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The Relation Between Surface Activity and Fiber-Bond Strength in a Papermaking Pulp

by Henry Johnston Allison, Jr.

June, 1940

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THE RELATION BETWEEN SURFACE ACTIVITY AND FIBER-BOND STRENGTH IN A PAPERMAKING PULP

A thesis submitted by

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HISTORICAL INTRODUCTION

The strength development of paper pulp during the beating process, generally termed "hydration" by the papermaker, has been known almost as long as paper; however, it has not yet been explained by known physical and chemical laws to the satisfaction of most pulp and paper technologists and scientists. Some of the more comprehensive discussions and evaluations of the many current theories proposed to explain this phenomenon have been given by Campbell (1), Clark (2), Cottrall (3), Jayne (4), and Simmonds (5).

THEORIES OF BEATING

The several theories for the cause of this hydration or strength development in the papermakers' beater (and allied equipment) may be divided into three main groups: the chemical, the physical, and the physicochemical concepts.

The Chemical Concept

The first explanations proposed for the phenomenon of hydration were based on the chemical concept. The more outstanding proponents of these were Cross and Bevan (6), Schwalbe and Becker (7), and Minor (8). Clark (2) has summarized this concept as follows:

> It was considered that, during beating, part of the cellulose fibers gradually passed into the condition of a gelatinous hydrate, or in other words, the cellulose in part combined chemically with water, just as for example, soda ash takes on or combines chemically with ten parts of water to give a hydrate commonly known as soda crystals or washing soda, which has physical properties entirely different from the original salt.

This explanation was accepted quite widely throughout the industry because it was based on seemingly reliable data showing that beaten pulp was more hygroscopic than unbeaten pulp and that a hydrate was accordingly formed. On these facts, the papermaker based his opinion that the purpose of beating was to cut and fibrillate the fiber to promote the formation of cellulose hydrate and that the strength obtained in the dry sheet was realized through this cellulose hydrate acting as a cement upon drying.

This chemical concept predominated until 1926 when it was attacked quite successfully in a rather radical paper by Strachan (9). Strachan objected to the concept on numerous grounds: viz., that there is no change in the x-ray pattern during beating, that beaten pulp has the same chemical composition (carbon, hydrogen, and oxygen) as unbeaten pulp, that the rate of imbibition of water by beaten pulp is typical of absorption rather than of compound formation, that the amount of water which can be pressed from beaten pulp varies with the pressure applied, and that temperature affects the combination of water and pulp as it would affect imbibition rather than compound formation. Since this paper was published, the chemical concept of hydration has been adversely criticized by a number of investigators.

Kress and Bialkowsky (10) found no appreciable change in the various chemical constants of pulp as a result of extensive beating. Campbell (1) carried out numerous careful moisture content-relative humidity experiments on pulps of various degrees of hydration and found the differences between beaten and unbeaten pulp to be negligible. Nakano (11,12) concluded that it is impossible for a chemically combined hydrate to be formed from cellulose and water as a result of beating.

He based this conclusion on a study of slowness development (loss in freeness). He found that a certain portion of the slowness developed by beating is lost by boiling or by freezing the beaten pulp suspension. Because it can be destroyed by these operations, it cannot have been developed by the formation of a true chemical cellulose hydrate. The remaining portion of the slowness development he attributed solely to the reduction in fiber diameter as the result of beating; this conclusion was based on a study of the nature of the pulp after boiling. Harrison (13) objected to the chemical or (as he designated it) mucilage theory because the three most important promoters of mucilage formation, overcooking, overbleaching, and bacterial action, are precisely the three factors which reduce the strength of pulp. Cottrall (3) found that no lattice expansion of cellulose occurs as a result of beating (x-ray investigations substantiating Strachan's data) and that there is no appreciable swelling of the fibers during beating. He thought that both of these functions should occur were a true chemical compound (cellulose hydrate) formed. Bell (14) found no difference in the amount of bound water associated with pulp as a result of beating; there would be some if water combined at all with cellulose.

Despite all these attacks, the proponents of the various chemical theories have, according to Clark (2), continued to defend them. They pointed out that, as compared to the total amount of cellulose involved, the amount affected by the formation of cellulose hydrate is too small for changes in chemical constants to be detected by the chemical tests used. Further, they showed that the errors in tests such as those of Campbell (adsorption and desorption curves)--differences

usually attributed to experimental error--are always in favor of the formation of a small amount of cellulose hydrate. (Campbell and others have claimed that these differences are due to errors because of the much longer time required for beaten pulp to come to equilibrium at any given humidity.) Finally, it was contended that much of the strength in pulp is developed before the formation of fibrils.

