The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Study of the Relation Between Sheet Strength and Fiber Surface Conditions

by Henry Philip Dixson, Jr.

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A STUDY OF THE RELATION BETWEEN SHEET STRENGTH AND FIBER SURFACE CONDITIONS

A thesis submitted by

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I. HISTORICAL INTRODUCTION

A large number of surface-active compounds have come into industrial use recently as wetting agents, emulsifiers, detergents, and penetrants. These compounds have already been used in the pulp industry to shorten the reduction time of hard-sized broke, to assist in deinking old paper, and to aid in processing latex and absorbent papers (1).

Since surface-active compounds, even in very dilute solution, reduce the surface tension of water and cause very rapid penetration of water into textiles, it would seem worth while to investigate the effect of such agents upon the beater processing of pulp. The beating and sheetmaking processes are chiefly concerned with the cellulose-water relationship, and, in spite of a large number of investigations, the change in cellulose-water systems during beating and sheet formation is not very well understood. It is quite possible that experiments with surface-active compounds in small concentrations which reduce surface tension might throw some light on the changes taking place in the paper-maker's beater and during the formation and drying of a fiber web.

The Theory of Wetting

Wetting is concerned chiefly with the relation of the surface tensions of the components of a system. Adam (2) states that briefly surface tension of liquids is due to a strong inward attraction of surface molecules. This inward attraction causes the surface to contract

until the maximum number of molecules are in the interior. "The fact that a liquid surface contracts spontaneously shows that there is free energy associated with it.... This free energy in the surface is of fundamental importance; a vast number of problems relating to the equilibrium of surfaces can be solved without knowing more than the magnitude of this free energy. In the solution of such problems a mathematical device is almost invariably employed to simplify the calculation; it is to substitute for the surface free energy a hypothetical tension, acting in all directions parallel to the surface, equal to the free energy of the surface. This is what is generally known as surface tension."

The above explanation includes liquid-liquid and solid-liquid interfaces, as well as the liquid-air interface, although the liquid-solid interfacial tension is difficult to measure.

Gortner (3) has given a simple picture of wetting. He explains that if a drop of a liquid is placed on a solid surface the resulting equilibrium will be determined by the surface tension of the solid, γ_s, the surface tension of the liquid, γ_l, and the interfacial tension of the solid-liquid, γ_{ls}. If $\gamma_s > \gamma_l + \gamma_{sl}$, the drop will spread and become a film on the solid surface. If, however, $\gamma_s < \gamma_l + \gamma_{ls}$, there will be a definite contact angle between the solid and the drop.

The above concepts of wetting, and the role of surface-active compounds, are not strictly applicable to very porous surfaces. Adams (4), in a discussion of detergent action and wetting, has stated that for porous surfaces $\gamma_A \cos\theta = W_{AS} - \gamma_A$ must be as large as possible

instead of merely cos θ, as in the case of a plane surface; θ is the contact angle, γ_A is the surface tension of water, and W_{as} is the adhesion between solid and liquid. When a solution is adsorbed by a fiber (5), the permeation is due to capillary attraction. The greater the surface tension and the lower the viscosity, the more rapid will be the penetration, providing cos θ, the contact angle, is unity (i.e., the surface is perfectly wetted).

Wetting agents make cos θ approach unity on surfaces where the contact angle is small (i.e., where cos θ is of a low magnitude). Therefore, in maximum penetration of capillary hydrophobic surfaces, just enough wetting agent must be added to attain some intermediate position between maximum penetration due to capillary attraction and a perfectly wetted surface.

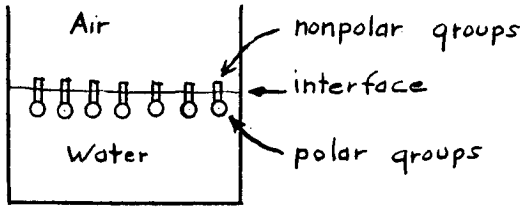
Orientation of Molecules at Surfaces

It is very difficult to sum up in a few sentences the amount of work which has been done on the subject of orientation of molecules at surfaces. Harkins (6) and Langmuir (7) have developed the basic concepts.

Molecules may be divided into two groups, the essentially symmetrical types and the unsymmetrical types. In symmetrical molecules, such as pentane, the two ends of the hydrocarbon are the same and behave identically toward an interface. In the case of acetic acid, the two ends are dissimilar, one being a hydrocarbon and the other a hydroxyl group (-OH) similar to water. Thus the two ends of acetic acid would act differently toward an interface.

Groups which have an affinity for water are termed polar groups. Such groups are -OH, -COOH, -CHO, $-NO_2$, $-CH{:}CH_2$, and -C:CH. The polar group confers solubility on organic molecules. Hydrocarbon (nonpolar) surfaces have much less free energy than water or polar surfaces. Hence, molecules containing both polar and nonpolar groups will orient at interfaces in such a manner as to produce the least amount of surface energy.

In an aqueous solution of long chain hydrocarbon molecules which have very strong polar groups attached, the molecules will orient at the air-water interface as shown in the accompanying sketch, and the surface energy of the system will be at a minimum.



Orientation of Surface-Active Molecules at an Interface

Application of Surface-Active Compounds to Wetting Problems

Wilkes and Wickert (8) have explained that wetting agents are strongly polar compounds comprising a nonhydrocarbon portion of high molecular weight at some point in which is located a sufficiently polar or water-soluble group to endow the molecule with properties of at least colloidal solubility in water. Thus these molecules in suspension will endow a hydrophilic medium with an ability to wet and penetrate materials more or less hydrophobic in character, or vice versa, by orientating at interfaces and reducing the surface energy.

It can be seen that any wetting power of a solution of these molecules toward any given substance is dependent upon the hydrophilic-hydrophobic balance in the surface-active molecule, and the surface energy of the substance to be wet. In order to avoid confusion, it might be pointed out that in this paper the term hydrophobic indicates a low surface energy as compared with water. Since it is impossible to measure by any practical means the surface energy of a solid surface, surface-active compounds have been evaluated by empirical methods for their ability to aid wetting. For example, the textile industry officially uses the Draves test (9). In this method, the time required for 5-gram skeins of two-ply unboiled cotton yarn to sink when weighted with a 1.5-gram sinker and submerged in a wetting agent solution is measured.

Types of Wetting Agents Available and Their Use in the Paper Industry

Dean (10) has described the structure and synthesis of wetting agents. He pointed out that innumerable wetting agents can be made from the various hydrocarbon chains, aliphatic and aromatic, and from the polar groups -OH, $-SO_3H$, $-SO_4H$, -Cl, -Br, $-NH_2$, and many others. Wilkes and Wickert (8) classified wetting agents as follows:

Group A	Group B
R-COONa	R_2^1-$CHOSO_3Na$
$R-OSO_3Na$	R'-OOC-CH_2
$R-CONHC_2H_4OSO_3Na$	R'-OOC-$CHOSO_3Na$
$R-COOC_2H_4OSO_3Na$	R'-Ar-SO_3Na

R is a fatty alkyl group; R' is a primary or secondary nonfatty alkyl group; and Ar is an aryl group.

Group A includes soaps, fatty alcohol sulfates, and sulfated fatty acid esters and amides. Group B includes secondary alcohol sulfates, sulfated esters of higher alcohols and dibasic acids, and alkyl derivatives of aryl or aromatic sulfonates.

Cupples (11) has prepared an extensive list of commercial wetting agents, and of their uses and chemical composition as far as they have been revealed by the manufacturers.

Harrison (12), (13) has carried out preliminary investigations on the use of wetting agents in beaters. In a study of the reduction of hard-sized broke he found that, in the range of 0.06 to 0.1 per cent of Perminal W (alkylated naphthalene sulfuric acid), the broke showed a maximum resistance to wetting, but that in larger concentrations the wetting time was reduced. He also stated that "It might be expected from current theories regarding the nature of wetness and hydration, that the presence during beating of a substance which facilitates water penetration would increase the rate of adsorption and so facilitate both strength and wetness development. The opposite effect was obtained when pulp was ball-milled in the presence of 5 per cent (fiber basis) alkylnaphthalene sulfonic acid."

Beating Time	60 min.	60 min. (With Agent)	25 min.
Burst	83.5	67.0	69.1
Tear	229	261	275
S.R. Wetness	51	19	19

If 2 per cent of kerosene were added, frothing was prevented and the pulp was beaten about the same as in the absence of wetting

agent. He stated that "frothing alone is sufficient to account almost completely for the inability of kraft pulps to develop when a wetting agent is present. Frothing may, by flotation, remove the fibers from the sphere of action of the ball mill, or there may be a more obscure explanation, depending on the changes in the degree of gelatinization of the cellulose surface in the presence of an air film." Noll (14), in a thermal study of beating, found that beating decreased with surface tension decrease. He decreased the surface tension by increasing the temperature. He also showed that wetting agents decrease the beating degree and, on the basis that wetting agents also decrease surface tension, he concluded that in his thermal studies the decrease of beating was a function of surface tension. It is obvious from the above experiments that there is much to be clarified in the cellulose-water-surface active agent relationships.

Morphology of Cellulose Fibers

In the consideration of the subject of wetting and of the functions of cellulose surfaces during beating development and sheet formation, it is necessary to explain briefly the modern concept of cellulose fibers. Ritter (15) has summarized the knowledge of fiber structure in an orderly manner and has pointed out the significance of the fiber structure in beating. Springwood fibers are thin-walled and in chemical pulps collapse to ribbons on slight processing. Summerwood fibers are thick-walled and resist beating. Cotton fibers are too long to form paper webs and must be cut to secure sheet formation. The fiber walls are composed of compactly wound cellulosic filaments,

termed fibrils. A smooth sleeve results from a filling of interstices between fibrils with hemicellulosic material, which in normal fibers must be removed before fibril windings become discernible. In the outer layer of the cell wall, the windings are at right angles to the fiber axis. The remaining fibrils in other layers are at angles of from 5 to 30 degrees to the long fiber axis.

Under controlled conditions, fibrils have been dissected into fusiform bodies which have been reduced to smaller spherical units. Submicroscopically, cellulose consists of micelles or crystallites. The crystallites are believed to be rectangular parallelopipeds about 50 by 50 by 500-1000 Angstrom units in size. The micelles are supposedly held together by tertiary valence forces.

Primary valence chains are the substructures of the micelles. The chains are from 500 to 1000 Angstrom units long and are composed of anhydroglucose residues held together by primary valence. Bundles of these chains are held together by secondary valence to form the micelles. The unit cell is a regularly occurring unit diagram in the crystal lattice involving the glucose residues of the primary valence chains. It is comprised of the equivalent of four anhydroglucose residues. It is 7.8 by 8.3 by 10.3 Angstrom units as calculated from x-ray data.

In addition to an explanation of fiber morphology, Ritter added the following interesting view on beating as related to the fiber structure. He explained that during beating fibrils are loosened from the fibers. Generally, the effects of beating are, in

order of occurrence, increase in pliability of fibers, transverse cutting, gelatinisation of fiber surfaces, rupture of the outer layer, and fibrillation.

He stated further that, other factors being the same, the resistance of fibers to fibrillation depends upon the severity of their previous chemical and mechanical treatments. Pulps which have been drastically treated fibrillate easily because interfibril substance is removed. "This explanation may seem contrary to the well known experimental fact that alpha pulp is dissected and fibrillated with greater difficulty than a less purified pulp. That, however, occurs when the alpha pulp has been dried, allowing the modified cellulose materials to cement the fibrils together by a substance more resistant than that in the original fibers." In wood this interfibril substance seems to be composed of pentosans, hexosans, and uronic acid complexes. In cotton it might consist of anhydrouronic acids and anhydroglucose residues. This would correspond to Lüdtke's skin substance.

The surface of cellulose is very large. Campbell (18) calculated from the x-ray data of Meyer and Mark (17) that one gram of cellulose has a total surface of 512 square meters, but the visible surface is only 0.4 square meter per gram. However, the total surface must be considered when one is dealing with sorption from vapors and liquids.

The Various Concepts of Beating

There is a large mass of literature on the subject of

"hydration" of papermaking fibers as they are processed in refining equipment. Simmonds (18), Clarke (19), Houser (20), Campbell (16), and Cottrall (21) have summarized the hydration literature, consolidated the various theories of hydration, and interpreted the findings in the light of their personal knowledge.

In this thesis, the term "hydration" as applied to pulp refining will be discarded so that it will not become confused with true chemical hydration. In place of "hydration," the term "pulp development" will be used to indicate the refining processes in which pulp fibers become increasingly slimy, fibrillated, and reluctant to part with water and in which the sheets of paper formed from these pulp fibers become increasingly strong to a maximum point and then become weaker and translucent.

Broadly speaking, there have been three concepts of beating: the chemical, the physical, and the physico-chemical or colloidal.

Early investigators, including Schwalbe and Becker (22) and Minor (23), tried to explain the development of pulp on the basis of a chemical change or a chemical addition of water during beating. As Clarke (19) pointed out, this theory explained most of the development phenomena as it was known in those days. But as progress in the knowledge of cellulosic materials advanced, many doubts were raised about the chemical theory of pulp development.

Strachan (24) was the first to point out that there is lit-

tle chemical change during beating. Furthermore, he could find no break in the curve of moisture content vs. time of drying, and thus he concluded that there was no evidence of true chemical hydration. Kress and Bialkowsky (25) offered the following conclusion on the basis of numerous experiments: "Practically no chemical changes in-so-far as the chemical constants, such as alpha content, copper number and soda soluble, have been observed in the various stages of beating an unbleached Mitscherlich spruce pulp to a degree far in excess of a stock prepared mechanically for the production of commercial glassine. The chemical changes noted with progressive beating in the cuprammonium viscosity determination and in the Schwalbe hydrolysis number are not, in our opinion, occasioned by chemical changes in the pulp but are caused solely by the fact that the fibre is more reactive, due to mechanical disintegration.

"Experimentally, we have definitely shown that during the so-called hydration, water does not chemically combine with the pulp and that no hydrates of the pulp exist."

The purely physical point of view of pulp development has been advanced and adhered to by Strachan (24), (26). He claimed that fibrillation alone is responsible for the strength development. This point of view has been refuted by many investigators. Kress and Bialkowsky (25) and Bell (27) have made sheets in alcohol and other hydrocarbon liquids and have found them to have little strength even if the fibers are well fibrillated. Nakano (28) has shown that, although wool and asbestos fibrillate, there is no strength. He con-

cluded that vegetable fibers alone seem to have colloidal surface conditions necessary for fiber bonding. Harrison stated (29) that fibrillation and imbibition usually occur together but fibrillation alone will not produce strength. Simmonds and Baird (30) pointed out that the maximum strength occurs before fibrillation begins.

The third concept of beating, the physico-chemical theory, accepts fibrillation as one of the chief factors causing strength in paper, but it incorporates a mechanism of fiber-fiber bonding also. The physico-chemical theory is held by such investigators as Campbell (16), Harrison (12), (29), Cottrall (21), Clarke (19), and Bell (27).

The chief difficulty in evolving any beating theory is that there are so many complicating factors. In the first place, measurements are made on the strength of a sheet of paper prepared from pulp under conditions of forming, sheet pressing, and drying that are often not rigidly controlled. Secondly, the fundamental basis of some of the usual strength tests is not well understood. Carson and Worthington (31) have shown that the Mullen strength is determined by the tensile strength and elongation in the machine direction. Doughty (32) has pointed out that tensile strength is a component of Mullen and fold, and that tensile strength is measured in fundamental units. Cottrall (33) has shown that the tear test is of little value. The test is not a measure of fiber length alone but also of hydration. Brecht and Imset (34) have pointed out that the Elmendorf tear tester does not indicate the extent of shortening of fibers on beating.

In view of the confusion existing concerning the tearing strength measurement, any strength development considered in this historical introduction will be in reference to Mullen, fold, and tensile strengths.

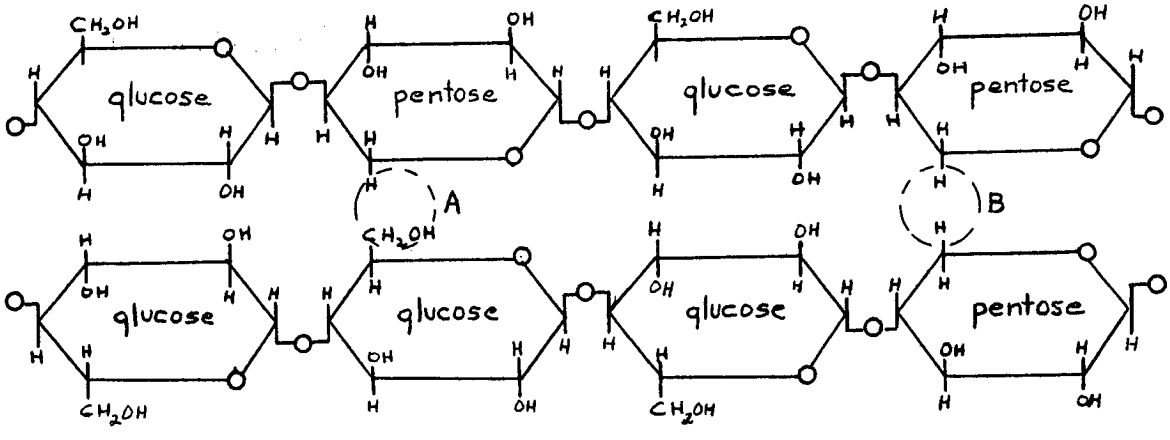
In general, it may be stated that the strength of a sheet of paper, from the physico-chemical viewpoint, is due to the individual fiber strength and the strength of the fiber-fiber bonds. The individual fibril and fiber strength is due chiefly to primary, secondary, and tertiary valence forces as previously indicated by Ritter (15). Steinschneider and Grund (35) have shown that the individual fiber strength decreases from the start of beating. Ritter (15) has further pointed out that the fiber strength is also dependent upon the severity of the isolation procedure.

One factor which affects the sheet strength due to individual fiber strength and the strength due to fiber-fiber bonds is the concentration of cellulose fibers per unit volume. Doughty (32) has made significant observations on the relation of the strength and the solid fraction present in a sheet. He found that the sheet strength as measured by the tensile strength is dependent upon the solid fraction of the pulp fiber. By employing wet pressing pressures from 0 to 1,000 pounds per square inch, the tensile strength increased with the solid fraction much the same as it would increase upon beating. Also, strength curves were constructed by plotting Mullen, fold, tensile, and tear against solid fraction. These curves were very similar to the familiar beating curves of strength vs. time. Thus, in beating,

the increase in solid fraction might account for most of the strength development. Doughty states that, except for a large increase in strength which takes place in the first few minutes of beating, there is little strength increase due to beating if the sheets are made at a constant solid fraction.

Effect of Constituents Other than Cellulose on Sheet Strength

Maass and Campbell (36) stated that foreign materials, such as pentosans, interrupt the regular cellulose structure, and thus there is a greater ease of fibril formation. Therefore, a sulfite pulp containing large amounts of pentosans will beat faster. Young and Rowland (37) found that the relation between pentosan content and swelling tendency of softwoods is nearly linear. In a theoretical explanation of their results, they pictured two cellulose chains lying side by side with pentose groups interspersed.



They postulate that, if there were two glucose chains lying side by side instead of glucose chains interspersed with pentose units, the attraction at points A and B would be between adjacent $-CH_2OH$ groups. This attraction is relatively strong. But the field of attraction

with pentose units present is very weak, because sometimes the field of force at A and B will be between -H H- and $-CH_2OH$ H-. This results in a greater ease of penetration of water, since cellulose-cellulose attractive forces are less and thus a greater swelling occurs. Clark (38), Meyer and Mark (17), and Kats (39) have shown that water does not enter into the micelles but between them. The concept of Rowland and Young would be limited to chains lying on the micelle surfaces.

Obermanns (40) has made extensive studies of hemicellulosic materials in relation to beating. He found that, either by introducing hemicellulose mechanically into rag stock or by producing it through overbleaching the pulp, the beating action took place more rapidly. The hemicellulose introduced mechanically was the beta and gamma fraction from a soda pulp.

The Mechanism of Fiber-Fiber Bonding

The mechanism of fiber-fiber bonding is not well understood. Campbell (16) theorized that the surface layer of cellulose is in solution and that fibers, brought into intimate contact by either pressure or surface tension effects, form on drying a bond of transition crystal layers. This terminology is rather unfortunate since Strachan (26) and others have pointed out that crystals form only when the crystal axes are in perfect orientation, and very few fibers would be arranged in that manner.

Cottrall (21) believed that free -OH groups are very reactive

and that at fiber-fiber surfaces these groups tend to unite. If two wet fibers are in intimate contact and drying takes place, the water bound to the -OH group is driven off and the -OH group will tend to be attracted to and bond with some other adjacent -OH group which has lost its water. If this -OH group happens to be one associated with the fiber in intimate contact, the phenomenon of fiber-fiber bonding takes place. This idea has also been expressed by Mark (41).

Cottrall's (21) entire concept of beating is very concisely presented and is worth reviewing. He stated that during beating the fibers first become softened and thus contact is more easily established upon pressing. This accounts for the strength increment before fibrillation. Contact is increased after fibrillation by the production of fibrils which are more mobile than the larger fibers and have a greater chance to form fiber-fiber bonds. Fibrillation will also lead to a reduction in bulk, since the fibrillae are capable of filling air spaces. Furthermore, it is noted that the major portion of bulk reduction occurs at the beginning of beating when there is considerable air space available. Cottrall restated Campbell's position regarding the relation of surface tension to the contraction of a sheet on drying. The smaller the fibrillae, the greater the attractive force and thus the greater the shrinkage.

Jayme (42) expressed approximately the same idea. He stated that, in the first place, for beating action to occur, it must take place in a medium that allows cellulose to swell. By swelling, the fibers become plastic, enabling them to fibrillate and form large

capillaries which fill with water. Beating also produces a larger surface by fibrillation and fiber cutting, thus improving the mechanical felting of fibers.

The Cellulose-Water Relationship

It is clear that fiber-fiber bonding and also fibrillation are intimately associated with the relationship of cellulose to water. Most discussions on this subject are centered on the problem of how and to what extent water is bound to cellulose. Peirce (43) has made an exhaustive experimental study of the relationship of water to cotton and expresses the water adsorption by several mathematical equations. He found that "moisture adsorption occurs in two phases in one of which one molecule of water attaches itself to one hexose group, whereas in the other an indefinite number of molecules are loosely adsorbed on all available surfaces, being limited only by conditions of space and external vapor pressure." The first class of water affects rigidity, elasticity, and strength whereas the second class maintains a vapor pressure. He pointed out that any removal of the second class disturbs the equilibrium of the first class. Maass and Campbell (36) hold also that water sorbed by cellulose is sorbed in two ways. The first is "bound" water and the second is held under tension in capillaries.

Balls (44) has carried out careful conductivity measurements on single cotton hairs. He stated that "the greater amount of water taken up after mercerisation must be held by cellulose in a different manner because although the hair is wetter by weight, the

conductivity is less.

"The cotton and water may be combined in various phases, which we may designate quite provisionally as follows: [% relative humidity] 0-15% Phase of chemical hydration. 15-40% Phase of monopolar adsorption. 40-77% Phase of tri-polar adsorption. 77-90% Phase of molecular association. 90-150% Phase of capillarity."

