PROFESSOR E. HEUSER

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Effect of the Hydroxyl Groups of Cellulose on Its Papermaking Properties

by J. O. Fleischer

June, 1948

LOAN COPY
To be returned to
EDITORIAL DEPARTMENT

THE EFFECT OF THE HYDROXYL GROUPS OF CELLULOSE ON ITS PAPERMAKING PROPERTIES

A Thesis Submitted by

J. G. Bletzinger

B.A., 1936, Allegheny College

M.S., 1938, Lawrence College

in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy, from Lawrence College, Appleton, Wisconsin, June, 1940

J G Bletzinger

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL REVIEW	3
HYDRATION AND THE BONDING STRENGTH OF PAPER	3
Chemical Theory	4
Physical Theory of Hydration	9
Campbell's Theory	14
Mechanism of Bonding	16
THE NATURE OF ACETYLATED CELLULOSE	21
ORIENTATION EXPERIMENTS: STUDY OF METHODS AND STANDARDIZATION	26
STUDY OF RAW MATERIALS	26
Procedure	27
Beater Runs for Cotton Linters	27
Beater Runs for Rag Stock	29
Discussion of Results	29
STUDY OF ACETYLATION	35
Method of Acetylation	37
Acetyl Determination	38
Data and Discussion of Results	39

TABLE OF CONTENTS (Continued)

	Page
Study of Beating in a Miniature Beater	49
Experiments with the Stainless Steel Beater Roll	49
Experiments with Rubber-covered Lead Balls	51
Standard Beater Runs	53
Discussion of Results	55
BEATING STUDIES OF ACETYLATED CELLULOSE PULPS	58
PREPARATION OF PULPS FROM RAG STOCK FOR STRENGTH STUDIES	58
Acetylation of Standard Rag Stock	58
Pulps of High Acetyl Content	58
Pulps of Low Acetyl Content	58
Acetylation of Highly Beaten Rag Stock	59
Saponification of Acetylated Rag Stock Beaten to a Low Freeness	61
Data and Discussion of Results	64
THE EFFECT OF ACETYLATION ON MOLECULAR WEIGHT, TENSILE STRENGTH, HYGROSCOPICITY, AND SURFACE CONDITIONS OF THE FIBERS	66
Effect of Acetylation on the Molecular Weight of the Cellulose	67
Effect of Acetylation on the Strength of Individual Cotton Fibers	70
Preparation of Bleached Cotton Fibers	71
Preparation of Acetylated Bleached Cotton Fibers	73
Determination of Tensile Strength of Individual Cotton and Acetylated Cotton Fibers	73
Data and Discussion of Results	75
Effect of Acetylation on Hygroscopicities of Prepared Pulps	75

TABLE OF CONTENTS (continued)

	Page
EFFECT OF ACETYLATION ON PAPERMAKING PROPERTIES OF CELLULOSE FIBERS	76
Processing the Pulps in Water	78
Procedures for Processing Pulps of Acetylated Standard Rag Stock	78
Processing in the British Disintegrator	78
Processing in the Miniature Beater	79
Testing of Handsheets	80
Calculations of Results	81
Procedures for Processing Pulp Which Had Been Beaten Before Acetylation	81
Data and Discussion of Results for Processing in Water	82
Processing in Acetone	96
Processing in British Disintegrator	96
Processing in the Miniature Beater	97
Testing of Handsheets	97
Discussion of Results	97
THEORETICAL DISCUSSION AND SUMMARY	104
CONCLUSIONS	112
REFERENCES CITED	113
APPENDIX	118

INTRODUCTION

The pronounced affinity of cellulose for water, as shown by its hygroscopicity, swelling, and the like, has commonly been attributed to the hydroxyl groups of the cellulose. Also, the bonding of paper has been thought to occur through the secondary valencies arising from them, similar to those bonds associated with the cellulose molecules of an individual fiber.

If all or part of these groups in the cellulose fiber were substituted by less hydrophilic groups such as methoxyls, acetyls, nitrate groups, or other ether and ester groups, the behavior of these modified fibers could be studied in the process of "beating" and the bonding in paper.

Cellulose esters and ethers can be prepared with the original fibrous structure maintained and without degrading the cellulose. By gradually increasing the degree of substitution and by subjecting the products to a beating action, a technique is available for investigating the phenomena of "hydration," fiber bonding, and other water-binding reactions.

From the possible choices of groups that could be introduced, the acetyl group was studied, because acetylation has been investigated extensively and cellulose acetate may be readily prepared in fibrous form with little degradation and reduction of tensile strength. Further, the possibility of subsequent saponification to regenerate the

original cellulose provides an additional point of study and means of control.

HISTORICAL REVIEW

The study of the hydration of pulp and the bonding strength of paper has been carried out by numerous investigators for many years. Excellent summaries of their work are available, as well as bibliographies on the subject--Bialkowsky (1), Bell (2), Simmonds (3), Clark (4), Campbell (5), Strachan (6)--so that a repetition of the general aspects will not be included here. The specific problem of this investigation is concerned with the effect of the hydroxyl groups themselves on the bonding strength between the fibers and their contribution toward the action which occurs during the hydration of the pulp. In this thesis, unless otherwise qualified, the term "hydration" will be reserved to describe the action which occurs when processing a pulp in a beater or similar mechanical device to increase the bonding strength between the fibers.

As mentioned in the introduction, the method of attack was to cover the hydroxyl groups progressively with less lyophilic groups and to follow the effect on bonding, paper properties, and beating characteristics. This procedure requires a division of the historical review into two parts: (1) hydration and the bonding strength of paper; (2) the nature of acetylated cellulose.

HYDRATION AND THE BONDING STRENGTH OF PAPER

The nature of hydration has been a matter of controversy and speculation since paper formation and bonding were first studied.

Many theories have been advanced, but for the most part they can be classified into three groups: chemical theory; physical theory; and Campbell's theory. Evidence from time to time has given preference first to one theory and then to another. Probably a reconciliation and combination of all three concepts will be required for the ultimate explanation.

In the following discussion, each group will be treated in turn.

Chemical Theory

Early investigators considered that a chemical change occurred on beating to form a cellulose hydrate compound which caused the greasy feel, the slowness of the stock, and the subsequent binding of the fibers. For example, Cross and Bevan (1) explained the beating action as given in the following summary. The separation of the fibers into independent units is the first essential condition for realizing their felting and interlacing qualities in the formation of paper. A second important condition for uniform felting is "the development of the flexibility of the fibers, the so-called 'softening' or 'hydration' effect of the beating process," whereby the fibers, originally stiff, become sufficiently flexible to combine with each other to form a uniformly close web when the pulp is drained on the paper machine wire. Thirdly, the ultimate fibers in most cases have to be reduced in length to an extent required for the formation in the type of paper to be produced. Other physical changes occur, such as the bruising and

flattening of the ultimate fibers and, in many cases, their further reduction into smaller units or fibrillae. "A fresh change takes place in the fibers as the result of their contact with the watery medium"; the continual beating causes the cell wall of the fiber to "absorb water and pass into the condition of a gelatinous hydrate." The "greasy" or "wet" feel may be regarded as "due to a solution of water by and in the cellulose (hydrate)," and may be compared with the "homogeneous, gelatinous mass which is obtained by the setting of the sulfo-carbonates."

The formation of oxycellulose during beating was postulated by Seibert and Minor (8) from their study of the increase of copper number with the processing. They also considered that with long beating there is a progressive formation of hydrocellulose.

The above work was referred to by Schwalbe and Becker (9) in their attempt to find an explanation for the formation of a cellulose slime on beating. The first step in the decomposition of cellulose was assumed to consist of the formation of an insoluble hydrocellulose or oxycellulose which has properties very similar to the hemicelluloses of wood incrustation, in that it reduces Fehling solution and is in general unstable and reactive. They concluded that "Cellulose-schleim" arises through mechanical crushing accompanied by an increase of reducing power (from copper number determination) and degree of swelling on beating. To substantiate their argument, they found that slime formation is accelerated when cellulose is treated with acid before mechanical processing. Therefore, it was concluded that slime formation seems to depend upon the formation of a hydrolytic degradation

product (cellulose dextrin) which differs from cellulose in its high reduction power. This substance was considered the cementing material of papers, particularly of parchment papers.

On the other hand, recent investigations by Curran, Simmonds, and Cheng (10) and by Kress and Bialkowsky (11) have shown that, with but two exceptions, no definite chemical changes during the beating can be observed. These are an increase in the hydrolysis number and a slight drop in the cuprammonium viscosity. Alpha-cellulose, pentosans, beta-cellulose, and gamma-cellulose remain almost constant during the beating experiments.

Although chemical analysis of the pulps for alpha-, beta-, and gamma-cellulose during the beating failed to show an increase of the low molecular weight celluloses, yet experiments with stocks in which these easy swelling celluloses are present or are added to the system have shown that these materials (celluloses of low molecular weight) facilitate the beating action. In confirmation of the work of Schwalbe and Becker mentioned above, Nakano (12) and Seibert and Miner (13) found that under certain conditions, an acid pretreatment accelerates the beating process tremendously and produces transparent and parchmentized papers. Bassett (14) has taken out a patent on the process of converting cellulose linters into papermaking fibers by mechanically treating them in dilute acids.

Similarly, the presence of hemicelluloses has been shown to be very effective in facilitating the beating action and increasing the strength of the paper prepared from the pulp. Rumbel (15), in

discussing the effect of hemicelluloses in papermaking, pointed out that they are partly responsible for the strength of a pulp. Jonas and Rieth (16) processed two pulps of almost the same chemical characteristics in which the copper number, viscosity, lignin content, and resin content were about the same but in which the pentosans and mannans were higher in one than in the other. On processing for 20 minutes, the pulp with the higher content of pentosans and mannans gave much greater strength and lower freeness. The difference seemed due only to the amount of pentosans present. Therefore, they treated a third pulp with xylan, mannans, and a mixture of the two, respectively, which resulted in an acceleration of the beating action and achieved greater strength when the xylan and mannans had been added to the beater. Of the two, mannans were the more effective.

Obermann (17) investigated more extensively the effect of hemicelluloses on beating. Increasing the beta- and gamma-cellulose content of a rag stock by overbleaching accelerated the beating action as shown by a more rapid drop in freeness but the strength of the pulp was also greatly reduced because of degradation of the cellulose. On the other hand, he found that the addition of xylan to rag stock not only accelerated the beating action but also increased the strength, particularly the tensile. Similarly, the addition of beta-cellulose, extracted from pulp, was shown to have the same beneficial effect.

Except for the one experiment by Jonas and Rieth, all the hemicelluloses in the above work were added as such to the pulp in the beater. To maintain the hemicelluloses structurally in the fibers

Kouts and Kurth (18) prepared a pulp of holocellulose in which the beta- plus gamma-cellulose content was 18.44 per cent and the pentosan content was 12.63 per cent. On processing, the pulp was beaten to a glassine condition after 33 minutes in a standard beater run with only 3600 grams on the bedplate. After extracting with ammonium oxalate, which removed some of the polyuronides and a small amount of pentosans, the pulp showed a slower beating rate and produced slightly less strength. Over-chlorination and hydrolysis of this second fraction increased the beta- plus gamma-cellulose content and subsequently accelerated the beating action slightly, although lower strength resulted. Finally, extraction with 17.5 per cent sodium hydroxide to remove most of the hemicelluloses left the pulp with 10.16 per cent beta- plus gamma-cellulose and 2.36 per cent pentosans. Processing of this pulp was very slow, the rate being comparable with that of alpha pulp; the resulting strength was less than half that of the original holocellulose.

The effect of hemicelluloses on beating is particularly interesting when correlated with the effect of pentosans on swelling. Young and Rowland (19), using a dilatometer method, showed that there was a straight-line relationship between the pentosan content of a pulp and its ability to swell in water. Thus, in consideration of the work of Kress and Bialkowsky (11), who found that the medium for beating must swell the cellulose in order to obtain strength, the effect of hemicelluloses on processing may not be so much a catalytic action for the beating itself, but a means of accelerating and extending the swelling of the fibers.

Therefore, one must conclude in the light of the above work on hemicelluloses and hydrocelluloses that the chemical constituents of the pulp have an appreciable effect on the beating action; yet, apparently, other factors as well are involved.

Physical Theory of Hydration

In opposition to the chemical view of hydration is the physical theory, which disregards any need for a chemical substance to explain hydration but postulates a structural phenomenon to characterize the beating action. Strachan, a foremost exponent of this concept, attributes the hydrating action and the strength of paper to the intertwining and bonding of the small fibrils which are formed by the beating process. His original viewpoint has been modified from time to time to agree with further investigations. In 1926, he proposed (5) that the taking up of water in beating should be termed imbibition instead of hydration because his experiments had indicated that the drying of beaten and unbeaten stock showed no break in the curve relating moisture content to vapor pressure which indicated the lack of a hydrate formation in the chemical sense. He considered that the main difference between beaten and unbeaten pulp is in the water which the cellulose has imbibed in swelling, and that the mechanical action of beating aids the swelling process by increasing the area of surface exposed.

> Hydration of the fibres in papermaking consists in an increased degree of imbibition due to increase of specific external surface of the cellulose masses (fibre). The latter is produced by slight or extensive fibrillation of the fibres, whereby a portion

of the latter is increased in specific external surface up to one hundred times that of the normal fibre.

His experiments with Methylene Blue adsorption showed that the beating caused no appreciable increase in total surface. Therefore, he concluded that "hydration during the beating is thus purely a physical action" (20).

In general, Strachan's viewpoint was one that follows a colloidal conception of cellulose. He said (20): "Cellulose in the form of fibres as used in papermaking exhibits all the properties associated with an elastic gel"; yet "cellulose differs from other elastic gels in being porous and holding considerable quantities of adsorbed air and gases." He considered that there exists capillary water between the fibers and colloidal water comprising water of imbibition adsorbed by the unbeaten fiber and water of hydration due to the beating action. (One should note that, in the terminology of the colloid chemist, solvation, imbibition, and hydration are used interchangeably in referring to the process by which water is taken up by hydrocolloids or lyophylic colloids. Hydration is the term reserved specifically to the taking up of water, whereas the other two are general and may refer to any medium (21).) In 1926 Strachan concluded that "the immense surface created by fibrillation plus the pressure to which the sheet is subjected are sufficient to account fully for the increase of imbibition which we call hydration."

In 1932 (22), Strachan postulated that the strength increase in beating was due mainly to the fibrillation and entanglement of the

resulting fibrils and to an adhesion between the swollen cellulose fibers. Concerning the mechanism of adhesion he says: "The force binding the fibers together during the felting on the paper machine is simply that of cohesion between colloidal surfaces according to well-known physical laws." The intertwining of the hydrated fibrillae is the principle factor in felting and sheet formation.

Strachan was not certain as to the nature of the bonding between the fibers. At least, a hydrocellulose or oxycellulose as the bond was excluded, although conceived possibly to be present; "the formation of hydrocellulose" may be considered "coincidental with the beating process." In 1935, he discussed the nature of a colloidal film of cellulose (23): during the beating process, the surface of the fiber becomes fibrillated or covered with a velvetlike pile of fibrillae which attract more water than the unbeaten fiber; consequently, a well-beaten fiber is covered with a thin film of jellylike cellulose and water in which state it is described as being "hydrated." This hydrated film plays an important role in the formation of a sheet of paper.

In fact, Strachan seemed to think that a film of colloidal water held mutually by adjacent fibrillae is necessary to bond the fibers together rather than an attraction, for the most part, between the cellulose molecules themselves. He stated that "cohesion of well-beaten fibers having fibrillated surfaces in a highly hydrated condition depends upon the attraction of the cellulose for water. The closer the fibers are pressed together and the smaller the film of water between them, the more strongly the fibers adhere to each other."

On drying the paper, the increased strength is conceived as being due to a closer association of the fibrillated surfaces and to depend upon the fact that the water most closely associated with the cellulose is most strongly attracted and that the extent of the attractive force depends upon the area of the hydrated surface. "The presence of the film due to the attraction of cellulose for water plays the part of bringing the fibrillae into intimate contact with each other at the contact surfaces of the fibers, upon which the final mechanical strength of the paper depends" (24, 25).

Swelling is a standard method of measuring the extent of imbibition or colloidal hydration. Kress and Bialkowsky (11) found that strength in pulp could not be developed by beating when the medium was one which did not swell the fibers. Using a dilatometer to measure the increment in volume, a good correlation was found to exist between the degree of swelling of the fibers and the extent to which strength was developed. Glycerin and formamide as mediums for beating produced results comparable to that obtained in water; methyl and ethyl alcohol produced a much poorer sheet, whereas hydrocarbons gave the least beating action. A comparison of the mediums which were used with their dielectric constants (or polarity) showed that a satisfactory beating action occurred in the same order as their dielectric constants.

Similar results have been reported by Stamm; he found that the swelling of cellulosic materials in dry organic liquids was, in general, less than in water, decreasing with a decrease in the polarity of the liquid. Normal alcohols from methyl to butyl alcohol gave a decreased

swelling with an increase in molecular weight. Sorption experiments by Sheppard and Newsome (26) showed similar results. Stamm (27) also found that a series of benzene derivatives gave an increasing swelling in the same order as that of the increasing dipole moments of the liquids.

The necessity of a gel formation for fiber strength and beating action has also been postulated. From a series of experiments involving various chemical and mechanical treatments of cellulose fibers of different origin, Bailey and Brown (28) found that a resistant fibril of approximately 1.0 microns in diameter always occurred after disintegrating the fiber. Evidence for the presence of a gel formation was discovered which suggested that at least two physical states of cellulose occurred in the fiber wall: a cementing gel and a compact fibril incapable of gelatinization in water by ordinary methods. They attributed possible changes in beating, such as freeness drop and development of strength, to this dense-structure. They reasoned that if cellulose in the fiber did not exist in two forms, one more resistant and the other less resistant to swelling in water, then the beating action should not cause the formation of discreet fibrils in the fibers but a general crushing of the fibers.

Brauns and Lewis (29a, 29b), experimenting with a highly purified wood pulp containing 99.1 per cent alpha-cellulose and having a low copper number (0.049), and a fairly high cuprammonium viscosity (32 centipoises), found that beating failed to hydrate the pulp or to produce strength. A structural change had occurred in its preparation

which, although it left the fiber composed of cellulose in a good chemical condition, could not exhibit the properties associated with the beating of pulp and fiber bonding. Furthermore, swelling experiments produced no ballooning which has been shown to be associated with a pulp capable of beating (30). The action was described as follows: "When this pulp was treated with cuprammonium solution instead of ballooning as expected, the sleevelike lamella of the secondary wall slipped off with apparent ease, one from the next, as though the amorphous membrane-like material had been removed."

In summarizing, the physical theory places emphasis upon the structural changes of the fiber which take place during beating and upon the apparent necessity for the existence of certain physical conditions in both the fiber and the medium in order to produce a successful processing of the pulp and to obtain paper formation.

Campbell's Theory

This hypothesis, proposed by Campbell (5, 11), combines the fibrillation concept of the physical view with another explanation for the bonding between fibers. A chemical formation of a mucilage is entirely abandoned; instead, a hydrated layer of cellulose in contact with water is considered to form. This lowers the attraction of fibrils for each other and permits water to enter the structural lattice causing swelling. Beating produces further disruption of the structure so that fibrils become frayed out. According to Campbell (5),

When the sheet of paper is formed, its strength depends largely on the adhesive bonds formed between the fibers, and these are formed wherever two wet cellulose surfaces dry in contact with each other. Because of the increase of external surface produced by beating, the number of contacts and subsequent bonds is much increased and results in the strength increased in the finished paper. The nature of the bonds is not definitely known, but in the opinion of the author [Campbell] they are due to the same secondary valence forces which cause crystallization. The strength of the bonds individually depends on the degree to which the two contacting cellulose crystals are oriented similarly. If identical in orientation a bond of maximum strength and insolubility is produced. Bonds of lower strength and greater solubility are produced if the two contacting crystals are less perfectly oriented.