As a result of the numerous attacks and its relatively weak defense, the chemical concept of strength development has passed almost into oblivion in recent years.

The Physical Concept

The physical concept of strength development during beating seemed to be the logical successor to the chemical concept, for it apparently offered explanations for all the phenomena used to attack the chemical concept. Actually, it was the theory proposed by most of those who objected to the chemical theories.

Strachan (9,15) was the first supporter of the purely physical theory. He theorized (15) thus:

> ...during beating the surfaces of the fibers are rendered plastic by fibrillation. The fibrillae of the two beaten surfaces become intertwined and bind together. We have not only intertwining of the fibers themselves but intertwining of minute fibrillae. The latter is clearly a surface action and depends almost entirely on capillarity or surface tension effects between surfaces. As the external specific surface of the fiber increases with beating so the cohesion between such surfaces increases in the presence of water which brings them into contact.

When the beaten fibers are pressed together, they unite according to

their plasticity and specific surface and, when dried, the water of imbibition is forced out and the fibers shrink. The outer layers of the fiber also shrink together and the dried fiber becomes coated with a layer of denser structure than it had before it was beaten. The fibers are no longer porous, for the air spaces are closed up, thus producing hardness and transparency in the mass. The beaten fibers will hold more water while they are still wet because of the increased amount of specific external surface resulting from fibrillation and because of the imbibitional effects. As the fibers are soft and fibrillated, they will adhere together more strongly on the wire and under the action of the presses and calenders. In answer to the criticism (especially by Harrison (13)) that the fibrillation theory cannot explain the large increase in strength early in the beating process, before fibrillation seems to occur, Strachan (15) stated that, on the contrary, fibrillation does occur but that the fibrillae are too small to be seen except, perhaps, under the strongest of magnifications. (In his more recent papers, however, Strachan has followed the trend of investigators away from the purely physical theories toward the physicochemical concept.)

Although Kress and Bialkowsky (10) disagreed with Strachan quite pointedly, they also viewed pulp strength development as a purely physical phenomenon. Like others (11,14), Kress and Bialkowsky beat pulp in various liquids to determine if fibrillation alone could produce strength in a sheet. They found that the sheet strengths obtained by beating in different nonaqueous liquids ranged from no strength at all to a strength comparable with that obtained by beating

in water. Investigating this further, they proved that the sheet strength which could be developed in pulp by beating in a given liquid was directly proportional to the ability of that liquid to swell the pulp fibers. On the basis of this intensive investigation, they concluded:

> ...these physical changes are mainly occasioned by the swelling of the fibers by the liquid in which the stock is beaten with the result that there is an increase in the volume of the fibers. In the wet, swollen condition the fibers are low in strength but highly plastic or ductile and any mechanical action will tend to bruise or fibrillate the fibers rather than produce a sharp cutting action. The hard close nature of the paper made from so-called hydrated stock seems to be due entirely to the fibrillation of the fibers and the shrinkage of the fibers when the liquid producing the swelling and imbibition is removed by drying.

Cottrall (3) approached the whole problem from a fundamental consideration of the nature of the individual fiber structure which, by that time, was fairly well understood. He claimed that the nature of the cellulose was such that it possessed, at all time, an affinity for a certain amount of water. Thus, hydration is in evidence before beating and is not increased by beating and the effects of beating are attributable to factors other than increased hydration. During beating, some small degree of breaking of bonds between the fibers takes place. This causes a very slight increase in hydration (and explains the increase in hydration which Campbell found in his moisture content-relative humidity experiments and attributed to experimental error), but it is so very small as compared with that which occurs spontaneously when pulp is immersed in water that it does not explain the effects on strength and other properties obtained by beating. Cottrall (3, p. 310) summarizes his theory as follows:

> ...for ordinary degrees of beating...the water-cellulose union is scarcely increased at all, and the character of the paper sheet is the result of other causes..., for example, changes in dimensions (fibrillation) and increased contact of the fibrous elements and, perhaps, also, partly to...the possible effect of exposing the various layers of fiber structural units. It is possible, however, that, as the beating becomes very intensive, the slightly increased water-cellulose union..., which is negligible at first, begins to have an appreciable effect on certain properties of the paper. As I have explained, the hypotheses I have put forward do not exclude the effect of gamma-cellulose, hemi-cellulose, lignin residues and derivatives, dextrin bodies, etc., which may be present in the half stuff.