Sheppard and Newsome (45) have shown that esterification reduces the moisture content of pulp and that the sorption is reduced in proportion to the molecular weight of the esterifying group. These results show that the hydroxyl groups play an important part in moisture sorption.

Sheppard (46) found 5 per cent of water to be held by primary sorption in native cellulose and 7 per cent in dispersed cellulose. Walker (47) stated that multimolecular layers of water are condensed on fiber surfaces. Each -OH group in the cellulose surface is the base of a water chain. Filby and Maass (48) in a study of the volume of cellulose and water vapor, claimed that the water content below 4 per cent is condensed, but that a water content of more than 8 per cent is taken up at normal density. Bancroft and Calkin (49) found that, after centrifuging at a high speed, cellulose which contained 27 per cent of water in saturated air still contained 17 per cent of moisture.

It is well to point out the hydrous condition of other materials present in pulp besides cellulose. Klingstedt (50) has

pointed out that since the materials in beta-cellulose are easily peptized by bases, it is possible that they are easily hydrated on beating. Haas and Hill (51) stated that beta- and gamma-cellulose may differ from alpha-cellulose only in degree of polymerization, hydration, or dispersion. Schroger (52) claimed that pentosans are much more hydrophilic than hexosans.

Many studies have been carried out on the water-cellulose relationship after beating. Seborg, Simmond, and Baird (53) made careful moisture sorption studies on cellulose and reported the well-known hysteresis loop obtained on adsorption and desorption. Sheppard and Newsome (54) found that although repeated adsorption-desorption cycles narrowed the hysteresis loop, the loop could not be eliminated. Pidgeon and Maass (55) found a decrease in sorption as the temperature was raised, thus adding weight to the idea that the bound⇌free water equilibrium is dependent upon the temperature. Seborg and Stamm (56) in a series of careful adsorption-desorption measurements could find no change in the hysteresis loop or electrical conductivity of pulp after eight hours of beating. Russell, Maass, and Campbell (57) in a very carefully controlled experiment found the ratio of moisture content of excessively beaten to unbeaten pulp to be 1.05. Kress and Bialkowsky (25) could find no change in Methylene Blue sorption in beaten and unbeaten pulps.

The evidence points to the fact that the "bound" water does not increase upon beating. Yet there is a mass of evidence that cellulose becomes reluctant to part with its water as it becomes

gelatinized by beating. Jahn and McCarthy (58) pressed pulp under 10,000 pounds per square inch pressure for 12 minutes and found that the water retention increased during beating. Bell's method (59) of measuring the volume contraction and the densities of pressed pulp cakes showed the same effect. Rowe (60) pointed out that the water retained by a material is dependent upon its physical state. By evaporation curves, obtained upon drying thin pulp pads, sharp breaks were obtained. These breaks were associated with pulp development. This "hydration" increased on beating. It is suggested that beating causes partial reduction to the amorphous state.

Jahn, Sedoff, and Holmberg (61) in a later series of measurements arrived at the following conclusions: "Increased pressures up to 5000 pounds per square inch decrease the per cent water retained for any constant time of pressing. Increased time of pressing at any constant pressure decreases the water content ... due to beating. Beating has no effect on the water retained if the pulp is subjected to pressure sufficiently long (44 hours). Determining the per cent water retained by pulp pressed at 4000 pounds pressure per square inch for 10 minutes gives a good measure of beating changes for drastically beaten or gelatinized pulp."

These authors show very clearly the difference between sorption measurements and other water retention measurements. "The term 'gelatinization' is sometimes used in connection with beating where it may be considered synonymous with colloidal hydration in that it means the dispersion of water into a solid or the increase

in internal water with resultant swelling. However 'gelatinization' is often used, though rather loosely, to imply not only colloidal hydration and resultant swelling but micellar disorientation and slime or gel formation.

"Colloidal hydration results on simple immersion or contact of pulp with water and drastic beating causes only very slight increase in this hydration as measured by sorption experiments...

"The changes in pulp properties by beating cannot, therefore, be explained by colloidal hydration or capillary imbibition, but are the result of physical changes termed 'paper makers' hydration.' If gelatinization be defined as synonymous with colloidal hydration, a measure of per cent water retained does not measure gelatinisation. If the changes in the physical character of the fibers, i.e., decreased effective particle size, slime formation, and micellar disorientation, be brought into the picture, these would cause a higher water retention due to the greater resistance to water flow."

II. PRESENTATION OF THE PROBLEM

From the historical introduction, it can be observed that beating and sheetmaking processes are closely related to the condition and amount of water retained on fiber surfaces and in fiber capillaries. It is proposed to investigate some of the relationships which apparently exist between sheet strength and the water present on fiber surfaces and within minute surface capillaries.

Experiments will be made employing variable surface tension conditions, and the hydrophilic character of pulp fiber surfaces will be varied by the use of surface tension depressants and several highly hydrophilic colloids. The effects of these variations on pulp fiber surface characteristics and upon sheet strength will be studied.

III. GENERAL EXPERIMENTAL PROCEDURES

A large number of experimental procedures have been followed, but in most cases procedures have been based on the following general methods. The merits of various methods used will be dealt with in the general discussion of results.

Pulp Processing

Beater runs were made according to TAPPI Standard Method T 200 m-54.

Ball mill runs were carried out as follows. Ninety grams (oven-dry basis) of pulp in two liters of water were disintegrated 75,000 revolutions in the British disintegrator. The pulp was then washed into a porcelain-lined 10½ by 13½-inch Abbé ball mill with one liter of water (3 liters total water). Seventy-seven flint pebbles (weight 5000 grams, volume 1892 cc., pebbles 60 to 70 grams each) were added, and the mill rotated at 60 r.p.m., After the desired number of revolutions, the pulp and pebbles were removed and separated and the pulp was diluted to ten liters. This pulp suspension was stirred with a small "Lightnin" mixer for fifteen minutes.

Forming and Testing of Handsheets

Handsheets were formed by TAPPI Standard Method T 205 m-36, except for the wet pressing pressure which was varied from 0 to 500

pounds per square inch, depending upon the experiment. Handsheets were tested by Institute methods:

Mullen strength - Institute Method 510
Tensile strength - Institute Method 511
Tearing strength - Institute Method 512

The porosity of the handsheets was estimated with the Gurley Densometer. This test measures the time required for 100 cc. of air to diffuse through the sheet under a given pressure.

Sheet thickness was determined by a Schopper caliper; five determinations were made on each sheet. The apparent density of the sheets was determined by dividing the ream weight (25 X 40--500) by the caliper expressed in thousandths of an inch. The folding endurance was measured on the M.I.T. folding endurance tester.

Surface Tension Measurements

Surface tension measurements were made on the du Noüy Interfacial Tensiometer (Central Scientific Co. Model No. 70540). The instrument was calibrated by placing a 0.800 gram weight on the ring and adjusting the torsion wire by the method described by the Central Scientific Co. so that the scale would read directly in dynes per cm.

Except where otherwise specified, measurements were made as follows. All glassware was boiled in sulfuric acid-potassium dichromate cleaning solution and rinsed with distilled water. Before each measurement, the tensiometer ring was flamed over a Bunsen burner, washed, and flamed again. The sample was then stirred violently and

a small portion poured into the tensiometer cup. In the case of pulp suspensions, the pulp was held back with a stirring rod and only the liquor was allowed to flow into the cup. The tensiometer ring was then lowered below the surface of the liquid and, after exactly one minute, the ring was pulled through the surface at a uniform rate. The reading was taken when the ring broke through the liquid surface. This reading was multiplied by 0.94, which is a constant depending upon the ring diameter and was supplied with the operating directions for the instrument. The du Noüy Ring Tensiometer was selected because of the ease of manipulation and the rapidity of operation.

Preparation of Colloidal Systems

Pulp-wetting agent systems were prepared by adding the wetting agent in the form supplied by the manufacturer to pulp suspensions of 0.9 per cent consistency. The suspensions were agitated slowly for one hour so as not to produce foaming. This procedure was followed in all cases unless otherwise specified.

The cellulose gel added to the pulp was prepared as follows. Fifteen grams of air-dry cotton linters (98.5 per cent alpha cellulose) were added to two liters of cuprammonium hydroxide solution. Care was taken to exclude air as much as possible, and the mixture was allowed to stand in the dark for three days. At frequent intervals the bottle was shaken on a motor-driven rocking device.

After the three-day dispersion time, the cellulose was completely dispersed. The cuprammonium dispersion was then allowed to

run slowly into 20 liters of cold distilled water which was moderately agitated; the cellulose precipitated as a light blue floc. The precipitate was allowed to settle over night in a stoppered bottle. The clear supernatant liquid was then siphoned off and the precipitate filtered in small portions on a large Büchner funnel. The wet, amorphous cellulose was washed in small portions with ten per cent acetic acid on a Büchner funnel until the blue color disappeared. During the washing, the cellulose changed to a gelatinous mass.

The colorless cellulose gel was washed with distilled water until the filtrate was neutral to litmus. The material was placed in two liters of water and agitated 30 minutes in a British disintegrator. The resulting cellulose gel had the appearance of a one per cent starch dispersion and did not settle out. One hundred cc. of solution contained 0.695 grams of oven-dry cellulose.

A one-fourth per cent locust bean gum suspension was prepared by adding slowly and with agitation 8.82 grams of Italian locust bean gum to 3450 cc. of cold water. The temperature was then slowly raised to 85° C., and the solution was allowed to cool. Agitation was continued throughout the preparation. The dispersion was used three hours after preparation.

A one-fourth per cent gelatin dispersion was made by adding the requisite quantity of pure sheet gelatin to warm water. The gel was allowed to cool before it was added to the pulp.

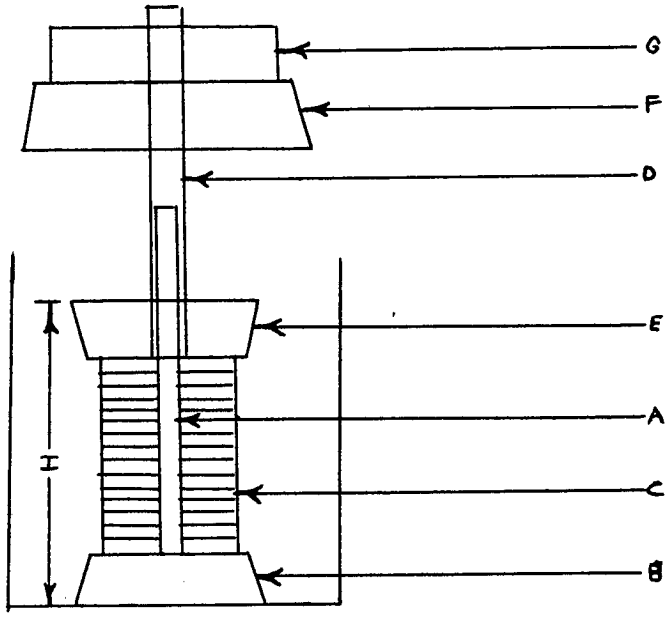
Methylcellulose was precipitated on pulp in the following

manner. Twenty grams of commercial methylcellulose (about five per cent methoxyl content) was treated with 170 cc. of cold water. After allowing the methylcellulose to soak for one hour, 26.6 grams of fifty per cent cold sodium hydroxide were added and the constituents kneaded with a stirring rod. After thorough mixing, the methylcellulose was diluted to 5 per cent by adding 184 cc. of water. The resulting methylcellulose solution was a thick, clear, viscous dispersion. The desired amount of methylcellulose was added to a 0.9 per cent pulp suspension and stirred slowly for three-fourths of an hour. The alkalinity was then reduced by adding ten per cent acetic acid until a phenolphthalein end point was obtained. The pulp suspension was stirred an additional fifteen minutes.

Pulp was mordanted with a tannic acid solution prepared by adding 20 grams of tannic acid to 1500 cc. of warm water. Enough pulp was then added to make a 0.9 per cent suspension, after which the mixture was brought to 80° C. and allowed to cool slowly. The tannic acid-treated pulp was filtered on a Büchner funnel, and the pulp fibers were diluted to 1300 cc. with water containing 10 grams of tartar emetic. This procedure mordanted the tannic acid to the fibers. After fifteen minutes of slow agitation, five grams of sodium carbonate were added and the suspension was filtered on a Büchner funnel. The pulp was again diluted to 0.9 per cent consistency (1500 cc.) with water containing 5 grams of tannic acid and was made into sheets.

Measurement of Swelling Action of Solutions on Cellulose

A modified procedure of Jayme' (62) was used to determine the relative swelling power of aqueous wetting-out agent solutions.



Measurement of Pulp Swelling

FIGURE 1

A calibrated thermometer stem (A) was placed in a No. 9 one-holed stopper (B). One-inch pulp squares (C) were cut and punched with a one-fourth inch hole. Thirty of these squares were weighed and then slipped on the thermometer stem (A). A glass tube (D) was inserted in a second No. 9 one-holed stopper (E). A No. 14 one-holed stopper (F) was also fitted on the glass tube as indicated in Figure 1. The glass tube (D) was placed over the thermometer stem (A) with the smaller stopper (E) resting on the pulp disks. An 800-gram lead disk (G) was placed on the No. 14 stopper, and the height, H, was measured by reading the thermometer stem (A) which was calibrated in

millimeters. The weight and glass tube holding the No. 9 and No. 14 stoppers were removed, and the disks and thermometer were placed in a glass cylinder. Enough of the desired liquid was then carefully added to cover the disks.

After 30 minutes, the glass tube and lead weight were placed on the pulp disks. If necessary, some of the liquid was removed so that the top surface of the stopper (E) was no longer submerged. After five minutes, the height H' was determined. The tabs were then removed, quickly blotted with paper toweling, and weighed immediately.

The following calculations were made:

$$\frac{H' - H}{H}(100) = \text{Percentage of Thickness Increase}$$

$$\frac{\text{Final Weight} - \text{Original Weight}}{\text{Original Weight}}(100) = \text{Percentage of Weight Increase}$$

Determination of Bound Water

The degree of hydration of colloidal materials was measured and correlated with sheet strength. The meaning of the term hydration is certainly not clear, particularly in the paper industry. Hydration, in the chemical sense, means the actual binding of water. However, the term has been loosely extended to include water held by capillary forces as well as that held by secondary valence. The line of differentiation between bound and capillary water is difficult to find in many cases. Therefore, the term hydration must be given an empirical limitation. For example, Newton and Gortner (63) term

"bound water" as that water which is not available as a solvent for sugar in a colloidal system.

In the case of pulp, several methods of determining the water of hydration were considered. The drying rate of pulp pads has been used by Rowe (60), but this method is dependent upon the rate of diffusion which varies with the pad density. Stamm (64) has used electrical conductivity to determine the fiber saturation point of wood and pulp, but pulp fibers treated with wetting agents might show erroneously high conductivity because many wetting-out agents are weak electrolytes. The method would not be suited for measurements in this thesis.

Barkas (65) has measured the bound water in Sitka spruce by determining the amount of water in the wood not available as a solvent for sucrose. The sugar concentration was measured interferometrically.

Newton and Gortner (63) and Gortner and Gortner (66) have been successful in making bound water measurements on plant materials by the cryoscopic method. They measured that water bound to a colloid which was not available as a solvent for sucrose. The sugar concentration was measured by the freezing point depression of the solution.

The validity of the determination as an absolute measure is dependent upon two factors. First, the colloid must not sorb sugar in preference to water and, secondly, the bound $\rightleftharpoons$ free water

equilibrium must not shift appreciably with change of temperature. Sugar and glucose are both negatively sorbed by pulp (65). The equilibrium between free and bound water probably changes during the freezing point determination; however, only relative measurements are necessary for the present investigation. The cryoscopic method was thought to be most applicable to the colloidal systems dealt with in this work.

The procedure employed is as follows. The freezing point depression of a sugar solution containing 0.5427 grams of sugar per gram of water was determined with the customary freezing point apparatus. A Beckmann thermometer calibrated to 0.01° C. was used to measure the temperature. Estimations were made of the thousandths of a degree. The freezing point was first determined approximately. Afterward each sample was supercooled 0.1° C., ± 0.020° C. A very small ice crystal was introduced and the system agitated very rapidly. The temperature then rose quickly to a constant value. This was taken as the freezing point. For any colloidal system under consideration, the oven-dry weight (after 24 hours) was determined. Preliminary experiments were carried out to determine the maximum concentration which could be used and still have sufficient mobility at the freezing point so that agitation was not too seeverely impaired.

A sample of the colloid containing this maximum amount of dry material was weighed. Let A be the water in this sample. On the basis of approximately 100 grams of total water in the final system, a portion of water, B, i.e. (100 - A), was weighed out and sufficient

sugar was added to B to give a sugar concentration of 0.7427 grams per gram of water in the mixture of A and B. After the sugar was dissolved, the weighed colloid was added and mixed thoroughly. The system was allowed to stand one hour to attain equilibrium. A measurement made after 48 hours showed that the one-hour period was sufficient for this purpose.

After the one-hour period, a portion of the solution was removed and a freezing point was determined as described above. Ten determinations were made on each sample. The freezing point depression of the colloid in the absence of sugar was also determined. It was found that a pulp suspension did not depress the freezing point.

If Δ_s is the freezing point depression of pure sugar, Δ_c the depression of the colloid, and $\Delta_{(c+s)}$ the freezing point depression of the mixture, the bound water may be calculated by the formula of Newton and Gortner (65):

$$\frac{\Delta_{(c+s)} - (\Delta_c + \Delta_s)}{\Delta_{(c+s)} - \Delta_c} \left[\begin{matrix}\text{Weight of Water} \\ \text{in System}\end{matrix}\right] = \begin{matrix}\text{Weight of Water} \\ \text{Bound}\end{matrix}$$

The percentage of hydration is determined by dividing the grams of water bound by the oven-dry weight of the colloid.

As there was no measurable Δ_c for pulp suspensions, the presence of the pulp during the freezing point determination was not necessary. To facilitate the freezing point measurement, the sugar liquor was pressed from the pulp-sugar-water system after equilibrium was attained. The freezing point depression of this sugar solution

was determined. The removal of the fibers from the system eliminated the mechanical difficulty experienced in attaining rapid agitation of the system as freezing occurred.

A verification of the method as a means for evaluating hydration (i.e., bound water) was made on starch-soap systems prepared by Heald (67). He found that the addition of sodium oleate to 0.5 per cent starch dispersions produced maximum turbidity at an optimum soap concentration of 12.18 per cent sodium oleate calculated on the starch present. On the basis of this and other experiments, Heald concluded that 12.18 per cent soap produced the minimum hydration of the system. By the procedure outlined above, the bound water determinations given in Table I were made. The results indicate that hydration is actually being measured by the procedure followed.

The Alkali Binding Power of Pulp

The amount of sodium hydroxide removed from solution by pulp was used as another measure of its hydrophilic nature. This was used by Jahn and McCarthy (58) as a measure of pulp development.

Bialkowsky (68) has shown that pulps remove alkali from dilute solutions. He found that the removal was greatest for easy-beating, impure pulps and that alpha and rag pulps bound the least amount of alkali. Downs (69) carried the work much farther and found that the binding of alkali was due in part to the acid constituents of the pulp and in part to sorption. No exchange sorption took place between the inorganic constituents of pulps and the sodium hydroxide.

TABLE I

WATER BINDING POWER OF SOAP-STARCH SYSTEMS

Sample	Weight of Water g.	Weight of Colloid g.	Weight of Sugar g.	Δ_{c+s} °C.	Δ_c °C.	Water Bound g.	Water Bound %	Average Water Bound %
0.5 % Starch	97.603	0.500	33.4670	2.132	0.000	0.545	110	101
0.5 % Starch	97.645	0.500	33.4485	2.130	0.000	0.456	92	
0.5 % Starch 12.18 % Sodium Oleate	99.184	0.561	33.9904	2.122	0.002	0.465	82	84
0.5 % Starch 12.18 % Sodium Oleate	99.127	0.561	33.9708	2.123	0.002	0.466	84	
0.5 % Starch 30.40 % Sodium Oleate	98.835	0.652	33.8708	2.143	0.007	0.741	114	105
0.5 % Starch 30.40 % Sodium Oleate	98.827	0.652	33.8700	2.141	0.007	0.608	95	

Δ_s 1.120

Repeated treatment with alkali resulted in decreasing alkali binding until a constant value was obtained. In a series of pulps the alkali binding observed was in the following order: kraft, unbleached Mitscherlich, unbleached sulfite, bleached sulfite, alpha, and rag. This is roughly in the order of the ease of beating. The order did not change when the pulps were extracted repeatedly until a constant binding was attained. Downs believed that the final values represented sorption only.

Walker (47), Sheppard and Newsome (45), and Pierce (43) have shown that the initial water sorption (bound water) takes place at primary hydroxyl groups. Therefore, alkali binding should take place there also and should give an index of the hydrophilic nature of pulp.

The following procedure was employed for determining the alkali binding power of pulps. To exactly 5 grams (oven-dry basis) of pulp, 60.00 grams of distilled water and 50 cc. of 0.01 N sodium hydroxide were added. The mixture was stirred well and the tightly stoppered bottle was placed in a water bath at 30° C. for various time intervals. The sample was removed and the liquor was filtered from the pulp on a small Büchner funnel. The pulp acted as the filter pad. The liquor was poured through the pad a second time. Fifty cc. of the filtrate were titrated with 0.01 N sulfuric acid to a phenolphthalein end point. From this titration, the milligrams of alkali retained by the pulp were calculated. Results were expressed as percentage of original sodium hydroxide removed by the pulp.

In cases where foreign materials were added to the pulp

(e.g., locust bean gum, glue, and wetting-out agents), a blank sample was titrated with 0.01 N sodium hydroxide to determine if any correction need be applied for acidity introduced into the pulp. As only one pulp was used, repeated alkali extractions were not undertaken since the acid constituents would be constant for a given pulp. Furthermore, repeated extractions were impossible on samples treated with wetting-out agents as these materials might be washed away.

IV. PRESENTATION OF RESULTS AND DISCUSSION

The Effect of Surface Tension Conditions During Beating and Sheetmaking

The surface tension in the beater was reduced by adding commercial wetting agents. Duponol WA, a sodium lauryl sulfate, was used in one experiment and Nacconol KP, an alkyl-aryl sodium sulfonate, in another. These agents foamed excessively and only 0.668 grams of Duponol WA (0.0029 per cent based on total volume) and 5.00 grams of Nacconol KP (0.22 per cent based on total volume) could be used. Duponol WA reduced the surface tension to 47 dynes per cm. and Nacconol KP reduced it to 46 dynes per cm. The original surface tension was only 57 dynes per cm. The results are given in Tables II, III, and IV and in Figures 2 and 3.