Campbell has shown further from mathematical calculations that the surface tension of water exerts an enormous pressure as the fibers approach each other on drying to compact the fibers in the wet sheet. Contact of fiber to fiber is necessary to produce a bonding between them. Roughly (32) has found that this contact can be attained by external pressure on the wet sheet; unbeaten stock can produce a well-bonded sheet by simply applying higher pressures to the wet web. He has shown that the "solid fraction" (a term similar to apparent density) correlates with the tensile strength of a paper, regardless of whether this density is attained by beating action or by high pressure. Yet, a small amount of beating will greatly increase the strength if the paper is prepared by a subsequent pressure method. However, a maximum is attained after a short interval of beating and strength does not continue to increase.

This is in accord with the work of Harrison (33), who concluded from a study of photomicrographs that the greatest strength was reached during the beating before fibrillation begins but that the

latter action is a means to an end: the increase of apparent density by facilitating the felting through greater pliability, more satisfactory distribution of fiber length, and change in fiber structure.

Thus, the fibrillation is thought to increase the external surfaces which, in turn, causes a greater tension on the sheet from the water. A denser sheet is formed with the subsequent increased contact of fiber to fiber which, as the water evaporates on drying, bond together as in crystallization.

Mechanism of Bonding

According to the x-ray work of Spencler and Dore (34) and Meyer and Mark (35) the cellulose chains are thought to be held together by secondary valences. This usually is attributed to the attraction between the hydroxyl groups.

As Urquhart (36) has postulated, when the cellulose is formed inside the cotton hair, it is precipitated in the presence of water and, hence, the hydroxyl groups will have water molecules attached. As the cotton hair dries, these hydroxyl groups are freed from water and tend to rearrange themselves so that their residual valences will be mutually satisfied by adjacent molecules, which action results in the bonding together of the cellulose. When rewetted, some of these molecules reattach themselves to water to give a looser form, but the fiber structure still is retained. Urquhart advanced the idea of "partial solubility" which is another concept of the same process:

part of a molecule may be solvated while, at the same time, the remainder of the cellulose chain is still attached to the fiber.

A similar situation may exist when pulp is beaten or mechanically treated. It is conceivable that solvation of the molecular surfaces can be facilitated by the flexing action and pressure which occurs during the physical treatment. With pulp, it is difficult to measure the amount of water of swelling (37) but some investigations (5, 38) indicate that it is increased with beating. One may interpret these results as indicating that the beating action increases the number of available hydroxyl groups by breaking down the original bonds between the cellulose hydroxyls and thus increases the capability of water binding and consequently of fiber to fiber bonding.

Hygroscopicity experiments should not be expected to measure the water of swelling (or imbibition), for the initial readings of sorption isotherms are taken in the range of 95 per cent relative vapor pressure, which means that the fibers at equilibrium have been dried out to a great extent from their water of swelling. Campbell (5) and Goberg, Simmonds, and Baird (38) have found by accurate measurements with a refined sorption balance that the hygroscopic water held by the dried fiber is slightly higher for the beaten pulp than for the unbeaten pulp; the ratio has been determined to be 1.04 to 1.06. This ratio persists even after several desorptions and adsorptions, suggesting that more hydroxyl groups permanently have been made available to the moisture, possibly to some extent from the formation of fibrillae in the beating action. Yet, one is not justified in assuming that these data

indicate the actual condition when the fibers were still in the liquid medium, for even at 100 per cent relative vapor pressure, great inhibition is known to occur when a solid is immersed in the solvent than when it is in contact with the vapor (von Schroeder paradox).

The true water of imbibition taken up during heating has yet to be measured. The method to be used finally may be an indirect one, such as a measurement of fiber swelling and shrinking in water before and during heating, instead of a direct analysis of imbibed water.

The nature of the residual valences arising from hydroxylic compounds (which includes cellulose as a polyalcohol) has been discussed from the physicist's viewpoint by Glasstone (39). Hydrogen is considered to be capable of becoming bivalent and, hence, acting as a bridge between two atoms. From a consideration of atomic structure, hydrogen when attached in a stable manner to a strongly electronegative element such as oxygen, is capable under certain conditions of accepting another pair of "spinning electrons" which bond the elements together with electrical forces.

One common example occurs in the formation of ice; x-ray analysis (41) seems to show each hydrogen atom to be symmetrically placed between two oxygen atoms, whereas each oxygen atom is surrounded by four hydrogen atoms. Sidgwick (42) accounts for the association of compounds containing hydroxyl groups in a similar manner by postulating that the oxygen atom donates a pair of electrons to the hydrogen atom of another molecule as would be the case for an alcohol.

A similar analogy is found in cellulose which is a polyalcohol. X-ray diagrams of cellulose show diffraction bands which are the same as that of ordinary ice. Hellmajer and Pavejee (43) believed that this indicates a hydration film surrounding the particles. From a study of entropy change, Katz (44) has pointed out that the initially adsorbed water, if not in the form of ice, is at least oriented and associated in a manner similar to ice. It is interesting that the experimental results from x-ray analysis and the thermodynamic relationships should also indicate that the cellulose molecules in a fiber are held together by hydroxyl groups through bivalent hydrogen atoms and that some water entering the structure orientates with respect to these hydroxyls in a manner which supports the postulation of Sidgwick above.

The cellulose lattice can be so expanded on swelling (for example, by 17.5 per cent sodium hydroxide) that the elastic limits seem to be exceeded and the fiber does not return to its original condition. Cellulose which has been thus "mercerized" has an increase in hygroscopicity ratio of 1.40 which could be explained on the assumption that a greater number of hydroxyl groups have become accessible. Probst (45) found that the mercerization of a rag stock caused a loss in strength of the paper sheet which varied with the extent of the mercerization. This loss in strength he attributed partly to the large number of hydroxyl groups available, causing a stable film of water to surround the molecules which prevented bonding in the usual manner. One can reason that this tightly held water film prevents the molecular surfaces of adjacent fibers in a sheet from attaining sufficiently intimate contact to bond together.

Approved for Public Release

McGregor (46) has shown that the combining of water during beating is not one of direct proportions. Considering the large molecules, it is conceivable that a heterogeneous combination does occur; yet, this may be effected by a condition in which a definite number of water molecules combines per glucose unit while only a part of these units of the molecular chain enters into the reaction. The work of Pierce (47), from rigidity measurements, indicates that one molecule of water combines per glucose unit but that, on further addition of water, the molecules do not attach themselves in any definite relationship. Sheppard (48) held a similar point of view.

Brown (49), in studying the bonding between multi-ply sheets of paperboard, found that the greater the amount of water present during the pressing, the greater the strength of the bond between the fibers and plies which increase was finally limited by the tendency for the sheets to crush during pressing.

In order that bonding may occur between the fibers, their surfaces must touch. Cottrell (50) has presented a logical interpretation of the mechanism of bonding; he assumed that a greater part of the strength depends on the number of fiber-to-fiber contacts to form the bonds through the linkage of free hydroxyl groups of the cellulose. These contacts can be produced through wet pressing, fibrillation in a beater, or friction in a Lampén mill.

Hence, in summarizing, it seems that the cellulose fibers when placed in a water medium react in a manner suggested by the

Forest Products Lab

surface solution or partial solubility concept of Campbell and Urquhart. Part of the hydroxyls of the cellulose chains have their secondary valence forces satisfied by water molecules. Mechanical action permits a greater exposure of these chain-ends by rubbing the surface and fleeing the fiber but this action is limited for effective bonding by two factors: (1) Too great an action changes the fiber structure beyond the limits of arrangement whereby it obtains its greatest strength. (2) An optimum film of water molecules is desirable for the greatest bonding action.

Upon drying, the fibers are pulled into close contact by the surface tension of the water as pointed out by Campbell, until the secondary valence forces are effective. As the water molecules are removed, these valences become satisfied by those of the cellulose hydroxyls in other (adjacent) fibers, causing a bonding to occur similar to that which exists between chains in an individual fiber.

Increasing the external pressure assists in creating these close fiber-to-fiber contacts and, consequently, increases the number of bonds. If preceded by mechanical action (even though slight) more fibrils and solvated molecules are available for contact; the resulting strength is increased when at the same solid fraction. Fiber arrangement in the sheet and fiber sizes (2, 11) affect these contacts and consequently the bonding which results.

THE NATURE OF ACETYLATED CELLULOSE

As compared to native cellulose, acetylated cellulose is characterized by its greater hydrophobic properties. The triacetate

and the diacetate are insoluble in water and only swell a negligible amount in this medium. On the other hand, the lyophilic properties with respect to organic solvents are enhanced. When prepared by most common methods (51) the diacetate is soluble in acetone and the triacetate is soluble in chloroform. However, when prepared without degradation from a high-grade cellulose of a degree of polymerization above 1000 glucose units, only swelling occurs with the above solvents regardless of the acetyl content (52).

Acetylated cellulose prepared by partial saponification of cellulose triacetate (51) with an acetyl content between 15 per cent and 19 per cent is soluble in water when the degree of polymerization is sufficiently low but insoluble when prepared from native cellulose by controlling the acetyl content with the time of reaction (52). Such hydrolyzed cellulose acetates with an acetyl content up to 26 per cent are permeable to water and, in the range of 24 to 26 per cent acetyl content, are soluble in ethylene glycol mono-methyl ether.

The structure of acetylated cellulose fiber, when prepared from native cellulose by the acetic anhydride-pyridine method (52), is very similar to that of the original cellulose fiber. Staudinger and his co-workers (54, 55), in studying the effect of this method of acetylation on degradation, have found that the molecular weight remains unchanged both with the cellulose acetate or when this product is carefully saponified to the original cellulose. From x-ray analysis, the fiber structure of the acetylated cellulose prepared from unmercerized native cellulose is the same as that of the untreated

cellulose except for the acetyl groups, which seem to extend out from the molecular chain into the intermolecular spaces (56). Saponification yields a cellulose fiber which gives the x-ray pattern of native cellulose. In contrast, acetylated fibers which are prepared from mercerized fibers give the x-ray patterns of a "hydrate-cellulose"--a cellulose in which the fundamental structure has been expanded by previous swelling or by regeneration from a dispersion--on saponification. An excellent review of the literature, summarizing the work on the submicroscopic structure of the cellulose acetate derivative and containing a copious bibliography on the subject, has been prepared by Sisson (57).

The strength of the cellulose fiber is seemingly not impaired by acetylation. Such acetylation Sakurada (58) has tested the effect of acetylation both on cellulose fibers and on viscose rayon and found that no decrease in tensile strength can be detected.

Cellulose may be considered as a semielastic gel--i.e., exhibiting some of the properties both of an elastic gel and of an inelastic gel. (Sheppard has chosen to describe cellulose as belonging to a group named "xerogels," which are colloids in a relatively dry state substantially free from liquid and volatile dispersion media (45).) The relation of a gel to a particular medium is displayed by the sorption of its vapor. Increased swelling or solubility in a solvent is accompanied by an increase in the ability to adsorb that solvent and hence a study of vapor sorption gives an indication of the attraction of the gel for the particular medium under consideration.

This affinity is often attributed to certain groups in a molecule, particularly when the molecule is large. This is true of cellulose, in which the attraction of the long chain molecule for water is attributed to the presence of hydroxyl groups. In simple sugars, such as glucose or cellobiose (the building units for cellulose), covering the hydroxyl groups with acetyl groups reduces the water solubility and limits the hygroscopicity at 100 per cent relative humidity to less than 1 per cent. In a similar manner, the cellulose triacetate, in which all the hydroxyl groups are covered, shows a hygroscopicity at 100 per cent relative humidity of about 9 per cent as compared with 16 per cent for the original cellulose (48).

Sheppard and Newsome (59) have shown that, as the acetyl content of a native cellulose is increased from the untreated to the triacetate, the hygroscopicity decreases in an almost linear manner. When a so-called "hydrate-cellulose" is progressively acetylated, the initial hygroscopicities are higher than those for the native cellulose but they converge as the acetyl content approaches that of the triacetate. Reducing the number of hydroxyl groups decreases the hydrophilic nature of the cellulose. On the other hand, the same investigators (60), when studying the sorption of alcohols by acetylated cellulose, found that increasing the acetyl content over the range from untreated to 44.5 per cent increased the sorption of ethyl or methyl alcohol in the same ratio as the sorption of water had decreased. In contrast to what might have been expected, increasing the number of carbon atoms of the alcohols in the homologous series reduced the

amount of alcohol which was adsorbed, calculating throughout on a mole basis.

Acetylated cellulose shows even greater affinity for the vapors of some other organic solvents. Kanamaru and Chao (61) reported that acetone and chloroform were highly adsorbed on a cellulose triacetate prepared from native cellulose by the Hess and Ljubitsch method (52). At 96 per cent relative vapor pressure, 41 grams of acetone were adsorbed per 100 grams of acetylated cellulose, as compared with 2.5 grams for native cellulose. Chloroform vapor was taken up to the extent of 96 grams per 100 grams of cellulose triacetate; standard fibrous cellulose showed an adsorption of only one per cent of this solvent, whereas viscose rayon took up but a negligible amount and cellophane, none at all.

Acetylated cellulose exhibits hysteresis with the vapor pressure sorption isotherm in a manner similar to native cellulose (58, 62). However, instead of the usual sigmoidal form of curve obtained with cellulose, the initial rise at low vapor pressure is absent and a gradual continuous increase of sorption is observed. Several investigators (58, 62) have noticed this phenomena and accounted for the difference by the fact that, since the hydroxyl groups were covered, an initial high adsorption, due to the attraction of water for hydroxyl groups, could not occur. The same phenomenon is observed in heat of adsorption measurements (29); the integral heat of adsorption approaches closely the heat of condensation--more so for the triacetate than for the diacetate. Thus, with cellulose triacetate, the sorption seems to be almost entirely capillary condensation.

ORIENTATION EXPERIMENTS

STUDY OF METHODS AND STANDARDIZATION

STUDY OF RAW MATERIALS

The pulp for this investigation had to be one which could be used for all experiments in order to eliminate the possible variable of differences in raw material. Hence, the following requirements were to be satisfied by the source material for cellulose before it was acceptable.

1. The stock or pulp should be in a physical state that retains papermaking qualities (beating in water, "hydration," bonding of fibers to give a normal strength evaluation).

2. Interfering and foreign substances present with the cellulose, such as lignin and cellulose of a low degree of polymerization, should be minimized; conversely, a high alpha-cellulose content is desired.

3. Fiber length and fiber distribution should be of such a nature that sheets of good formation can be obtained without further fiber reduction in beating experiments.

4. Strength properties should be within the normal range obtained in commercial papers and should be sufficient to show changes caused by covering the hydroxyl groups.

Two indications of a mercerized cellulose are its high hygroscopicity and, as Probst (45) has shown, an increase in opacity (scattering coefficient) with beating; hence, any pulp to be used in the present work must show normal characteristics in this respect.

Since untreated wood pulps have a relatively low alpha-cellulose content and contain traces of lignin, cotton was selected as the first source material because of its higher degree of purity.

Two sources of cotton were considered: linters and high-grade rag stock. The types of linters which were evaluated are listed as follows: (1) Hercules cottonseed hull shavings in sheet form--linters cut short for papermaking and pressed into dry lap; (2) Hercules seed hull shavings--in sheet form as above but of longer fibers; (3) cottonseed linter from Hercules Powder Company--a fluffed cotton linter with a much longer fiber than those in sheet form for the paper industry; and (4) cottonseed HS pulp from Hercules Powder Company--a fluffed linter similar to 3 but having a longer fiber.

In addition, four samples of commercial number one rag stock all from the same mill were evaluated.

Procedures

Beater Runs for Cotton Linters

The pressed cotton linters (Materials 1 and 2) were disintegrated and slushed in the laboratory Valley Iron Works beater with no

weight on the bedplate; the charge was 400 grams of air-dry pulp. After all slots and lumps were completely broken up, actual beating was started with 6500 grams on the balanced bedplate. For the pressed linters (Material 1), samples were removed after five minutes and then at 20-minute intervals until the Schopper-Riegler freeness had dropped to 450 cc. For the pressed linters (Material 2), the samples were removed at 30-minute intervals.

The fluffed linters (Materials 3 and 4) required more vigorous slushing action to break up the "pills" and slots. For fluff linters (Material 3), the charge was 375 grams of air-dry linters (consistency of 1.53 per cent). During the first fifteen minutes of slushing, a weight of 1700 grams was carried on the balanced bedplate; subsequently for forty-five minutes, 3100 grams were used. Samples were taken after the 60-minute slushing period and at intervals of twenty minutes thereafter. After seventy-five minutes of beating, the freeness had dropped to 195 cc. S.R. (in subsequent discussions in this thesis, S.R. will refer to freeness measured on the Schopper-Riegler freeness tester) but the stock did not feel "hydrated." Hence, a weight of 2200 grams was placed on the bedplate and the beating was continued for 135 minutes.

For the fluffed linters (Material 4), which were longer fibered and harder than the previous linters tested, a charge of 395 grams (air-dry) was used in the beater. The stock was slushed for one hour with a weight of 200 grams on the balanced bedplate. Even after this length of time, the stock was not completely defibered; therefore,

6500 grams were placed on the bedplate and the first sample was taken after thirty minutes of beating. Sampling was continued at 30-minute intervals.

Beater Runs for Rag Stock

The fibers of rag stock were too long to be evaluated directly in the 1.5-lb. laboratory Valley Iron Works beater. Hence, precutting in the 5-lb. beater was necessary. After thirty minutes of cutting (until the fibers appeared satisfactory for the smaller beater) the pulp was drained through cheesecloth to increase the consistency, and transferred to the smaller beater, the balanced bedplate of which was weighted with 4500 grams. The pulp was found to beat very rapidly so that the second sample was taken fifteen minutes after removing the slushing sample; a third sample was taken after twenty-five minutes of beating.

Subsequent beater runs on the rag stock in the 5-lb. beater were intended to determine the conditions for obtaining the maximum amount of cutting with the least drop in freeness. Consistency and time of beating were varied to approach this condition. When these requisites had been obtained, a source supply was prepared for further experiments.

Discussion of Results

In all cases, the cotton linters were difficult to handle in the laboratory equipment (see Tables I-A and I-B). Furthermore, the

TABLE I-A

BEATER RUNS* ON COTTON LINTERS

Beating time min.	Schopper-Riegler freeness cc.	B. & L. opacity %	Apparent density	Bursting strength points per 100 lb.	Tear %
		1. "O.Q." Pressed Linters			
5	865	73.2	—	15.0	66.2
25	805	79.3	—	15.0	98.8
45	645	80.7	—	21.0	96.2
65	435	84.7	—	25.9	88.9
85	310	85.7	—	28.5	81.5
		2. "H" Pressed Linters			
10	845	70.7	6.3	8.5	85.2
40	830	71.4	8.1	13.0	96.8
70	780	—	—	—	—
100	620	77.1	9.8	23.3	118.5
130	415	81.2	11.0	27.5	110.6
160	350	81.2	11.3	31.2	100.5
		3. Fluff Linters #1 Cottonseed Linters			
0	895	66.5	8.5	14.8	216.0
20	835	69.0	10.1	25.9	274.0
40	690	77.5	11.2	36.0	270.0
60	485	79.0	11.9	44.7	225.0
75	395	82.5	12.3	48.0	231.0
210	210	83.0	12.5	65.0	197.0

* In 1 1/2-pound Valley beater

TABLE I-A (continued)

BEATER RUNS* ON COTTON LINTERS

Beating time min.	Schopper-Riegler freeness cc.	B. & L. opacity %	Apparent density	Bursting strength points per 100 lb.	Tear %
		4. "H" Special Fluff Linters			
30	880	**	----	----	----
60	875	**	----	----	----
90	840	75.2	8.17	27.4	----
120	775	76.5	9.38	34.5	240.0
150	650	78.9	10.34	40.3	239.8
180	510	80.8	11.00	45.7	204.2

* In 1 1/2-pound Valley beater

** Formation so irregular that no tests were made on the handsheets

TABLE I-B

EVALUATION AND CUTTING OF RAG

Trial no.	Consistency %	Beating time min.	Schopper-Riegler freeness cc.	B. & L. opacity %	Apparent density	Bursting strength points per 100 lb.	Tear %
"G.Q." No. 1 Bleached Rag Stock - Sample 1 (Evaluated in 1 1/2-pound Valley Laboratory Beater)							
		Initial after 30 min. cutting in 5-lb. Valley beater, 0	740	82.6	10.3	33.0	161.5
		15	360	87.7	12.2	45.2	105.8
		25	215 (30 sec. drainage time)	88.8	12.9	46.4	90.6
"G.Q." No. 1 Bleached Rag Stock - Sample 1 (In 5-lb. Valley Beater, 25 lb. on bedplate)*							
1	0.423	20	510	----	----	----	----
2	0.219	5	665	----	----	----	----
"G.Q." No. 1 Bleached Rag Stock - Sample 2							
	0.407	10	510	81.8	12.0	53.2	263.0
"G.Q." No. 1 Bleached Rag Stock - Sample 3							
	0.402	5	710	----	----	----	----
	0.408	6	695	----	----	----	----

* Used on all the following beater runs

TABLE I-B (continued)

EVALUATION AND CUTTING OF RAG

Trial no.	Consistency %	Beating time min.	Schopper-Riegler freeness cc.	B. & L. opacity %	Apparent density	Bursting strength points per 100 lb.	Tear %
	"G.Q." No. 1 Bleached Rag Stock - Sample 3 (With addition of 2% butanol and 10% ethanol on butanol by volume)						
	0.486	5	710	——	——	——	——
	"G.Q." No. 1 Bleached Rag Stock - Sample 5						
1	0.30	5	710	——	——	——	——
2	0.30	5	725	——	——	——	——
3	0.30	5	710	——	——	——	——
4	0.30	5	715	——	——	——	——
5	0.30	5	710	——	——	——	——

fact that the opacity increased with beating suggested that the fibers had properties of a mercerized material.