Cottrall stressed the idea of true hydration (although not developed by beating), because it was the only way he could explain the loss of strength in a sheet when it is wet.

Harrison (13) objected to the purely physical concept because: (a) It does not explain why the major strength development in pulp occurs before any fibrillation can be seen; (b) it does not explain why there is no strength development during that period of beating when fibrillation does occur; (c) he treated dry pulp in a suitable disintegrator to fibrillate it and subsequently suspended it in water only to find that it would not give a strong sheet unless it were subjected to an extensive beating treatment after wetting; hence fibrillation, per se, is of no value (Neale (16) answered this objection with the statement that Harrison failed to obtain true fibrillation because the internal forces in a dry fiber are such that the dry disintegration treatment would cause just as many fractures across the length of the fiber as it would fibrillation--i.e., fractures along the length of the fiber); and (d) he boiled pulp to increase the softness of the fibers and provide more fiber contacts (Cottrall's theory) but found that the

treatment decreased the sheet strength rather than increased it.

Doughty (17) objected to the fibrillation theory because, although the strength of a sheet can be increased by increasing the fiber contacts through more intensive wet pressing, an unbeaten pulp, by this means, cannot be made into a sheet with a strength comparable to that of a sheet made from beaten pulp--showing that a certain amount of beating is essential for strength despite the amount of wet pressing applied in making the sheet. Thus, although, as Cottrall has proposed, the flexibility of the fiber is improved by beating and will, therefore, permit more fiber contacts and as a result greater sheet strength, some other factor is involved.

The Physicochemical Concept

Many of the facts used for the arguments in favor of the mechanical or fibrillation theory are indisputably correct, but the arguments used against these theories are, for the most part, equally true. Out of this paradox has grown the physicochemical concept, the concept which serves as the basis for most of the theories held at the present time on pulp strength development during beating.

Apparently the first proposal of a physicochemical theory for strength development was that made by Forrvik (18) who proposed a theory that was almost purely colloidal. He said that water held to the fibers is adsorbed (a) in large canals, (b) in the lumen, and (c) on the surfaces of the fibers by imbibition. He stated that sheet formation is essentially a colloidal chemical glueing manifestation,

not a mechanical felting. Thus, the purpose of beating is to cause the fibers to swell and in so doing make the fiber walls more adhesive and more plastic. The fiber walls consist of many layers of cellulose and allied materials. In the swelling of the outer layer, glueing is made possible and thus the strength is developed. If the under portions break through, fibrillation occurs and a weaker paper is produced.

The beating process is not a homogeneous, continuous process but one which may be divided into three processes differing essentially one from another. In the first, the capillaries and submicroscopic interstices become filled with water with the expulsion of air. At the same time a colloidal swelling of the fiber walls occurs. The result of these factors is to increase the volume and plasticity of the fiber; the effect is to permit the formation of more fiber-to-fiber contacts which, on pressing, will stick together. As a consequence, the fiber bond strength in the sheet increases, the sheet strength becomes greater, and the extensibility decreases. During the second period of beating the swelling caused by the kneading of the fibers increases. This contributes especially to the plasticity of the fibers. The third process of beating is recognized as the active splitting of the fibers into fibrils, whereby the inner capillaries cease to exist. Between the fibrils new capillary surfaces form which are very resistant to pressure. This action causes the great increase in shrinkage properties of the sheet.

Another early theory based on the physicochemical concept was that developed by Nakano (11,12,19). As mentioned above, he studied the effects of boiling beaten pulp on the change in its degree of wetness.

From this work he concluded that there was no water bound to pulp by the mechanism of true chemical hydration. Subsequently he beat pulp in various liquids and noncellulose fibers in water. From the various data which he obtained, Nakano (19) proposed that the beating process can develop adhesive properties on the fiber and fibril surfaces of only vegetable (cellulose) fibers because they alone possess the proper colloidal nature; this adhesive property is a most important characteristic of the fibers and the felting property (fibrillation) is of secondary importance.

From his fundamental study of the physics involved in the action of the beater, Smith (20) concluded that the fibers are cut and hydrated during the beating operation. The hydration effect is produced on the fibers by pressure and abrasion, drawing, brushing, and carding. The result of these actions is to soften the fibers and to increase the tendency for surface adsorption of water. (Since Smith speaks of surface adsorption of water, his use of the term hydration apparently does not imply true chemical hydration.)