TABLE II

BEATER EVALUATION OF BLEACHED SULFITE PULP

Time (min.)	0	15	30	45	60	75
S. R. Freeness	850	810	730	640	470	405
Basis Weight (lb.)	41.8	43.1	43.1	43.7	43.8	44.4
Mullen Points	27.8	82.1	80.1	100	93.5	95.0
Tear Factor	2.18	1.41	1.04	0.93	0.83	0.86

TABLE III

BEATER EVALUATION OF BLEACHED SULFITE PULP
IN 0.0029 PER CENT DUPONOL WA

Time (min.)	0	15	30	45	60	75
S. R. Freeness	850	810	745	675	580	480
Basis Weight (lb.)	43.5	42.1	40.5	41.1	43.8	45.2
Mullen Points	27.6	58.5	85.0	86.0	100.0	97.0
Tear Factor	2.33	1.46	1.16	1.07	1.04	1.04

TABLE IV

BEATER EVALUATION OF BLEACHED SULFITE PULP
IN 0.022 PER CENT DUPONOL WA

Time (min.)	0	15	30	45	60	75
S. R. Freeness	845	795	735	640	510	480
Basis Weight (lb.)	45.1	41.7	41.7	42.2	43.6	41.9
Mullen Points	22.2	52.8	69.0	80.0	91.5	95.5
Tear Factor	1.94	1.74	1.23	1.07	0.95	0.99

Various wetting agents were added to pulp and evaluated 45 minutes in the ball mill. A one-gram sample of the following agents was added to the ball mill charge of 100 grams of air-dry bleached sulfite and 5000 cc. of water. This gave a wetting agent concentration of 0.032 per cent on a total weight basis or 0.1 per cent based on the pulp present.

Wetting Agent:	Approximate Chemical Composition:
Tergitol 7	Sodium salt of sulfated secondary higher alcohol
Onyxsan S	Cation active compound derived from high molecular weight tertiary amine
Duponol WA (flakes)	50 per cent sodium lauryl sulfate
Sodium Retene Sulfonate	Sodium retene sulfonate
Ultrawet	Sodium salt of a sulfonic acid containing about 16 carbon atoms
Aerosol OT	Dioctyl sodium sulfosuccinate
Triton W-30	Sulfonated aromatic ether alcohol
Avitex AD	Sulfated and acetylated oleyl alcohol

The results are given in Table V.

TABLE V

EFFECT OF BALL MILL DEVELOPMENT OF PULP IN THE PRESENCE OF WETTING AGENTS

Wetting Agent	Freeness S.R.	Mullen Points %	Tear Factor	Fold	Basis Weight lb.	Surface Tension dynes/cm.
None	750	78.0	1.58	719	46.1	52
Onyxsan S	800	41.0	1.52	22	46.5	41
Duponol WA	750	65.0	1.99	118	46.6	38
Na Retene Sulfonate	740	80.0	1.50	415	46.5	44
Ultrawet	760	76.5	1.73	217	50.5	—
Aerosol OT	750	75.6	1.58	252	46.0	37
Triton W-30	760	76.0	1.56	261	47.0	39
Avitex AD	765	53.4	2.56	51	45.6	38
Tergitol 7	800	36.0	1.93	89	44.3	36

Onyxsan S and Duponol WA were selected from the group of wetting agents listed above, and complete ball mill evaluations were made. Two grams of the desired wetting agent were added to each ball mill charge. After the milling period, half of the pulp was

FIGURE 2

EFFECT OF WETTING-OUT AGENTS ON THE CHANGE IN MULLEN AND FREENESS DURING BEATING

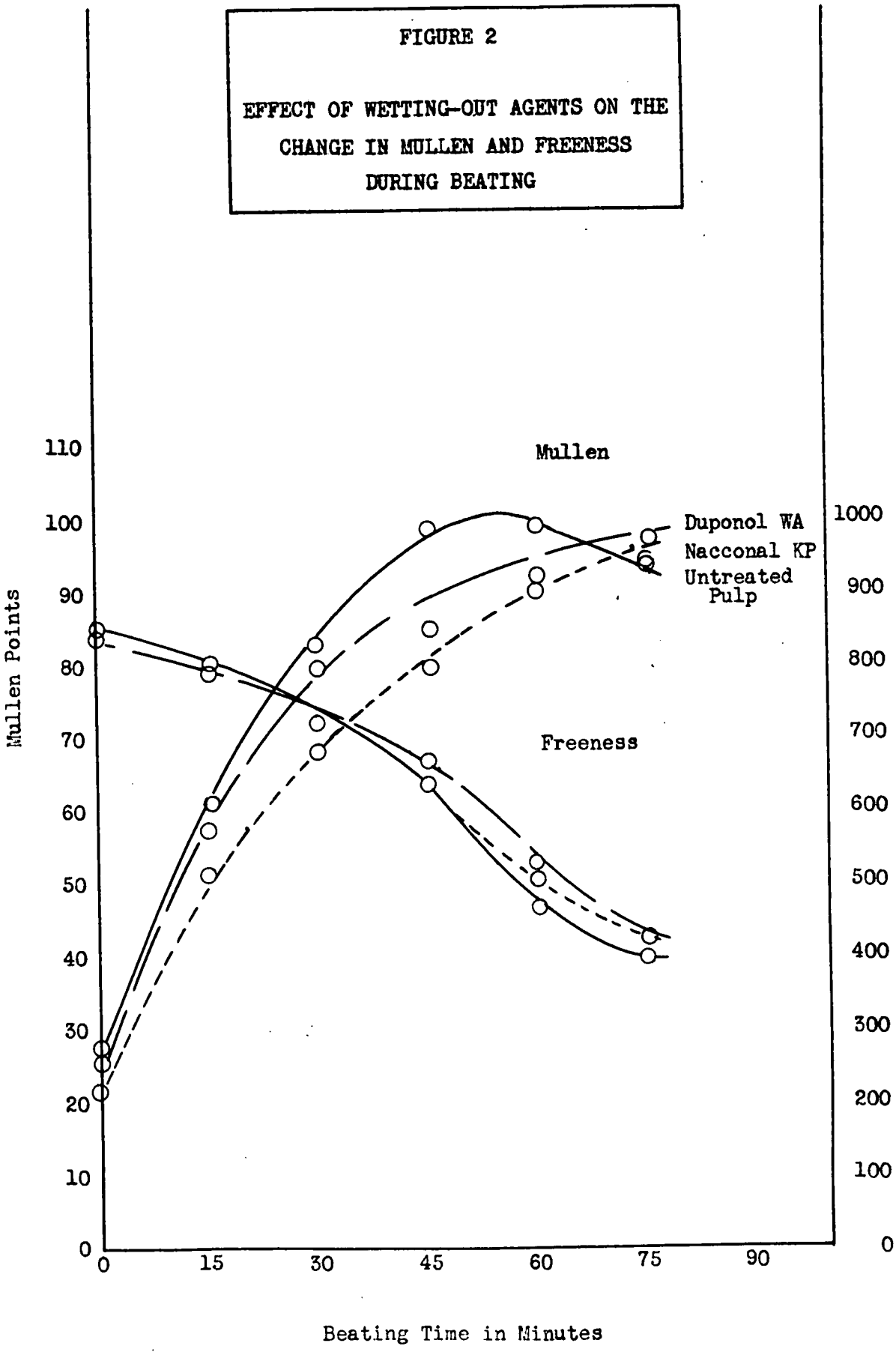
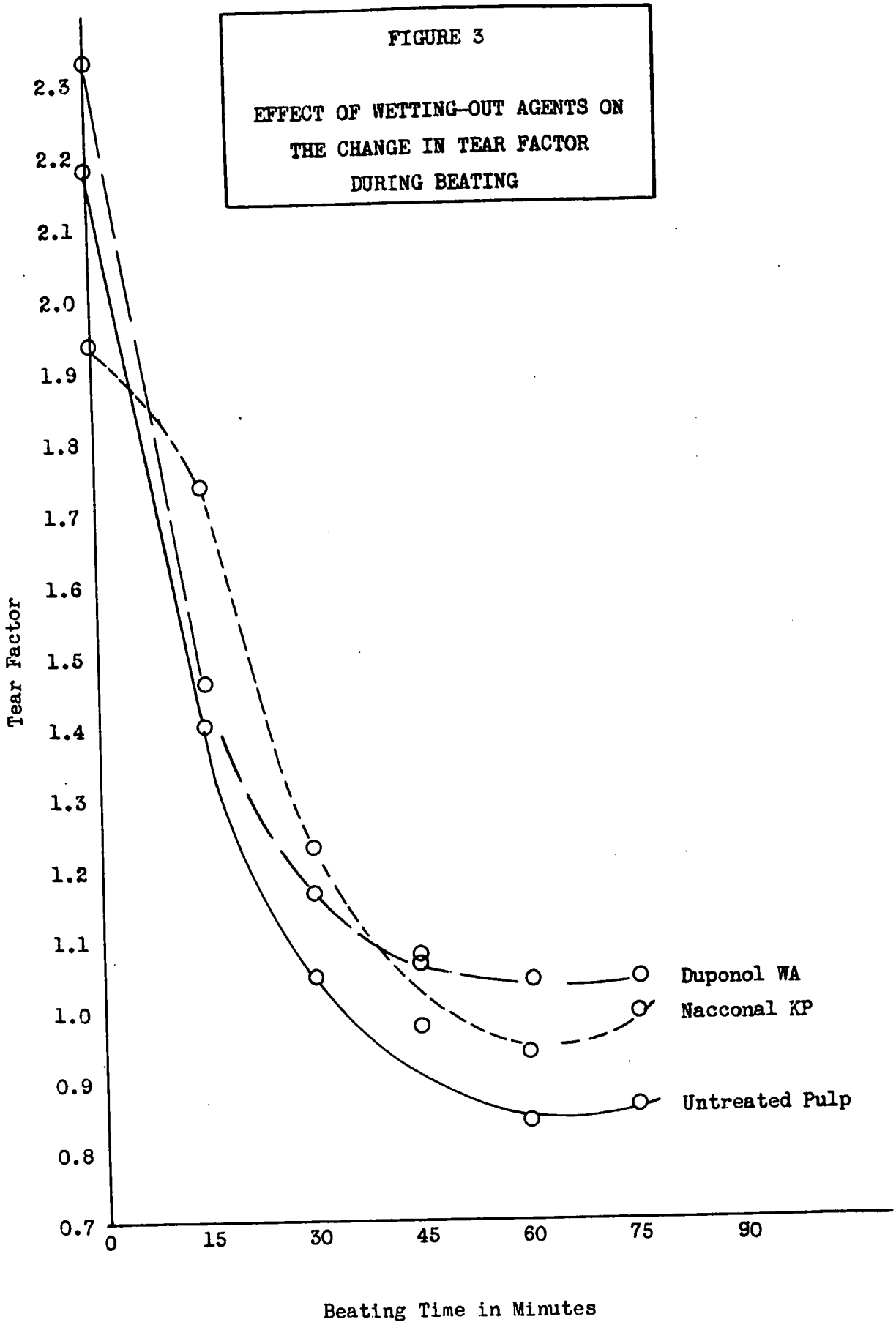


FIGURE 3

EFFECT OF WETTING-OUT AGENTS ON THE CHANGE IN TEAR FACTOR DURING BEATING



very thoroughly washed. Sheets were made from the pulp still containing Duponol WA and from the washed pulp. The results of this procedure are shown in Figure 4 and Table VI.

In general, all wetting agents apparently reduced the rate of pulp development. The sheets felt soft, and the pulp fibers were not well knit. From Figure 4 it is noted that the chief cause for a reduction in strength was due to the presence of the surface-active material during sheet formation and drying. The reduction of surface energy must have some effect on the rate of beating, however, as the difference in sheet strength between the untreated pulp and the treated pulp tended to increase with beating (Figures 2 and 3). This tendency is also well illustrated in the Mullen of the washed pulp plotted in Figure 4.

It is readily observed that a considerable difference existed between the effect of various wetting-out agents. In the case of Onyxsan S, at least, this was probably largely due to the greater sorption of the wetting agent on the pulp, as Onyxsan S has a positive potential and cellulose has a negative charge. Table V shows that there was no correlation between the surface tension of the system in the ball mill and the strength of the handsheets. The surface tension depression of water due to the presence of cellulose will be considered later.

Noll (14) has claimed that the rate of beating is inversely proportional to the surface tension. However, in changing the surface tension by increasing the temperature, viscosity and colloidal

FIGURE 4

EFFECT OF BALL MILLING PULP IN THE PRESENCE OF WETTING-OUT AGENTS ON STRENGTH

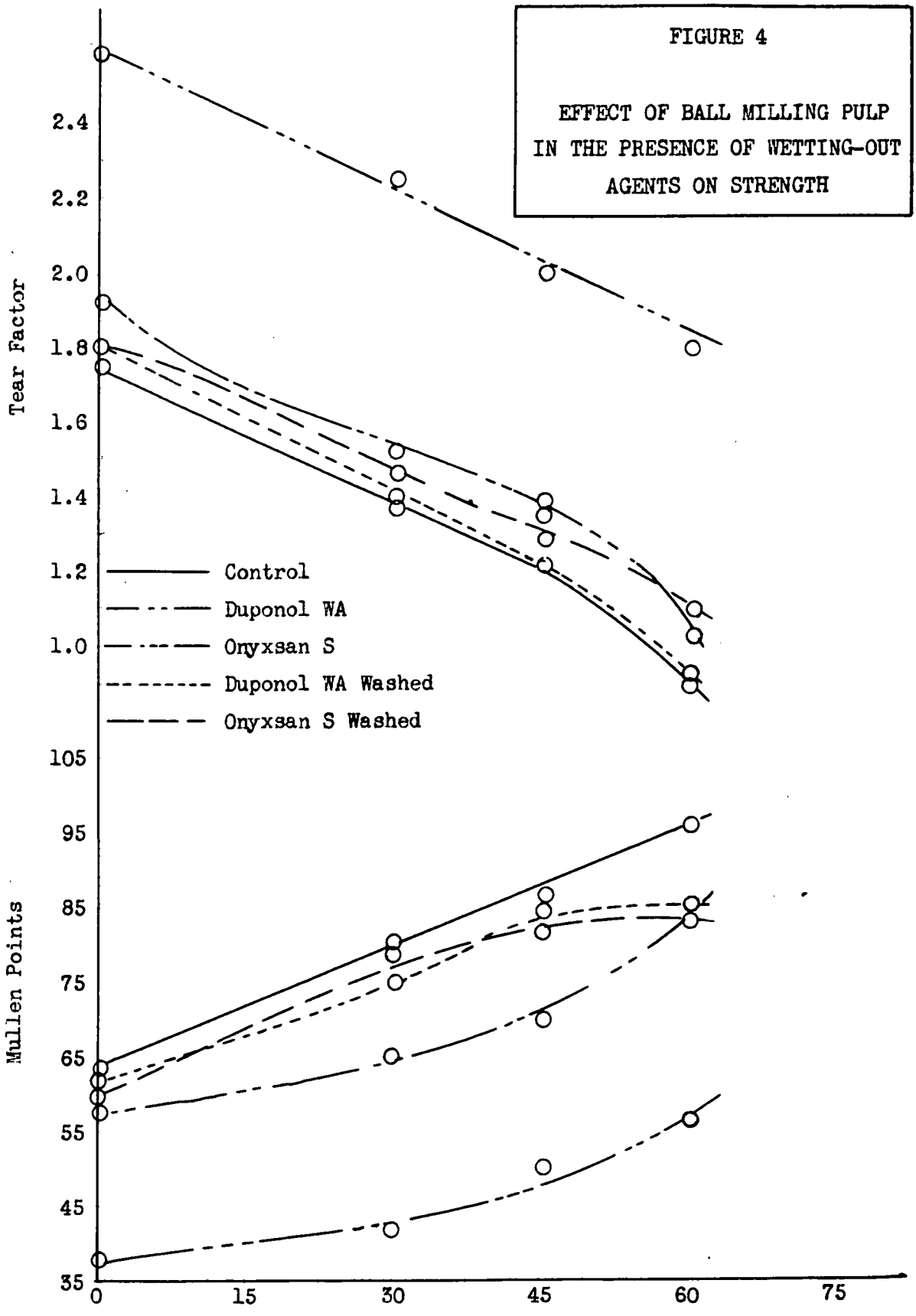


TABLE VI

EFFECT ON STRENGTH OF BALL MILLING PULP IN THE PRESENCE OF WETTING AGENTS

	Mullen Points				Tear Factor				Caliper (thousandths of an inch)			
Beating Time (min.)	0	30	45	60	0	30	45	60	0	30	45	60
Untreated pulp	63.4	80.5	87.0	96.0	1.75	1.38	1.28	0.90	3.58	3.24	3.06	2.60
Onyxsan S	38.2	42.1	50.0	56.7	2.58	2.25	2.00	1.79	4.10	3.50	3.30	3.05
Onyxsan S (washed)	60.0	80.0	82.0	85.0	1.80	1.47	1.35	1.10	3.59	3.20	3.10	2.85
Duponol WA	58.0	65.0	70.0	85.0	1.95	1.52	1.39	1.07	3.82	3.50	3.10	2.82
Duponol WA (washed)	62.7	75.0	85.0	94.0	1.80	1.40	1.22	0.91	3.60	3.27	3.00	2.64

	Basis Weight (lb.)				Apparent Density			
Untreated pulp	46.3	45.2	44.5	43.5	12.9	13.9	14.5	16.7
Onyxsan S	47.2	47.0	46.7	46.6	11.5	13.4	14.1	15.3
Onyxsan S (washed)	46.5	48.0	46.0	45.9	12.9	14.5	14.8	16.1
Duponol WA	47.2	46.2	45.0	44.5	12.4	14.0	14.5	15.8
Duponol WA (washed)	48.3	45.3	46.2	44.3	13.4	13.8	15.4	17.0

reactivity are changed also; therefore, the conclusions are based on several variables. He justified his hypothesis by reducing the surface tension with a wetting agent, but the magnitude of his results might be explained as due to the effect of sorption of the surface-active molecule rather than to a surface tension depression. This point will be clarified in a later section.

Harrison (12), (13) claimed that the decrease in rate of ball milling might be due to frothing. "Frothing may remove fibers from the sphere of action." This stand has been largely disproved by observations on the behavior of Duponol WA and Onyxsan S. No foaming was noted when positively charged Onyxsan S was ball milled, although considerable foam was formed when Duponol WA was used. Yet Onyxsan S caused the greatest loss of strength.

The Effect of Making Handsheets Under Reduced Surface Tension Conditions

From the foregoing results it is evident that the greatest reduction of sheet strength in a pulp treated with a surface tension depressant is caused by some condition established during sheet formation and drying.

Campbell (16) has proposed that sheet shrinkage and the forces which bring fibers into intimate contact so that fiber-fiber bonds will form are due to the surface tension of the water held in the interstices of the fiber mat. When water in a sheet is removed to the extent that only thin layers exist between fibers, the water tends to draw the fibers together. This force, based on the surface tension

of water at 75 dynes per cm., is 150 dynes per cm. of fiber length if two fibers are lying parallel to each other.

Campbell visualized a fiber as a beam and considered the force of surface tension as a uniform loading. He calculated the fiber deflection to be 0.0002 cm. for a fiber 0.1 cm. long and 0.003 cm. in diameter. If a fibril had a diameter of only 0.0003 cm., the deflection would be 2.0 cm. or 10,000 times as much. Campbell stated that such a deflection is absurd, but it shows that a fine fiber network would collapse and shrink together under surface tension forces.

In a qualitative study, pulp was treated with Duponol WA for ten minutes before the sheets were made. The results are shown in Figure 5 and Table VII. It might be concluded from these data that Campbell's theory had been verified. However, the results given in Figure 6 and Table VIII give rise to some interesting contradictory facts. If no sorption period was allowed, the strength was only slightly affected by decreasing the sheet mold surface tension. The Duponol WA was added directly to the sheet mold and the maximum sorption time could not have been in excess of one minute.

Although the sorption of Duponol WA appeared necessary to cause a reduction in strength, it is not entirely in disagreement with Campbell's concept (16). The surface tension effect considered is not effective until the greater bulk of the water is removed. This would be in the later stages of pressing and during the drying period. If the surface tension depressant were not sorbed, it would leave the sheet mold with the water when the sheet was formed. There-