As great a strength as for linters was obtained for the rag stock, but less rise in opacity was experienced. Hence, rag stock appeared to be the more suitable raw material for obtaining papermaking properties.

For a source material, the fiber length of the original rag stock from the commercial paper mill was too long to form satisfactory sheets and had to be shortened by a cutting action in a beater without greatly "hydrating" the pulp. It was arbitrarily decided that, for this purpose, freeness, as a measure of the hydration, was to be kept above 700 cc. S.R. After several trial beater runs, it was found that by reducing the consistency to 0.30 per cent and beating for only five minutes in the 5-lb. Valley beater, the freeness dropped to only 710 cc. S.R. Further, these fibers were short enough to produce handsheets of good formation. Therefore, 25 lb. of the hardest sample (Material 4) of the commercial rag stock were beaten (cut) according to the above conditions. Periodic testing of the freeness showed it to range between 710 cc. and 725 cc. S.R. Subsequently, the beaten stock was pressed, air-dried, and stored in sealed glass containers for further use. The above prepared rag stock, beaten to 710 to 725 cc. freeness and air-dried, will be called "Standard Rag" in this thesis and abbreviated "S.R.P." At the same time, 15 lb. of the unbeaten commercial rag stock were stored wet in the sealed glass containers for emergency.

STUDY OF ACETYLATION

For the purpose of this thesis, two conditions were prerequisites for any method of preparing a cellulose derivative: (1) the product must be insoluble in water; (2) the cellulose must remain in the original physical state and with the original degree of polymerization or change in such a manner that the untreated cellulose can be brought to a comparable condition.

Two general types of derivatives which may have been used are the ethers and the esters. Since the esters are easier to prepare and their degradation more capable of control, they were selected for study. The ethers, on the other hand, are less reactive as a substitution group but the methods of preparation require treatment which produces swelling of the cellulose (even to mercerization). Furthermore, the methyl ethers are soluble in water between 0.6 and 0.7 alkyl groups per glucose unit when prepared with a quartenary ammonium compound and between 1.2 and 1.6 groups per glucose unit when prepared from alkali-cellulose in the usual way (63); Book (63) postulated that the alkyl groups force open the bundle structure to permit a greater solvation of the cellulose chains. This is sufficient to completely dissolve the fiber in cold water when 0.6 to 0.7 alkyl groups per glucose unit are present in a homogeneous product. The higher alkyl celluloses are insoluble in water because the methoxyl group itself exhibits less solvation than the hydroxyl group and hence repells the water when sufficient amount is present. Hence, acetylation offers a more promising method for preparing cellulose derivatives.

The most critical prerequisite of the present study is that the acetyl group should be introduced into the cellulose material without destroying the original fibrous structure and without impairing the original strength properties of the fiber.

For accomplishing this aim, several methods have been considered (64, 65, 66). The method using acetic acid without a catalyst (67) and the procedure in which acetic anhydride alone is the acetylating agent (68) were discarded because of the high temperature required and the slowness of the reaction. The method selected was one modified from the procedures suggested by Hess and Ljubitsch (52) wherein the derivative is formed by the action on cellulose of acetic anhydride in the presence of pyridine at room temperature for twenty-four hours and continuing at 40° C. for several weeks; the time of reaction controls the amount of acetyl groups introduced. It will be noted that a catalyst, such as sulfuric acid, is not required in this procedure.

The original method provides for steeping the cellulose in strong alkali (5 per cent for sixty minutes or 16 per cent for thirty minutes) before acetylation. Since, in view of the purpose of the present investigation, alkali treatment had to be avoided, the cellulosic material was not subjected to such treatment. It was simply washed with pyridine in order to remove the moisture as far as this was possible. Thereafter, the material was left in pyridine overnight at room temperature. In those experiments where the pulp had been slushed first in water, as much of the latter as possible was displaced with pyridine by repeated extractions before allowing the material to stand overnight in the pyridine.

The effect of the following factors in acetylation were investigated: (1) time of acetylation, (2) temperature, (3) ratio of acetylation mixture to cellulose, (4) several pretreatments, and (5) the type of cotton and its physical state.

Method of Acetylation

The cotton cellulose in fibrous form--both cotton linters and rag stock were used--was pretreated several times with pyridine to displace the water. (In case the pulp was air-dry, no pretreatment was applied.) Then, the cellulose was covered with pyridine and permitted to stand overnight at room temperature.

After the solvent had been filtered off on a Büchner funnel, the pulp was broken up with a "Lightnin'" mixer. The acetylation mixture (10 cc. of acetic anhydride to 16 cc. of pyridine for each gram of cellulose on ovendry basis) was then added with stirring. When the pulp had been thoroughly suspended, the container (a glass canning jar) was sealed and placed for a maximum of twenty-four hours on a horizontal rotator which revolved the charge at 60 r.p.m.; beyond that time the acetylation mixture was not agitated except for an occasional manual shaking.

After a given time for acetylation, the cellulose acetate, which retained its fibrous structure, was filtered from the acetylating mixture on a Büchner funnel, then returned to the glass jar, washed with pyridine recovered from previous acetylations, and again filtered. After a brownish color of the reaction mixture had been removed by

several such extractions, a final wash with fresh pyridine was made to remove the last traces of color. (Some experiments were made in order to determine the source of the discoloration. Apparently, the color originates from a reaction between pyridine and acetic anhydride. Light is a catalyst for the reaction; water impedes the formation.)

The next step consisted of displacing in a similar manner the pyridine with ethanol until no odor of the organic base could be detected. When the ethanol had been displaced finally with ether, the fibrous cellulose acetate was air-dried by passing dry air through the product.

In those preliminary experiments where only the acetyl content was to be determined, the products were subsequently dried further in a vacuum desiccator over calcium chloride.

Acetyl Determination

The method of Murray, Stead, and Gray (64), in which the cellulose acetate is saponified with alcoholic sodium hydroxide after swelling in 75 per cent ethanol, was employed to determine the acetyl content. It is rapid and accurate to 3 per cent error, which was regarded as being satisfactory for this investigation.

To check the reproducibility of the method, the acetyl content of a commercial cellulose acetate was determined. Two portions were saponified for twenty-four hours and one for forty-eight hours. The results are summarized below:

Time of Saponification hr.	Acetyl Content %
24	40.2
24	39.9
48	40.2

Data and Discussion of Results

The experimental data concerning the factors which affect acetylation are summarized in Table II. In the following discussions, reference will be made to the experiments by number from this table.

Under the conditions described above, acetylation proceeds rather slowly. This is illustrated in Experiments 1 to 6, in which, all other conditions being the same, the time of acetylation was lengthened from 5 to 117 hours. Even after this long time, the acetyl content of the cotton linters (Material 1) had reached only 10.65 per cent, corresponding to a degree of substitution of 14.9 per cent of the available hydroxyl groups. It also will be noted that the maximum acetyl content obtainable under the conditions applied in these experiments was almost reached after eight hours; beyond that, an increase in the time of reaction increased the degree of acetylation only a little.

Acetylation proceeded even more slowly with the special linter (Material 2); even after twenty-seven hours only 7.56 per cent and after 168 hours only 10.5 per cent acetyl had been reached (Experiments 7 and 8).

TABLE II

ACETYLATION OF CELLULOSE PULPS

	Type	Pulp preparation	Acetylation method*	Acetylation time hr.	Acetyl content %
1	Hercules Original Linters No. 1	Disintegrated by stirrer in water, replaced with pyridine	Ac_2O + pyridine in test tube with stirring	5	7.79
2	Same	Same	Same	8	9.26
3	Same	Same	Same	17	9.16
4	Same	Same	Same	26	8.12
5	Same	Same	Same	41	8.73
6	Same	Same	Same	117	10.65
7	Hercules Special Linters No. 2	Disintegrated by stirrer in water, replaced with pyridine	Ac_2O + pyridine on rotation machine--60 r.p.m.	24	7.56
8	Same	Same	Same	168	10.50
9	Commercial Rag Stock--cut in beater 510 cc. freeness	Filtered; water replaced with pyridine	Ac_2O + pyridine on rotation machine--60 r.p.m.	26	10.98
10	Same	Same	Same	168	15.60

* At room temperature unless stated otherwise

TABLE II (continued)

	Acetylation mixture	Periods of acetylation hr.	Temperature ° C.	Total acetylation time hr.	Acetyl content %
		Hand Cut Commercial Rag Stock - Sample 2*			
11	5 g./130 cc.	24	25	24	8.89
12	5 g./260 cc.	24	25	24	8.51
		Beater Cut Commercial Rag Stock - Sample 3 (695 cc. Freeness)			
13	5 g./130 cc.	24	25	24	11.57
		Hand Cut Commercial Rag Stock - Sample 2			
14	5 g./130 cc.	24 121	25 38	145	14.62
		Commercial Bleached Sulfite (Previously steeped in butanol and air-dried)			
15	5 g./130 cc.	24 121	25 38	145	16.56
		Machine Cut Commercial Rag Stock: S.R.P. No. 5** Rag - 710 cc. Freeness			
16	5 g./130 cc.	144	25	144	13.63
		Machine Cut Commercial Rag Stock: S.R.P. No. 5**			
17	5 g./130 cc.	24 120	25 38	144	15.04
		Machine Cut Commercial Rag Stock: S.R.P. No. 5**			
18	5 g./130 cc.	72***	25	72	14.03
19	5 g./130 cc.	72****	25	72	12.72

* Preparation consisted of steeping the pulp in pyridine overnight and breaking it up with a stirrer

** Source supply for all further cotton cellulose experiments

*** Pretreatment of 72 hours in pyridine at 4° C.

**** Pretreatment of 72 hours in water at 25° C.

TABLE II (continued)

EFFECT OF PRETREATMENT ON ACETYLATION

Standard Rag Used in Each Reaction as Raw Material

	Pretreatment	Period of acetylation hr.	Temperature ° C.	Acetyl content %
20	72 hours in pyridine at 38° C.	72	25	13.31
21	72 hours in pyridine at 4° C.	72	25	14.03
22	72 hours in methanol at 25° C.	72	25	13.65
23	72 hours in ethanol at 25° C.	72	25	13.64
24	72 hours in 50 per cent butanol and 50 per cent ethanol at 25° C.	72	25	13.87
25	72 hours in water at 25° C.	72	25	12.72

On the other hand, the commercial rag stock (Experiments 9 and 10) acetylated more easily, the acetyl content being 10.98 per cent after twenty-six hours and 15.75 per cent after 168 hours (which corresponds to 23.4 per cent of the hydroxyl groups covered).

Hess and Ljubitsch (52) found that acetylation with temperatures higher than room temperature increased the rate of substitution but that little was gained when 50° C. was exceeded. In Experiment 14, with hand-cut rag stock, the temperature of acetylation, after the first twenty-four hours, was increased to 35° C. with the result that an acetyl content of 14.62 per cent was obtained, an appreciable increase over that in comparable experiments conducted at room temperature. The same was shown to be true with beater cut rag stock in Experiments 16 and 17.

In all acetylations, the reaction quickly reached a point where further introduction of acetyl groups proceeded very slowly. Considering the law of mass action, this might have been caused by the consumption of acetylation mixture to the extent that further reaction was greatly retarded. To show that this was not the case, however, two simultaneous acetylations were conducted (Experiments 11 and 12), in which the ratio of reacting mixture to pulp in one was double that in the other—i.e., the usual ratio. No more acetyl groups could be introduced by this procedure than by the customary method as described.

Taniguchi and Sakurada (70) have pointed out that a pretreatment of the pulp with organic solvents will increase the rate of

acetylation. These authors found methanol particularly effective. Experiment 15, which was simultaneous with Experiment 14, showed that bleached sulfite pulp gave the highest acetylation rate of any experiments which were tried. However, this pulp had been treated previously with butanol. To show whether it was this alcohol which caused the more efficient reaction and in consideration of the work of Taniguchi and Sakurada, a series of pretreatments with subsequent acetylation of the beater-cut rag stock (Experiments 19 to 25) were carried out, using alcohols, pyridine, water, and mixtures of alcohols.

After an acetylation time of seventy-two hours, no advantage was observed in any of the pretreatments of the cellulosic material. The experiment involving treatment with water before displacing it with pyridine showed the slowest reaction, contrary to expectation, since water should be a better swelling agent than the alcohols. On the other hand, Wilson and Hughes (71) have found that the acetylation reaction proceeded most rapidly when the water present in the pyridine was between 0.3 and 0.6 per cent. It is likely that in those pretreatment experiments in which the cellulosic material was air-dry, the final water content in the pyridine located within the micellar system amounted to just this favorable percentage. However, in case water was used for pretreatment, the final water content was, no doubt, considerably above this point.

The factor which had the greatest effect on the rate of acetylation was the type of cotton and its physical state. The linters showed greater resistance to acetylation than rag stock and seemed to

approach the saturation point quickly even after only eight hours of reaction (Experiments 1 to 6). Hand-cut rag stock, although more reactive than linters, was more resistant than the beater-cut rag stock. However, the difference was greater during the first hours of the reaction, indicating the contrast in exposed external surface. After 144 hours, the acetyl content was almost the same with both materials (Experiments 14 and 17). This is in contrast to the linters, which approached a limit of 11 per cent acetyl content regardless of the acetylation time.

In summarizing, it may be stated that the acetic anhydride-pyridine method of acetylation introduces a certain amount of acetyl into the fibrous cellulose even though preswelling in a mercerizing concentration of sodium hydroxide is omitted from the procedure. The reaction is slow but carrying out the operation at 35 to 40° C. increases the rate somewhat. Pretreatments with alcohols and organic solvents appeared to give little or no advantage. Commercial rag stock was more readily acetylated than linters and seemed to have a higher saturation point for the amount of acetyl groups that could be introduced.

Therefore, rag stock, which had been selected for beating experiments, was also the most satisfactory for acetylation purpose.

STUDY OF BEATING IN A MINIATURE BEATER

The usual method for evaluating a pulp is to beat it in water and prepare handsheets which subsequently are evaluated for

physical strength. So-called "hydration" is estimated from the time required for water to drain from the pulp after a predetermined period of beating.

On the other hand, the strength properties of a paper sheet are very complex and fundamental rules of stress and strain are difficult to apply. However, since this investigation is concerned primarily with strength in paper, it seems appropriate that the measurement of bonding should be accomplished by preparing and testing handsheets rather than by attempting to develop a method for measuring the bonding strength between individual fibers or a small group of fibers.

As mentioned in the historical review, the bonding between fibers accounts for part of the sheet strength; in addition, the strength of the individual fibers is also a factor. Of the many possible physical tests available, tensile strength seems to be the most applicable and the most easily interpreted. Three primary factors contribute to this property: (1) the bonding between the fibers; (2) the strength of the individual fibers; and (3) the alignment and felting of the fibers. When the bonding between fibers is less than the tensile strength of the individual fibers, the interface is the point of rupture or, in other words, a slippage of the fiber surfaces occurs; when the bonding strength approaches that of the fibers, failure occurs within the fibers, as well as between the bonding surfaces. Gradations of these two factors occur simultaneously.

Except in the case of highly degraded or beaten pulps, the strength of the fiber as compared with that of a paper sheet is

extremely high. Mark (72) calculated the strength of the bonds in a cellulose fiber to be 800 kg. per square mm. for a longitudinal linkage due to principal valency bonds as compared with 200 kg. per square mm. for transverse linkage due to secondary valency bonds. Berg (73) has tested the tensile strength of individual fibers during beating and has found that the range is from 6650 to 26800 lb./sq. in. as compared with 6000 lb./sq. in. for a well-bonded sheet of paper (by beating).

The method of sheet preparation is an important factor affecting strength tests. Doughty and Curran (74) have shown from a comparison of five standard types of sheet machines that the differences in strength of the sheets prepared on these machines are very small but that the procedures of pressing and drying are critical. Doughty showed earlier (32) that the tensile strength of a paper sheet was a function of the "solid fraction" (ratio of volume of solid fiber in a sheet to volume of the sheet), even though different methods (beating, wet pressing) of obtaining this were used. The fiber length (75) was found to have little influence on the tensile strength at any given solid fraction; the main contribution of fiber length was the effect on shrinkage and subsequent increase of solid fraction.

Simmonds and Baird (76) in their study of processing to develop strength, found that the maximum bursting strength was obtained in a mill using rubber-covered lead balls, as compared with a pebble mill or laboratory beater. Larocque (77) has developed a "microbeater" for processing small amounts (1 to 2 grams) of pulp on

the principle of a single-rod mill; he showed that this compares well with the action of the laboratory beater.

Thus, the mechanical treatment of pulps could be carried out in either of these pieces of equipment. More important is the pressing procedure and the maintenance of a constant solid fraction. For a satisfactory comparison between the original celluloses and their derivatives, the pulp should be formed into handsheets--first, in the unbeaten condition and then, after milling for a predetermined period. By pressure methods, in consideration of Doughty's work, a series of sheets of increasing apparent densities should be prepared to obtain the range available from beating and subsequently should be tested for tensile strength and other characteristics.

Excellent discussions of the evaluation of pulps have been presented by Harrison (33), MacGregor (46), Doughty (32, 74, 75, 78), Simmonds and Baird (76), and Cottrall (50), so that further treatment will not be included here.

On account of the time and expense involved in preparing the acetylated materials and because of the waste involved in using common laboratory equipment (beater and pebble mill), a special beating device was designed and constructed for processing small amounts of pulp (10 to 25 grams), using as a pattern the equipment which has been described by Larocque (77).

The "miniature beater" used in the present investigation is a simplified rod mill utilizing but a single rod. This is enclosed in

a rotating chamber that contains the pulp to be processed and is motivated by two rotating shafts on which the flanges of the beater rest (see Fig. 1).

The outer chamber of the beater is a 6-inch extra strong pipe with round machined flanges on each end to engage the driving shafts. The ends are closed water-tight with blind flanges employing rubber gaskets.

The rod consists of a 4-inch standard pipe with a machined plug welded into each end. Its weight may be varied by changing the number of lead shot inside. This is possible through a water-tight plug in one end.

The entire beater is made of Misco-"C" stainless steel.

The above apparatus was converted into a ball mill simply by replacing the beater rod with rubber-covered lead balls.

Experiments with the Stainless Steel Beater Roll

The operation of the miniature beater required a few modifications as indicated from preliminary experiments which were conducted. The original speed of 39 r.p.m., it was found, permitted the suspended stock to rest behind the beater roll instead of flowing over it. By changing the driving pulley from 8 to 12 inches, the speed was increased to 60 r.p.m. and the above difficulty was no longer evident.

At first the driving wheel on the rotating shafts were covered with friction tape to prevent slipping and to reduce noise and



Miniature Heater

and vibration. However, this tape would wear off in a short time and frequently would slip into knots during the run causing the beater roll to bump. Finally, rubber floor matting with the treads running parallel to the shafts was used to cover these driving wheels, which material when successfully adhered to the metal gave a satisfactory surface for operation.