Doughty's (17) work, showing the necessity of a theory which embodies more than simply increasing the number of fiber contacts to produce sheet strength, has already been cited. He carried out his several investigations on both beaten and unbeaten fibers by testing sheets formed from each pulp with different percentages of solid fiber content (obtained by using different amounts of wet pressing) for various physical and optical properties. Doughty summarizes his theory as follows:

> Hence the beating process may be divided into two principal stages, an initial one in which adsorption, absorption, or imbibition of water on and in the fibers is the preponderant effect, and a final one in which decrease of fiber size is most important. These stages naturally overlap somewhat, but the transition need not be considered as a separate one. Likewise the strength changes on beating may be considered as occuring in two successive stages: first, a strength increase at constant solid fraction, caused by the adsorption or imbibition effect and its consequent surface changes, and second, a strength change caused by increasing solid fraction, the strength at constant solid fraction remaining constant. The increase in solid fraction may be attributed to increased shrinkage of the sheets on drying which may in turn be ascribed principally to a decreased particle size of the pulp.

Further elaborating on his theories, Doughty claimed that the purpose of the first stage of beating is to increase the actual availability of the potential bond strength in the pulp. That these bonds are not already available may be explained by the theory of Urquhart (21) that the bonds are mutually satisfied in dry pulp or by the possibility that the potentially active bonds are saturated by adsorbed air or other material. The function of the second stage of beating is to so alter the fibers by softening them and breaking them down that greater compactness and thus greater contact area may be realized to permit greater utilization of the fiber bond forces made available in the first stage of beating.

Kanamaru (22,23) investigated the phenomenon of beating in an entirely different way. In the course of his investigations of the zeta (electrostatic) potential of pulp fibers against water, he studied the effect of beating. In a translation (22) of one of his earlier articles, it was reported that Kanamaru found a decrease in the zeta potential with an increase in the degree of beating. It was stated, however, that this was only preliminary data and that further findings would be re-

ported later. In citing a later article (23), Strachan (24) reported that Kanamaru found the zeta potential to increase with beating. Subsequent work reported by Kanamaru (25,26,27) seemed to indicate that Strachan's interpretation was correct, for Kanamaru explained how he reduced the zeta potential on beaten cellulose fibers with the result that these fibers lost part of the slowness gained by beating. On the basis of this zeta potential work, Kanamaru (28) developed the following theory to explain hydration: The hydration of cellulose in pure water may rationally be understood as depending primarily on the electrical attraction of the water dipole for the polar hydroxyl group of the cellulose. When cellulose is placed in water, an interfacial potential is set up because of the differences in electrical properties (as dielectric constants, polarity, and electrical conductivity) in which the cellulose assumes a charged state with regard to the water. The water dipoles or ions are oriented on the surface of the cellulose in such a way as to reduce the free energy of the system to a minimum. In this way, hydration (or, in general, solvation) occurs. Thus the double layer on the cellulose-water interface is formed.

The amount of moisture adsorbed by cellulose at a given vapor pressure is not a direct measure of the degree of hydration; however, like the swelling manifestations in water, it is produced primarily by hydration—i.e., through the electrical attraction between the water dipole and the polar hydroxyl group in the cellulose. Therefore, one may expect a parallelism between hygroscopic behavior and the ease with which the pulp can be beaten.

Kanamaru did not explain, in any of the articles available for study, how this condition is realized during the beating process. From his work on the neutralization of the zeta potential by the formation of aluminum hydroxide in the presence of beaten fibers (25,26,27), it might be inferred that the polar hydroxyl groups on the cellulose, the presence of which give rise to the zeta potential, are of major importance in fiber bonding because, as he showed, this neutralization reduced hygroscopicity and dielectric strength in sheets made from the fibers.

Campbell's (1) theory, proposed about this time, differed markedly from Kanamaru's ideas, for it postulated that crystallization rather than colloidal forces produced the major part of the fiber bonding. Because there is a very large specific surface in a mass of fibers on which water adsorption may occur and because cellulose is very hygroscopic, Campbell considered that there was no reason to believe that water molecules would not bind onto the surface layers and, in effect, form a layer of hydrated cellulose. In fact, these attractive forces for cellulose and water may form a state of "partial solubility," but complete solution is unlikely as the molecule is too long.