FIGURE 5

EFFECT ON STRENGTH OF ADDING DUPONOL WA TO BEATEN PULP

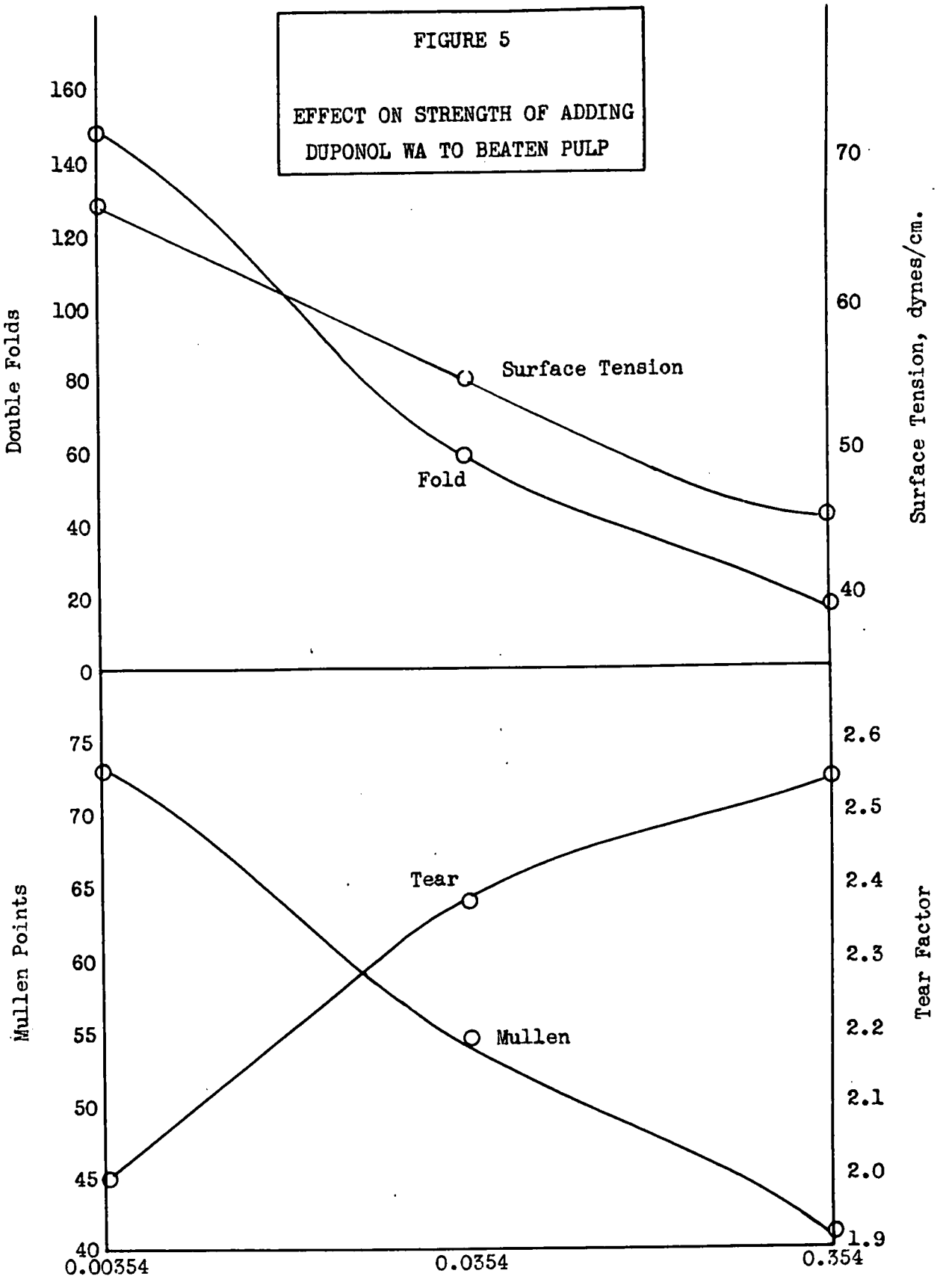
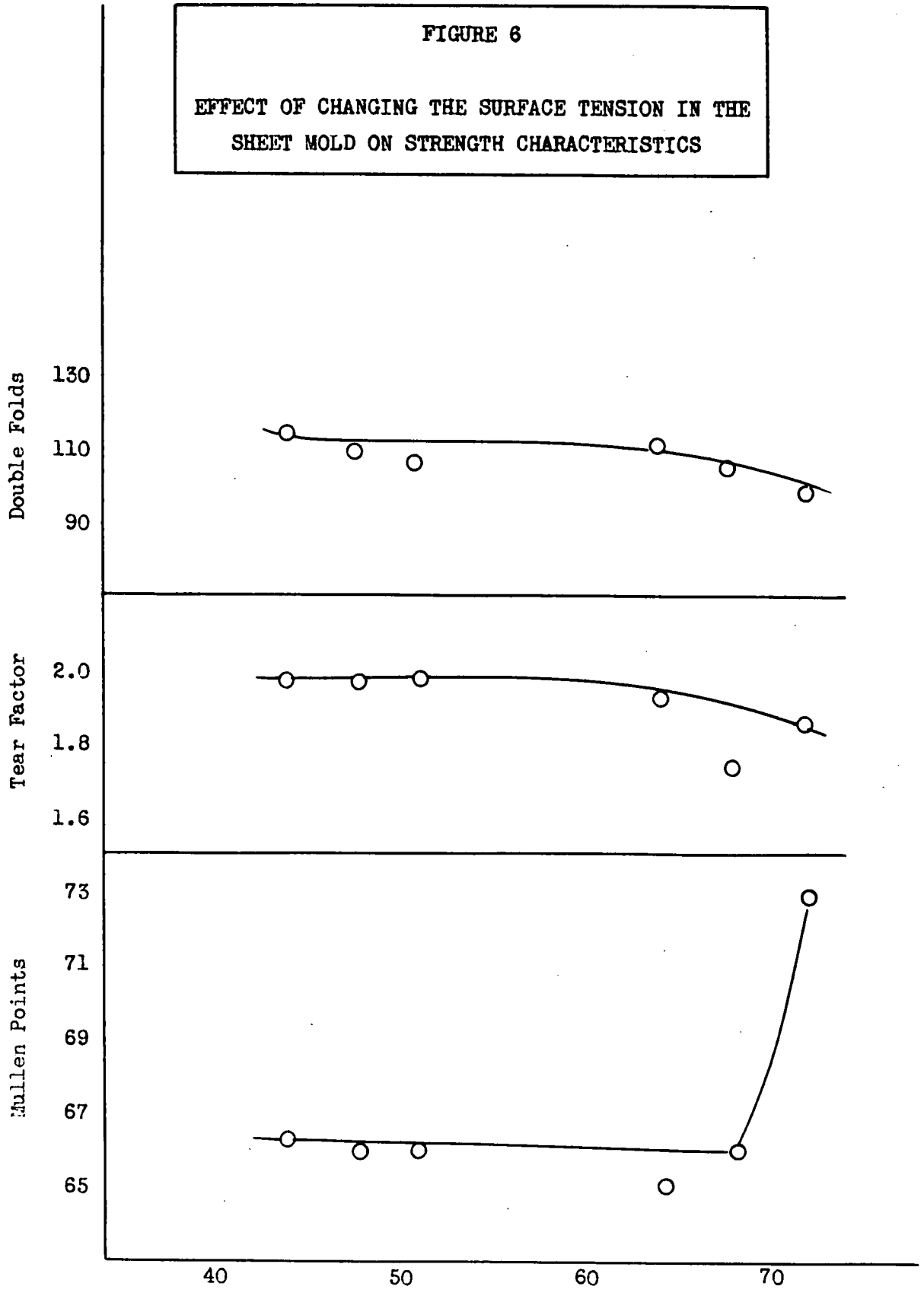


FIGURE 6

EFFECT OF CHANGING THE SURFACE TENSION IN THE SHEET MOLD ON STRENGTH CHARACTERISTICS



fore, if a surface tension depressant is expected to alter the forces Campbell had in mind, the surface-active material must be present in the sheet during pressing and drying.

However, sorption of a polar molecule with a large hydrophobic group oriented on the cellulose surface may change characteristics other than surface energy (e.g., the amount of water bound to cellulose, etc.). This has been found to be the case as will be described subsequently. At present, some of the causes which lead to the conclusion that surface tension forces are probably secondary to other factors causing fiber-fiber bonding will be considered.

TABLE VII

EFFECT ON STRENGTH OF ADDING DUPONOL WA TO BEATEN PULP

Grams Duponol WA Per Gram Pulp	Mullen Points	Tear Factor	Fold	Basis Weight (lb.)	Surface Tension dynes/cm.
0.0000	74.6	1.98	189	47.4	71
0.00354	73.5	2.00	147	47.6	67
0.03540	59.3	2.38	58	47.8	55
0.35400	40.5	2.54	17	49.3	45

TABLE VIII

EFFECT ON STRENGTH OF ADDING DUPONOL WA
DIRECTLY TO THE SHEET MOLD

Grams Duponol WA Per Sheet	Mullen Points	Tear Factor	Fold	Basis Weight (lb.)	Surface Tension dynes/cm.
0.0000	74.6	1.98	189	47.4	71
0.0384	72.9	1.85	99	46.2	75
0.0773	66.0	1.76	107	45.8	69
0.1558	65.0	1.94	112	47.8	64
0.2558	66.2	1.98	105	46.5	51
0.3840	66.1	1.99	110	48.5	48

The Depression of the Surface Tension of Water by Cellulose

The addition of pulp to water was found to reduce the surface tension of water to a marked degree. Various commercial pulps were made into two per cent suspensions in distilled water. The surface tensions of the filtrates from these suspensions are given in Table IX.

TABLE IX

EFFECT OF COMMERCIAL PULPS ON THE
SURFACE TENSION OF WATER

Pulp	Surface Tension
Unbleached Kraft	55
Unbleached Sulfite	50
Rag	52
Soda	60
Bleached Kraft	63
Water	75

du Nouy (71) has shown that surface tension drops as a function of time. Figure 7 and Table X show that the surface tension of pulp suspensions first increased and then dropped to a minimum value. However, as time progressed the surface tension increased again, and after 70 hours a maximum value was obtained.

TABLE X

EFFECT OF TIME ON THE SURFACE TENSION OF PULP SUSPENSIONS

Bleached Sulfite		Cotton Linters	
Time hr.	Surface Tension dynes per cm.	Time hr.	Surface Tension dynes per cm.
water	73	water	73
0.08	49	0.16	60
0.66	50	0.70	59
1.00	54	1.50	62
2.50	56	3.25	59
4.50	51	6.50	48
7.50	47	10.00	52
10.00	49	70.00	72
70.00	65		

The only conclusion that can be drawn is that the surface tension change is very sensitive and that it must be due to very minute quantities of material. This material must be readsorbed when the pulp stands for a long period of time.

To determine whether the material responsible for the surface tension depression could be washed out, two-gram samples of bleached sulfite and pure cotton linter cellulose were disintegrated in a Gösta Hall shredder and suspended in 100 cc. of distilled water. After stirring by hand (about 15 seconds, or just sufficient to break

FIGURE 7

EFFECT OF TIME ON THE SURFACE EQUILIBRIUM OF PULP SUSPENSIONS

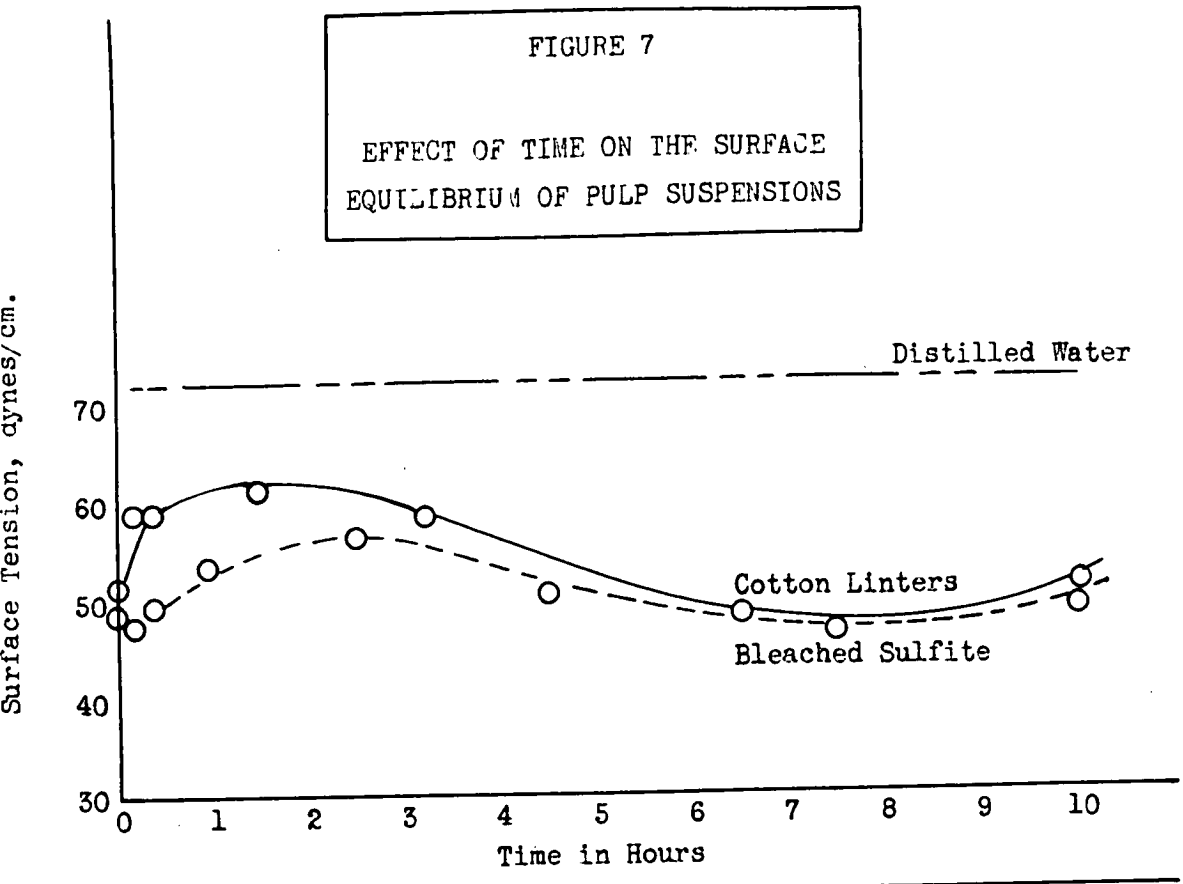
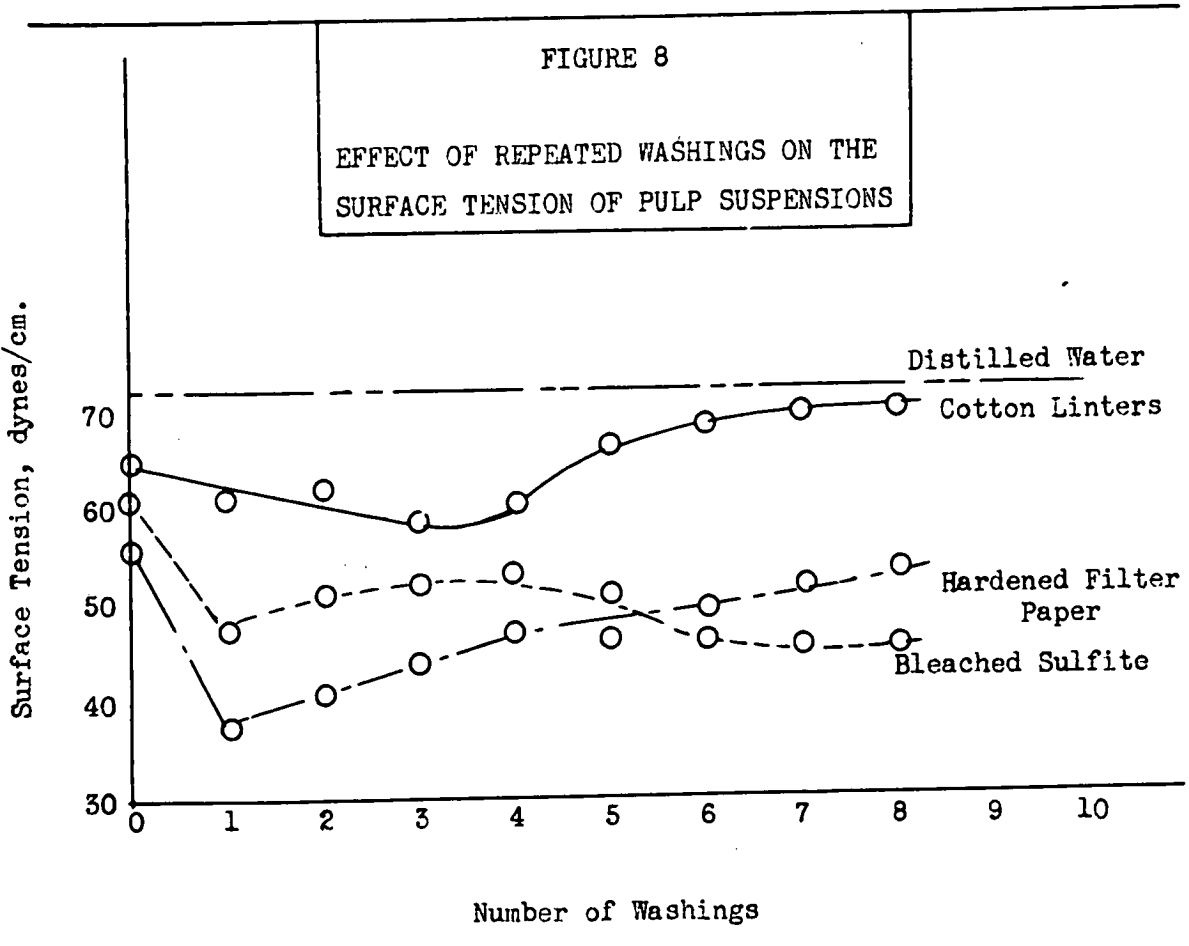


FIGURE 8

EFFECT OF REPEATED WASHINGS ON THE SURFACE TENSION OF PULP SUSPENSIONS



up the fiber suspension), the surface tension of the liquor was determined. The pulp was then diluted to 600 cc. with distilled water and agitated in a malted milk mixer for two minutes. After 20 minutes the pulp was filtered on a small Büchner funnel and resuspended in 100 cc. of distilled water. Surface tension determinations were made after each washing. The results shown in Figure 8 and Table XI indicate that the material producing the reduction in surface tension is removed with great difficulty. In the case of bleached sulfite, severe mechanical agitation probably serves to loosen the material from the cellulose fibers, and washing appears to increase the tendency of the pulp to reduce the surface tension.

TABLE XI

EFFECT OF REPEATED WASHINGS ON THE SURFACE TENSION OF PULP SUSPENSIONS

	Surface Tension (dynes/cm.)								
Number of Washings	0	1	2	3	4	5	6	7	8
Cotton Linters	65	61	62	58	60	66	63	63	59
Filter Paper	57	38	41	44	47	46	49	52	53
Bleached Sulfite	61	48	52	52	53	50	46	46	45

A number of experiments were performed in a study of the causes of surface tension depression of water in the presence of pulp. These experiments will now be discussed. Practically, there is no such material as pure cellulose. There are always some of the lower carbohydrates, degradation materials (oxycelluloses), and lignin.

A two per cent suspension of highly purified alpha wood pulp gave a surface tension of 50 dynes per cm.. The liquor was filtered through a hardened filter paper and found to have a surface tension of 44 dynes per cm.. Particles exhibiting Brownian movement were plentiful when this liquor was examined under dark field illumination.

The liquor was then centrifuged for 10 minutes (acceleration of 675 x g) and the top liquid produced a surface tension of 64 dynes per cm.. Most of the particles exhibiting Brownian movement had been removed by this operation. The centrifuged sample was treated with coarse charcoal for one-half hour and then filtered through glass wool. The surface tension of this liquid was 70 dynes per cm.. The charcoal had removed most of the active material.

The possibility of microscopic particles, regardless of their nature, being responsible for the surface tension depression was eliminated by suspending a very fine bentonite clay in distilled water. The surface tension was 73 dynes per cm.. Bleached sulfite was treated in a variety of ways to see if the surface tension of a pulp suspension could be altered. The treatment which changed the surface tension might offer a clue as to the nature of the surface tension depressant present. Cellulose was slightly oxidized by treating pulp with oxidizing agents and by heating in an oven. Pulps were suspended in alkali and in acid to see if sorption and neutralization affected the resultant surface tension. All surface tension measurements were made in two per cent sus-

pensions. The results are given in Table XII.

TABLE XII

VARIOUS TREATMENTS GIVEN BLEACHED SULFITE TO CHANGE THE SURFACE TENSION OF TWO PER CENT SUSPENSIONS

	Treatment	Surface Tension dynes/cm.
1.	Bleached sulfite suspended in water.	58
2.	Pulp suspended in 5 per cent potassium dichromate for three minutes, washed and suspended in water.	52
3.	Pulp suspended in cold 10 per cent potassium permanganate for 1 minute, washed and suspended in water. Pulp a light brown color.	55
4.	Pulp suspended in cold alkaline 10 per cent potassium permanganate for 10 minutes. Black material washed and suspended in water.	47
5.	Pulp suspended in cold alkaline 10 per cent potassium permanganate for 30 seconds. Light brown pulp washed and suspended in water.	50
6.	Pulp boiled 30 minutes and then cooled.	45
7.	Pulp boiled 30 minutes, washed with 5 per cent acetic acid and suspended in water.	55
8.	Pulp suspended in 0.01 N sulfuric acid.	56
9.	Sample 8 after 24 hours.	56
10.	Sample 9 washed and suspended in water.	45
11.	Pulp suspended in 0.01 N sodium hydroxide.	56
12.	Sample 11 after 24 hours.	63
13.	Sample 12 washed and suspended in water.	42

Oven aging of cotton linters and bleached sulfite for 6 hours at 105° C. did not change the surface tension of a two per cent suspension. Also the treatments listed in Table XII indicate

that oxidation of pulp reduced the surface tension only slightly. In general, acid treatment reduced the surface tension and alkaline treatment increased it. The effects were slight and inconclusive.

An alpha cellulose was prepared from bleached sulfite by treating the pulp with 17.5 per cent sodium hydroxide (Institute Method 421). The original sample in 2 per cent suspension gave a surface tension value of 60 dynes per cm.. The freshly prepared alpha cellulose in 2 per cent suspension increased the surface tension to 67 dynes per cm.. After 4 hours, this value had decreased to 53.5 dynes per cm.. The beta and gamma fraction after neutralization produced a surface tension of 50 dynes per cm. in a one liter solution. Upon concentration to 150 cc., the surface tension was still further reduced to 47 dynes per cm..

A variety of high molecular weight organic compounds were suspended in distilled water to see if they would depress the surface tension. About 0.1 gram samples of the materials listed in Table XIII were suspended in 75 cc. of distilled water. From the trend of the data in Table XIII it may be stated that polymerized organic molecules appear to have the property of reducing surface tension. This may be due to a very slight solubility of the material. du Noüy (71) has shown the surface tension of water to be reduced to 55 dynes per cm. in concentrations of less than one part per 100,000 of sodium oleate. Strachan (72) claimed that cellulose is soluble in water in about the same order as calcium carbonate (6.5 parts per 100,000), and that the "soluble cellulose"

is noncellulosic due to break down during formation.

TABLE XLII

EFFECT OF HIGH MOLECULAR WEIGHT COMPOUNDS ON THE SURFACE TENSION OF WATER

Material	Surface Tension dynes/cm.
Distilled water	72.5
Locust bean gum from a prepared 2 % dispersion	53.1
Soya bean protein	55.5
Egg albumin	40.8
Potato starch	62.0
Gum arabic	65.0
Ethylcellulose (0.1% solution water soluble product)	44.0
Methyl cellulose (0.1 % solution water soluble product)	51.0

Two hundred grams of disintegrated bleached sulfite were extracted with distilled water in a Soxhlet extractor for 110 hours. During the course of extraction, the water became a light yellow color, and toward the end of the extraction, rather turbid. A weak foam persisted on the boiling surface after 70 hours. After cooling, the extract (1 liter) had a surface tension of 41.5 dynes per cm.; a sample diluted 10 times gave a surface tension of 47.6 dynes per cm.; and when 950 cc. of the original liquor was concentrated to 500 cc., the surface tension was 39.6 dynes per cm..

The cause of surface tension depression of water by organic complexes is not clear. If cellulose is considered to be slightly soluble, as Strachan claims, and as is indicated by the extraction experiment above, beta and gamma cellulose must be even

more soluble, as they are less polymerized. This concept would account for the surface tension depression of water by pulp, the greater depression by beta and gamma fractions, and the low surface tension of the liquor obtained by extended extraction of pulp with distilled water.

Although the cause of surface tension depression is not definitely established, the effect is measurable and appreciable. The forces calculated by Campbell (16) (from the surface tension of water at 75 dynes per cm.) which pull fibers together and cause sheet shrinkage must be of a smaller magnitude than he assumed, but these forces could still produce the fiber distortion necessary to cause shrinkage. It is sufficient to point out that the surface tension forces at fiber-fiber interfaces must be complex, and possibly theoretical calculations would lead to erroneous conclusions.

Other Effects of Wetting Agents on Handsheets

There are several other indications that wetting agents do not reduce sheet strength solely by virtue of their ability to reduce the forces of surface tension. Sheets made from pulp beaten 75 minutes and treated with Duponol WA (0.3 gram per sheet) were wet pressed until the solid fraction (i.e., concentration of fibers per unit volume) was identical to that of untreated sheets. The results in Table XIV indicate that sorbed polar molecules which contain large hydrophobic groups must interfere with fiber-fiber bonding, since the fibers in both treated and untreated samples were

forced into contact by mechanical pressure and the chances of fiber-fiber bonding were the same in both cases.

TABLE XIV

EFFECT OF WET PRESSING TREATED SHEETS TO THE SAME DENSITY AS UNTREATED SHEETS

Sheet Treatment	Untreated Pulp	Treated Pulp	Treated Pulp
Wet Pressing Pressure (lb. per sq. in.)	100	100	125
Basis Weight (lb.)	48.1	48.0	46.2
Caliper (thousandths in.)	3.06	3.20	2.94
Mullen Points	101	78.6	77.6
Tear Factor	1.08	1.30	1.27
Double Folds	1908	178	160
Gurley Density	1625	154	160
Moisture Content (%)	10.32	10.27	10.30
Apparent Density	15.71	15.00	15.71

The presence of wetting agents in pulp during formation and drying might produce a change in the pulp-water relationship which would reduce the ability of fibers to form fiber-fiber bonds upon drying. The following studies were carried out to help clarify the problem.