As mentioned in the description of the apparatus, the beater roll is filled with lead shot which can be varied at will through a plug in one end. During the series of experiments, the total weight of the roll was changed from 49.2 pounds (completely filled with shot) to 35 and to 30 pounds.

The standard procedure adopted for beater runs was as follows: The 12 to 24 grams of pulp to be processed were defibered in the British disintegrator for 12,500 revolutions in one liter of water; this slush pulp was diluted to about 1550 cc., mixed by hand, and washed into the beater with a measured amount of water to give the desired consistency. The most satisfactory results were obtained when the total volume in the beater was 2000 cc. The end flange was bolted on tightly and the beater was placed on the driving wheels of the machine (see Fig. 1). After the allotted beating time, the pulp was removed from the cylinder by hand, returned to the British disintegrator to break up the clumps and balls of fiber which formed (usually stirring for 2500 revolutions except as noted in the results when a longer time was given) and, subsequently, diluted to 6 liters from which a freeness sample was taken. The remaining stock was diluted to about 0.15 per cent

consistency and formed into handsheets according to TAPPI standard method T 205 m-40.

When the wet pressure was to be increased above that of 50 lb./sq. in. as required in the TAPPI standard method, the handsheets, having been couched onto the blotters, were stacked in a hydraulic press capable of exerting a total pressure of 30 tons or another press capable of 130 tons. Metal plates were inserted as in the TAPPI standard method and a total pressing time of five minutes was given. The second pressing was continued in the standard press of the British sheet machine using 50 lb./sq. in. for two minutes.

The results of the miniature beater runs with bleached sulfite (sul.) and standard rag stock (S.R.P.), in which the consistency, charge, and the weight of the beater roll were varied, are summarized in Table III.

Experiments with Rubber-covered Lead Balls

The miniature beater was converted into a ball mill by substituting rubber-covered lead balls for the stainless steel beater roll. Two sizes were used: a ball 1.5 in. in diameter and one 1.75 in. The weight of the balls for a run was 14 pounds of each size or a total of 28 pounds.

The standard procedure adopted duplicated that using the steel roll except that the stock had to be washed from the balls at the end of a run. Consequently, less total volume of water was used

TABLE III

SUMMARY OF MINIATURE BEATER RUNS

No.	Pulp	Consistency %	Beating time min.	Freeness cc.	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Wet pressure lb./in.^{2}
1	Sul.	0.80	90	860	3.8	12.20	65.7	38.9	——	——	50
2	Sul.	0.30	33.3	855	——	——	——	——	——	——	——
3	Sul.	0.60	33.3	870	——	——	——	——	——	——	——
4	Sul.	1.20	33.3	845	4.0	12.00	67.6	34.8	2.700	——	50
5	Sul.	1.20	126	845	——	——	——	——	——	——	——
6	Sul.	1.20	430	700	3.4	13.93	62.8	67.5	1.158	28.3	50
7	S.R.P.	1.00	100	670	4.0	10.90	77.6	36.2	3.044	——	50
	S.R.P.	1.00	100	670	3.5	12.20	73.8	41.8	3.218	——	130
8	S.R.P.	0.90	100	700	——	——	——	——	——	——	——
9	S.R.P.	0.70	90	715	——	——	——	——	——	——	——
10	S.R.P.	0.70	150	675	4.4	10.10	78.0	32.7	3.350	——	50
11*	S.R.P.	——	——	755	5.4	8.2	81.4	26.6	3.560	——	50
12	S.R.P.	1.00	300	625	4.3	11.00	78.0	38.2	2.921	——	50
13	S.R.P.	1.00	510	525	4.0	11.58	78.1	35.6	2.590	——	50
14	S.R.P.	1.20	780	410	3.9	11.81	79.4	30.3	1.506	16.25	50

* In British disintegrater for 12,500 revolutions

TABLE III (continued)

SUMMARY OF MINIATURE BEATER RUNS

No.	Pulp	Consistency %	Beating time min.	Freeness cc.	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Wet pressure lb./in.^{2}
						Miniature beater run of Standard Rag - 1.0% consistency; 45.2 lb. roll					
			0	755	5.4	8.20	81.4	26.6	3.560	——	50
			100	670	4.0	10.90	77.6	36.2	3.044	——	50
			300	625	4.3	11.00	78.0	38.2	2.921	——	50
			510	525	4.0	11.58	78.1	35.6	2.590	——	50
						Beater roll weight of 35.0 pounds					
15	S.R.P.	1.00	600	500	4.2	11.03	79.2	43.1	2.590	17.90	50
16*	S.R.P.	1.00	885	455	4.0	11.57	78.9	43.2	2.670	17.65	50
17	S.R.P.	1.00	615	540	3.9	11.33	78.3	40.2	2.828	17.35	50
18	S.R.P.	1.00	315**	510	4.2	11.10	79.1	46.3	3.120	17.30	50
19	S.R.P.	1.25+	720	365	3.9	11.77	78.8	37.0	1.861	16.74	50
20	S.R.P.	1.25+	360++	430	4.0	11.78	78.2	46.2	2.536	17.82	50
	S.R.P.	1.25+	360++	430	3.4	13.65	75.3	50.6	2.402	——	1610
21†	S.R.P.	——	——	490	5.1	9.44	82.7	49.8	3.662	13.95	50
						Beater roll of 30.0 pounds					
22	S.R.P.	1.00	720	505	3.9	11.32	78.1	44.2	2.718	17.62	50
23	S.R.P.	1.00	360++	515	4.2	11.12	78.5	54.4	3.310	17.21	50

* The friction type around the wheels of the driving shaft became loose and caused the beater to bump

** An additional deflibering in the British disintegrater for 75,000 revolutions after beating

\+ Although the consistency was 1.25%, the charge was but 20.0 grams; volume = 1600 cc.

++ An additional deflibering in the British disintegrater for 150,000 revolutions after beating

† In British disintegrator for 12,500 revolutions

TABLE III (continued)

SUMMARY OF MINIATURE BEATER RUNS

No.	Pulp	Consistency %	Beating time min.	Freeness cc.	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Wet pressure lb./in.^{2}
			Standard beater run on commercial bleached sulfite								
			5	660	4.6	10.71	74.8	——	2.331	10.44	50
			20	800	3.8	12.48	68.8	——	2.291	21.88	50
			35	640	3.5	13.63	65.7	——	1.509	30.21	50
			50	435	3.4	14.05	63.2	——	1.338	31.18	50
			65	305	3.3	14.45	60.7	——	1.140	32.90	50
			Standard beater run on standard rag stock								
			5	730	5.1	8.66	79.2	32.3	3.438	9.74	50
			25	600	4.7	9.91	79.6	49.1	3.374	15.22	50
			45	450	4.6	9.94	77.7	61.7	3.700	18.14	50
			65	260	4.5	10.45	79.2	68.7	3.735	20.79	50
			Ball mill run on standard rag stock								
		B.D.	0	755	5.4	8.2	81.4	26.6	3.560	——	50
		1.00	98	650	5.1	9.61	——	48.4	3.645	14.05	50
		1.25	120	575	4.5	10.31	——	54.7	3.351	16.80	50
		1.25	180	520	4.5	10.40	——	50.4	3.670	17.20	50
		1.25	270	425	4.6	10.65	83.4	51.1	3.798	18.00	50
		1.25	370	355	4.2	10.45	80.3	62.7	3.300	19.98	50

in beating: 20 grams of stock were slushed into 1600 cc. of water. Four hundred cc. of water added in washing brought up the total volume to 2000 cc., the same as for the runs with the stainless steel roll. Otherwise, the procedure followed that previously outlined. The results are given in Table III.

Standard Beater Runs

Standard beater runs on the commercial bleached sulfite pulp and on the standard rag stock were conducted according to the TAPPI standard method T 200 m-40. The pulp was soaked in water for at least two hours before disintegrating which proceeded for fifteen minutes. Handsheet samples were taken at 15-minute intervals for the sulfite pulp and at 30-minute intervals for the rag stock. A weight of 4500 grams was used on the balanced bedplate in both cases. These results are also given in Table III.

Discussion of Results

From the results in Table III, it is seen that the miniature beater processes in a manner similar to that of the standard laboratory beater. For the bleached sulfite pulp, after determining (in Experiments 2, 3, and 4) that 1.20 per cent consistency with a 48.2-pound roll caused the greatest drop in freeness per period of beating, a miniature beater run of 430 minutes produced a tensile strength of 28.3 per cent at an apparent density of 13.93 and freeness of 700 cc. Comparing this with the standard beater (see Table IV) at thirty-five minutes processing, where the tensile strength is 30.2 per cent at a

freeness of 640 cc. and 13.63 apparent density, one notes a close agreement. However, the tear is lower for the miniature beater run, indicating that more cutting of the fibers occurs.

The processing of the rag stock was found to be more dependent upon consistency than the sulfite pulp and required a lighter roll to keep a high tear while the tensile was developed. An increase in bursting strength was more difficult to obtain than an increase in tensile strength. A tensile of 17.5 to 18.0 pounds per 100-pounds basis weight was reached readily with the stainless steel beater roll whether its weight was 46.2, 35, or 30 pounds. On the other hand, the maximum bursting strength that could be attained by the miniature beater alone was only 40 to 43 points per 100-pound basis weight, regardless of beating time or weight of roll.

TABLE IV

COMPARISON OF MINIATURE BEATER PROCESSING WITH THE PROCESSING IN A STANDARD LABORATORY BEATER

	Beating time min.	Freeness cc.	Apparent density	Tensile lb. per 100 lb.	Tear factor
		Bleached Sulfite Pulp			
Miniature beater	430	700	13.93	28.3	1.158
Standard beater	35	640	13.63	30.2	1.509
		Standard Rag Stock			
Miniature beater	300*	515	11.12	17.2	3.310
Standard beater	25	600	9.91	15.2	3.374

* Additional defibering: British disintegrator for 150,000 revolutions after beating in miniature beater

However, subsequent processing in the British disintegrator was found to increase the bursting strength, indicating that a whipping action, in addition to a crushing action, is necessary to develop strength.

Finally, by using a 30-pound roll and, after beating by whipping, in the British disintegrator for 150,000 revolutions, a bursting strength of 54.4 per cent, a tear factor of 3,310, and a tensile of 17.21 pounds per 100-pounds basis weight (see Experiment 23) were obtained, which compares favorably with the standard beater run at the same freeness (515 cc.).

The British disintegrator alone (for 375,000 revolutions) was capable of producing a bursting strength of 49.8 lb./sq. in. per 100-pounds basis weight but the tensile was low (13.95 pounds per 100-pounds basis weight), even though the freeness indicated a well hydrated stock.

When rubber-covered lead balls were used for processing, a greater bursting strength was obtained with a higher tear than by either of the above methods. After 370 minutes of processing, a bursting strength of 62.7 lb./sq. in. per 100-pounds basis weight and a tensile of 19.98 pounds per 100-pounds basis weight were developed, which compared well with the beater run at a similar freeness.

Hence, from the above results, one concludes that the greatest strength can be developed in the miniature equipment by combining a limited crushing action of the miniature beater, using the stainless steel roll, with the whipping action of the British

disintegrator (as in Experiment 23), or by a ball-mill action using rubber-covered lead balls.

BEATING STUDIES OF ACETYLATED CELLULOSE PULPS

PREPARATION OF PULPS FROM RAG STOCK FOR STRENGTH STUDIES

Acetylation of Standard Rag Stock

Pulps of High Acetyl Content

According to the procedure described in the section on study of methods, the acetylations for an acetyl content of more than 9 per cent were carried out as before with the small test batches; however, in the present case 60 grams (on ovendry basis) of rag stock were used for the starting material and the acetylating reagents were increased proportionally to 600 cc. of acetic anhydride and 960 cc. of pyridine. The only pretreatment was to steep the air-dry stock in pyridine overnight.

Pulps of Low Acetyl Content

As was shown in the introductory experiments, the chemical reaction of acetylation with acetic anhydride-pyridine is one which proceeds rapidly at first but which slows down with the introduction of the groups, particularly after the surface molecules have been acetylated. To obtain greater homogeneity throughout the pulp, in a mechanical sense, with the products of lower acetyl content,

precautions were taken to see that the fibers were readily accessible to the acetylating mixture by complete suspension and vigorous agitation. Thus, instead of treating the air-dry fiber with pyridine as before, the rag stock was defibered in water with a quick stirring action, filtered, treated with pyridine to displace the water, and then acetylated.

For the acetylation in which thirty minute reaction time was given, the rotator was used for the agitation after the initial mixing with the reaction chemicals. For the acetylation of the relatively short reaction time of ten minutes, the rag stock and acetylating mixture were shaken continuously during the reaction by hand.

This method was expected to give a low acetyl content but in the pulp acetylated for thirty minutes an acetyl content of 5.11 per cent was obtained. Possible reasons for this behavior will be given later.

Acetylation of Highly Beaten Rag Stock

A portion of the rag stock from the standard beater run (described in the studies of beating), which had been processed sixty-five minutes and tested for a freeness of 260 cc., was filtered to about 18 per cent dry on a Büchner funnel. Approximately 50 grams (ovendry basis) had been taken. The precaution, necessary to prevent a "horny" formation, required that the pulp at no time be permitted to dry out; hence, the water in the slush pulp was displaced by pyridine.

To do so, the filtered rag stock was placed in a ground glass-stoppered two-liter bottle, covered with wet pyridine, and mixed well by manual shaking and rolling. After soaking overnight, the wet pyridine was filtered off and fresh pyridine added. This was repeated twice more to remove almost all the water. Mathematically about 50 per cent was removed with each treatment so that less than 3 per cent water remained.

The final filtered pulp, moist with pyridine, had a weight of 277 grams. Sixty per cent or 166.2 grams were acetylated with 350 cc. of acetic anhydride and 560 cc. of pyridine. The remainder of the pulp was covered with pyridine and carried through the operations with the other for control. According to the usual procedure, the charges were rotated at room temperature for twenty-four hours; subsequent reaction was conducted at 39° C. for forty-eight hours to give a total acetylation time for seventy-two hours.

When the reaction period was completed, the rag stocks were filtered, washed first with pyridine to remove the acetylating mixture, then with 50 per cent ethanol, and finally with distilled water until no odor of the organic solvents could be detected. Instead of drying, the moist rag stocks (about 15 per cent ovendry) were placed in a ground stoppered two-liter bottle and kept sealed. Thus, as intended, the beaten stock was not permitted to form hard clumps or to become horny through drying. An acetyl content of 14.20 per cent was obtained.

Saponification of Acetylated Rag Stock Beaten to a Low Freeness

The saponification of acetyl cellulose* with alkali can be conducted in such a manner that little or no degradation occurs, provided oxygen is excluded during the reaction (see Staudinger and coworkers (79-81)). In addition to eliminating degradation of chain length, dehydration of the fibers had to be guarded against, since considerable strength is known to be lost when nearly all the water is removed from cellulose either by drying or by dehydrating agents as alcohol (82). Hence, such a method as that of Zemplén (83), which utilizes a mild treatment with little sodium dissolved in absolute alcohol, is not suitable for saponification in the present case.

On the other hand, Sakurada and Tukahara (84) found that acetyl cellulose was readily saponified in 0.2 N alcoholic or aqueous potassium hydroxide at 30° C. within two hours. The method of determining acetyl content of the Eastman Kodak Laboratories (69), previously mentioned and employed in this thesis, uses 0.25 N sodium hydroxide in a 50 per cent alcoholic solution, first at a temperature of 50 to 60° C. for fifteen minutes, and then at room temperature for twenty-four to forty-eight hours. The water which is present in the 50 per cent alcohol inhibits the dehydration of the cellulose. For the requisites of saponification mentioned above, this last method seemed most suitable, provided the initial, high temperatures were eliminated and oxygen was excluded. A longer period of saponification was to be employed to compensate for carrying out the reaction at room

---

* The terms acetyl cellulose, cellulose acetate, and acetylated cellulose will be used interchangeably in the following discussion.

temperature. The modified method was as follows: The unused paper and clippings from the physical tests on the handsheets of acetylated rag stock, which had been beaten previously to 260 cc. freeness, were saponified under nitrogen atmosphere to regenerate the original cellulose pulp without degradation. The equipment consisted of a one-liter three-necked round-bottom flask into which were connected, respectively, a separatory funnel, a drain-off line for washing purposes, and a line to the nitrogen and vacuum which could be reversed by a three-way stopcock.

The saponifying mixture for 11.2 grams of acetylated cellulose consisted of: (1) 200 cc. of sodium hydroxide, (2) 250 cc. of 95 per cent ethanol, (3) 50 cc. of distilled water, and (4) 25 cc. of 95 per cent ethanol for wash purposes.

The order of procedure was as follows: After the paper clippings had been placed into the bottom of the flask, the rubber stoppers of the lines and funnel were inserted and sealed with a film of cellulose acetate. The apparatus and pulp were washed free of air by alternately evacuating and filling the vessel ten times with oxygen-free nitrogen.* The saponifying mixture was added through the separatory funnel by maintaining sufficient vacuum in the flask to pull in the liquid. The level in the separatory funnel was drawn down to about 5 cc. The sides of the funnel were rinsed with the 25 cc. of ethanol and the liquor was drawn down to about 5 cc. again. The

---

* The apparatus employed in molecular weight determinations according to Orem (to be described later) was used to supply the oxygen-free nitrogen.

pressure in the flask was brought back with nitrogen gas until a slight excess over atmospheric pressure (about 2 mm. of mercury) existed to prevent the infiltration of air at any possible leaks.

After a 65-hour period of saponification, the liquor and residual alkali were drawn off by a slight vacuum, carefully replacing this volume with nitrogen. A 20 per cent alcohol solution of 500 cc. was added to the pulp residue in the flask; the mixture was then shaken, allowed to stand with the regenerated pulp for a few minutes, and drained off as above. This operation was repeated twice more with distilled water, the latter time adding a few drops of phenolphthalein to the wash water. A pink color appeared, indicating that some alkali was still present. The liquor was drawn off and fresh water added (plus phenolphthalein) which gave but a very faint pink color. Half of this liquid was removed and the remainder neutralized with 1 per cent acetic acid solution until the pink phenolphthalein color was removed and a slight excess of acid was present. After standing a few minutes, the above liquid was drained off; freshly distilled water was added to cover the pulp, and the mixture was allowed to stand for a half hour.

The entire procedure was conducted under oxygen-free nitrogen until the final addition of distilled water.

The wet pulp was processed immediately with one liter of tap water in the British disintegrater for 12,500 revolutions. Handsheets were prepared according to the TAPPI standard method T 205 m-40.

Data and Discussion of Results

In Table V, the rag stocks which were prepared according to the above procedures are listed with their acetyl contents. A supply of 40 grams or more of each was available for strength evaluations. Also included in the table are those control samples in which the pulp was steeped in pyridine only, as indicated.

In Pulp 2, a higher acetyl content was obtained than was expected from the allotted time of reaction. The increased rate of reaction may have been caused by higher temperature maintained by the exothermic reaction with residual water present (which did not appear in previous reactions) or may have been due to the defibering of the pulp in water before acetylating which, in addition to providing a more homogeneous suspension, may have produced a more reactive surface for the acetylation.

The acetylation reaction greatly slows up after 11 days and appears to be approaching 27 per cent acetyl content as an upper limit, which corresponds to covering very nearly half of the total hydroxyl groups present in the cellulose. It is interesting to note the coincidence that Mark and Meyer (85) have calculated the number of hydroxyl groups present on the outside of the micelle surfaces to be 50 per cent of the total reactive groups present. Also, Hess (86) found that no change in x-ray diagram occurred until 47.7 per cent of the hydroxyl groups were covered by acetyl groups; this corresponds to an acetyl content of 27.9 per cent.