Thus, when fibers are immersed in water, a layer of water is adsorbed on every exposed crystal surface and a layer of hydrated cellulose is thus produced. This combination of hydroxyl groups with water lowers the attraction of the crystallites for each other and allows additional water to enter interstices between the crystallites and thus produce further imbibition and swelling. Beating causes stressing and bending of the softened structure, the fiber is made more

flexible and fibrillation occurs, and a very much greater external surface is so produced.

When paper is produced from pulp, the fibers and fibrils are first caused to compact together by the large surface tension forces of the water. Subsequently, they are bound together either weakly by secondary valency forces such as those by which the water is held or more strongly by crystalline forces developed upon drying at regions where partly solubilized crystallites have become oriented properly to a crystalline face of an adjacent fiber.

Campbell admitted (according to Clark (2)) that his theory did not explain the rapid increase in strength obtained in the early part of beating. Another shortcoming of his theory was pointed out by Strachan (24): the wetting of a sheet would not break such crystalline bonds as Campbell proposed.

After reviewing all the theories previously formulated, Clark (2) proposed the following as a sort of compromise theory:

> The bonds between the rod elements of cellulose formed by the hydroxyl groups (the secondary bonds) are not very strong and have a chemical affinity for water. When immersed in water the fibers swell and the component parts are loosened, certain of the hydroxyl groups combining with water, thus destroying these particular bonds and forming a potentially adhesive layer. Beating cuts, bruises, and flexes the fiber, opens it up further, and softens and fibrillates it. When the sheet is formed, depending on the fineness and flexibility of the cellulosic material, the fibrillae of all dimensions intertwine and the whole is compacted to a greater or less degree by the effects of surface tension, the magnitude depending on the fineness of the particles. When the paper is dried the combined water is driven off and mutual hydroxyl linkages form to hold the structure together, aided perhaps by other effective noncellulosic materials present. The strength of the sheet primarily depends on the effectiveness with which the

> fibers and fibrillae are prevented from slipping along and apart from between each other and not by direct tensile effects, which also explains the important function of length of fiber on the strength of the sheet.

Bell (14) carried out an extensive study to show the importance of fibrillation in sheet strength development. His work showed that fibrillation was quite important but was insufficient for explaining the whole of strength development. After making a thorough study of this function, he concluded:

> ...apart from the purely mechanical fiber cutting and fibrillation, beating causes the formation of a colloidal surface film on the water wetted fibers which results in fiber bonding when the sheet is formed. The mechanism of the sheet formation is through a chain of oriented water molecules linking the active hydroxyl groups of the cohering cellulose micelles in such a way that the strength of cohesion depends on the shortness of the chain.

Strachan in his more recent papers (24,29) has agreed to supplement his purely mechanical theory with a colloidal concept to explain fiber bonding. He believed the forces involved result from some sort of colloidal surface phenomenon which exhibits, as Kanamaru has shown, an electrostatic potential. Even in an earlier paper, Strachan (15) reported data showing the manifestations of the negative zeta potential but seemed to explain it as one of the factors of the fibrillation theory.

Mark (30) proposed a theory which was, seemingly, quite similar to Strachan's more recent theory. Mark believed that beating has the effect of diminishing the size of the fibers and at the same time of fundamentally altering the fiber surface properties by mechanical and chemical action. The nature of this action is to produce a roughened,

spongelike surface layer containing minute splits and cracks. This change in nature of the fiber surface is of foremost importance not only for the binding of water but also for the felting of fibers.

There is one other group of strength development theories which, although quite different from all the physicochemical or colloidal theories presented above, seems to lend itself quite logically to classification as, basicly, a physicochemical concept. It is the theory that noncellulosic or hemicellulosic materials (pentosans, hexosans, beta- and gamma-cellulose, and similar materials) produce or aid in the development of sheet strength. This idea has been supported as a theory or as an addition to some other accepted theory by many investigators, including Schwalbe (31), Cottrall (3), Bell (14), Young and Rowland (32), Obermanns (33), Brauns and Lewis (34), and Routz (35).

Some of these investigators arrived at their conclusions by removing the hemi- and noncellulosic materials from pulp by alkaline treatments, whereas others added more of such materials to pulp just before beating. Routz, however, prepared holocellulose (that fraction of wood containing all the carbohydrate materials and tested it in the experimental beater. He found that it could be beaten to a low freeness unusually rapidly and that it gave very good sheet strength.