Change in Equilibrium Moisture Content in the Presence of Wetting Agents

Handsheets formed from pulp beaten 45 minutes and treated with wetting agent were very soft. This velvet quality of sheets treated with excessive wetting agent might be attributed to a higher equilibrium moisture content. Such conditions would give rise to a

low Mullen and a high tear. Figure 9 and Table XV show, however, that the equilibrium moisture content gradually decreased as Duponol WA was added to the pulp. The decrease was small but presistent. Measurements made on other samples are also given in Table XV. It is evident that the sorption of wetting agents (i.e., polar molecules with a large hydrophobic group) causes a change in the cellulose-water relationship. If sorbed polar molecules cause a decrease in the colloidally sorbed water on cellulose surfaces, it might account for the decreased ability of fibers to form bonds when brought into contact, since fiber wettness has been proved an essential condition for fiber-fiber bonding (16),(21).

TABLE XV

EFFECT OF DUPONOL WA ON THE EQUILIBRIUM MOISTURE CONTENT OF HANDSHEETS

Duponol WA grams/sheet	Equilibrium Moisture, %	Remarks
0.00	9.35	Pulp beaten 45 minutes
0.05	9.43	" " " "
0.10	10.00	" " " "
0.30	9.60	" " " "
0.50	9.60	" " " "
Moisture determined in other experiments (not plotted)		
0.00	11.80	Pulp beaten 45 minutes
0.30	10.79	" " " "
0.00	9.94	" " " "
0.30	11.05	" " " "
0.00	10.05	Pulp unbeaten
0.30	10.65	" "
0.00	10.32	Pulp beaten 75 minutes
0.30	10.50	" " " "
0.30	10.27	" " " "

Effect of pH on the Action of Duponol WA on Pulp

The pH of pulp suspensions was adjusted by means of a buffer solution. A 0.5 molar solution in respect to phosphoric, boric, and acetic acids was prepared. Pulp suspensions of 0.8 per cent consistency were made 0.04 molar with the concentrated acid solution. Enough normal sodium hydroxide was added to give pH values of 4.5, 5.5, 6.5, 7.5, and 8.5. To each sample, containing 6 grams of pulp, 1.5 grams of Duponol WA were added. After a four-hour sorption period, handsheets were made. The pH of the tap water in the sheet mold was corrected to the sample pH with either hydrochloric acid or sodium hydroxide. The resulting strengths of the handsheets are shown in Figure 10 and Table XVI.

TABLE XVI

EFFECT OF pH ON THE SORPTION OF DUPONOL WA AS MEASURED BY HANDSHEET STRENGTH

pH Value	4.5	5.5	6.5	7.4	8.4
Caliper (thousandth in.)	3.12	3.10	3.02	2.96	3.18
Basis Weight (lb.)	50.2	50.8	48.5	49.0	50.5
Apparent Density	16.2	16.4	15.9	16.5	15.9
Mullen Points	57.5	62.1	64.8	65.5	31.5
Tear Factor	1.60	1.51	1.52	1.52	2.06
Double Folds	68	66	53	82	15
Mullen Points*	70.0	73.4	75.0	74.0	71.1
Basis Weight *	50.0	51.1	50.3	49.7	48.0

* Sheets not treated with Duponol WA

FIGURE 9

EFFECT OF DUPONOL WA ON EQUILIBRIUM MOISTURE IN HANDSHEETS

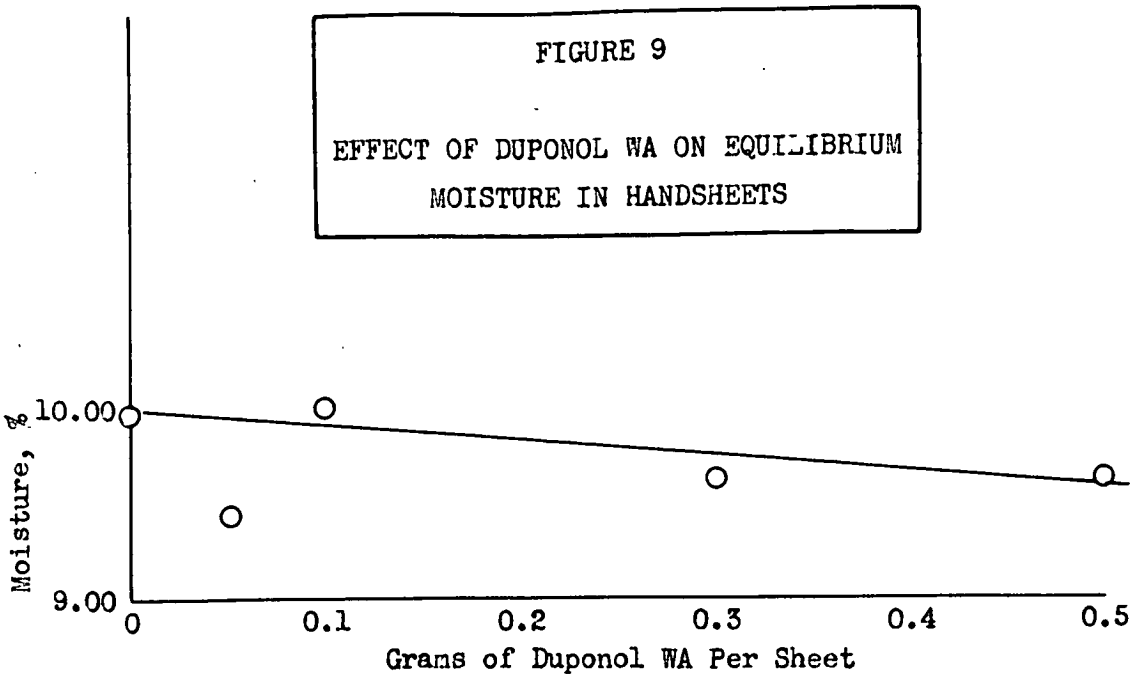
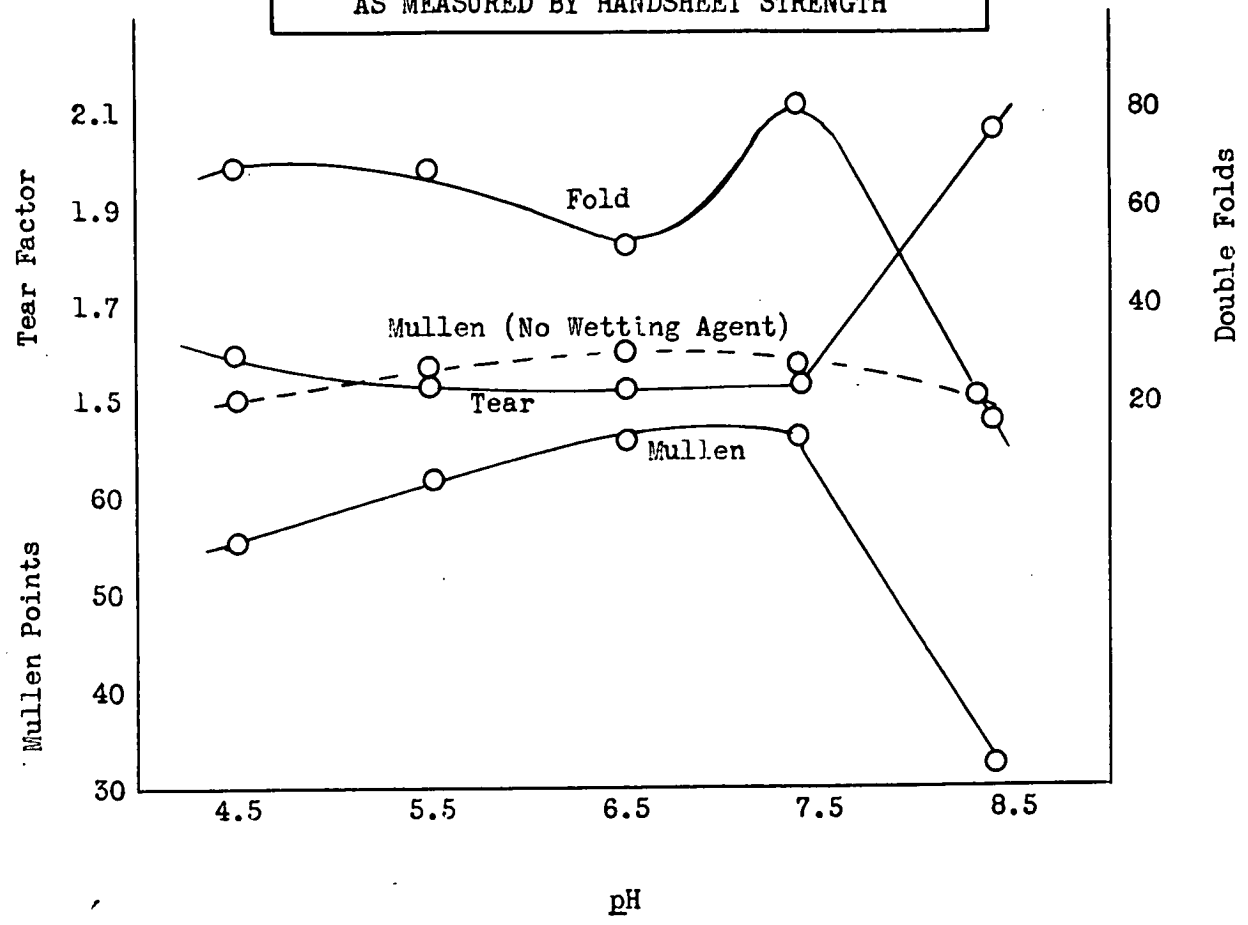


FIGURE 10

EFFECT OF pH ON THE SORPTION OF DUPONOL WA AS MEASURED BY HANDSHEET STRENGTH



The pH had little effect on the action of Duponol WA on handsheets except at high pH values. The effect was not as great as might be concluded from Figure 10 as the scale is rather large.

Effect of Extracting Duponol WA from Handsheets

In order to verify the concept that a surface-active molecule functions only during sheet formation and during the drying process, Duponol WA was extracted from treated handsheets with butyl alcohol. Sodium Lauryl sulfate, the active ingredient in Duponol WA, is soluble in higher alcohols. Handsheets formed and air-dried in the usual way were soaked in dry butyl alcohol for one hour and then air-dried on the drying plates and rings used in the TAPPI standard sheetmaking procedure. Sheets not treated with Duponol WA were also soaked in butyl alcohol to determine if any strength loss occured because of the treatment.

Removal of the wetting agent caused only a small increase in the sheet strength as is clearly illustrated in Figure 11 and Table XVII. The butyl alcohol soaking procedure was not detrimental, because untreated sheets soaked in butyl alcohol did not lose strength. The Duponol WA treatment was 0.3 gram of agent per sheet. On the basis of this experiment it is evident that the presence of Duponol WA in the sheet during strength testing was not responsible for the reduction in strength characteristics.

FIGURE 11

EFFECT OF EXTRACTING DUPONOL WA FROM HANDSHEETS ON STRENGTH CHARACTERISTICS

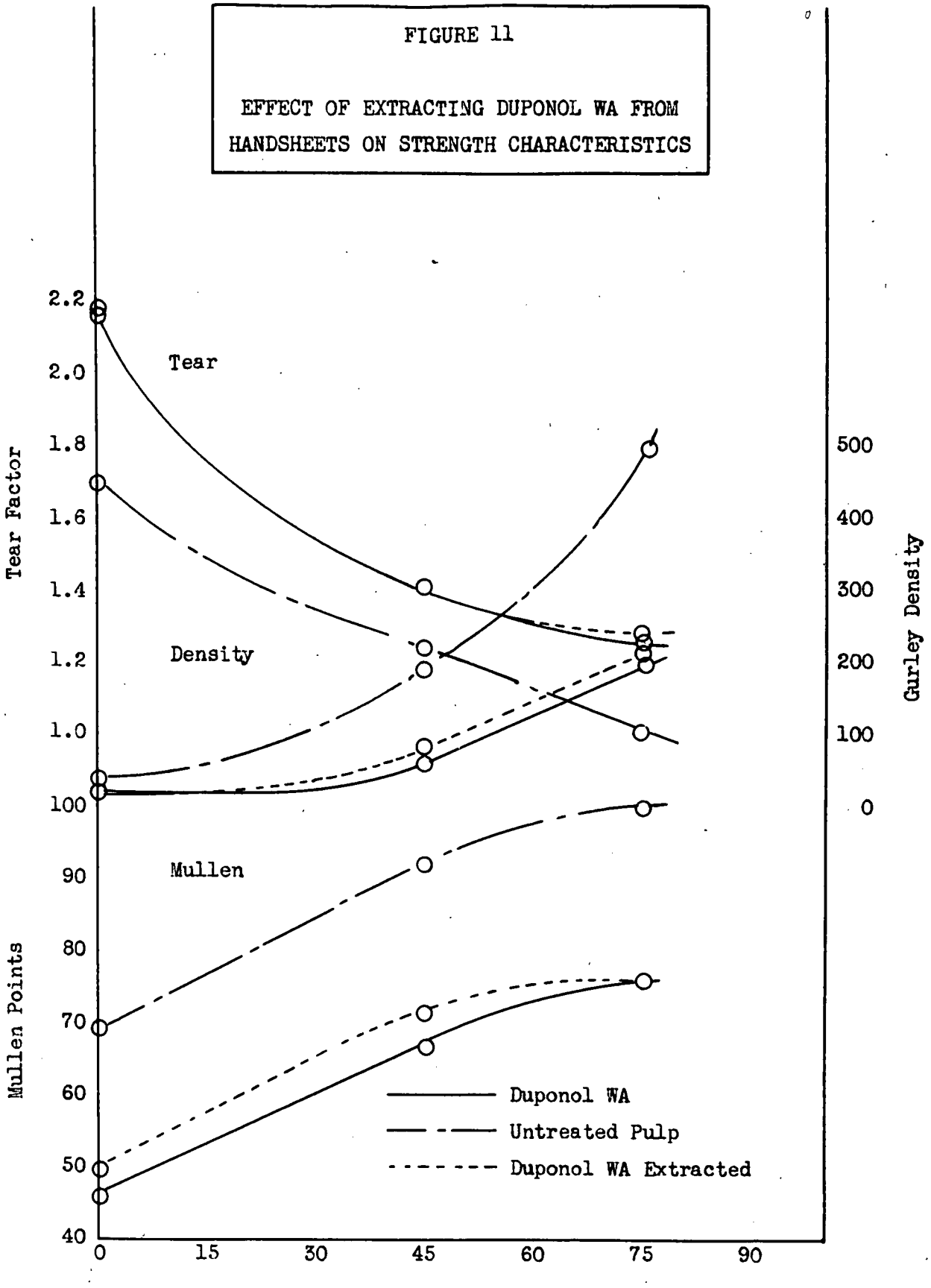


TABLE XVII

EFFECT OF EXTRACTING DUPONOL WA FROM HANDSHEETS

Sample	Beating Time min.	Mullen Points	Tear Factor	Gurley Density sec.	Basis Weight lb.
No Treatment	0	69	1.69	46	48.6
Duponol Treated	0	46	2.16	18	49.3
Duponol Treated, Extracted	0	50	2.18	17	46.9
No Treatment	45	92	1.23	134	46.2
Duponol Treated	45	67	1.39	64	47.2
Duponol Treated, Extracted	45	72	1.40	62	45.9
No Treatment, Extracted	45	89	1.28	240	48.0
No Treatment	75	100	1.00	480	45.8
Duponol Treated	75	76	1.26	219	47.6
Duponol Treated, Extracted	75	75	1.27	217	44.5

Effect of the Swelling Power of Wetting Agent Solutions on Cellulose

The susceptibility of a pulp to beating is dependent upon the swelling power of the beating medium (25). The possibility of a dilute solution of a wetting agent enhancing the swelling power of cellulose was investigated by the procedure outlined in Chapter III. The swelling power of several wetting agent solutions is given in Table XVIII. The swelling power of sodium hydroxide and a higher alcohol were also determined to demonstrate the sensitivity of the procedure.

It may be concluded that dilute solutions of surface-active agents did not enhance the swelling power of water. The relatively simple swelling experiment was fairly sensitive as was indicated by the swelling powers of octyl alcohol and sodium hydroxide.

TABLE XVIII

SWELLING POWER OF VARIOUS SOLUTIONS IN RESPECT TO PULP FIBERS

Sample	Thickness of Disks		Increase Thickness	Thickness Increase
	Original mm.	Final mm.	cm.	%
Water	28.5	39.3	10.8	38
Water	28.5	39.3	10.8	38
Duponol WA*	28.5	39.6	11.1	39
Triton W-30*	28.5	39.3	10.8	38
Tergitol 7*	29.7	40.4	10.7	38
Pure Tergitol 7	28.5	36.6	8.1	28
Octyl Alcohol	28.5	30.6	2.1	7
17.5 % NaOH	28.5	110.5	82.0	286
NaOH*	28.5	41.1	12.6	44

* 3 grams per liter concentration

Effect of Duponol WA on Colloidally Bound Water

Aside from the possible effect of reduced surface tension conditions during drying, the effect of sorbed polar molecules on cellulose-water relationships is strongly indicated. Since the reduction in equilibrium moisture content is not sufficient to explain the large losses in strength, it is possible that the manner in which water is held by fibers has been affected by the sorption of polar molecules. As indicated in the historical introduction, the water which is bound to cotton fiber has a profound influence on the strength of the thread (43). This effect may easily be extended to pulp fibers matted into a sheet of paper.

If a sorbed polar molecule should reduce the hydrophilic nature of a fiber surface by virtue of the large hydrocarbon portion, and if such fibers would not form fiber-fiber bonds when brought into

close contact, it would demonstrate the importance of the hydrophilic character of the fiber surface. Such a measurement has been undertaken.

The "bound water" determination by the cryoscopic method was adapted from the work of Newton and Gortner (63) and Gortner and Gortner (65) as the most applicable to the colloidal systems at hand. The merits of this method have been previously described. The determination was carried out on pulps which had not been made into handsheets, because the irreversible effect of drying might disturb the relations between bound and free water which existed during sheet formation. The original pulp was dry-lap, however.

Six grams of shredded pulp in 650 cc. of water were treated with 6 grams of Duponol WA for 24 hours. The pulp was filtered on a Büchner funnel and washed with 100 cc. of water. Another sample of the original dry-lap was also shredded. The percentage of hydration of these pulps was determined by the procedure and calculation outlined in the section on experimental methods. The results are presented in Table XIX.

Such a large decrease in the hydration of cellulose surfaces in the presence of surface-active agents was rather unexpected. However, an excessive amount and an excessive sorption period were employed. The hydration of untreated cellulose fiber was higher than expected. Stamm (64) has found the fiber saturation point of wood to be about 27 per cent. In aqueous suspension, it is possible that more water is associated with cellulose than is measured on fibers at

100 per cent relative humidity. The results of cryoscopic bound water measurements are interpreted in relation to each other rather than in an absolute sense, and indicate that pulps not treated with surface-active agents are much more hydrophilic. It will be shown in a later section that the hydrophilic character of fiber surfaces has considerable bearing on the fiber-fiber bonding of cellulose fibers.

TABLE XIX

EFFECT OF SORBED WETTING AGENT ON THE PERCENTAGE OF HYDRATION OF PULP FIBERS

Sample	Dry Colloid g.	Water g.	Sugar Added g.	$\Delta_{(c+s)}$ °C.	Water Bound g.	Hydration %
Duponol treated	1.818	99.280	34.2440	2.122	0.09	5
Duponol treated	1.818	99.280	34.2440	2.124	0.18	9
Duponol treated	1.818	99.280	34.2440	2.125	0.13	7
Average percentage of hydration of Duponol treated sheets						7
Untreated	4.765	100.055	34.2388	2.153	1.54	32
Untreated	4.765	100.055	34.2388	2.156	1.67	35
Untreated	4.765	100.055	34.2388	2.155	1.62	34
Untreated	4.765	100.055	34.2388	2.153	1.54	32
Average percentage of hydration of untreated sheets						34

Δ_s without pulp 2.120° C; Δ_c 0.000° C.

It was pointed out in the discussion of the alkali binding procedure that the alkali binding power of cellulose may well be used as a measure of the hydrophilic character of pulp. A 5-gram sample of pulp was treated with 1 gram of Duponol WA for 24 hours at 0.9 per cent consistency. This sample was filtered on a Büchner funnel and made up to the proper dilution as explained under the section on experimental procedure. A 5-gram sample of untreated pulp was also

subjected to the alkali binding procedure. Treated and untreated samples were also put through the experiment except that the sodium hydroxide was omitted. The filtrates were titrated with 0.01 N sodium hydroxide instead of sulfuric acid to see if the Duponol treatment had introduced any acidity into the pulp. The results for the wet lap Mitscherlich pulp used are given in Table XX. The sodium hydroxide added to each sample was 0.01970 grams. The blank titration of the treated pulp required 1.15 cc. of 0.01 N sodium hydroxide as compared to 1.20 cc. for the untreated pulp; therefore, the alkalinity was changed very little by the Duponol WA.

TABLE XX

EFFECT OF SORBED DUPONOL WA ON THE ALKALI BINDING OF BLEACHED MITSCHERLICH PULP

Sample	0.01 N H_2SO_4 cc.	Normality of Filtrate	NaOH in Filtrate g.	NaOH Bound g.	Per Cent Binding
Treated	6.0	0.00120	0.00520	0.01460	73.8
Untreated	3.60	0.00072	0.00302	0.01668	85.0

These alkali binding experiments showed that the hydrophilic nature of pulp had been reduced by the sorption of a polar molecule containing a large hydrophobic group.

It has been demonstrated that surface-active molecules reduce the hydrophilic nature of pulp, and this fact accounts, in part at least, for the loss of strength in handsheets.

Effect of Changing the Hydrophilic Character of Pulp Fibers on Sheet Strength

Since wetting agents have been shown to decrease the hydrophilic nature of pulp, studies were undertaken in which the hydrophilic character of pulp was increased. Several hydrophilic materials were added to pulp. It was assumed that these materials coated the fibers and thus produced a more hydrophilic surface. Gelatin, locust bean gum, and a cellulose gel were selected as the hydrophilic colloids. These materials were compared with Duponol WA in their effect on pulp fibers.

The hydrophilic character of gelatin has been the subject of numerous investigations, and its affinity for water is well known. Locust bean gum is almost pure hemicellulosic material which is extremely hydrophilic and forms viscous gels at high dilutions. The cellulose gel was prepared from a high alpha cellulose to demonstrate the hydrophilic character of a pure, finely dispersed cellulose. Before dispersion, the alpha pulp had a copper number of 0.075. After the treatment, the copper number had increased to only 0.146 and degradation was assumed to be very slight.

Doughty (32) has shown that the solid cellulose per unit volume is the controlling factor which determines the sheet strength after the first few minutes of beating. By wet pressing, the solid fraction of a handsheet may be varied. Pulps treated with various hydrophilic materials were pressed at different wet-pressing pressures so that strength characteristics could be compared at a constant solid

fraction. The number of fibers of a given kind in a given volume would be practically the same at a fixed density. Thus the comparison of sheet strengths at a given solid fraction (apparent density) would be a comparison of the ability of a given number of fibers to form bonds.

The hydrophilic materials were added to 0.9 per cent consistency unbeaten bleached sulfite in a quantity of 0.15 gram per sheet and stirred for 1 hour. Since Duponol WA is only 50 per cent sodium lauryl sulfate, 0.3 gram per sheet was employed. The results of these experiments are given in Table XXI. The Mullen and tear are plotted against apparent density in Figures 12 and 13.