TABLE V

ACETYLATIONS OF RAG PULPS

Pretreatment	Periods of acetylation	Temperature ° C.	Total reaction time	Acetyl content %
		Standard Rag Stock		
(1) Broken up in water; filtered; steeped twice in pyridine	10 min.	25	10 min.	4.25
(2) Broken up in water; filtered; steeped overnight in pyridine	30 min.	exothermic reaction 25+	30 min.	8.12
(3) Air-dry stock steeped overnight in pyridine; broken up by mixer	60 min.	25	60 min.	6.18
(4) As in 3	5 hr.	25	5 hr.	9.22
(5) As in 3	24 hr. 10 days	25 39	11 days	20.05
(6) As in 3	24 hr. 20 days	25 39	21 days	22.52
(7) As in 3	24 hr. 23 days	25 39	24 days	23.35
(8) As in 3	24 hr. 30 days	25 39	31 days	25.00
(9) As in 3	24 hr. 30 days 59 days	25 39 25	90 days	26.46
(10) As in 3	48 hr. in pyridine only	25	48 hr.	none

The average room temperature was considered to be 25° C. which is the value reported for all acetylations carried out at room temperature.

TABLE V (continued)

ACETYLATIONS OF RAG PULPS

Pretreatment	Periods of acetylation	Temperature ° C.	Total reaction time	Acetyl content %
Rag Stock Beaten in Laboratory Beater (260 cc. Freeness)				
(11) Water displaced with pyridine	24 hr.	25		
	24 hr.	39	72 hr.	14.20
(12) Same as for 11	24 hr.	25		
	48 hr.	39	72 hr.	
	in pyridine only		72 hr.	none
(13) Number 11 after saponification	------	--	------	0.00

One may speculate that under the conditions applied no more acetyl groups can be introduced into the cellulosic material than those which would cover the surface hydroxyl groups of the micelles provided that a preswelling of the micelles (for example, by alkali mercerization) has not taken place, and that degradation of the molecular chains is inhibited.

THE EFFECT OF ACETYLATION ON MOLECULAR WEIGHT, TENSILE STRENGTH, HYGROSCOPICITY, AND SURFACE CONDITIONS OF THE FIBERS

It is conceivable that any losses in sheet strength which would be observed after acetylating a pulp may be due to other possible causes that could occur simultaneously as the hydroxyl groups of the cellulose were replaced with acetyl groups rather than to a

covering of the hydroxyl groups. These possibilities are: (1) a reduction of the strength of the individual fibers because of degradation affecting the molecular weight of the cellulose chains; (2) a reduction in tensile strength of the fibers when the hydroxyl groups are covered because the bonds between chains are greatly reduced and slippage of the molecules takes place; (3) a reduction of fiber surface activity due to the possible influence of organic solvents employed in the acetylation and washing which, in themselves, would cause an appreciable loss in sheet strength.

To investigate these other possibilities, the molecular weight before and after acetylation was determined; the tensile strength of individual acetylated fibers was measured and compared with that of the original fibers; a blank pulp was carried through "acetylation" without acetic anhydride; that is, all the procedures involved and subjected to solvent treatments (see Experiment 10 of Table V) and evaluated. Finally, an acetylated rag stock was regenerated to the original cellulose pulp by saponifying off the acetyl groups and restoring the hydroxyl groups; the reclaimed pulp was compared with the acetylated pulp and with the original pulp for strength properties and other characteristics (see Pulps 11, 12, and 13 in Table V). These experiments will be described in detail below.

Effect of Acetylation on the Molecular Weight of the Cellulose

The molecular weights of the cellulose samples were determined according to the method of Staudinger (57), in which the material is

dissolved in Schweizer's reagent (cuprammonium solution) and the viscosity of the solution measured. All operations were conducted in nitrogen atmosphere. In order to carry this out, special equipment which permitted transfer of the solution from the dissolver to the viscosity capillary without introducing oxygen to the system was necessary; such an apparatus has been designed and constructed by Dr. J. W. Green of this laboratory and represents a modification of the apparatus used by Lettermoser and Waltsch (55). A description of this apparatus is to be published elsewhere.

In determining the viscosity of the cellulosic materials in cuprammonium solution, it is necessary that complete dispersion be obtained; hence, the change of viscosity with time must be measured in order to ascertain the maximum value. Once the required period for complete dispersion has been found (by following the change of molecular weight with time), the viscosity should be evaluated at approximately that time and possibly checked eight or ten hours later to see if any change has taken place.

Furthermore, to minimize association of the molecular cellulose, the concentration of the cellulosic material had to be very low; thus, solutions of less than 0.03 per cent or 0.00185 gram/162 (here, 162 is gram weight of the anhydro-glucose unit; the expression grams/162 is called, though somewhat erroneously, gram moles in the literature) per liter were prepared in this case. The samples were air-dry but of known moisture content; the results were based on ovendry cellulose. For the acetylated materials, the samples were calculated back to the

TABLE VI

EFFECT OF ACETYLATION ON MOLECULAR WEIGHT OF RAG CELLULOSE

Material	Dispersion time hr.	Concentration $C = \frac{g/l}{162}$	Specific viscosity η_{sp}	$\frac{\eta_{sp}}{C}$	Molecular weight	D.P.*
1. Standard rag cellulose steeped in (a) pyridine 45 hours	22	0.00128	0.1280	100.0	200,000	1235
	42	0.00128	0.1496	117.0	234.000	1444
	66	0.00128	0.1500	117.0	234,000	1444
2. Standard rag cellulose (a)	100	0.00137	0.1590	116.0	233,000	1437
	150	0.00137	0.1592	116.3	233,000	1438
(b)	78	0.00104	0.1148	110.4	221,000	1364
3. Acetylated rag cellulose Ac = 9.22% (a)	90	0.00141	0.1492	105.9	212,000	1309
	97	0.00141	0.1484	105.3	211,000	1302
(b)	92**	0.00137	0.1605	117.2	234,000**	1444
	115	0.00137	0.1401	102.3	205,000	1261
4. Acetylated rag cellulose Ac = 25.00% (a)	114	0.00150	0.1591	106.1	212,000	1309
(b)	108	0.00171	0.1850	108.5	217,000	1340

* Degree of polymerization

** In this determination, the capillary had been clogged with mercury which was cleaned out with nitric acid for the next run; hence, this value is probably too high.

original cellulose present, since complete saponification occurs in the alkaline cuprammonium solution (see Staudinger and Daumiller (54)).

The results of the molecular weight determinations are summarized in Table VI. These values indicate clearly that no appreciable degradation of the cellulose occurs from acetylation by the acetic anhydride-pyridine method. The maximum drop after 31 days of acetylation (25.00 per cent acetyl cellulose)* was less than 6 per cent, which is almost within the allowable experimental error. Staudinger and Jurisch (53) have shown that negligible loss in strength for native cellulose, degraded by acid hydrolysis, occurs with a change in degree of polymerization above a molecular weight of 160,000 which means that, in this sense, little loss might be expected from the acetylated fiber. This assumption was confirmed in experiments to be discussed in the next section where the tensile strength for the acetylated fibers was found to be unchanged by the acetylating reaction.

Effect of Acetylation on the Strength of Individual Cotton Fibers

Lower strength properties in handsheets of acetyl cellulose fibers, as compared with those of the original cellulose, may be questioned on the grounds that acetylation has reduced the tensile strength of the individual fibers to such an extent that failure is due to fiber rupture for the most part and not to the rupture of bonding between fibers. Since it is the latter feature which is of particular interest, the above premise had to be substantiated experimentally.

---

* "Per cent acetyl cellulose" is equivalent to acetylated cellulose of "per cent acetyl content."

As already mentioned, Sakurada (58) found that acetylation did not impair the tensile strength of fibrous cellulose acetate. However, his method of acetylation was not the one employed in this investigation. Therefore, it seemed advisable to ascertain the effect of the acetic anhydride-pyridine method of acetylation on the tensile strength of the individual fibers.

Ideally, it would have been desirable to have determined the tensile strengths of the rag stock from which the handsheets were prepared. However, because these fibers were too short to be placed in the tensile tester with any facility or assurance of accuracy, raw cotton of long seed hairs was utilized for this purpose. Preparation and testing of the materials are described below.

Preparation of Bleached Cotton Fibers

Raw crude cotton fibers, obtained through the courtesy of Mr. Thomas Kerr of the North Carolina State College, Raleigh, North Carolina,* were separated by hand from the seed hulls and leaves which were still present. To remove the fats and waxes, the above fibers were extracted in batch lots in a Soxhlet extractor with ethanol for at least twenty-four hours.

The method of bleaching was a careful quick bleach in a slightly alkaline medium. The agent was "Chlorox," a commercial

* Upland cotton, Mexican variety, grown at Statesville, N. C. in 1938. "The cotton was picked a relatively short time after opening and no rain fell in the interim; therefore, any degradation should be a minimum."

preparation of sodium hypochlorite on the alkaline side. Sufficient amount of this liquor to make a 1.0 per cent sodium hypochlorite bleach (3.5 per cent chlorine on the ovendry cellulose) was diluted to 400 cc. and added to the raw cotton fibers. The mixture was shaken vigorously for ten minutes, agitated on the rotator for fifteen minutes, and finally shaken by hand for five minutes more. The pulpy mass was filtered on a Büchner funnel, and the filtrate was titrated to determine the residual caustic (0.132 per cent) to be sure that the bleaching continued in an alkaline medium to the end; the pH was above 8.4 from phenolphthalein end point. After the reaction, considerable excess of chlorine remained in the solution, which quickly turned starch-iodide paper a deep bluish purple.

After the liquor had been filtered off, the cotton fibers were suspended immediately in distilled water, agitated for a few minutes and again filtered. This process was repeated; then the fibers were suspended in 400 cc. of 0.5 per cent acetic acid for fifteen minutes to remove any retained sodium hydroxide, and filtered. After two more suspensions in distilled water to remove all the acid, the acid-free fibers (to litmus and odor) were suspended in ethanol and filtered. Finally, acetone was used to remove the alcohol and the residual water.

The traces of acetone were removed from the filtered fibers, first in a vacuum desiccator and then by blowing dry air through the fluffed cotton until no odor of the solvent could be detected. The material thus treated was very white, similar to that found in commercial absorbent cotton.

Preparation of Acetylated Bleached Cotton Fibers

Two one-gram samples of the above bleached cotton fibers were carefully weighed out into 200 cc. ground-stoppered bottles and steeped in pyridine overnight. The excess pyridine was filtered off on a Büchner funnel; the fibers were returned to the bottles and 25 cc. of the Hess and Ljubitsch acetylating mixture were added to each. The bottles were placed on the rotator for agitation (at 60 r.p.m.). After forty-seven hours of acetylation, the first sample was removed from the rotator, filtered from the reaction mixture, and washed with pyridine, ethanol, and ether. When air-dried, the acetylated cotton was placed in the constant humidity room for tensile evaluation. The acetyl content was 9.43 per cent, which corresponds to 12.90 per cent of the hydroxyl groups covered.

The other sample was placed in the constant temperature bath at 39° C. for long period acetylation. After 37 days of reaction, it was removed, filtered, and washed as for the above sample. The acetyl content was 18.38 per cent, corresponding to 26.1 per cent of the hydroxyl groups covered.

Determination of Tensile Strength of Individual Cotton and Acetylated Cotton Fibers

The tensile strength of the three samples of cotton fibers (numbers 1, 2, and 3 of Table VII) were determined on the Saxl Tensile tester, an instrument for determining the tensile strength of individual fibers. At least 25 fibers were evaluated in each case to obtain a fair

TABLE VII

TENSILE STRENGTH OF INDIVIDUAL FIBERS

	Description	Initial length cm.	Length at break cm.	Tensile g.	No. tested
(x)	Kerr raw cotton-unbleached Saxl tester without rider	0.92	----	3.8	6
(y)	Crude cotton from Berry Saxl tester with rider	0.77	----	3.1	10
	Kerr raw cotton-bleached				
(1-a)	in R.H. room 1¼ hr.	1.14	----	3.7	10
(1-b)	in R.H. room 6¼ hr.	0.57	----	3.2	10
(1-c)	in R.H. room 2¼ days	0.57	0.63	5.0	10
(1-d)	in R.H. room 2 months	0.63	0.72	4.5	10
(1-e)	in R.H. room 3 months	0.63	0.69	4.7	8
(2-a)	Kerr raw cotton-bleached acetylated, Ac = 9.43%	0.60	0.68	4.9	25
	omitting four questionable values			5.4	21
(1-f)	Kerr raw cotton-bleached simultaneous with tests (2-a)	0.58	0.67	4.1	5
(2-b)	Kerr raw cotton-bleached acetylated, Ac = 9.43%	0.53	0.61	4.2	10
(3-a)	Kerr raw cotton-bleached acetylated, Ac = 15.38%	0.54	0.60	5.5	10
(3-b)		0.56	0.63	5.6	8
(3-c)		0.56	0.61	5.5	18
Summary of above evaluations:					
(1)	Kerr raw cotton-bleached, unacetylated	0.64	0.75	4.2	53
(2)	Kerr raw cotton-bleached, acetylated, Ac = 9.43%	0.57	0.65	4.6	35
(3)	Kerr raw cotton-bleached, acetylated, Ac = 15.38%	0.55	0.61	5.5	36

average. Natural fibers vary in size and strength so that a sufficiently large number must be tested. To obtain as representative a test as possible, the tensile strengths were evaluated on fibers from different portions of the cotton sample. Moreover, acetyl determinations were not carried out until the tensile strength had been evaluated. In this way, the fibers tested would be more representative of the entire lot rather than of a separate portion remaining after the chemical determination had been conducted. Furthermore, the acetyl content would also represent the portions from which samples for tensile strengths were selected.

Data and Discussion of Results

In Table VII, the results of the above tests are summarized. It will be noticed that the acetylation did not decrease the tensile strength of the fiber but apparently increased it, if anything. Therefore one can conclude that any loss in strength observed in handsheets of acetylated pulps as compared with the original pulps, will not be due to a reduction in tensile strength of the individual fibers.

Effect of Acetylation on Hygroscopicities of Prepared Pulps

The acetylation of cellulose has been shown to reduce its hygroscopicity (Sheppard (4g)). An attempt was made in the present investigation to show the effect of acetylation on the hygroscopicity of the pulps under consideration. For accurate measurement, careful control should be exercized to eliminate hysteresis effects and slight changes in relative humidity. However, these desirable conditions were

not available so that the values obtained can be considered only as indicating trends rather than as an exact measurement of hygroscopicity at any given acetyl content.

The method of procedure was as follows: The handsheets for strength evaluation, which had been conditioned in the constant humidity room at 65 per cent relative humidity and 70° F. according to Institute Method 503, were sampled for hygroscopicity measurements; the test strips were left in the controlled atmosphere for several days. The samples were then weighed, placed in weighing bottles, and dried in an Abderhalden at 55° C. over phosphorous pentoxide for three to four hours. The samples were weighed in the weighing bottles and quickly removed, after which the bottles were resealed and weighed to obtain their tare values. The percentage of moisture was based on the ovendry pulp present.

The results (see Table VIII) show that, as the acetyl groups are introduced, the hygroscopic moisture of the pulps is reduced, even when based on the original cellulose present instead of the weight of the acetylated cellulose. (See Appendix for calculations.)

EFFECT OF ACETYLATION ON PAPERMAKING PROPERTIES OF CELLULOSE FIBERS

As mentioned in the section on the Study of Beating, a satisfactory comparison between the native cellulose and the cellulose derivatives requires that the pulps should be formed into handsheets, first in the unbeaten condition, and then after milling for a predetermined period. By pressure methods, one can prepare a series of

TABLE VIII

HYGROSCOPICITIES OF PROCESSED ACETYLATED AND STANDARD RAG STOCKS

Acetyl content	Processing received	Moisture content %	Moisture content Based on cellulose present %
0	Miniature beater 615 min.	7.83	7.83
0	Miniature beater 885 min.	9.42	9.42
0	Miniature beater 300 min. + action in British disintegrator	8.96	8.96
0	British disintegrator 375,000 revolutions	8.97	8.97
4.25	Miniature beater standard run	8.00	8.32
6.15	Miniature beater standard run	8.22	8.73
8.12	Miniature beater standard run	7.81	8.54
9.22	British disintegrator, 12,500 revolutions	7.62	8.37
14.20	Beaten rag, acetylated, defibered in British disintegrator for 12,500 revolutions	6.11	7.10
20.05	Miniature beater standard run	5.16	6.36
23.35	Miniature beater standard run	5.26	6.93
25.00	British disintegrator, 12,500 revolutions	4.25	5.99
25.00	British disintegrator, using acetone, 12,500 revolutions	4.31	5.67

TABLE VIII (continued)

HYGROSCOPICITIES OF PROCESSED ACETYLATED AND STANDARD RAG STOCKS

Acetyl content	Processing received	Moisture content %	Moisture content Based on cellulose present %
	Rag Stock Beaten in Laboratory Beater Before Acetylation		
0	Pyridine steeped, in British disintegrator, 12,500 revolutions	5.76	5.76
14.20	British disintegrator, 12,500 revolutions	6.11	7.10
0	Saponified from 14.20% acetyl content; in British disintegrator, 12,500 revolutions	5.70	5.70

sheets of increasing apparent densities to simulate any further range which might be obtained by beating and to make possible comparisons of the handsheets at similar apparent densities.

Processing the Pulps in Water

Procedures for Processing Pulps of Acetylated Standard Rag Stock

Processing in the British Disintegrator. To obtain an initial strength value of unbeaten pulp, it was desired to find the original strength with a minimum of hydrating action. As was shown in the results of the Study of Beating, an appreciable strength can be developed in the British disintegrator alone after long continued agitation but without resorting to an actual beating device. However, defibering pulps for a short period of agitation should cause little

strength development and, for comparative purposes, standardization of the procedure should compensate for most of that difference.

Hence, the pulps were defibered in the British disintegrator for only 12,500 revolutions or approximately four minutes. This action was sufficient to break up any clumps and to give an even slush stock. Twelve to 14 grams of pulp (ovendry basis) were placed in the disintegrator cup with one liter of water to give a 1.2 per cent suspension. For acetylated pulps, sufficient acetylated material was used to give 14 grams of the original cellulose.

The pulps were evaluated for freeness on the Schopper-Riegler freeness tester, and handsheets were prepared on the British sheet machine. With the acetylated pulps, two sets were prepared: one according to TAPPI standard method T 205 m-40; the other, at a higher wet pressure of 1550 or 1800 lb./sq. in. for the first pressing in order to approximate the same apparent density in the dry sheet as that of the native cellulose pulps. Otherwise, the standard procedure was followed.

Processing in the Miniature Beater. From a consideration of the results of the experiments in the Study of Beating, the standard procedure adopted for processing pulps in the miniature beater was as follows. Twenty grams of pulp (ovendry basis; for acetylated pulps, calculated to the actual cellulose content) were defibered in the British disintegrator with one liter of water for 12,500 revolutions; the slushed pulp was diluted to 1600 cc., mixed well by hand, and

washed into the miniature beater with 400 cc. more water, bringing the total volume in the beater to 2000 cc. The end flange was bolted on tightly, and the beater was placed on the driving wheels of the machine. After 300 minutes of processing, the beater was opened; the stock was removed from the cylinder by hand without dilution and returned to the British disintegrator, where it was given a defibering and whipping action for 150,000 revolutions or about forty-eight minutes.

The completely processed pulp was diluted to a consistency of about 0.25 per cent, tested for consistency, and sampled for Schopper-Riegler freeness tests. The remaining stock was diluted to a consistency of approximately 0.20 per cent and formed into handsheets. Where possible, three sets were prepared: one, according to TAPPI standard method T 205 m-40 and two at higher initial wet pressures of 645 and 1500 lb./sq. in., respectively. Otherwise, the standard procedure was followed.

Testing of Handsheets. Handsheets were conditioned for six or more hours at 65 per cent relative humidity and 70° F. according to Institute Method 503 and tested for basis weight, caliper, bursting strength, tensile strength, and opacity, according to the corresponding Institute Methods 504, 506, 510, 511, 512, and 518. Since in many cases, the formation of the handsheets was very irregular and "wild," it was necessary to measure the immediate test sample for basis weight; calculations were based on a 24 by 40--500 ream size for the sample which was tested; hence, basis weights are not reported in the results.

Calculations of Results. In the results obtained, calculations have been made both for the observed strength values of the acetylated handsheets based on their actual weight and for the strength values based on the weight which the sheet would have if the increase in weight from the acetyl groups was subtracted to give the weight of the cellulose present. Details and samples of calculations are given in the Appendix.