One of the first objections to this general theory was that proposed by Probst (36): that the effects found upon the removal of hemi- and noncellulosic materials might be attributable to some effect that the process of removal with caustic had on the cellulose itself. He showed that treatment of pulp with caustic soda solutions of mercer-

ising strength would cause a reduction in the papermaking qualities of the pulps—i.e., of the ability of the pulps to develop strength upon mechanical treatment. He proved that this was not entirely a matter of the removal of caustic-soluble materials by preparing a pulp of high alpha-cellulose content through successive weak alkaline treatments on an ordinary bleached sulfite pulp and by showing that the papermaking qualities of the pulp thus prepared were quite good. He concluded that "it is the treatment which is the important factor in determining the papermaking properties of purified pulps, not the materials removed."

Dixson (37) explained the process involved when various hemi- and noncellulosic materials are added to pulp to increase the strength of sheets formed from it. He showed that such materials have a greater hydrophilic nature than does pure cellulose and that the hydrophilic character of fiber surfaces is the predominant factor which causes fibers to bond and thus give strength to a sheet of paper. Hence, it follows that the hemi- and noncellulosic materials cause a sort of glueing action which produces a stronger bond between the fibers than could be produced by the fibers alone. Such an effect as this has been shown in the past by Rowland (38) and by Rowland and Bauer (39), who were able to increase sheet strength by the addition of starch to the pulp; the starch was caused to adhere by the use of alumina as an electrostatic binder. This factor has been investigated still further by Houtz (40).

PROPERTIES OF FIBER SURFACES AND FACTORS WHICH INFLUENCE THESE PROPERTIES

The Zeta Potential

The nature and properties of the phenomenon of zeta (electrostatic) potential as a function in colloidal chemistry have been discussed quite thoroughly by Gortner (41) and by many others. The data and discussions occurring in the literature concerning the zeta potential as it relates to the cellulose fiber in water has been reviewed extensively by Erspamer (42) and discussed by Rowland (43) and by Strachan (24).

Rowland (43) attributed the occurrence of the phenomenon to a difference in dielectric properties between cellulose and water. Because of the higher dielectric value of the water, it takes a positive charge and leaves the cellulose negative.

Kanamaru (22) has investigated the effect on the zeta potential of various chemicals (KCl, NaOH, HCl, H_2SO_4, and $Al_2(SO_4)_3$) in different concentrations. With increasing amounts of aluminum sulfate, the zeta potential decreased regularly to zero. With each of the other chemicals used, it increased to a maximum and then decreased with increasing concentrations of the chemical.

In general, the nature of the zeta potential of cellulose is such that it is a property of the surface of the fiber and any change exhibited by it is a direct indication of some change occurring on the fiber surface.

The Effect of Beating on the Fiber Surface Conditions

Although many of the investigators of the problems of strength development in the beater have agreed that fiber surface activity, condition, or nature plays a major role, only a very few have studied this factor specifically.

Kanamaru (22,23) investigated the zeta potential on the cellulose fiber, using a streaming potential apparatus for his studies. He reported at first (22) that the zeta potential decreased with beating. In the abstract of a subsequent paper (23) it is reported that he found the zeta potential to vary with the time of beating according to the equation:

$$-\frac{d\zeta}{dt} = a(\zeta - \zeta_\infty)$$

where: t is the time of beating,
ζ is the zeta potential at this time,
ζ_∞ is the zeta potential after an infinite period of time, and
a is a constant determined by the beating conditions.

From this equation is developed the following:

$$\log \frac{\zeta_o - \zeta_\infty}{\zeta - \zeta_\infty} = Kt$$

where: ζ_o is the initial zeta potential, and,
K is a constant similar to a in the above.

In reviewing this article, Strachan (24) quoted Kanamaru as stating that the zeta potential rises with beating.

In subsequent work Kanamaru (25,26,27) showed that, by producing aluminum hydroxide in the presence of pulp fibers, he could reduce the electrostatic charge, completely neutralize it, or even

convert it to a positive electrostatic charge. He found (25) that the degree of beating (as measured by slowness) decreased when he reduced the zeta potential. Thus "the inference taken that the free charge on cellulose in water solution is to be considered as a determining factor for the hydration or beating of pulp has received a new support." When beating pulp on which the zeta potential had, before beating, been partly discharged, Kanamaru found that the degree of beating (slowness) increased unusually rapidly at first, but more slowly as the beating proceeded. This he explained by the fact that, through violent mechanical action in the beating and through the splitting of the fibers, the aluminum hydroxide is partly dispersed and thus the negative charge on the fibers increases.