Pulp processed in the ball mill was also pressed to various densities and the results given in Table XXII and Figure 14 and Figure 15 are offered for comparison with pulps treated with various hydrophilic materials. In Table XXIII the percentage hydration of various materials is presented. The values were obtained by the cryoscopic method previously described. The hydration of locust bean gum, cellulose gel, and gelatin was measured on the material in the form in which it was prepared (see Chapter III on experimental procedure).

FIGURE 12

EFFECT OF VARIOUS HYDROPHILIC MATERIALS ON THE MULLEN STRENGTH OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

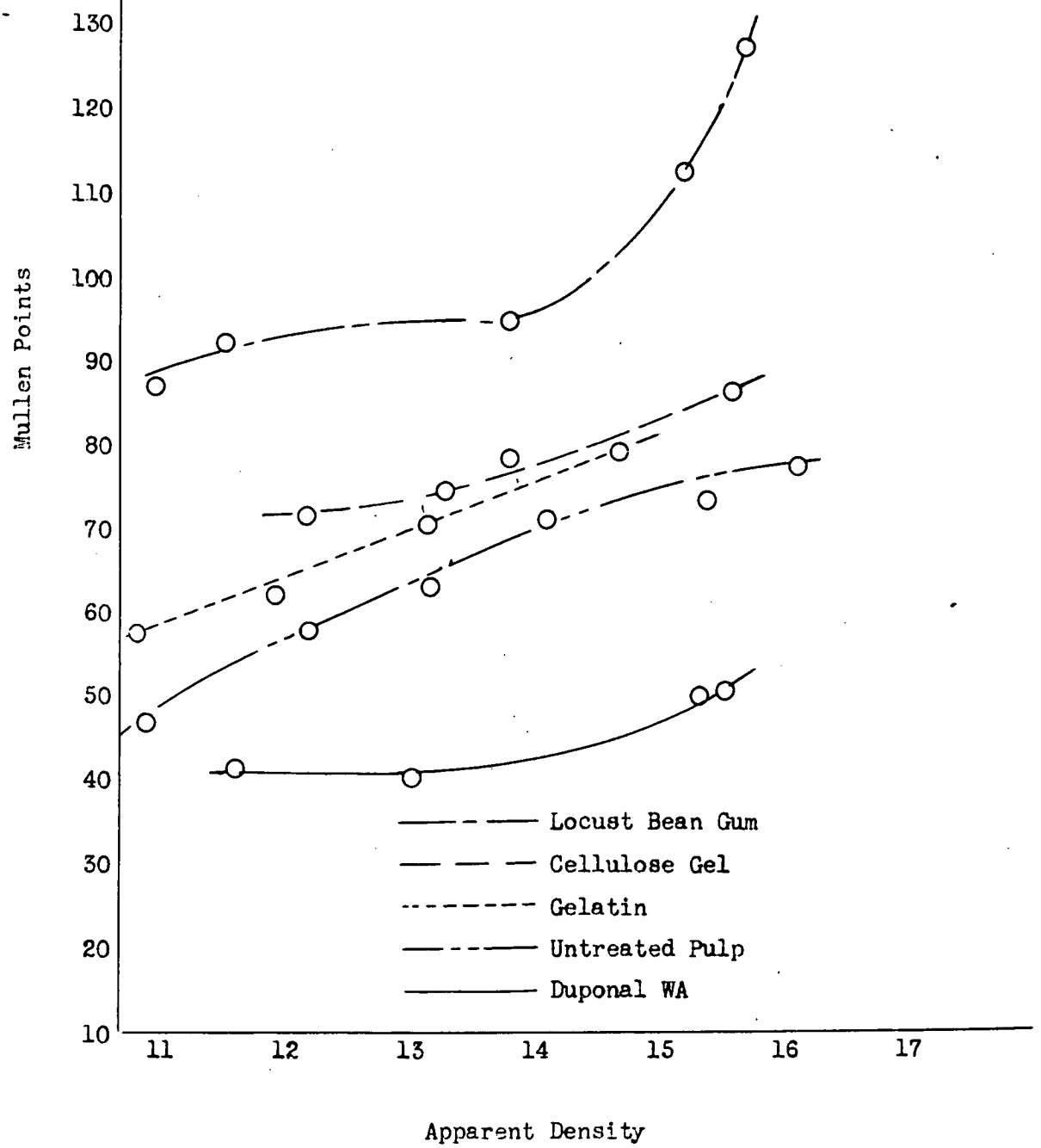


FIGURE 13

EFFECT OF VARIOUS HYDROPHILIC MATERIALS ON THE TEARING STRENGTH OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

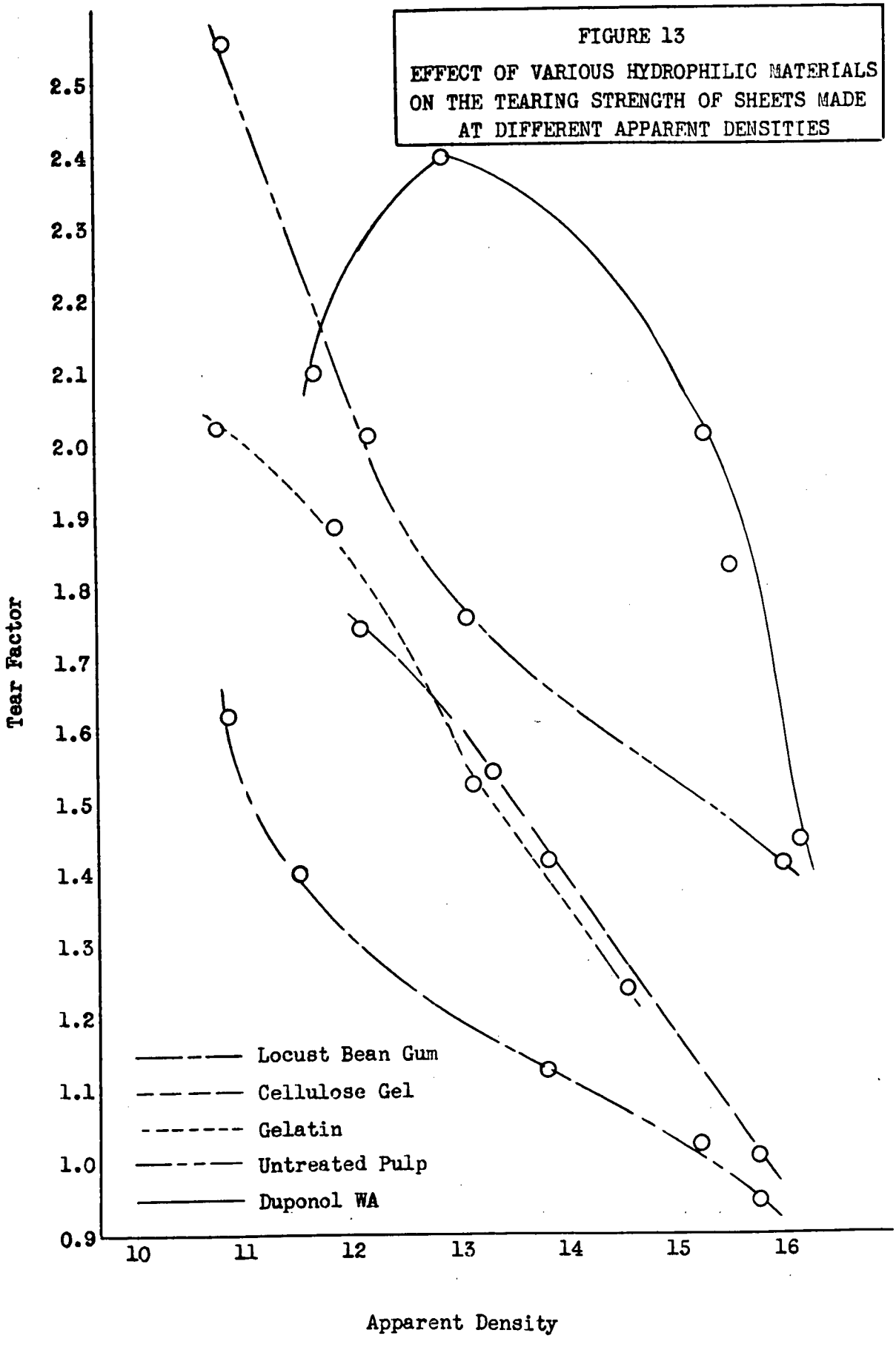


TABLE XXI

EFFECT OF HYDROPHILIC MATERIALS ON THE STRENGTH CHARACTERISTICS OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

Sheet	Pressing Pressure lb./sq.in.	Material Added	Basis Weight lb.	Caliper thousandths of an inch	Mullen Points	Tear Factor	Gurley Density	Double Folds	Apparent Density
A	25	—	48.2	4.42	47.6	2.56	4	35	10.9
B	50	—	48.1	3.94	57.0	2.02	8	47	12.2
C	100	—	46.9	3.58	65.4	1.75	16	73	13.1
D	200	—	50.2	3.12	78.0	1.41	76	146	16.0
E	30[illegible]	—	50.0	3.20	73.6	1.26	103	206	15.6
F	500	—	46.4	3.26	71.1	1.61	26	108	14.2
G	25	A	50.5	4.16	72.0	1.75	30	98	12.1
H	50	A	51.8	3.90	74.0	1.54	51	151	13.3
I	100	A	49.8	3.60	78.0	1.41	77	160	13.8
J	200	A	47.9	3.04	86.0	1.00	472	304	15.7
K	25	B	47.8	4.44	56.5	2.02	4	41	10.8
L	50	B	45.6	3.84	61.7	1.86	6	75	11.9
M	100	B	45.0	3.44	69.9	1.52	14	85	13.1
N	200	B	51.5	3.52	79.5	1.24	32	311	14.6
O	5	C	49.0	4.62	87.0	1.61	16	---	10.9
P	15	C	47.7	4.14	92.0	1.41	568	---	11.5
Q	50	C	49.2	3.58	94.0	1.12	878	---	13.8
R	100	C	48.8	3.24	107.0	1.08	1000	---	15.2
S	300	C	48.9	3.12	127.0	0.94	1456	---	15.7
T	5	D	45.6	3.80	41.6	2.10	0	---	11.7
U	100	D	49.7	3.84	40.1	2.40	7	13	12.9
V	200	D	47.5	3.10	50.5	2.00	38	52	15.3
W	300	D	48.7	3.14	50.5	1.82	51	37	15.5

A Cellulose Gel
B Gelatin
C Locust Bean Gum
D Duponol WA

FIGURE 14

EFFECT OF BEATING ON MULLEN STRENGTH OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

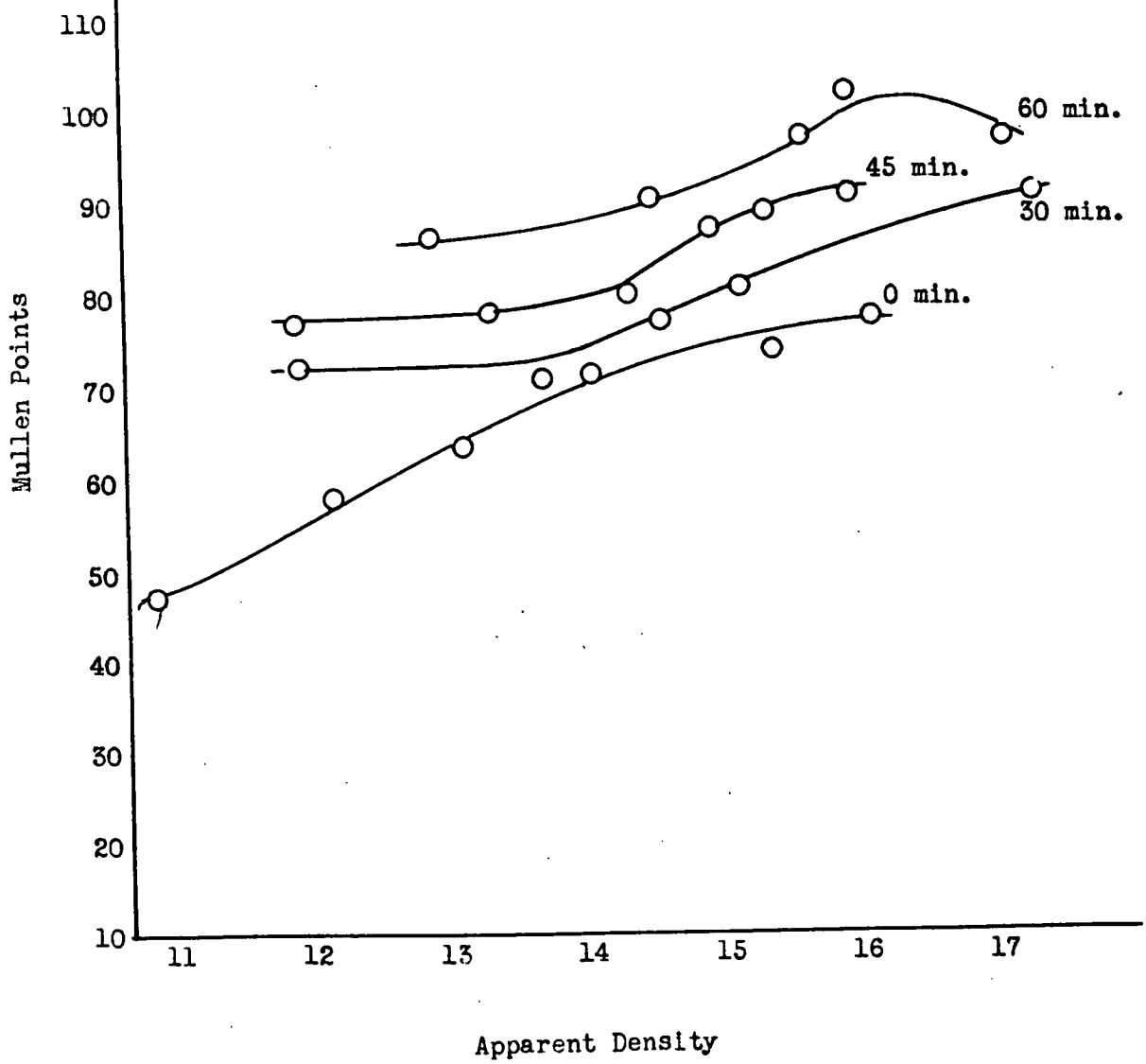


FIGURE 15

EFFECT OF BEATING ON TEARING STRENGTH OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

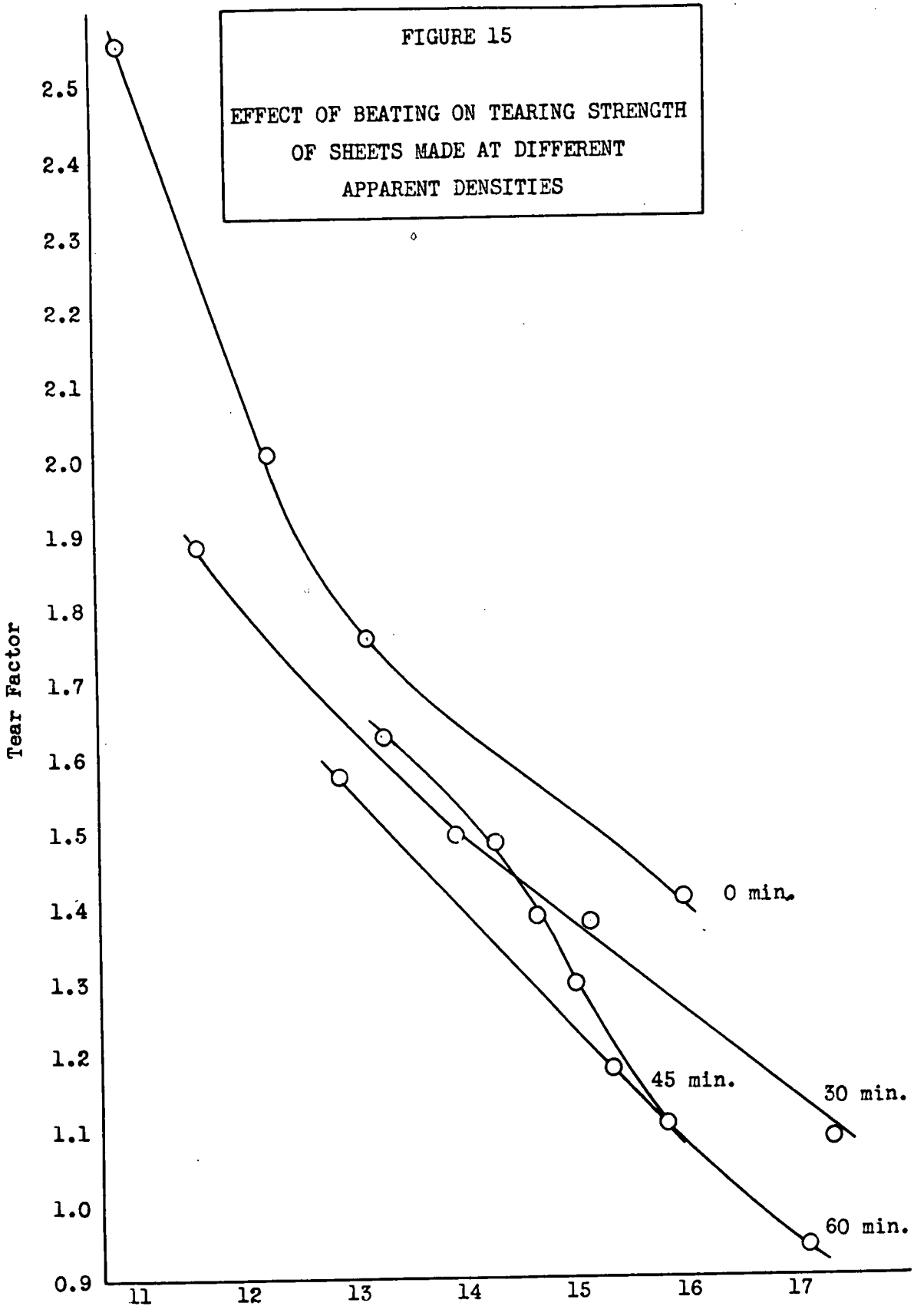


TABLE XXII

EFFECT OF BEATING ON THE STRENGTH CHARACTERISTICS OF SHEETS MADE AT DIFFERENT APPARENT DENSITIES

Sheet	Beating Time min.	Pressing Pressure lb./sq.in.	Basis Weight lb.	Caliper thousandths of an inch	Mullen Points	Tear Factor	Gurley Density Double Folds		Apparent Density
AA	30	5	47.3	4.06	71.9	1.88	0	100	11.6
AB	30	25	44.8	3.28	70.5	1.50	0	147	13.7
AC	30	50	45.6	3.12	78.0	1.38	15	158	14.6
AD	30	100	46.4	3.06	80.5	1.38	82	187	15.1
AE	30	300	49.6	2.86	90.0	1.08	147	680	17.3
AF	45	5	47.0	3.96	77.5	1.65	7	89	11.9
AG	45	25	49.1	3.68	78.5	1.62	25	299	13.3
AH	45	50	47.4	3.30	79.3	1.48	44	339	14.3
AI	45	100	48.3	3.24	87.0	1.28	77	344	14.9
AJ	45	150	48.5	3.16	8[illegible].7	1.17	110	525	15.3
AK	45	200	50.2	3.16	90.5	1.08	279	1093	15.9
AL	60	5	49.4	3.84	86.0	1.57	---	359	12.8
AM	60	30	46.7	3.20	90.0	1.09	---	987	14.6
AN	60	50	48.3	3.06	96.5	1.10	---	1097	15.7
AO	60	100	46.2	2.90	102.0	1.08	---	1288	15.9
AP	60	200	47.0	2.74	96.0	0.93	---	1197	17.1

TABLE XXIII

PERCENTAGE HYDRATION OF VARIOUS HYDROPHILLIC MATERIALS
AS DETERMINED BY THE CRYOSCOPIC METHOD

Sample	Dry Colloid g.	Water Added g.	Sugar Added g.	$\Delta_{(c+s)}$ °C.	Δ_c °C.	Water Bound g.	Hydration %	Average Hydration %
Average for untreated pulp (from Table XIX)								54
Average for Duponol FA treated pulp (from Table XIX)								7
Locust Bean Gum	0.214	99.786	34.1967	2.212	0.000	4.16	1940	1940
Cellulose Gel	1.030	99.820	34.2170	2.383	0.208	2.53	250	241
Cellulose Gel	1.030	99.820	34.2170	2.375	0.204	2.36	232	
Gelatin	1.000	99.947	34.2620	2.168	0.008	1.85	185	194
Gelatin	1.000	99.947	34.2620	2.170	0.006	2.07	203	
Alpha Wood Pulp	4.625	100.375	34.3985	2.141	0.000	0.936	21	
Alpha Wood Pulp	4.625	100.375	34.3985	2.140	0.000	0.936	20	23
Alpha Wood Pulp	4.625	100.375	34.3985	2.145	0.000	1.170	25	
Pulp Milled 60 min.	4.779	100.041	34.2841	2.155	0.000	1.62	34	
Pulp Milled 60 min.	4.779	100.041	34.2841	2.155	0.000	1.62	34	33
Pulp Milled 60 min.	4.779	100.041	34.2841	2.154	0.000	1.58	33	
Pulp Milled 60 min.	4.779	100.041	34.2841	2.155	0.000	1.58	32	

Δ_s in absence of pulp 2.1900 C.

In Table XXIV, the values of the Mullen strength taken at a constant apparent density of 14.0 (from Table XXII) are compared with the degree of hydration of materials added to unbeaten pulp. A striking parallel is definitely illustrated.

TABLE XXIV

COMPARISON OF MULLEN STRENGTH OF HANDSHEETS WITH THE DEGREE OF HYDRATION OF MATERIALS ADDED TO PULP

Material	Mullen Points	Hydration %
Unbeaten Pulp Treated with Duponol WA	42	7
Unbeaten Pulp	69	54
Gelatin	75	194
Cellulose Gel	77	241
Locust Bean Gum	95	1940

The conclusion may be drawn that the ability of pulp fibers to form fiber-fiber bonds is dependent upon the hydrophilic character of the fiber surface. This concept is supported by a large volume of evidence from the literature.

Campbell (16) stated that "The nature of the bond between fibers in paper must be identical, or practically identical, with that between the solid particles which constitute the structure of a gel. It is the realization of this which has led chemists generally to the hypothesis of a gelatinized layer on cellulose in water, particularly on beaten pulp."

Campbell has pointed out further that the surface of cellulose must be in solution or rather the surface molecules must be

continually dissolving and others continually redepositing on the cellulose surface.

Probably very few of the cellulose macromolecules get far away from the surface and it is not difficult to visualize a layer on cellulose surfaces composed of dissolved cellulose and water held at a reduced activity by the cellulose surface. The bound water measurement probably gives an index to the amount of the water held under the conditions just outlined. If two cellulose surfaces are brought closely enough together so that the shells of cellulose solution meet, drying will cause the fibers to stick together by the same mechanism which causes glue to bind, or two wet crystals of copper sulfate to stick together on drying.