Freeness determinations were carried out on a sample of the acetylated pulp which would give 2.00 grams of the original cellulose; therefore, the approximately same number of fibers were involved in each freeness test regardless of acetyl content.

Procedures for Processing Pulps Which Had Been Beaten Before Acetylation

The preparations of the rag stock, which had been beaten in a standard beater to a freeness of 260 cc., then acetylated to an acetyl content of 14.20 per cent, and finally saponified to the original cellulose, have been described in the Section on Pulp Preparations. The processing of these materials was limited to defibering in the British disintegrator for 12,500 revolutions. Handsheets were prepared according to TAPPI standard method T 205 m-36. With the acetylated pulp, one set of sheets was prepared with a wet pressure of 1610 lb./sq. in. in the first pressing for five minutes instead of the customary 50 lb./sq. in.; otherwise the standard procedure was followed. The method of testing the handsheets was the same as that for those processed in the miniature beater.

Data and Discussion of Results for Processing in Water

From the data listed in Table IX, it is seen that, in general, replacing the hydroxyl groups of the cellulose in a pulp with acetyl groups, increases its resistance to beating and reduces the bonding between fibers in a sheet of paper. In attempting to process an acetylated pulp, it was found that even the introduction of a small amount of acetyl groups, such as 4 or 6 per cent, reduced the tendency for water to wet the surface. With higher acetyl contents, the repulsion of water was more noticeable. While attempting to defiber the 20 or 25 per cent acetyl cellulose in the British disintegrator, the pulp was found to float on the surface because the entrained air was not readily displaced by the water. However, defibering could be accomplished after stirring for the allotted 12,500 revolutions; even then, a few scattered clumps remained in the pulp and could be observed in the finished handsheets.

A phenomenon, that was particularly noticeable with the acetylated stocks during the formation of handsheets, was the persistent tendency of the fibers to flocculate and clump together. This condition was observed for both the beaten and unbeaten stock, although much more manifest in the former. In fact, with the pulp of 25 per cent acetyl content processed in the British disintegrator, the flocculation was sufficiently prevalent to prevent sheet formation; part of the handsheet would be heavy, whereas other parts would be completely without fiber. Beating greatly reduced this tendency to flocculate (even in the 25 per cent acetyl cellulose) but a slight clumping was still evident.

TABLE IX

SUMMARY OF PROCESSING OF STOCK IN BRITISH DISINTEGRATOR IN WATER MEDIUM

Acetyl content	Freeness	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Stretch %	Wet pressure lb./in.^{2}
				Observed Strength Values					
Original-1	755	5.4	8.20	81.4	26.6	3.560	—	—	50
pulp 2	775	6.0	7.83	84.5	27.9	3.154	7.0	2.8	50
Pyridine steeped	770	5.6	8.34	83.8	25.8	3.199	6.9	—	50
4.25	775	7.1	7.32	83.2	23.4	2.610	6.2	3.8	50
(5.57)*		5.5	9.40	81.2	27.1	2.768	7.4	3.4	1800
6.18	790	5.7	7.94	80.7	20.0	2.058	4.9	2.5	50
(8.17)*									
9.22	800	6.7	6.70	85.3	12.3	1.679	2.9	—	50
(12.68)*		5.0	8.26	80.9	14.5	—	3.4	—	1550
20.00	820	9.5	4.68	88.0	9.9	—	1.7	—	50
(31.43)*		6.0	7.52	85.2	10.9	—	1.5	—	1800
25.00	820	15.0	3.19	—	—	—	0.6	—	50
(41.60)*		7.0	5.22	—	—	—	1.6	—	1800

* Percentage of hydroxyl groups covered by acetyl groups

TABLE IX (continued)

SUMMARY OF PROCESSING OF STOCK IN BRITISH DISINTEGRATOR IN WATER MEDIUM

Acetyl content	Freeness	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Stretch %	Wet pressure lb./in.^{2}
Strength Values Calculated to Original Cellulose Content									
4.25	775	7.1	7.00	83.2	25.3	2.727	6.4	3.8	50
(5.57)*		5.5	8.99	81.2	28.2	2.892	7.6	3.4	1800
6.18	790	5.7	7.45	80.7	21.3	2.190	5.2	2.5	50
(8.17)*									
9.22	800	6.7	6.10	85.3	13.5	1.845	3.2	—	50
(12.68)*		5.0	7.52	80.9	16.0	—	3.7	—	1550
20.00	820	9.5	3.77	88.0	12.3	—	2.1	—	50
(31.43)*		6.0	6.05	85.2	13.6	—	1.9	—	1800
25.00	820	15.0	4.47	—	—	—	0.8	—	50
(41.60)*		7.0	6.87	—	—	—	2.1	—	1800

* Percentage of hydroxyl groups covered by acetyl groups

Microscopic examination of the beaten pulps showed that less fibrillation occurred with the acetylated pulps than with the original rag stock. The ends did not brush out but tended to remain blunt. On the other hand, no great increase in cutting was apparent, although this is difficult to estimate for the rag stock because of the numerous fibrils which are present.

The unbeaten pulps (processed in the British disintegrator) showed a rise in freeness when the hydroxyl groups were replaced. However, the entire range of freeness between the acetylated and unacetylated pulp is so small with an unprocessed pulp that experimental errors tend to obscure the results. In Table IX, the pyridine treatment is shown to have caused no change in freeness as compared with that of the original rag stock but 4.25 per cent acetyl content produces a slightly freer pulp; the 6 per cent acetyl cellulose was appreciably more free; after an acetyl content of 20 per cent had been reached no further rise in freeness was observed.

In the same table, it may be observed that the apparent density and the strength properties decrease as more and more acetyl groups are introduced. At a constant wet pressure of 50 lb./sq. in., the apparent density decreased from 5 to 4 per cent as the acetyl content was increased from zero to 20 per cent. This indicates (1) that the acetylated fibers are less pliable and more rigid and hence not as compressible as the original cellulose and (2) that the acetylated fibers do not bond well enough to retain the density of the sheet after removing the wet pressure.

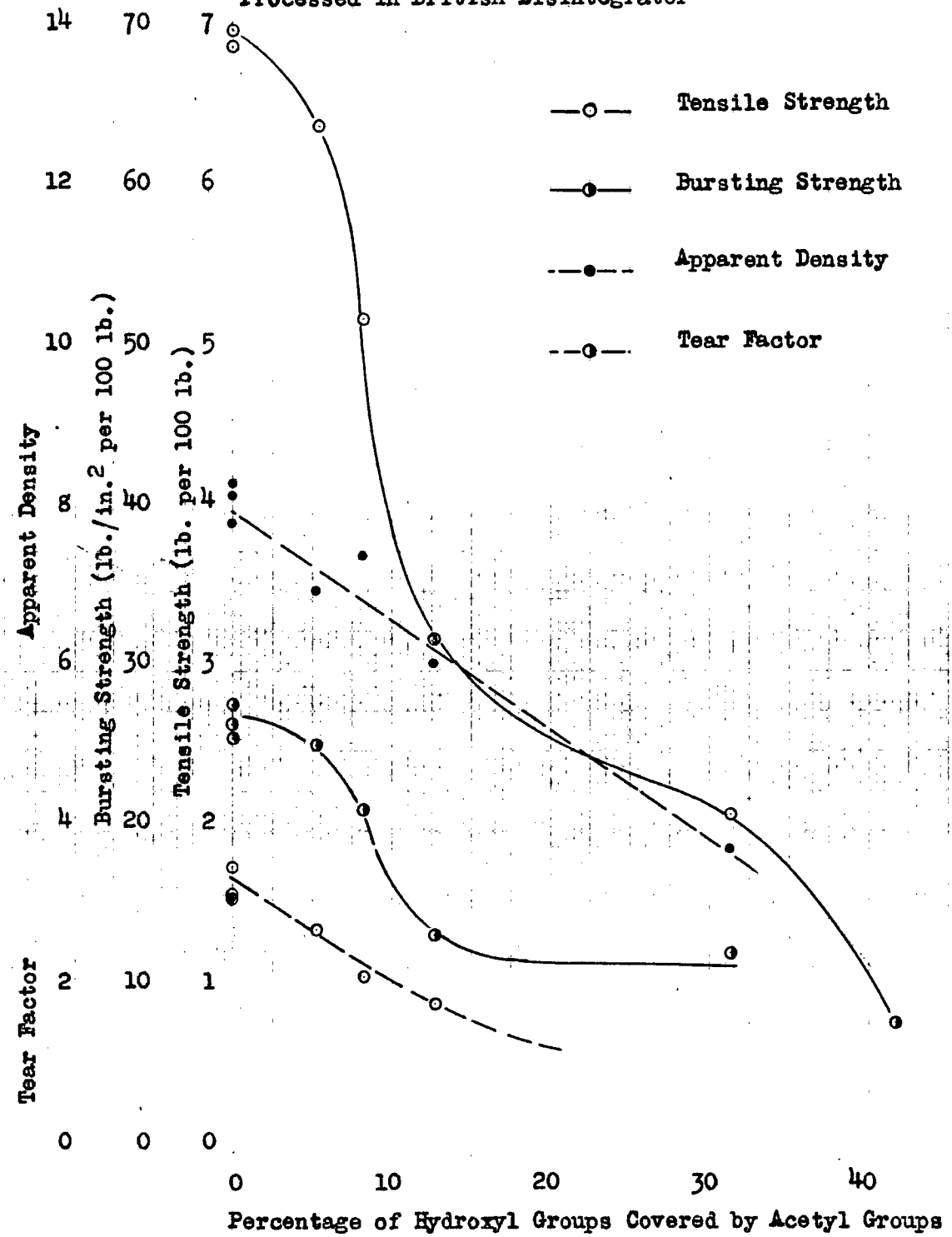
This reduction in bonding, shown by the loss in tensile and bursting strengths, permits slippage of the fibers to occur. When 20 per cent acetyl content had been introduced, the bursting strength dropped from 26 lb./sq. in. to 12 lb./sq. in.; tensile decreased from 7 to 2 pounds per 100-pound basis weight. Figure 2 shows a continual drop of strength values as the hydroxyl groups are replaced.

On the other hand, a comparison of the values at the same apparent densities gives a clearer picture of the bonding capacity of the fiber surface than when judging at constant pressure. For example, interpolating to obtain the tensile strength of the pulp with an acetyl content of 4 per cent at an apparent density of 7.63 (that obtained for the original pulp), a value of 6.9 pounds is obtained, whereas that for the untreated cellulose was 7.0 pounds; the bursting strength at the same apparent density interpolates to 26.5, whereas the original pulp had a value of 27 per cent.

Hence, when the acetylated fibers have been compacted sufficiently by increasing the wet pressure in order to produce approximately the same number of contacts between the fiber surfaces, then the strength of the handsheets is almost the same but still slightly lower for the acetylated pulp than for the original pulp. This means, apparently, that the potential ability of the surface to bond has been changed very little by the introduction of a small amount of acetyl groups. On the other hand, when the handsheets are prepared at the same wet pressure, the rigidity of the fibers in water has been increased to such an extent by acetylation that, compared to

FIGURE 2

THE EFFECT OF ACETYLATION ON STRENGTH PROPERTIES OF UNBEATEN PULPS
Processed in British Disintegrator



the original fiber, they are unable to make as many contacts and hence, the overall strength of the handsheet is much lower.

In a similar manner, properties of the 6 per cent acetyl cellulose can be compared with that of 4 per cent acetyl cellulose at the same apparent density of 7.45. Interpolation gives a tensile strength of 6.7 pounds per 100-pounds basis weight and a bursting strength of 26.0 lb./sq. in. per 100-pounds basis weight for the 4 per cent acetyl cellulose in contrast to 5.2 and 21.3, respectively, for the 6 per cent acetyl cellulose. This means that, even when the contact between the fibers is similar (sheets at the same apparent density), the strength of the handsheet with higher acetyl content has been reduced; this may be interpreted to mean that the bonding between these surfaces in mutual contact is less for the higher acetylated cellulose than for the less acetylated fiber. Furthermore, since this bonding decrease as more acetyl groups replace hydroxyl groups, the attraction between the fibers must depend to a great extent upon the hydroxyl groups present in the cellulosic material.

In contrast to defibering the pulps in the British disintegrator, beating the pulps in the miniature beater produced some interesting results which were not indicated with the unbeaten pulps. In the first place, handsheets were more easily formed for all acetylated pulps as compared with the difficulties experienced with the unbeaten materials. In fact, those acetylated pulps which had an acetyl content below 8 per cent "hydrated" better and felt as "wet" as the original beaten rag stock. Physical tests, listed in Table X, manifested this similarity to

TABLE X

SUMMARY OF MINIATURE BEATER RUNS*

Processing in Water

	Acetyl content	Freeness	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Stretch %	Wet pressure lb./in.^{2}
					Observed Strength Values					
1-a	0	550	4.3	10.78	79.8	54.6	3.218	18.3	4.3	50
			3.7	12.53	76.7	56.0	3.340	18.7	4.8	1610
1-b	0	585		freeness check run - separate beater run						
1-c	0**	515	4.2	11.12	78.1	54.4	3.310	17.2	4.3	50
1-d	Pyridine treated Ac = 0.00	550	4.6	10.47	80.7	55.7	3.061	18.4	4.8	50
1-e***	0	515	4.4	10.71	——	51.2	2.931	18.0	3.8	50
2	4.25 (5.57)+	440	4.4	10.83	74.2	55.2	3.262	18.0	4.0	50
			3.8	12.10	71.1	59.7	2.941	18.8	4.3	645
			3.6	12.76	69.7	58.7	3.188	18.7	4.3	1800
3	6.11 (8.17)+	365	4.3	10.90	74.1	57.6	3.016	18.1	4.6	50
			4.0	12.07	71.8	60.3	2.900	18.6	4.4	1800
4	8.12 (11.07)+	475	4.5	10.84	77.7	45.2	3.079	15.8	4.3	50
			4.0	11.74	73.9	50.2	2.890	16.8	4.5	645
			3.8	12.28	72.7	52.1	2.754	17.4	4.3	1800
5	9.22 (12.68)+	445	5.2	11.30	83.2	47.8	2.780	16.0	4.0	50
			4.9	12.47	83.2	49.7	2.421	16.2	3.8	645
			4.7	12.83	82.0	52.1	2.514	16.7	4.0	1800
6	20.05 (31.43)+	715	6.2	8.78	91.4	11.1	1.096	4.0	1.8	50
			5.2	10.51	89.8	14.6	1.020	5.1	1.8	645
			4.8	11.30	89.2	15.1	1.133	6.1	1.6	1800
7	23.35 (37.80)+	780	6.4	8.92	91.7	7.67	0.653	2.6	1.0	50
			4.8	11.59	89.0	9.9	0.867	3.8	1.3	1800

TABLE X (continued)

SUMMARY OF MINIATURE BEATER RUNS*

Processing in Water

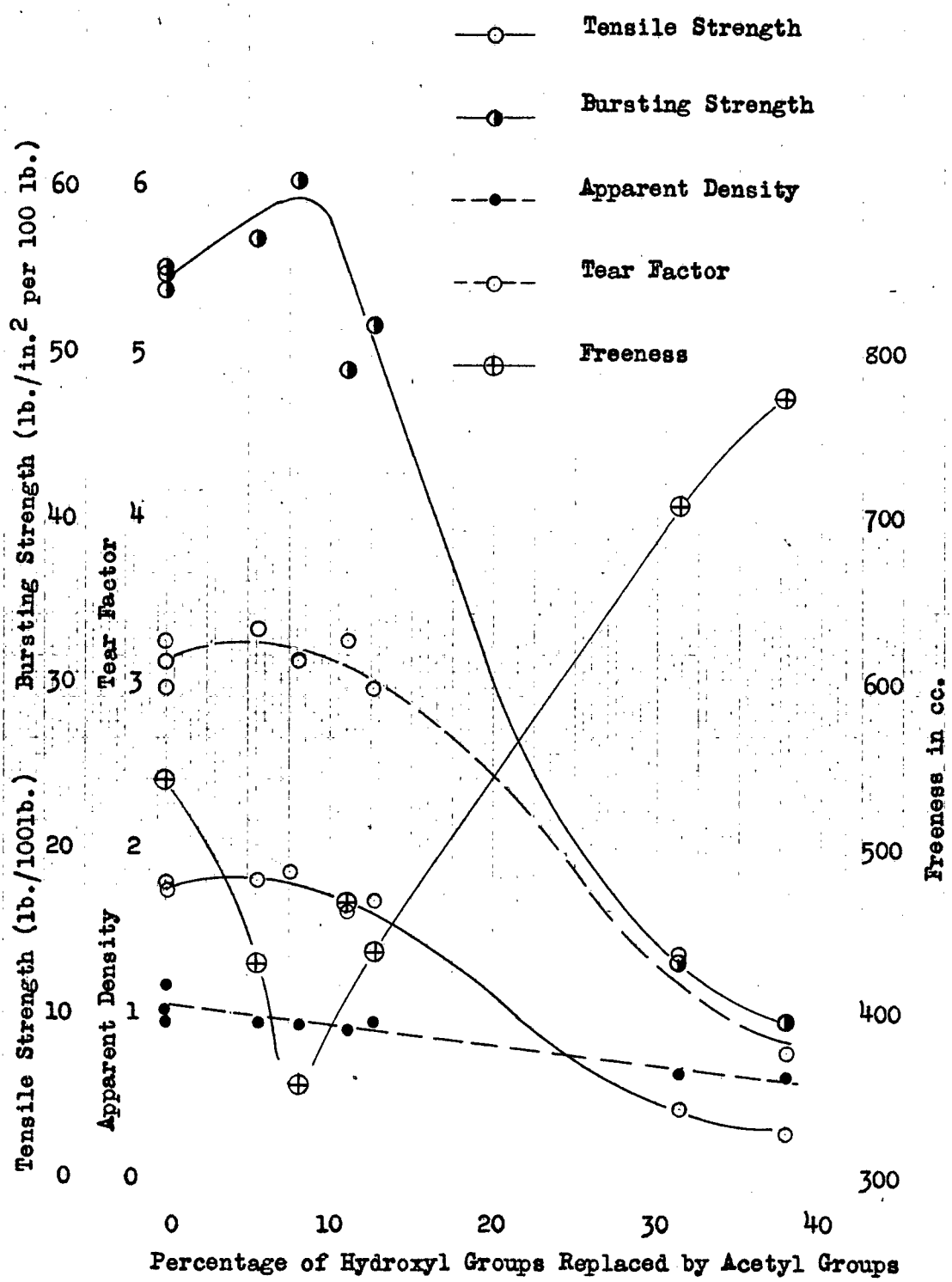
	Acetyl content	Free-ness	Caliper .001 in.	Apparent density basis wt./ caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Stretch %	Net pressure lb./in.^{2}
			Strength Values Calculated to Original Cellulose Content							
2	4.25 (5.57)+	440	4.4	10.38	74.2	57.7	3.409	18.8	4.0	50
			3.8	11.61	71.1	62.3	3.074	19.7	4.3	645
			3.6	12.21	69.7	61.4	3.328	19.5	4.3	1800
3	6.11 (8.17)+	365	4.3	10.25	74.1	61.3	3.214	19.3	4.6	50
			4.0	11.34	71.8	64.2	3.090	19.8	4.4	1800
4	8.12 (11.07)+	475	4.5	9.99	77.7	49.8	3.348	17.1	4.3	50
			4.0	10.79	73.9	54.6	3.134	18.3	4.5	645
			3.8	11.29	72.7	56.5	2.990	18.9	4.3	1800
5	9.22 (12.66)+	445	5.2	10.28	83.2	52.5	3.050	17.6	4.0	50
			4.9	11.34	83.2	54.8	2.646	17.8	3.8	645
			4.7	11.70	82.0	57.3	2.760	18.4	4.0	1800
6	20.05 (31.43)+	715	6.2	7.07	91.4	13.8	1.361	5.0	1.8	50
			5.2	8.48	89.8	18.2	1.284	6.4	1.8	645
			4.8	9.10	89.2	16.8	1.409	7.6	1.6	1800
7	23.35 (37.80)+	780	6.4	6.89	91.7	10.2	0.847	3.4	1.0	50
			4.8	8.93	89.0	12.9	1.119	4.9	1.3	1800

* 300 minutes in miniature beater + 150,000 revolutions in British disintegrater
** Beater under different mechanical operation
*** 410 minutes in miniature beater + 150,000 revolutions in British disintegrater
\+ Percentage of hydroxyl groups replaced by acetyl groups

FIGURE 3

THE EFFECT OF ACETYLATION ON PAPERMAKING PROPERTIES

Processing in Miniature Beater



the unacetylated pulp. Pulps with an acetyl content between 4 per cent and 5 per cent were "slower" than the original rag stock with the same amount of processing; furthermore, bursting and tensile values were definitely higher than those of the original cellulose. However, for these acetylated pulps of 9 per cent acetyl content and above, the strength of the handsheets was lower than that of the standard rag stock. When as much as 20 per cent acetyl content had been introduced, the strength was far less than that of the unacetylated stock. The bursting and tensile values were only one third of that of the original pulp. Even less strength was obtained when the acetyl content was increased to 23 per cent.