When he reduced the negative potential with aluminum hydroxide (26,27), the hygroscopicity of the pulp dropped correspondingly until the zeta potential was zero. As the zeta potential was increased to a positive value, the hygroscopicity of the pulp increased. The dielectric strength of sheets formed from this pulp was found to vary in a similar manner.

Thus Kanamaru's findings clearly indicate that the changes occurring in beating are, at least in part, fundamental fiber surface changes.

Strachan (15) showed that increasing the degree of beating of pulp increased the degree to which silver oxide (a positive colloid which he formed in the presence of the fibers) is adsorbed by the cellulose. (The curve for the adsorption of silver oxide roughly

paralleled the slowness development curve.) This increase was attributed partly to crystal growth, to increase in fiber surface area (as the result of fibrillation), and to mechanical retention, and partly to an increase in electrostatic adsorption. Experiments conducted with other positive colloids, which were formed in the presence of the fibers, showed similar results and proved that the factor of electrostatic adsorption was involved because the quantities of solid adsorbed was greater for the more strongly positive precipitates. Strachan proved that the effect was not wholly a matter of electrostatic condition by repeating the test with a negative colloid, clay, and showing that its retention increased with increased beating. From these data he concluded: "...we are compelled to return to the colloidal adsorption theory which deals with physical retention of the particles in capillary spaces by surface tension effects, which latter might be resolved into terms of electrical charges and potentials." He explained the increase in the adsorption of the negative colloid through a "coholding of their hydrophilic envelopes" in addition to the mechanical retention mechanism.

Studies of the adsorption of dyes on pulps to indicate changes in fiber surface properties have been made. Kress and Bialkowsky (10) concluded that the degree of beating had no appreciable effect on the amount of basic, acid, or direct dye which would be adsorbed. They found that the depth of color of sheets prepared from the more highly beaten pulps was greater; they explained this entirely as a change in optical properties in the sheet rather than a result of any increase in the adsorption of dyestuff. Strachan (15) reported no increase in the adsorption of Methylene Blue, a basic dye, with increases in the degree

of beating of pulp. Likewise, Clark (2) reported that beating does not affect dye adsorption.

Clark (2) stated that beating of pulp increases the degree to which that pulp will be sized by a given amount of rosin and alum. In view of certain current opinions as to the fundamentals of rosin sizing (44), this fact might be taken as an indication that the zeta potential of pulp increases with beating.

The Effect of Drying on the Fiber Surface Properties

It is generally appreciated by the industry that the drying of pulp reduces not only the rate at which it can be beaten to a given sheet strength but also the maximum sheet strength which can be developed. The nature of this has been explained by some proponents of the physico-chemical concept of strength development as an irreversible colloidal change (perhaps dehydration) on the fiber surface (45). Harrison (13) objected to this view because he was able to develop the same strength in either wet lap or air-dried (to 10 per cent moisture content) pulp by a one-hour treatment of each in his Lampén Mill (a sort of ball mill using one 10-kilogram bronze ball).

Urquhart (21) has postulated a theory for the effect of drying upon the hydroxyl groups on cellulose. In the natural state, cellulose is precipitated in the presence of water and these groups have water attached to them. As the material dries, the water is driven off leaving free hydroxyl groups. It is natural, then, to assume that these active hydroxyls mutually satisfy each other, since such a re-arrangement would decrease the over-all free energy of the system.

Naturally, such a mutual satisfying process would tend to twist and distort the fiber and the rigid nature of the fiber would tend to resist this distortion. The result would be that some of the hydroxyls would be completely satisfied, some partly satisfied, and some almost entirely unsatisfied. It is likely that these different degrees of satisfaction of the hydroxyls would affect their action when the fiber is rewetted. The unsatisfied hydroxyls would become active spontaneously, the partly satisfied ones would be rendered active by simple mechanical treatment, and the completely satisfied ones would be made active only by considerable mechanical action, if at all.

De Bruyne (46) believed that drying reduces the strength of the dipole character of the cellulose molecule because polar groups will no longer adhere to it and the adsorption of water is decreased. He accounted for this result through the reaction of two hydroxyls to form an ether linkage to give off water. He proposed this theory not as a contradiction to Urquhart's theory but as an addition to explain the mechanism of the complete mutual satisfaction that Urquhart proposes.