Materials vary in respect to their ability to bind water at their surfaces. This is illustrated in the bound water measurements. If cellulose surfaces are coated with materials which bind water more strongly than cellulose, the active layer will be much thicker. Thus, more fiber-fiber bonds will form when fibers are brought close to each other than would ordinarily form without the thickened active layer of hydrated material.

If a polar molecule is sorbed on a cellulose surface, the hydrophilic portion will be anchored to the hydrophilic cellulose surface. The large hydrophobic portion will orient away, and the sphere of influence of the hydrocarbon will reduce the tendency of cellulose to partially dissolve and form a hydrated layer. Hence, the probability of the cellulose forming fiber-fiber bonds is reduced.

The hydrophilic character of pulp varies to a great extent because pulps contain varying amounts of hemicelluloses which are extremely hydrophilic, as was evidenced by the water-binding power of locust bean gum. Generally speaking, the more a pulp is purified, the less hydrophilic it becomes. This is demonstrated by an increased amount of beating necessary to produce a given strength (37), (40). The water-binding power of high alpha wood pulp was less than that of ordinary bleached sulfite which contains hemicellulose (Table XXIII). The commercial high alpha wood pulp could not be made into sheets even after severe beating. Most of this effect was caused by mercerisation during purification (72), but a portion of the lack of sheet-forming ability of the fibers was probably due to a reduction in hydrophilic character.

It is not to be implied that pure cellulose is not hydrophilic; in fact, it is extremely so; but cellulose fiber differs from other gels in that the macromolecules are bound in a rigid structure as fiber walls. In the nonfibrous gel state, cellulose shows relatively high hydrophilic character but it certainly is not comparable with hemicellulose.

Figures 14 and 15 and Table XXII illustrate the effect of ball mill processing pulp and then making sheets at various apparent densities. The effect was the same as the effect of adding hydrophilic materials, yet no change in the degree of hydration could be measured by the cryoscopic procedure. The effect was not as anomalous as it appeared. The same result (i.e., an increase in sheet

strength) was attained by a different method. When fibers are beaten, the external area increases and the fibers become more pliable (18), (21), (25), (42); hence the probability of fiber-fiber bond formation is greater. It will be shown in a subsequent section that pulp does become slightly more hydrophilic in the first few minutes of beating.

Effect of Sheet Density on the Tearing Strength

It is interesting to note that the tearing strength was almost the reciprocal of the Mullen (Figures 12, 13, 14, 15). It is usually assumed that tearing strength loss on beating is due to fiber cutting. Little cutting takes place in the ball mill, and the reduction in tear must have been due to the formation of fiber-fiber bonds.

The sharp decline of tear below a certain critical amount of bonding was indicated by the curve of Duponol WA-treated fibers. Sheets were made by suspending dry fibers in dry butyl alcohol and then forming the sheets on a piece of Fourdrinier wire placed in the bottom of a Büchner funnel. The sheets were pressed at a pressure of 300 pounds per square inch for 7 minutes between blotters and dried on British plates and rings. The Mullen strength was nearly zero. The tearing strengths for various beating periods are given in Table XXV and are a measure of the fiber entanglement.

TABLE XXV

EFFECT OF MAKING HANDSHEETS
IN DRY BUTYL ALCOHOL

Beating Time min.	Tear Factor	Apparent Density	Basis Weight lb.	Caliper thousandth of an inch	Mullen Points
0	0.76	10.60	53.4	5.00	0.8
45	1.20	9.68	52.7	5.45	0.9
60	1.29	9.60	53.0	5.50	0.9

It may be concluded that for a given fiber furnish in a pulp processing apparatus, the tearing strength is inversely proportional to the Mullen strength and an increase in Mullen will be attended by a proportional loss in tearing strength. In other words, the tearing strength is inversely proportional to the amount of fiber-fiber bonding above a certain small degree of fiber bonding essential to hold the sheet together.

Experiments Testing the Validity of the Hypothesis that Fiber-Fiber Bonding is a Function of the Fiber Hydrophilic Nature

The hypothesis has been advanced that the ability of fibers to form fiber-fiber bonds is dependent upon the hydrophilic nature of the fiber surface, other factors being equal. Various experiments designed to test this hypothesis have been made.

A fresh cellulose surface has a marked affinity for water. Campbell (16) has shown that bone-dry cellulose will remove vapor sorbed on phosphorous pentoxide. Such a surface should be wetted almost perfectly, and the cosine of the contact angle of water on

cellulose must be very nearly unity. As Adam (4) has shown, the wetting of a porous surface is the product of the surface tension and $\cos\theta$ (contact angle). Thus the inability of wetting agents to increase the rate of imbibition of pulp in the beater is understood since the value of (surface tension)($\cos\theta$) is invariably reduced unless $\cos\theta$ is originally low due to sizing material on the fibers.

Wetting agents are employed to reduce the difference in energy between hydrophobic and hydrophilic surfaces. In the case of pulp-water systems, the two components are usually both highly hydrophilic and any auxiliary agent between the surfaces would tend to lessen the affinity of the surfaces for each other. In pulping processes, a wetting agent would be useful only when at least one component of the system is hydrophobic. Thus a wetting agent would be useful in a deinking process and in breaking down hard-sized broke.

Several compounds of the wetting agent type of low hydrocarbon content were added to pulp and after a one-hour sorption period sheets were made. The results are given in Table XXVI.

TABLE XXVI

EFFECT OF POLAR SUBSTANCES ON SHEET STRENGTH

Compound	Grams Per 5 Sheets	Mullen Points	Tear Factor	Basis Weight lb.	Surface Tension dynes/cm.
Added in Molecular Portions					
Sodium Lauryl Sulfate	5.10*	42.5	2.04	45.6	----
Sodium Benzenesulfonate	1.50	63.0	1.88	47.6	----
Sodium Sulfanilate	1.43	58.0	1.65	46.6	----
Control Pulp, No Agent	0.00	68.0	1.70	43.8	----
Added in Equal Weight Portions					
Sodium Benzenesulfonate	0.75	65.0	1.57	46.8	65.8
Sodium Lauryl Sulfate	1.50*	41.0	2.40	49.7	45.0
Naphthalene Lignin Complex	0.75	65.8	1.70	48.9	64.0
Control Pulp, No Agent	0.00	64.4	1.75	46.9	70.0

* Added as Duponol WA, 50% Sodium Lauryl Sulfate

From Table XXVI it is observed that the handsheet strength was greater if the size of the hydrophobic group in the surface-active molecule was reduced. The molecules of sodium benzenesulfonate and sodium sulfanilate sorbed on the cellulose surfaces did not reduce the surface hydrophilic character as much as sodium lauryl sulfate, which has a relatively large hydrophobic group. Although the naphthalene lignin complex made from lignosulfonic acid has a large carbon content, lignosulfonic acid has many polar groups and thus a hydrophilic nature. The lignin complex affected sheet strength very little, although it depressed the sheet mold surface tension to 64 dynes per cm..

It has been noted previously that little significance can be attached to the surface tension in the sheet mold; however, it may be pointed out that the depression of the surface tension by

sodium benzenesulfonate and the naphthalene lignin complex had no effect upon the strength of the sheet. The surface tension depression by Duponol WA was much greater and the handsheet strength was much less; but if the loss of strength of handsheets was due solely to surface tension conditions during forming and drying of the sheet, the surface tension lowering by sodium benzenesulfonate and the lignin complex would be reflected to some extent in the handsheet strength.

Bleached sulfite pulp was mordanted with tannic acid to make it less hydrophilic. Tannic acid is well known as a dehydrating agent in colloidal systems. The procedure of preparing tannic acid mordanted fibers is given in Chapter III. Sheets made from these fibers were compared with sheets treated with Duponol WA, locust bean gum, gelatin, and methylcellulose. The preparation of methylcellulose and its precipitation on the fibers has also been previously described. This material was selected as representative of a soluble cellulosic material, or rather a highly dispersed cellulosic material, in aqueous media.

Strength characteristics, sheet mold surface tension, and the alkali binding power of the shredded sheets were determined (Tables XXVII and XXVIII). No alkali binding determination was made on the tannic acid mordanted fibers due to the high acidity, although the acidity introduced into the pulp was corrected in other cases where it was only slight.

TABLE XXVII

RELATION OF SHEET MOLD SURFACE TENSION AND STRENGTH OF HANDSHEETS OF PULP TREATED WITH MATERIALS WHICH CHANGE THE HYDROPHILIC CHARACTER

Treatment	None	Tannic Acid	Gelatin	Methyl-cellulose	Duponol WA	Locust Bean Gum
Basis Weight lb.	45.1	44.1	46.3	52.5	48.1	47.5
Mullen Points	56.4	0.0	68.6	99.0	31.6	95.5
Tear Factor	2.12	0.65	1.56	1.02	2.31	1.30
Double Folds	49	0	89	1586	9	528
Caliper thousandths inch	5.78	5.50	5.80	5.81	4.26	5.61
Apparent Density	11.9	8.0	12.3	13.8	11.3	13.1
Surface Tension dynes/cm.*	72.5	71.5	67.7	64.0	48.0	72.5
Surface Tension dynes/cm.**	57.0	51.7	48.0	53.0	33.0	43.7

* in sheet mold
** at 0.9% consistency before making sheets

TABLE XXVIII

ALKALI BINDING OF PULPS TREATED WITH MATERIALS THAT CHANGED THE HYDROPHILIC NATURE OF THE FIBERS

Treatment	None	Duponol WA	Gelatin	Methyl-cellulose	Locust Bean Gum
0.01 H_2SO_4 cc.	13.40	14.40	12.20	12.80	13.00
Blank NaOH cc.	0.35	0.35	0.35	0.60	0.60
Corrected H_2SO_4 cc.	13.05	14.05	11.85	12.30	12.40
Normality NaOH in Filtrate	.00261	.00281	.00237	.00246	.00248
NaOH in Filtrate g.	.0110	.0118	.0110	.0103	.0104
NaOH Bound g.	.0079	.0071	.0089	.0086	.0085
NaOH Binding %	41.8	37.6	47.0	45.5	45.0

The strength characteristics given in Table XXVII are in the order anticipated from the treatment given. The sheets made from tannic acid mordanted fibers were merely a felted mass. The fibers could be brushed from the soft sheet by hand. The surface tension of the 0.9 per cent consistency treated pulp was determined as well as the surface tension in the sheet mold. The former is a closer approach to the concentration of the system in the wet sheet than the measurement made in the sheet mold before drainage is started. The surface tension had little relation to the finished sheet strength.

It might be inferred that the hydrophilic nature of a pulp surface and the surface tension are closely related. This is not necessarily true. If the hydrophilic nature of pulp is reduced by a surface-active agent, the surface tension of water between pulp fibers will be decreased. If, however, the pulp fibers are mordanted

with tannic acid, the surface tension is not reduced appreciably. In the case where fibers were treated with locust bean gum, the surface tension of the aqueous portion of the system was rather low, yet the fibers were extremely hydrated. Therefore, the degree of hydration and the forces of surface tension are not proportional.

The alkali binding of the shredded pulp showed a trend of hydrophilic character consistent with the hypothesis advanced. The binding power of the gelatin treated sheets was too high; however, too much value should not be placed on the alkali binding results because, on rewetting of the dried handsheets, the colloidal materials will not revert to their original hydrated state. This is especially true of methylcellulose which must be prepared in an alkaline medium.

Effect of Beating on the Hydrophilic Character of Pulp Fibers

It has been shown previously that the bound water as determined by the cryoscopic method did not increase during moderate beating. The changes in alkali binding and surface tension were observed as a pulp was beaten in a two-pound Valley beater. The results are shown in Figure 16 and Tables XXIX and XXX. The initial alkali binding was made on dry lap soaked and de-fibered by maceration with a stirring rod. The alkali binding of the zero beating interval sample was made on the pulp which had been beaten 5 minutes.

The sharp initial rise of alkali binding indicated that the hydrophilic nature of the pulp increased on slight mechanical treatment. No further increase was noted until the later stages of beating

when fiber disintegration became appreciable. The surface tension of the liquid in the beater decreased gradually during beating. This was interpreted as indicating that lower carbohydrates, which might be more susceptible to hydration, were slowly being peptized by the mechanical beating action.

TABLE XXIX

BEATER EVALUATION OF BLEACHED SULFITE PULP

Beating Time min.	0	15	30	45	60	75
S. R. Freeness	850	810	735	645	480	410
Basis Weight lb.	47.8	47.7	47.0	46.3	46.2	45.6
Caliper thousandth inch	3.94	3.48	3.12	3.02	3.00	2.70
Apparent Density	12.1	13.7	15.1	15.3	15.5	16.8
Mullen Points	36	65	78	90	94	91
Tear Factor	2.23	1.50	1.20	1.00	0.98	0.82
Surface Tension in Beater dynes/cm.	57	53	50	48	47	44

FIGURE 16

BEATER EVALUATION OF BLEACHED SULFITE

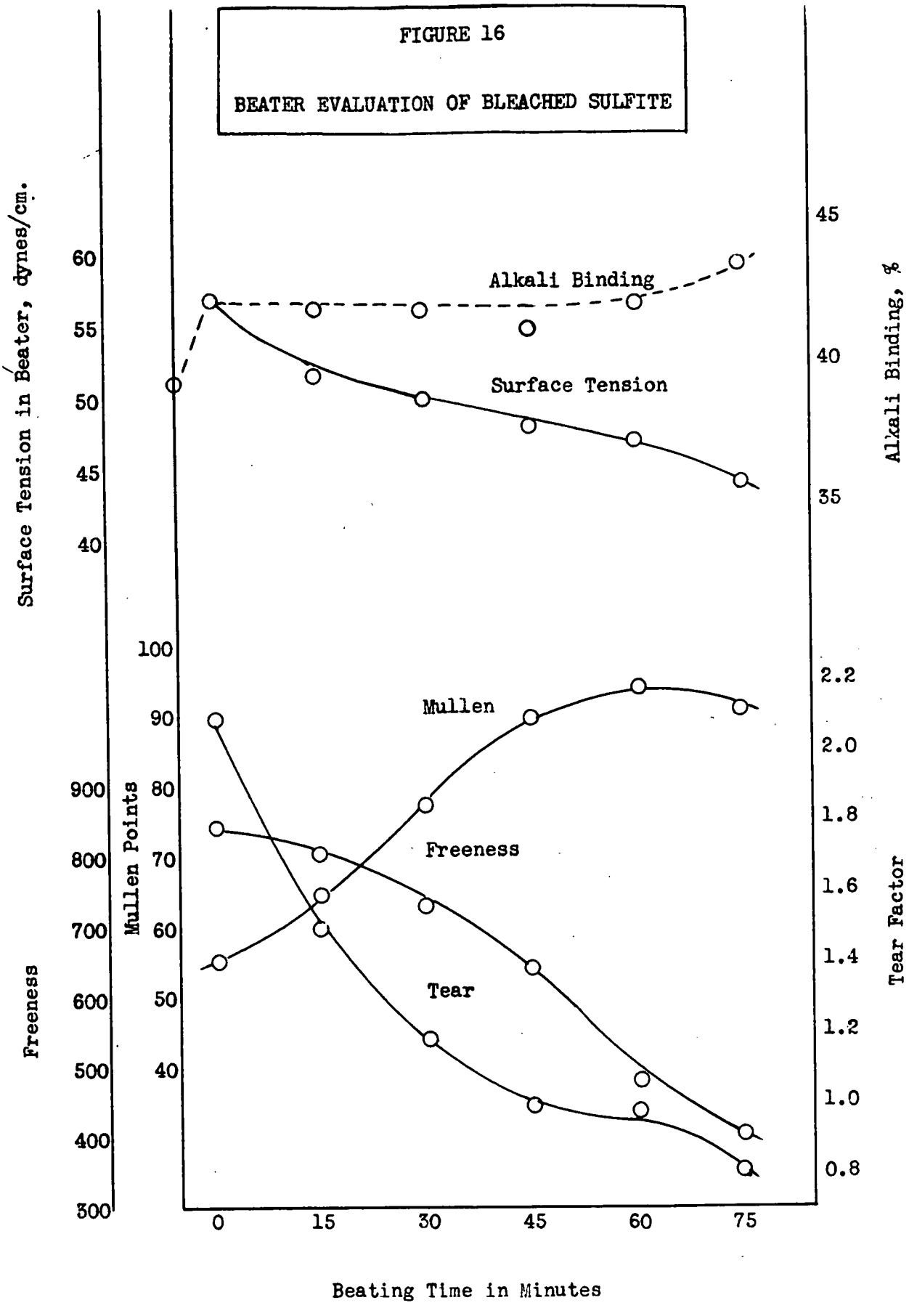


TABLE XXX

ALKALI BINDING OF BEATEN PULP

Beating Time min.	0*	0**	15	30	45	60	75
0.01 N H_2SO_4 cc.	13.6	13.0	13.1	13.1	13.2	13.0	12.6
Normality of Filtrate	.00292	.00260	.00262	.00262	.00264	.00260	.00254
NaOH in Filtrate, g.	.0114	.0109	.0110	.0110	.0111	.0109	.0107
NaOH Bound, g.	.0075	.0080	.0079	.0079	.0078	.0080	.0082
NaOH Binding, %	39.5	42.3	41.9	41.7	41.3	42.3	43.4

0.0189 grams of NaOH added to each sample
* Raw pulp de-fibered by slight agitation
** Pulp circulated in beater and beaten 5 min. (Official 0 interval)

The initial increase in alkali binding was interpreted as a removal by mechanical action of a film, or rather particles, of cellulosic materials rendered less hydrophilic by the action of air or by drying. This effect was further investigated by kneading pulp at 8 per cent consistency for 6 hours. The alkali binding of this pulp and of the original pulp which was disintegrated very slightly was determined at various alkali sorption periods. The results are given in Figure 17 and Table XXXI. The increased binding of pulp subjected to mechanical agitation was definite throughout the entire sorption period. The Mullen strength increased from 34.0 to 42.8 points per pound.

It was argued that if mechanical friction removed from fibers accumulated material which was less hydrophilic than cellulose, the fresh cellulose surface could be reduced in hydrophilic activity

TABLE XXXI

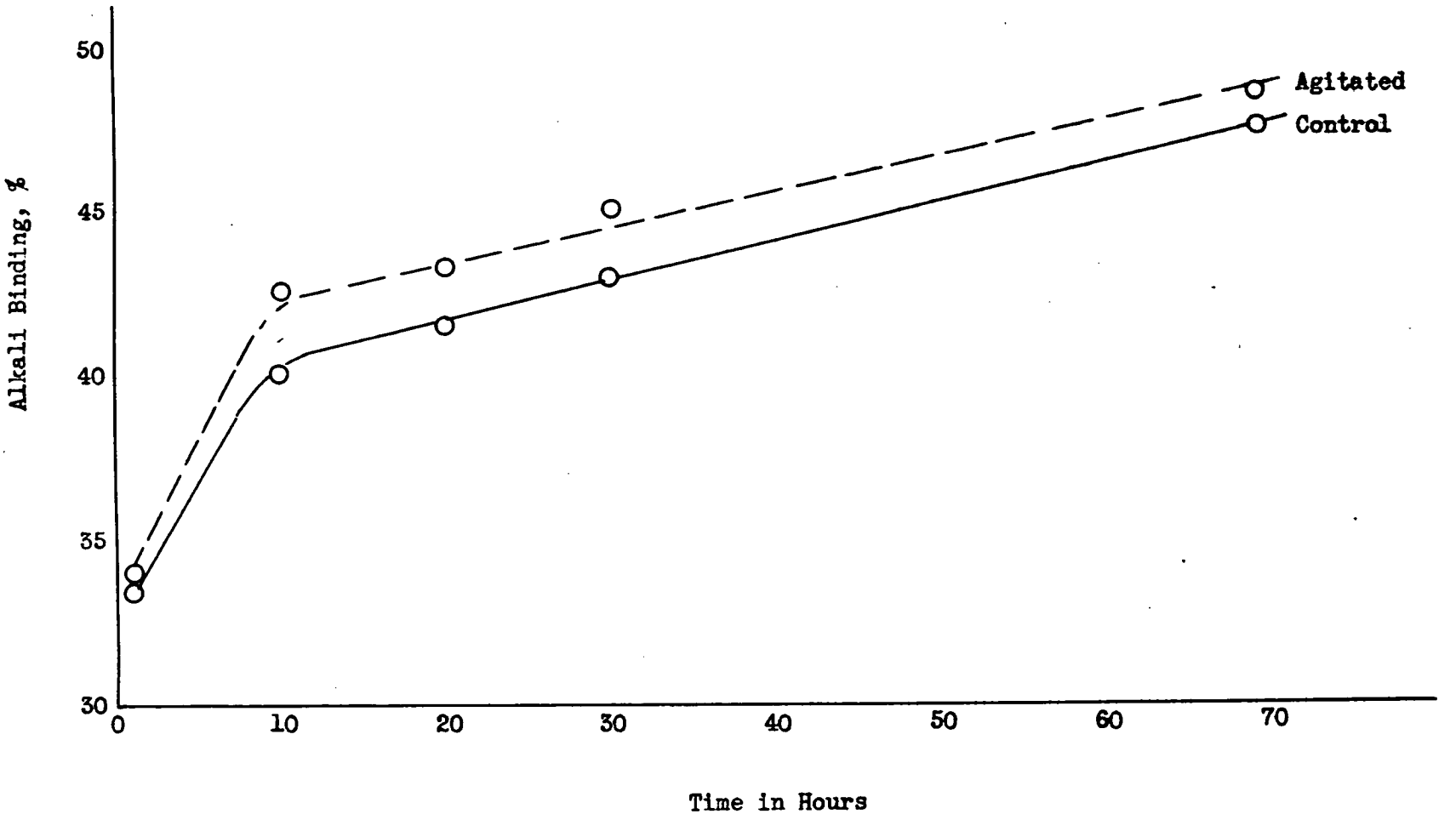
ALKALI BINDING OF PULP AGITATED SIX HOURS

NaOH Sorption Period hours	0.01 N H_2SO_4 cc.	Normality Filtrate	NaOH in Filtrate g.	NaOH Bound g.	NaOH Bound %	Average NaOH Bound %
1*	15.0	.00300	.0126	.0063	33.3	37.6
1	14.9	.00298	.0125	.0064	33.9	
10	13.6	.00272	.0114	.0075	39.7	40.1
10	13.3	.00266	.0112	.0077	40.6	
20	13.4	.00268	.0113	.0076	40.2	41.5
20	12.9	.00258	.0108	.0081	42.8	
30	12.9	.00258	.0108	.0081	42.8	43.0
30	12.7	.00254	.0107	.0082	43.4	
69	11.9	.00238	.0100	.0089	47.0	47.5
69	11.6	.00232	.0098	.0091	48.0	
1**	15.2	.00304	.0127	.0062	32.8	33.9
1	14.6	.00292	.0123	.0066	34.9	
10	13.2	.00264	.0111	.0078	41.2	42.6
10	12.7	.00254	.0106	.0083	44.0	
20	12.7	.00254	.0106	.0083	44.0	43.1
20	13.0	.00260	.0109	.0080	42.3	
30	12.3	.00246	.0103	.0086	45.5	45.0
30	12.6	.00252	.0105	.0084	44.5	
69	11.5	.00230	.0096	.0092	48.6	48.6

* unagitated control pulp
** agitated six hours

FIGURE 17

ALKALI BINDING POWER OF PULP AGITATED AT 8 PER CENT CONSISTENCY FOR 6 HOURS



in a controlled manner by the sorption of polar molecules. If a series of samples were treated with increasing amounts of a polar compound containing a large hydrophobic group, the decrease in hydrophilic character of the pulp subjected to mechanical friction would be greater, at least at small concentrations, than the decrease for the original pulp treated in the same manner.