In general, tear, which is a complex physical property, decreased with increasing acetyl content; as the bonding between the fibers decreased, the tear also decreased.

The increase in strength over the original rag stock, when a small amount of acetyl groups has been introduced, may be accounted for in two ways. First, one may think of the acetylated portion as located on the surface of the fiber which, upon beating, forces open the structure and permits the water to penetrate the inner sections of the fiber, thus exposing more bonding surface of hydroxyl groups than would be present in the unacetylated cellulose fiber. It is in this manner that Rook (63) explained the water solubility of low methylated cellulose; covering a few of the hydroxyl groups opens up the structure so that sufficiently more hydroxyl groups are made available to cause complete solvation of the cellulose and, hence, its solution.

A second explanation may be postulated as follows. In rag stock, the film of bound water surrounding the micelles may be sufficiently copious to prevent a close bonding of the hydroxyl groups of adjacent fibers. This film may be similar, though to a lesser degree, to that produced by strong caustic treatment producing mercerization. Soda pulp which is also prepared by a caustic treatment shows similar characteristics. Drying would not remove this film to the extent that the Van der Waal forces arising from the cellulose hydroxyl groups could be completely effective. On the other hand, the introduction of a small amount of acetyl groups would reduce this film but at the same time, upon beating, sufficient uncovered hydroxyl groups would remain to bond the fibers together. If this postulation is correct, the phenomenon of increased ease of beating with the introduction of a small amount of hydrophobic groups should be more pronounced with mercerized fibers or alpha pulps, since the hygroscopic moisture for these cellulosic materials is much higher than that for rag stock. Further investigation would be interesting.

On the other hand, one might attribute this increase in strength to a mechanical abrasion which could conceivably occur during the beating; that is, the small amount of acetyl groups present, which have been shown by other investigators (90) to be for the most part on the surface of the cellulose, would be scraped off during the processing, leaving a more active surface. However, acetyl determinations on the beaten acetylated pulp showed the acetyl content to be practically the same after beating as before.

Acetyl Content of Two Pulps

Before beating %	After beating %
4.25	4.50
6.12	7.72

In any case, after the hydroxyl groups have been covered to a greater extent than those on the surface, considerable strength loss is observed and the pulp becomes much more difficult to beat. Freeness, in addition, after processing for the standard beating period is much higher for these pulps than that obtained for the unacetylated rag stock. When a sufficient number of hydroxyl groups have been covered so that few are available even after beating, they cannot hold the fibers together through their secondary valences, and hence, the sheet strength is lost.

Regenerated Cellulose.

Convincing evidence that the reduction of the hydroxyl groups in a pulp was responsible for the loss in strength, as has been shown by the above experiments, could be presented if it were possible to destroy the papermaking qualities of a pulp by acetylation and then to restore these properties by regenerating the hydroxyl groups of the pulp. This complete cycle has been carried out on the native rag stock beaten in the standard beater run to a freeness of 260 cc.; the strength properties of this beaten pulp are given in Table XI. The method of acetylation, the procedure for carrying the control pulp through the acetylating operations, and the manner of saponification have been described in the section on Preparation of Pulps. The strength characteristics of handsheets prepared from these pulps are summarized in Table XI.

See pp. 59.

TABLE XI

EFFECT OF ACETYLATION ON A HIGHLY BEATEN RAG STOCK

Processed in British Disintegrator

Acetyl content	Free-ness	Caliper .001 in.	Apparent density basis wt./ caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Wet pressure lb./in.^{2}
Original beaten pulp Ac = 00.00	260	4.5	10.45	79.2	68.7	3.735	20.79	50
Pyridine control Ac = 00.00	340	4.3	10.92	80.7	74.3	3.578	21.7	50
Acetylated Beaten Pulp - Observed Values								
Ac = 14.20	565	5.6	8.70	92.7	24.5	2.120	7.1	50
	565	4.4	11.09	89.3	29.6	2.186	8.8	1550
Calculated to Original Cellulose								
	565	5.6	10.11	92.7	28.5	2.470	8.3	50
	565	4.4	12.90	89.3	34.3	2.542	10.2	1550
Saponified from 14.20 Ac = 00.00	——	4.2	11.43	83.5	55.7	3.416	18.42	50

It is seen that the introduction of 14.2 per cent acetyl content, which means covering 20.7 per cent of the total hydroxyl groups in the cellulose, caused a deleterious effect on the strength properties of the pulp and raised the freeness from 260 cc. to 565 cc. In contrast, treatment of the beaten stock with solvents alone raised the freeness slightly (to 340 cc.) but no loss in strength could be measured; in fact, bursting and tensile strengths were slightly increased by the treatment. A comparison of the properties of the acetylated stock at the apparent density of 11.09 (obtained by increasing the wet pressure to 1550 lb./sq. in.) with those of the pyridine-treated pulp at 10.92, shows that the bursting and tensile strengths have been reduced to 40 per cent of the original values by the introduction of acetyl groups. Thus, even when the fiber contact is approximately the same (the sheets pressed to equal apparent density), the strength is only a fraction of the original; this may be interpreted to mean that the bonding between fibers had been greatly reduced by the loss of available hydroxyl groups.

The data show that restoring the hydroxyl groups regenerates the papermaking properties of the pulp; the burst increased from 24.5 to 55.7 lb./sq. in. per 100-pounds basis weight; the tensile strength rose from 7.1 to 18.4 pounds per 100-pounds basis weight; and the tear factor reached 3.416, which was almost as high as that of the control pulp steeped in pyridine.

Therefore, it seems reasonable to conclude from the above experiment that the hydroxyl groups of the cellulose play a large part in bonding fibers together and in producing sheet strength.

Processing in Acetone

Papermaking fibers of native cellulose have been shown by Kress and Mialkowsky (11) not to beat in oils and most organic solvents, but only to beat to form a well-bonded sheet in a liquid medium which swells the cellulose and which contains a large percentage of potential hydroxyl groups such as are present in water. This condition suggested that acetylated cellulose fibers might bond to form a sheet in a medium which would swell the fibers and make them flexible, in the same manner as water does cellulose fibers. The organic solvent, acetone, produces these characteristics in cellulose acetate and, therefore, was selected as a beating medium for the acetylated fibers. The methods of processing and preparation of handsheets are the following.

Processing in British Disintegrator

For this processing, 14 grams of pulp (on the basis of the cellulose present in the acetylated pulps in an ovendry condition) were placed in the British disintegrator with 1100 cc. of commercial acetone (allowing 100 cc. for evaporation) and stirred for 12,500 revolutions. The defibered pulp was diluted with acetone to a consistency of approximately 0.2 per cent and formed into handsheets on the British sheet machine, using acetone throughout the operation. The organic solvent was collected from the effluent of the sheet machine and re-used for the subsequent preparation of sheets. TAPPI standard method T 205 m-40 was followed except that only two to three sheets could be pressed at a time (instead of the usual 7 or more) because of the rapid evaporation

of the acetone. Additional blotters were added in the press, as recommended in the method, to compensate for the lack of sheets.

Processing in the Miniature Beater

The standard procedure adopted for water was followed exactly in processing with acetone as the liquid medium. Handsheets were prepared in acetone and pressed at 50 and 1500 lb./sq. in. wet pressure, as discussed for processing in water. Freeness was not determined since the values that would be obtained could not be compared with those using water as a medium, considering the wide difference in viscosities of the two liquids.

Testing of Handsheets

The Institute Methods employed for testing sheets processed in water were followed in the case of testing the acetone-processed paper.

Discussion of Results

When the dry pulp of cellulose acetate, which had an acetyl content of 25.00 per cent, was placed in the acetone, it was immediately wetted and distributed itself throughout the liquid. Agitation in the British disintegrator readily broke up the clumps of pulp and produced a well-defibered stock. Of interest was the high transparency of the fibers--that is, the refractive index of the fibers appeared to be almost the same as that of the medium.

The visible physical characteristics of the fiber suspended in acetone were their flexibility and pliability; they appeared much softer than when native cellulose fibers were suspended in water. When handsheets were prepared in the British sheet machine, the formation was completely uniform; a tendency to flocculate or to associate into the customary bunches, so common with native rag stock in water, was not at all evident.

A highly hydrate pulp is commonly known to shrink on drying; in a similar manner, handsheets prepared in acetone from the 25 per cent acetyl cellulose shrank considerably as the organic solvent evaporated. The effect was more pronounced than for handsheets prepared from 8 per cent acetyl cellulose discussed below.

The cellulose acetate fibers of 8 per cent acetyl content when placed in the acetone were also soft, flexible, and pliable and they were wetted rather easily by the medium but not to the extent that was observed for the highly acetylated material above. The pulp did not defiber with the same ease in the British disintegrator and, when formed into handsheets, flocculation of the fibers was prevalent, making it difficult to prepare paper. Transparency of the fibers, so evident with the 25 per cent acetyl cellulose, was not observed; their refractive index appeared to be appreciably different from that of the acetone medium.

Dry standard rag stock was immediately wetted by the acetone and sank to the bottom of the liquid. However, after the usual 12,500 revolutions in the British disintegrator using acetone for the

suspending medium, no defibering whatsoever had occurred and the clumps of dry rag stock were completely intact. Hence, 200 cc. of water were added and 12,500 more revolutions of stirring in the disintegrator were given the pulp. Some fibers had broken off but even after this treatment many large clumps remained. Therefore, 300 cc. more water were added and the pulp was stirred for 500 additional revolutions, which was sufficient to break up the pulp. However, when the water was filtered off and acetone was again added, the pulp flocculated and tended to bunch together. Despite the apparent resistance to defibering, the rag stock was soft, pliable, and very flexible when wet with acetone. Handsheets were as difficult to form as in those experiments in which highly acetylated fibers were processed in water; large holes appeared in some parts of the sheet, while the stock piled up in others.

In general, the pulps seemed to retain the acetone better within the interstices of the handsheets with decreasing acetyl content. The handsheets of 25 per cent acetyl cellulose showed immediate shrinkage and extremely rapid drying; the pulps of 8 per cent acetyl cellulose showed less tendency to shrink and a lower apparent rate of drying, whereas the rag stock did not seem to shrink at all, although a tendency to shrink may not have been evident because of the higher rigidity of the fibers in acetone.

The papermaking characteristics of the handsheets prepared in acetone from these three pulps are listed in Table XII. It is clearly seen that the general trend is an increase in the strength of the handsheets with increasing acetyl content. Most surprising are the

TABLE XII

HANDSHEETS PREPARED IN ACETONE AS BEATING MEDIUM

Processed in British Disintegrator

Acetyl content	Caliper .001 in.	Apparent density basis wt./caliper	Opacity %	Bursting strength (lb./in.^{2}) per 100 lb.	Tear factor	Tensile lb. per 100 lb.	Stretch %	Wet pressure lb./in.^{2}
Observed Strength Values								
0	13.0	5.76	——	——	——	1.5	——	50
8.12 (11.07)*	14.7	5.17	——	19.0	1.382	2.1	2.2	50
25.00 (41.60)*	6.0	9.87	70.0	105.2	2.910	23.9	17.6	50
Strength Values Calculated to Original Cellulose								
8.12 (11.07)*	14.7	4.73	——	20.7	1.550	2.3	2.2	50
25.00 (41.60)*	6.0	7.50	70.0	139.0	3.822	31.4	17.6	50
Processed in Miniature Beater ~~with Acetone as the Medium~~								
Observed Strength Values								
8.12 (11.07)*	9.5 6.8	5.52 8.24	93.6 92.7	30.0 30.4	3.039 2.482	6.87 6.4	4.2 3.6	50 1800
Strength Values Calculated to Original Cellulose								
8.12 (11.07)*	9.5 6.8	5.07 7.58	93.6 92.7	32.8 33.0	3.299 2.708	7.5 7.0	4.2 3.6	50 1800

* Percentage of hydroxyl groups covered by acetyl groups

unusual strength properties obtained in the handsheets prepared from the acetylated pulp containing an acetyl content of 25 per cent (41 per cent of the hydroxyl groups in the cellulose were acetylated). A tensile strength of 31.4 pounds per 100-pounds basis weight was obtained when this pulp was defibered and formed into handsheets in acetone, as compared to 2.1 pounds per 100-pounds basis weight under the same processing in water. Moreover, this is appreciably higher than the best tensile strength that could be developed in the standard rag stock processed in water, either in the British disintegrator or after beating under optimum conditions in the miniature beater; in this latter case, a tensile strength of only 18.7 pounds per 100-pounds basis weight was attained. Bursting strength exhibits the same relationships; the acetylated pulp processed in acetone showed a burst of 139 lb./sq. in. per 100-pounds basis weight as compared with 56 lb./sq. in. per 100-pounds basis weight for the standard rag stock beaten in water. Tear was about the same for both pulps.

The apparent density of this well-bonded sheet, instead of being extremely high, as might be expected, was only 7.50, which is similar to that measured for the handsheets of the original cellulose processed with water in the British disintegrator for the same length of time. This may be interpreted to mean that, even though the contacts between fibers are numerically equivalent, yet the bonding forces between the acetylated surfaces are sufficiently greater to produce the increased strength.

Therefore, it seems that a bonding between acetyl groups can occur which is as strong or even stronger than that occurring between hydroxyl groups, provided the proper medium is used for processing the fibers.

One might attribute the close bonding of the sheet to the formation of surface films consisting of cellulose acetate dissolved in acetone. However, the solution of the 25 per cent acetyl cellulose in the acetone was negligible; the nonvolatile substances in the acetone filtered from the handsheets were 20 parts per million; or, based on the amount of pulp which had been suspended in the solvent, the nonvolatile material amounted to 0.67 per cent of the pulp.

The effect of beating the acetylated fiber in acetone was determined for the acetylated pulp of 8 per cent acetyl content; this was selected in preference to the acetylated material containing 25 per cent acetyl content, because the behavior in acetone of this lower acetylated fiber more nearly resembled that of standard rag stock in water. After standard processing in the miniature beater, the fibers could be made into handsheets more readily than when they were defibered in the British disintegrater. Flocculation was less prevalent but some tendency for the fibers to associate was observed. Sheet formation was much improved over that of the unbeaten material.

In Table XII, the evaluation of the handsheets shows that a development of strength properties was obtained by beating. Tensile strength increased from 2.3 to 7.5 pounds per 100-pounds basis weight;

bursting strength, from 20.7 to 32.8 lb./sq. in. per 100-pounds basis weight. The tear increase was most interesting, since the value of 3.299 is in the range obtained for the original rag stocks beaten in water; this indicates that little cutting had occurred.

When a higher wet pressure was applied in preparing the handsheets, the apparent density increased, but the tensile and bursting strengths remained the same. Appreciable tearing strength was lost, however, which is an anomaly, for, usually, this property is not reduced unless the bursting and tensile strengths are increased. These latter results may be due to experimental difficulties--that is, too great an evaporation of the volatile acetone occurred before the wet pressing could be carried out.

In summarizing, it appears that acetylated pulps can be processed in acetone (or possibly other organic solvents possessing a similar swelling effect) and that strength can be developed by beating in the same way that native cellulose fibers can be "hydrated" in water to develop strength.

THEORETICAL DISCUSSION AND SUMMARY

The results of the present investigation may be utilized as a basis for explaining some of the phenomena which occur during the beating of a papermaking pulp. Many of the concepts will need further substantiation by other methods of study; however, some factors influencing hydration and bonding are well founded from the work which already has been carried out.

In the first place, the experiments in this study clearly show that the hydroxyl groups of the cellulose play an important role in the processing of papermaking fibers in water and in their bonding to form a strong sheet of paper. With pulps which have had the surface hydroxyl groups replaced, the bonding strength between the fibers is lowered in proportion to the number of these groups that have been covered by acetyl groups--that is, if the pulps are only defibered and not beaten before the preparation of handsheets.

However, when these acetylated pulps were beaten, their strength-producing characteristics, without exception, increased two to three times over those of the unbeaten acetylated stock, even though many of the hydroxyl groups were covered. On the other hand, highly acetylated pulps, in which 40 per cent or more of the hydroxyl groups were covered, had very low strength properties even after beating. This increase on beating seemed to be due to a rise in apparent density rather than to an increase in the bonding activity of the surfaces, for at the same apparent density, little difference in strength

was observed. The data suggest that the effect of beating, in the case of highly acetylated pulps, is to make the fibers more flexible and pliable, so that they may compress into a denser sheet during the pressing operation.

In the second place, the beating action apparently splits open the fiber surfaces exposing more hydroxyl groups from the intermicellar surfaces. Since the acetyl groups are introduced into the cellulose fiber topochemically, the hydroxyl groups of the "superficial" surface are covered first. The slightest reduction in hydroxyl groups immediately affects the bonding strength of the fibers and has been shown by experiment to reduce the strength continuously as more and more acetyl groups are introduced, provided no beating action is given the acetylated pulp. However, when these surface-acetylated pulps were processed in a beater, the whipping and bruising action on the fibers seemed to crack open the shell of acetylated cellulose which is present or tended to unwind this external layer and to permit the under layers of hydroxyl groups to bond the fibers together. Such a condition is shown, for example, with the pulp of about 9 per cent acetyl content. In the unbeaten condition, its initial bursting and tensile strengths had dropped to approximately half that of the native cellulose rag stock; yet, when beaten, it attained about the same strength characteristics as those of the original beaten rag stock. Hence, in this case, fiber bonding appears to be due to the hydroxyl groups underneath the cellulose acetate shell. This supposition is supported by the fact that extending the acetylation to hydroxyl groups further within the fiber prevents a strong bonding from occurring even with beating.

Direct application of this concept to beating of the original rag stock must be made with reservations until further proof can be presented, since the presence of acetyl groups in the above experiments may greatly influence the phenomenon by facilitating the disruption of the surface and, hence, may obscure the conditions to be studied.

In any case, the investigation shows that when almost all the hydroxyl groups that can be covered without opening the intramicellar structure (e.g., through mercerization) have been replaced with acetyl groups, low strength characteristics result in the pulps even when processed in the beater. Hence, one may assume that beating does not open the intramicellar structure but only enlarges the intermicellar spaces; furthermore, one may conclude that it is the surface hydroxyl groups of the micelles (chain molecular bundles) which are effective in ~~co-ordinated~~ "hydration" and fiber bonding and not those hydroxyl groups within the micelles whose secondary valences are mutually well satisfied. (The concept of "micelles," as a term, is undergoing change; here, it refers to bundles of molecular chains.)

In the third place, the enhancing effect which a small amount of acetyl groups on the fiber surface has on the development of strength is enlightening and may set as a technique for studying the mechanism of strength loss after mercerization and alpha treatment. The fact that a rise in maximum strength could be obtained by the introduction of small amounts of a hydrophobic group suggests that a pulp can be too hydrophilic in nature to achieve the maximum bonding. In other words, the fiber surface can offer too great an attraction

for water or between hydroxyl groups to produce the optimum conditions of strength in a sheet of paper. Fortunately, the experiments of this thesis accomplish a change in surface without producing a major change in micellar structure of the fiber which beclouds the phenomenon in the case of mercerization.

In the previous discussion, it was suggested that this increase in maximum strength obtained by a low degree of acetylation may be due (1) to a reduction of the attraction of the surface hydroxyl groups for water and, hence, a reduction of the surface film of water or (2) to the opening up of the structure more readily on beating. Of the two, the latter explanation seems more capable of satisfying the facts.

It is possible to picture that in the rag stock, which has but small amounts of low molecular cellulose, the bonding which occurs between cellulosic micelles is due, for the most part, to the long chain molecules themselves. On the other hand, in wood pulps, many short chain cellulose molecules (hemicelluloses) intervene between these bonds in some places and act as a mutual "cement" between the micelles. Hence, when the fiber is placed in water, these cellulose molecules of low molecular weight, which readily solvate and swell, tend to shove open the intermicellar structure, and break the bonds between mutually satisfied hydroxyl groups of the long chain molecules. In this way, large number of micellar surfaces are available which increase the bonding between fibers.

In contrast, the cellulose fibers of rag stock which contains but a small amount of these readily solvated molecules are bound

together mostly through the long cellulose chains themselves. Swelling is more difficult and the intermicellar structure is not opened up readily to permit bonding between a large number of micelle surfaces. This hypothesis is substantiated by the experimental fact that the presence of increasing amounts of pentosans (hemicelluloses) will increase proportionally the swelling which occurs with cellulose fibers (Young and Rowland (19)) and that the presence of hemicellulose facilitates the "hydrating" action (16-18).

Applying this concept to the rag pulps of low acetyl content, one may speculate that the increased ease of beating is due to a similar condition of the intermicellar surfaces where, in this case, the presence of a small amount of the hydrophobic acetyl groups sufficiently reduces the "external"* surface bonding so that the micelles may split apart and open up new micellar surfaces for fiber bonding after mechanical beating, in the same way that solvation and swelling of the hemicellulose, if present, would open up the structure. The fact that great strength eventually can be produced in rag stock after long, careful bruising and flexing of the fibers, substantiates the above idea, if one can conceive that the mechanical action finally splits open the intermicellar spaces when given sufficient time; and hence, the bonding between fibers increases provided the macrostructure is not weakened.

In summarizing, a small amount of acetyl groups added to the surface of the cellulose fiber reduces the attraction between surface micelles and permits the intermicellar spaces to be opened up more

---

* Surface of micelle layer on outside of fiber

readily with mechanical fleming than if the hydroxyl bonds were left intact. However, since acetyl groups are hydrophobic in nature, covering more than just those on the surface prevents the water from entering the structure and solvating the molecules. Bonding and hydration are less when the introduction of a certain optimum number of acetyl groups is exceeded.

In the fourth place, the strength, which was obtained in the handsheets of acetylated cellulose fibers prepared in acetone, substantiates some proposed explanations of fiber bonding and opens the way for further speculation. First of all, these experiments show that fibers can be bonded by other groups than hydroxyl groups and that a similarity in the chemical nature of the suspending medium to the fibers is necessary to achieve this bonding.

To explain completely these two facts requires a satisfactory elucidation of the mechanism of swelling and solution; however, at the present time, no theory exists which will explain these two phenomena by satisfying all the known facts. But swelling and solution do occur and may be observed when a substance has had a similar molecular structure to that of the suspending medium.

Thus, cellulose acetates, with the proper acetyl content and corresponding satisfactory molecular weight, are known to dissolve in acetone; similarly, cellulose is suspected of being soluble in water (see Strachan (94)), and when the molecular chains of the cellulose are shortened to the extent that the polymerized cellobiose

units may be classified as oligosaccharides, solution in water of such "degraded" cellulose is a fact.

Hence, the postulation of a "surface solution" with cellulose fibers by Campbell (5) and by Urquhart (36) is quite feasible. The fact that acetylated fibers in acetone show similar papermaking properties to those of cellulose fibers in water makes the theory more convincing, for it is common knowledge that cellulose acetate can be dissolved in acetone and recombined into "celanese" yarn.

Therefore, the following hypothesis is presented. The beating medium (which is specific in chemical nature for the fibrous material under consideration) is imbibed into the fiber structure, causing it to swell and become pliable. Long chain molecules on the surface of the micelles are partially dissolved (solvated) when the valency bonds between the active groups (hydroxyl or acetyl in this thesis) have been satisfied by the liquid medium instead of by mutual groups of the molecule. Mechanical action facilitates the opening up of the micellar structure.

When the fibers are formed into a wet sheet, many of these micellar surfaces of one fiber come in contact with those of an adjacent fiber. As the liquid medium is removed by evaporation, the solvated active groups of the molecules on the surface of the micelles satisfy their secondary valences by auto-attraction with those of an adjacent fiber, instead of by those of the medium or of the same fiber. In this manner, the fibers bond together. The more bonds which can be

accomplished through these micellar surfaces, the greater the strength of the paper.

CONCLUSIONS

Experimental evidence has been presented to substantiate the following familiar hypotheses:

a. The hydroxyl groups of the cellulose in the fibers are largely responsible for the "hydration" which takes place during beating in water and for the bonding of the fibers in a sheet of paper.

b. The beating action appears to open up the intermicellar spaces of the fiber, permitting the water medium to penetrate and thus making these surfaces available for bonding between the fibers. Beating does not disturb the intramicellar structure.

c. Bonding between fibers appears to be due to a mutual satisfaction of the secondary forces of the hydroxyl groups in the cellulose of adjacent fibers.

Fibers which have over 40 per cent of the hydroxyl groups in the fiber replaced with acetyl groups (mathematically, the surface hydroxyl groups of the micelles are replaced) give practically no bonding when processed in water.

Intense bonding between these acetylated fibers can be accomplished to give a strong sheet of paper provided a suspending medium, such as acetone, is used for processing which will swell the fibers and tend to dissolve the acetylated cellulose.

to water

REFERENCES CITED

(1) Bialkowsky, Harold W., "Hydration-bibliography," Bull. Inst. Paper Chemistry 1, no. 4:14-21(December, 1939).

(2) Bell, J. M. B., J. Soc. Chem. Ind. 52:109T-116, 119-130(1933).

(3) Simmonds, F. A., Paper Trade J. 101, no. 3:35-39(July 18, 1935).

(4) Clark, James d'A., Paper Trade J. 97, no. 26:25-31(Dec. 28, 1933).

(5) Campbell, W. Boyd, "The cellulose-water relationship in paper-making," Canada, Dept. of the Interior, Forest Service, Bulletin 84. Ottawa, F. A. Acland, 1933. 52 p.

(6) Strachan, James, Proc. Tech. Sect. Paper Makers' Assoc. Gt. Brit. and Ireland 6, pt. 2:139-167(1925-26).

(7) Cross, C. F., and Bevan, E. J., "A text-book of paper-making," 5th edition, especially p. 206-233. New York, Spon and Chamberlain, 1920. 527 p.

(8) Seibert, Florence B., and Minor, Jessie E., Paper 24:1007-1012(1919).

(9) Schwalbe, Carl G., and Becker, Ernst, Z. angew. Chem. 32:265-269 (1919).

(10) Curran, C. E., Simmonds, F. A., and Chang, H. M., Ind. Eng. Chem. 23:104-108(1931).

(11) Kress, Otto, and Bialkowsky, Harold W., Paper Trade J. 93, no. 20: 35-44(Nov. 12, 1931).

(12) Nakano, Michinaro, Cellulose Ind. (Tokyo) 6, suppl. binding:15(1930).

(13) Seibert, Florence B., and Minor, Jessie E., Pulp Paper Mag. Can. 18:939-942(1920).

(14) Bassett, Harry P., U. S. patent 1,792,351(Feb. 10, 1931).

(15) Runkel, Roland, Papier-Fabr. 31:75-77, 86-89, 97-100(1933).

(16) Jonas, K. G., and Rieth, E., Wochbl. Papierfabr. 64:853-855(1933).

(17) Obermanns, Henry E., Paper Trade J. 103, no. 7:83-91(Aug. 13, 1936).

(18) Houts, Harold E., and Kurth, Erwin F., Paper Trade J. 109, no. 24: 38-41(Dec. 14, 1939).

(19) Young, George H., and Rowland, B. W., Paper Trade J. 97, no. 15: 44-46(Oct. 12, 1933).

(20) Strachan, James, Paper-Maker 87:TS51-52(1934).

(21) Gortner, Ross Aiken, "Outlines of biochemistry," 2nd edition, especially p. 263. New York, Wiley, 1938. 1017 p.

(22) Strachan, James, World's Paper Trade Rev. 97:576-582, even pages only: 667-668, 671-672, 675, 755-756, 759-760, 762, 764, 800, 802, 805(1932).

(23) Strachan, James, Paper-Maker 89:TS49-50(1935).

(24) Strachan, James, World's Paper Trade Rev. 109:606(1938).

(25) Strachan, James, Paper-Maker 95:TS49-52, 54(1938).

(26) Sheppard, S. E., and Newsome, P. T., J. Phys. Chem. 36:2306-2318 (1932).

(27) Stamm, Alfred J., Ind. Eng. Chem. 27:401-406(1935).

(28) Bailey, A. J., and Brown, R. M., Ind. Eng. Chem. 32:57-63(1940).

(29a) Brauns, Friedrich E., and Lewis, Harry F., Paper Trade J. 105, no. 10:35-37(Sept. 2, 1937).

(29b) Lewis, H. F., Brauns, F. E., and Buchanan, M. A., Paper Trade J. 110, no. 5:36-38(Feb. 1, 1940).

(30) Carpenter, Charles H., and Lewis, Harry F., Paper Trade J. 99, no. 3:37-42(July 19, 1934).

(31) Campbell, W. Boyd, Ind. Eng. Chem. 26:218-219(1934).

(32) Doughty, R. H., Paper Trade J. 93, no. 2:39-44(July 9, 1931).

(33) Harrison, H. Ainsworth, Proc. Tech. Sect. Paper Makers' Assoc. Gt. Brit. and Ireland 11:272-333(1930-31).

(34) Spengler, O. L., and Hoyt, W. H., "The structure of ramie cellulose as derived from x-ray data," In Weiser, Harry Boyer, "Colloid symposium monograph," vol. 4, p. 174-202. New York, Chemical Catalog Co., 1926.

(35) Meyer, Kurt H., and Mark, H., "Der Aufbau der hochpolymeren organischen Naturstoffe." Especially p. 143-144. Leipzig, Akademische Verlagsgesellschaft, 1930. 264 p.

(36) Urquhart, Alexander Robert, J. Textile Inst. 20:T125-132(1929).

(37) Kakuma, Michimaro, "Studies in beating," translated and compiled by Shiro Tashiro from Japanese periodical publications. Troy, John A. Manning Paper Company, 1930. 107 p.

(38) Sedoff, Arthur, Holmberg, C. V., and Jahn, Edwin C., Paper Trade J. 109, no. 26:42-49(Dec. 28, 1939).

(39) Seborg, C. O., Simmonds, F. A., and Baird, P. K., Paper Trade J. 107, no. 19:45-50(Nov. 10, 1938).

(40) Glasstone, Samuel, "Recent advances in physical chemistry," 2nd edition, especially p. 44-46, 98-99. Philadelphia, Blakiston's, 1933. 498 p.

(41) Lowry, Thomas Martin, J. Chem. Soc. 123:822-831(1923).

(42) Sidgwick, Nevil Vincent, "The electronic theory of valency," Oxford, The Clarendon Press, 1929. 310 p.

(43) Kolkmeijer, N. H., and Favejee, J. C. L., Nature 132:602-603(1933).

(44) Katz, J. R., "X-ray spectrography of swelling," paper presented at the general session of the Amer. Chem. Soc., Cleveland, 1934; quoted by Stamm, Alfred J., "Colloid chemistry of cellulosic material," U. S. Dept. Agriculture, Misc. Publication No. 240. Washington, U. S. Gov't. Print. Off., 1936, p. 63

(45) Probst, T. Richard, Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1939. 100 p.

(46) McGregor, Geo. H., Paper Trade J. 102, no. 11:27-39(March 12, 1936).

(47) Pierce, F. T., J. Textile Inst. 20:T133-150(1929).

(48) Sheppard, S. E., Trans. Faraday Soc. 29:77-85(1933).

(49) Brown, Duncan S., Doctor's Dissertation. Appleton, Wisconsin, The Institute of Paper Chemistry, 1939. 182 p.

(50) Cottrall, Leslie G., Proc. Tech. Sect. Paper Makers' Assoc. Gt. Brit. and Ireland 14, pt. 2:241-312(1933-34).

(51) Krüger, D., "Zelluloseacetate und die anderen organischen Ester der Zellulose," especially p. 77-92. Dresden and Leipzig, Theodor Steinkopff, 1933. 391 p.

(52) Mess, Kurt, and Ljubitsch, Noah, Ber. 61:1460-1462(1928).

(53) Perdyce, Charles R., U. S. patent 2,129,052(Sept. 6, 1938).

(54) Staudinger, H., and Daumiller, G., Ann. 529:219-265, especially 220-223(1937).

(55) Staudinger, H., and Eilers, H., Ber. 68:1611-1618(1935).

(56) Herzog, R. O., J. Phys. Chem. 30:457-469(1926).

(57) Sisson, Wayne A., Ind. Eng. Chem. 30:530-537(1938).

(58) Sakurada, I., Papier-Fabr. 36:252-257(1938).

(59) Sheppard, S. E., and Newsome, P. T., J. Phys. Chem. 33:1617-1635, especially 1625-1632(1929).

(60) Sheppard, S. E., and Newsome, P. T., J. Phys. Chem. 36:2306-2318 (1932).

(61) Kanamaru, Kisou, and Chao, Ju-yan, Kolloid Z. 84:85-99(1938).

(62) Urquhart, Alexander Robert, and Eckersall, Norman, J. Textile Inst. 23:T163-170(1932).

(63) Beck, L. H., Ind. Eng. Chem. 29:985-987(1937).

(64) Faust, O., "Celluloseverbindungen und ihre besonders wichtigen Verwendungsgebiete," vol. 1, especially p. 601-603. Berlin, Julius Springer, 1935. 1496 p.

(65) Ross, Kurt, "Die Chemie der Cellulose und ihrer Begleiter," Especially p. 411. Leipzig, Akademische Verlagsgesellschaft, 1928. 836 p.

(66) Sakurada, I., Papier-Fabr. 36:252-257, especially 255(1938).

(67) Malm, C. J., and Clarke, H. T., J. Am. Chem. Soc. 51:274-278(1929).

(68) Bernoulli, August L., Schenk, Max, and Hagenbuch, Werner, Helv. Chim. Acta 13:534-571, especially 551-553(1930).

(69) Murray, T. F., Jr., Stamm, C. J., and Gray, H. LeB., Ind. Eng. Chem., Anal. Ed. 3:269-273(1931).

(70) Taniguchi, H., and Sakurada, I., J. Soc. Chem. Ind., Japan 41, suppl. binding:71B-72B(1938).

(71) Wilson, H. N., and Hughes, W. C., J. Soc. Chem. Ind. 58:74-77(1939).

(72) Mark, H., Melliand Textilber.:695-700(1929).

(73) Berg, Kristian O., Papier-Fabr. 31:605-611; 617-622(1933).

(74) Doughty, R. H., and Curran, C. E., Paper Trade J. 97, no. 25:38-44 (Dec. 21, 1933).

(75) Doughty, R. H., Paper Trade J. 94, no. 9:29-34(March 3, 1932).

(76) Simmonds, F. A., and Baird, P. K., Paper Trade J. 98, no. 20: 33-42(May 17, 1934).

(77) Larocque, G., Forest Products Labs. Canada, Pulp Paper Lab., Quarterly Rev. No. 20:22-25(October-December, 1934).

(78) Doughty, R. H., Paper Trade J. 93, no. 15:44-49, 54(Oct. 6, 1931).

(79) Staudinger, H., and Eilers, H., Ber. 69:819-851, especially 838-839(1936).

(80) Staudinger, H., and Eilers, H., Ber. 68:1611-1618, especially footnote p. 1617(1935).

(81) Staudinger, H., and Schweitzer, O., Ber. 63:3132-3154, especially footnote p. 3133(1930).

(82) Porrvik, Gunnar, Pulp Paper Mag. Can. 28:133-136(1929).

(83) Zemplén, Géza, Gerecs, Árpád, and Kadácsy, Ilona, Ber. 69:1827-1829(1936).

(84) Sakurada, I., and Fukuhara, I., J. Soc. Chem. Ind. Japan 41, suppl. binding:384(1938); C.A. 33:2703(1939).

(85) Mark, H., and Meyer, Kurt H., Cellulosechemie 11:91-100, especially 96-97(1930).

(86) Hess, Kurt, Melliand Textilber. 15:29-32, especially 31(1934).

(87) Staudinger, H., and Reinecke, F., Ann. 535:47-100(1938).

(88) Lottermoser, A., and Vultsch, F., Kolloid Z. 63:180-196, especially 194(1933).

(89) Staudinger, H., and Jurisch, J., Zellwolle, Kunstseide, Seide 44: 375-376(1939); C.A. 34:1480(1940).

(90) Kanamaru, Kisou, Helv. Chim. Acta 17:1429-1440(1934).

APPENDIX

CALCULATION OF ACETYL CONTENT

The gram molecular weights of the chemical groups and molecular units to be considered are as follows:

anhydro-glucose unit of cellulose	162.0 g.
acetyl group, CH_3CO (or Ac)	43.0 g.
acetyl group after reaction with the hydroxyl group of the cellulose	42.0 g.

Let n be the number of hydroxyl groups covered with acetyl groups; then the weight of the acetyl groups introduced is $n(43.0)$ and the weight added to the anhydro-glucose unit of the cellulose is $n(42.0)$. Therefore, the equation expressing the percentage of acetyl content is,

$$\text{Acetyl content } (\%) = \frac{n(43.0)(100)}{162 + n(42.0)} \qquad (1)$$

In the acetyl determinations, the acetyl content was calculated from the titration by using the following equation:

$$\text{Acetyl content } (\%) = \frac{(0.0430)(N)\ (\text{cc. of alkali consumed})}{(\text{Weight of sample in grams})} \qquad (2)$$

where N is the normality of the alkali neutralized by the saponified acetic acid.

CALCULATION OF THE PERCENTAGE OF HYDROXYL GROUPS REPLACED BY ACETYL GROUPS

By combining equations (1) and (2) above, the percentage of hydroxyl groups covered in an acetylated cellulose can be calculated from the acetyl content. Since the total number of hydroxyl groups that can be replaced per anhydro-glucose unit is 3, and n is the number which has been replaced, then the percentage of the total number of hydroxyl groups that have been replaced is,

$$\text{Hydroxyl groups covered (\%)} = \frac{n(100)}{3} \qquad (3)$$

Solving equation (1) for n and substituting its value in equation (3) gives,

$$\text{Hydroxyl groups covered (\%)} = \frac{162\ Ac}{[43 - (42\ Ac)/100]}, \qquad (4)$$

where Ac is the acetyl content in per cent calculated from equation (2).

CALCULATION OF ORIGINAL CELLULOSE PRESENT IN AN ACETYLATED CELLULOSE PULP

By using the symbols and values employed in arriving at equation (1), the equation for the original cellulose present in an acetylated pulp can be written as

$$\text{Original cellulose (\%)} = \frac{162(100)}{162 + n(42.0)} \qquad (5)$$

Substituting in equation (5) the value of n in terms of acetyl content, obtained by solving equation (1) for the number of hydroxyl groups replaced by acetyl groups, gives

$$\text{Original cellulose } (\%) = \frac{6966 - 680^{4}\,Ac/102}{6966}, \qquad (6)$$

where Ac is the acetyl content in per cent.

CALCULATION OF OBSERVED STRENGTH VALUES TO VALUES BASED ON THE ORIGINAL CELLULOSE PRESENT IN THE ACETYLATED PULPS

In Table X, page 90, the observed tensile strength for the acetylated pulp of 23.35 per cent acetyl content was 1.5 pounds and the observed basis weight was 57.1 pounds per 25 by 40--500 ream size. The original cellulose content for this acetylated pulp was 77.3 per cent. Hence, the basis weight, calculated to the original cellulose content, is .773 by 57.1 or 44.1 pounds.

Calculating the observed tensile strength as pounds per 100-pounds basis weight gives,

$$\frac{1.5 \times 100}{57.1} = 2.6 \text{ lb./100 lb.}$$

Calculating the tensile strength to the original cellulose content gives,

$$\frac{1.5 \times 100}{44.1} = 3.4 \text{ lb./100 lb.}$$