This type of experiment was carried out by treating 5-gram samples of stock stirred at 8 per cent consistency for 6 hours with Duponol WA for 24 hours. The alkali binding power was then determined. Samples of the original stock were treated also and the results are shown in Figure 18 and Table XXXII. The rate of decrease of surface hydration of the agitated pulp decreased at a greater rate for activated pulp than for the original pulp. However, the difference between the original and the agitated samples were close to the limit of accuracy of the experiment.

TABLE XXXII

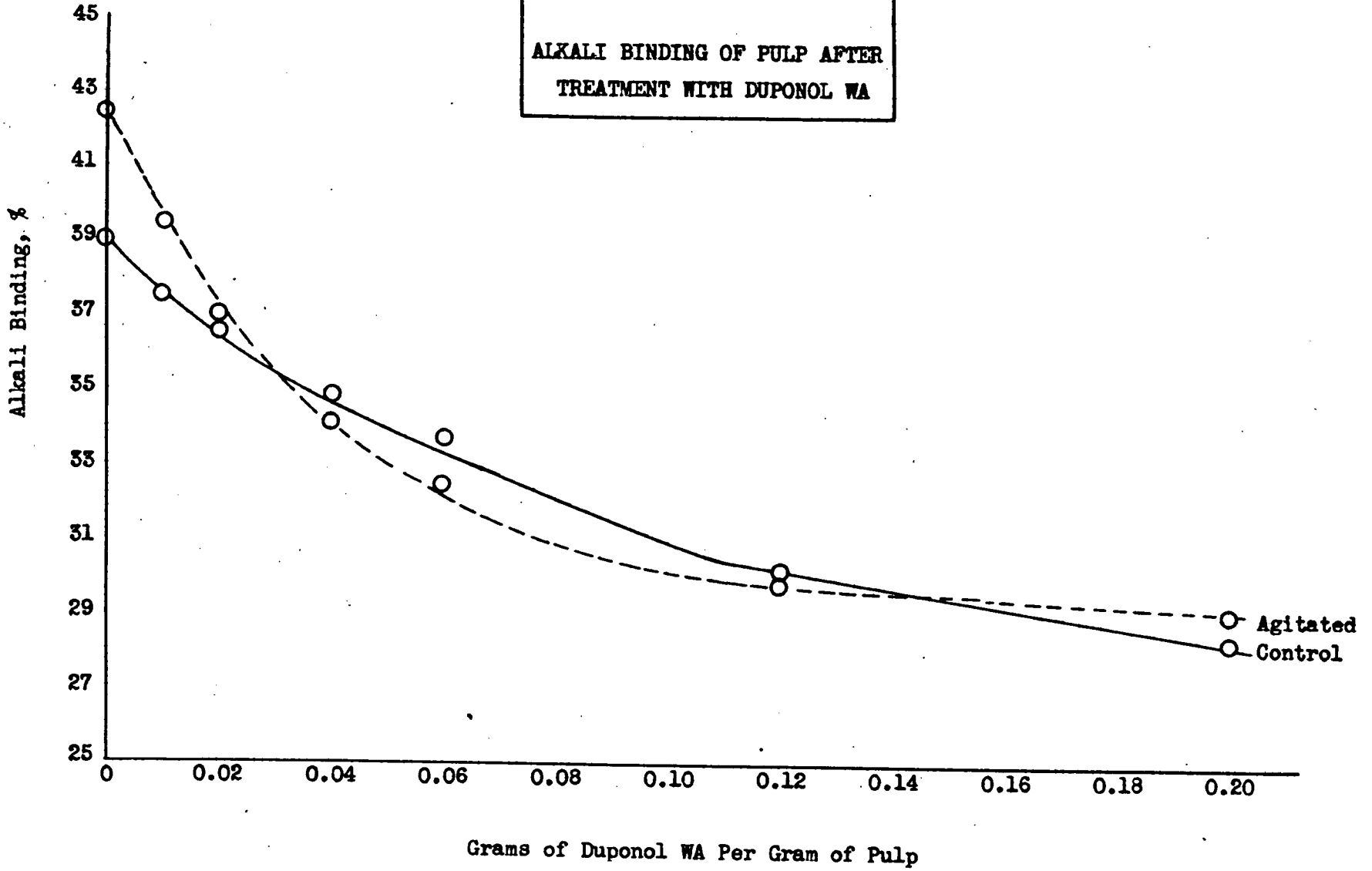
EFFECT OF TREATMENT OF RAW AND AGITATED PULP WITH DUPONOL WA ON ALKALI BINDING

Sample	0.01 N H_2SO_4 cc.	Normality of Filtrate	NaOH in Filtrate g.	NaOH Bound g.	NaOH Bound %
No Pulp	22.50	.00450	.0180	.0000	00.0
0 Raw	13.70	.00274	.0115	.0074	39.3
0 Ag.*	13.00	.00260	.0109	.0080	42.3
.05 Raw	13.90	.00278	.0117	.0072	38.0
.05 Ag.	13.45	.00269	.0113	.0076	40.0
.10 Raw	14.30	.00286	.0120	.0069	36.4
.10 Ag.	14.20	.00284	.0119	.0070	37.0
.20 Raw	14.60	.00292	.0123	.0066	34.9
.20 Ag.	14.90	.00298	.0125	.0064	33.9
.30 Raw	14.90	.00298	.0125	.0064	33.9
.30 Ag.	15.40	.00308	.0129	.0060	31.8
.60 Raw	15.70	.00314	.0132	.0057	30.2
.60 Ag.	15.85	.00317	.0133	.0056	29.7
1.0 Raw	16.20	.00324	.0136	.0053	28.0
1.0 Ag.	16.05	.00321	.0135	.0054	28.6
		Check Experiment			
0 Raw	13.70	.00274	.0115	.0074	39.3
0 Ag.	13.85	.00257	.0108	.0081	42.6
.05 Raw	14.05	.00281	.0118	.0071	37.5
.05 Ag.	13.70	.00274	.0115	.0074	39.3
.10 Raw	14.20	.00284	.0119	.0070	37.0
.10 Ag.	14.05	.00281	.0118	.0071	37.6
.20 Raw	14.60	.00292	.0123	.0066	35.0
.20 Ag.	14.75	.00295	.0124	.0065	34.5
.30 Raw	15.00	.00300	.0126	.0063	33.5
.30 Ag.	15.10	.00302	.0127	.0062	32.8
.60 Raw	15.70	.00314	.0132	.0057	30.2
.60 Ag.	15.85	.00317	.0133	.0056	29.7
1.0 Raw	16.05	.00321	.0135	.0054	28.6
1.0 Ag.	15.80	.00316	.0133	.0056	29.7

* agitated six hours

FIGURE 18

ALKALI BINDING OF PULP AFTER TREATMENT WITH DUPONOL WA



The Mullen strength of handsheets was determined for agitated pulp treated with Duponol WA in the same manner as in the alkali binding experiment. This Mullen strength was compared with the Mullen of the original pulp also treated with Duponol WA. These results are shown in Figure 19 and Table XXXIII. The greater susceptibility of the surface of mechanically agitated pulp to dehydrating effects of Duponol WA in respect to the original pulp was demonstrated. However, the Mullen strength does not parallel the alkali binding relations of the two pulps as a comparison of Figure 18 and Figure 19 readily shows.

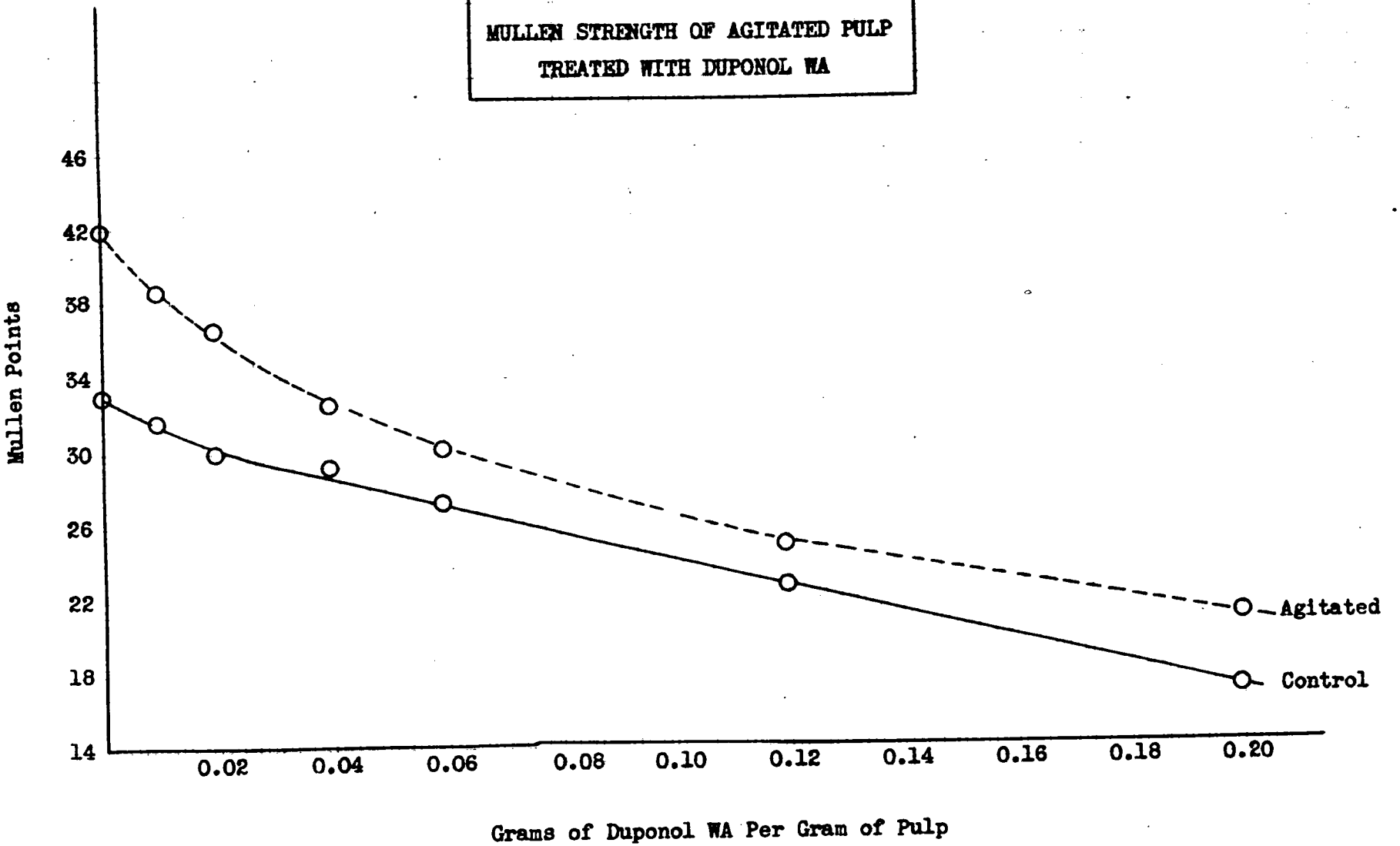
TABLE XXXIII

MULLEN STRENGTH OF RAW AND AGITATED PULPS AFTER TREATMENT WITH DUPONOL WA

Duponol WA Per Gram of Pulp g.	Mullen Points		Basis Weight lb.	
	Agitated	Raw	Agitated	Raw
0.00	42.0	31.8	46.7	47.0
0.01	38.4	31.6	47.0	46.2
0.02	36.7	28.3	47.1	47.2
0.04	32.5	29.4	46.9	47.8
0.06	30.3	27.2	47.3	47.1
0.12	25.2	23.0	47.5	47.3
0.2	21.0	17.0	47.0	47.3

FIGURE 19

MULLEN STRENGTH OF AGITATED PULP TREATED WITH DUPONOL WA



V. SUMMARY AND CONCLUSIONS

1. It has been demonstrated that the hydrophilic character of fiber surfaces is the predominate factor which causes fibers to bond and thus give strength to a sheet of paper.

2. The hydrophilic character of unbeaten pulp fibers was increased by treating suspensions of bleached sulfite with locust bean gum, cellulose gel, and gelatin. Handsheets of various apparent densities obtained by varying the wet pressing pressure were made and evaluated for strength properties.

3. The hydrophilic character of unbeaten bleached sulfite fibers was reduced by treatment with Duponol WA (sodium lauryl sulfate). The strength properties of the sheets made from these fibers were compared to the sheets made from fibers treated with hydrophilic materials.

4. The hydrophilic character was measured by the relative amounts of water bound to the various hydrophilic colloids, bleached sulfite, and bleached sulfite treated with Duponol WA. The amount of bound water was determined by a modification of the method of Gortner and Gortner.

5. By measuring the alkali binding power, the hydrophilic nature of treated bleached sulfite fibers as measured by bound water experiments was confirmed. The strength of the handsheets made from the fibers treated with materials to change the hydrophilic nature was in the same order as the amount of water bound by the materials added.

6. It was shown by bound water measurements that the hydrophilic character of bleached sulfite fibers did not increase during 60 minutes beating.

7. It was shown by alkali binding experiments, however, that beating slightly increased the hydrophilic nature of pulp during the first few minutes of beating and also somewhat after 60 minutes beating. It was postulated that a film of hydrophobic materials formed by the action of air and drying were removed by slight mechanical agitation.

8. The initial increase in alkali binding was confirmed by kneading pulp at 5 per cent consistency for 6 hours and comparing the alkali binding with the binding power of raw pulp.

9. A study of the effects of wetting agents on beating was made. Types of wetting agents were added to bleached sulfite in a laboratory beater and to bleached sulfite in a ball mill. These agents slightly decreased the rate of development. The handsheets were much weaker because sorbed polar molecules interfered with fiber-fiber bonding during sheetmaking.

10. Handsheets of bleached sulfite pulp beaten to various degrees were made in the presence of surface-active materials. A decrease in Mullen strength and folding endurance and an increase in tearing strength were brought about by surface-active substances, providing the material was allowed to sorb on the pulp fiber. The change in strength was roughly proportional to the surface tension of

the liquid in the sheet mold. If no sorption period was allowed, the strength characteristics of the handsheets did not change appreciably with a decrease in sheet mold surface tension.

11. Cellulose-water systems depressed the surface tension of water as much as 25 dynes per cm.. The greater the pulp purity, the less the surface tension depression. Severe washing of pulp in water did not remove the constituents which reduced the surface tension.

12. A number of organic constituents including ethylcellulose, wheat flour, egg albumin, etc., caused a similar decrease in surface tension of water. The surface tension depression was attributed to a slight solubility, which, in the case of cellulose, was presumably due chiefly to the solubility of the lower polymers of cellulose such as beta and gamma cellulose.

13. The sorption of Duponol WA on pulp fibers decreased the equilibrium moisture content slightly. It was shown further that wetting agents, specifically Duponol WA, reduced the hydrophilic character of pulp fibers, and that this effect caused most of the strength loss observed rather than the reduction of surface tension under which the sheets were formed and dried.

14. Fibers mordanted with tannic acid formed a soft sheet with very little strength. It was concluded that since tannic acid is not an exceptionally good surface tension depressant, the inability of the fibers to form bonds could not have been due to a reduction of the forces tending to pull fibers together. This con-

firms the concept that surface-active substances reduce sheet strength by virtue of their hydrophobic character in respect to pulp, as well as by any reduction in surface tension forces.

15. In regard to the application of wetting agents to pulping processes, it may be stated that, since pulp is extremely hydrophilic, the usual commercial wetting agents are either without effect or are detrimental to the strength of sheets made from treated pulp. In the case where one component of a system containing pulp is hydrophobic, wetting agents might assist in mixing pulp and the hydrophobic component compatibly.

VI. LITERATURE CITED

1. Anon., Chem. Ind. 40:171(1937).

2. Adam, Neil Kensington. "The physics and chemistry of surfaces." 2d edition, p. 2. Oxford, Clarendon Press, 1938. 402 p.

3. Gortner, Ross Aiken. "Outlines of biochemistry." 1st edition, p. 156-10?. New York, Wiley, 1929. 783 p.

4. Adam, N. K., J. Soc. Dyers Colourists 53:121-129(1937).

5. Röhm and Haas Company, Inc. "Triton K-30." p. 17-18. Philadelphia. 38 p.

6. Harkins, William D., Davies, Earl C. H., and Clark, George L., J. Am. Chem. Soc. 39:541-596(1917).

7. Langmuir, Irving, J. Am. Chem. Soc. 39:1848-1906(1917).

8. Wilkes, B. G., and Wickert, J. N., Ind. Eng. Chem. 29:1254-1259 (1937).

9. Draves, Carl Z., and Clarkson, F. G., Am. Dyestuff Reptr. 20: 201-208(1931); C. A. 25:5296(1931).

10. Dean, H. K. "Wetting agents." In International Society of Leather Trades' Chemists, "Wetting and detergency." p. 25-39. New York, Chemical Publishing Co., 1937. 207 p.

11. Cupples, H. L. "A list of proprietary detergents, wetting agents, and emulsifying agents." U. S. Bureau of Entomology and Plant Quarantine E-426. Washington, U. S. Govt. Print. Off., 1938. 24 p.

12. Harrison, H. A., World's Paper Trade Rev. 99, Technical convention number:27(March, 1933).

13. Harrison, H. Ainsworth, Ind. Eng. Chem. 26:458-461(1934).

14. Noll, August, Papier-Fabr. 35:393-398, 401-408(1937).

15. Ritter, Geo. J., Paper Trade J. 101, no. 18:92-100(Oct. 31, 1935).

16. 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.

17. Meyer, Kurt H., and Mark, E., Ber. 61:593-614(1928).

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

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

20. Heuser, E., Paper Trade J. 101, no. 21:39-46; no. 22:35-41; no. 23: 39-42(Nov. 21, 28, Dec. 5, 1935).

21. Cottrall, Leslie G., Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland 14:241-274(1933-34).

22. Schwalbe, Carl G., and Becker, Ernst, Z. angew. Chem. 33:14-16, 57-59(1920).

23. Minor, Jessie E., Ind. Eng. Chem. 13:131-133(1921).

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

25. Kress, Otto, and Bialkowsky, Harold, Paper Trade J. 93, no. 20: 38-44(Nov. 12, 1931).

26. Strachan, J., World's Paper Trade Rev. 97:576, 578, 580, 582, 667-668, 671-672, 675, 755-756, 759-760, 762, 764, 800, 802, 805 (1932).

27. Bell, J. M. B., Paper-Maker 89:Ts59-62, 79-80(1935).

28. Nakano, Michimaro, Cellulose Ind. 6:B25(1930).

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

30. Simmonds, F. A., and Baird, P. K., Paper Trade J. 98, no. 20:38-42(May 17, 1934).

31. Carson, F. T., and Worthington, F. V., Bur. Standards J. Research 6:339-353(1931).

32. Doughty, R. H., Paper Trade J. 95, no. 10:71-79(Sept. 8, 1932).

33. Cottrall, Leslie G., Paper-Maker 87:Ts127-132(1932).

34. Brecht, W., and Imset, O., Papier-Fabr. 31, no. 27A:46-60(July, 1933).

35. Steinschneider, M., and Grund, E., Papier-Fabr. 36:1-21(1938).

36. Maass, O., and Campbell, W. Boyd, Pulp Paper Mag. Can. 40:108-114 (1939).

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

38. Clark, George L., Ind. Eng. Chem. 22:474-487(1930).

39. Katz, J. R., Cellulosechem. 11:17-30(1930).

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

41. Mark, H., Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland 14:278-279(1933-34).

42. Jayme, G., Papier-Fabr. 35:409-417(1937).

43. Peirce, F. T., J. Textile Inst. 20:T133-150(1929).

44. Balls, W. Lawrence. "Studies of quality in cotton." p. 41-42. London, Macmillan, 1928. 278 p.

45. Sheppard, S. E., and Newsome, P. T., J. Phys. Chem. 39:143-152 (1935).

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

47. Walker, Albert C., Textile Research 7:229-239(1936-37).

48. Filby, Edgar, and Maass, O., Can. J. Research 7:162-177(1932).

49. Bancroft, Wilder D., and Calkin, John B., Textile Research 4: 371-398(1933-34).

50. Klingstedt, F. W., Svensk Papperstidn. 40:412-416(1937).

51. Haas, Paul, and Hill, T. G. "An introduction to the chemistry of plant products." 4th edition, vol. 1, p. 206. London, Longmans, Green, 1928. 530 p.

52. Schorger, A. W. "Chemistry of cellulose and wood." 1st edition, p. 143. New York, McGraw-Hill, 1926. 586 p.

53. Seborg, C. O., Simmonds, F. A., and Baird, P. K., Ind. Eng. Chem. 28:1245-1250(1936).

54. Sheppard, S. E., and Newsome, P. T., J. Phys. Chem. 33:1817-1825 (1929).

55. Pidgeon, Lloyd M., and Maass, O., J. Am. Chem. Soc. 52:1053-1069 (1930).

56. Seborg, C. O., and Storm, A. J., Ind. Eng. Chem. 23:1271-1275 (1931).

57. Russell, J. K., Maass, O., and Campbell, W. B., Can. J. Research B 15:13-37(1937).

58. McCarthy, Joseph L., and Jahn, Edwin C., Paper Trade J. 103, no. 9:21-29(Aug. 27, 1936).

59. Bell, J. M. B., J. Soc. Chem. Ind. 52:T109-116, 119-120(1933).

60. Rowe, J. W., Paper Makers' Monthly J. 66:22-25(1928).

61. Sedoff, Arthur, Holmberg, C. V., and Jahn, Edwin C., TAPPI Preprints of Papers. Twenty-Fourth Annual Meeting:141-147(1939).

62. Jayme, George, and Steinmann, Rudolf, Papier-Fabr. 35:337-364 (1937).

63. Gortner, Ross Aiken. "Outlines of biochemistry." 2d edition, Chapter 9. New York, Wiley, 1936. 1017 p.; Newton, R., and Gortner, R. A., Botan. Gaz. 74:442-446(1922).

64. Stamm, Alfred J. "Colloid chemistry of cellulosic materials." U. S. Dept. of Agriculture. Miscellaneous publication No. 240. especially p. 47. Washington, U. S. Govt. Print. Off., 1936.

65. Barkas, Wilfred W., Nature 135:545(1935).

66. Gortner, R. A., and Gortner, W. A., J. Gen. Physiol. 17:327-328 (1933).

67. Heald, A. M., Doctor's Thesis, Institute of Paper Chemistry, 1939.

68. Bialkowsky, Harold W., Paper Trade J. 97, no. 13:28-46(Sept. 26, 1933).

69. Downs, M. L., Paper Trade J. 107, no. 16:30-35(Oct. 20, 1938).

70. du Noüy, P. Lecomte. "Surface equilibria of biological and organic colloids." Chapter 2. New York, Chemical Catalog Company, 1926. 212 p.

71. Strachan, James, World's Paper Trade Rev. 109, Technical convention number:54, 57-58, 60, 62, 64, 66(March, 1938).

72. Probst, T. F., Doctor's Thesis, Institute of Paper Chemistry, 1939.