Rideal's data and opinions (47) substantiated this claim by De Bruyne; he stated further that highly polar groups are necessary on the cellulose fiber surface to produce wettability.

The Effect of Chemical Action on the Fiber Surface as it Affects Strength Development

Very little direct work has been done on the effect of various chemical treatments of the cellulose fiber surface as they relate to strength development and other properties involved in beating.

Nakano (46) showed that, if a lightly beaten stock is treated with sodium hydroxide its wetness is reduced below that of the original stock.

It has been pointed out by various authors that high alpha-cellulose content pulps (those treated with cold solutions of strong caustic soda to remove various hemi- and noncelluloses) beat only with difficulty. Generally this was attributed to the absence of hemi- and noncellulose components which were thought to be of prime importance in the beating process. Cottrall (3) proposed that it might be due to the formation of ONa radicals from the OH radicals, but he chose the other (absence of hemi- and noncelluloses) theory as the more likely. Probst (36) investigated this problem quite thoroughly. He showed that the treatment of pulps with caustic soda solutions of mercerizing strength (10 per cent or above) caused the pulps to lose their ability to form strong paper sheets upon beating. Pulps so treated were found to be altered in other respects too; they required greater concentrations of cuprammonium hydroxide to produce swelling, exhibited entirely different swelling characteristics in caustic soda, and were found to increase the sheet opacity with beating (rather than decreasing as ordinary pulps do). From this it was obvious that the pulp had undergone some fundamental change as the result of the mercerizing process. To further prove that the change in papermaking quality was not a matter of the removal of caustic-soluble materials alone, Probst subjected a pulp to successive mild caustic treatments (all well below mercerizing conditions) to produce a high alpha-cellulose content and showed that its papermaking properties were not changed appreciably.

Dixson (37) demonstrated that "the hydrophilic character of the fiber surfaces is the predominant factor which causes fibers to bond and thus give strength to a sheet of paper." To prove this, he showed that the addition of certain materials (locust bean gum, cellulose gel, and gelatin) to unbeaten pulp would increase its hydrophilic character and produce improved strength properties. On the other hand, the addition of certain common wetting agents reduced the hydrophilic nature of the fiber surfaces and decreased the sheet strength.

Bletzinger (49) has shown that the strength developed in a sheet by beating can be decreased by the acetylation of the cellulose, the decrease in strength becoming greater as the acetyl content of the pulp increased. He showed further that he could partly regain this strength loss by hydrolysis of the cellulose acetate to remove the acetyl groups.

The Effect of Storage of Beaten Pulp on its Strength Properties

Clark (2) has stated that under sterile conditions the storage of pulps for extended periods of time does not alter the character of the resultant paper. Harrison (13), in an investigation of variables involved in laboratory strength testing of pulp, reported that overnight storage of beaten pulp had a negligible effect on the sheets made from it. Guild and Mills (50) have reported that storage of beaten pulp over the week end does not change its freeness appreciably.

Nothing more definite than these data is reported in the literature on this subject although it is generally known in the industry

that the storage of beaten pulp over extended periods of time will cause a drop in strength without a significant change in freeness.

STATEMENT OF PROBLEM

Various investigators have shown that the zeta potential of pulp fiber surface increases as the pulp is beaten to develop sheet strength. Others have shown that various treatments which alter the nature of the fiber surface also alter the strength of sheets formed from the pulp.

The purpose of this investigation is to determine if the inference from these findings, namely that the fiber surface activity of the pulp, as related to the zeta potential, is a factor in the strength of the sheet formed from the pulp, is a fact. In addition to the study of strength development by mechanical treatment, it is proposed that a study be made of the effect of other treatments to which a pulp is subjected during the manufacture of paper; such treatments include the drying of pulp before beating, the standing of pulp after beating, and the soaking of pulp in a weak chemical solution.

MATERIALS, EQUIPMENT, AND PROCEDURES

MATERIALS

Pulp

The pulp used in the present work was a bleached Mitscherlich sulfite pulp obtained in the form of wet lap from a commercial pulp mill. All the pulp needed was obtained at one time and was stored in air-tight cans at about 36 per cent dry content until used.

It was deemed advisable to evaluate this pulp for the strength development and opacity obtained when beaten by standard methods. For this evaluation, the pulp was beaten in a 1-1/2 lb. Valley beater using the conditions specified in Institute Method 403 "Beater Processing of Pulp." A weight of 4500 grams was used on the balanced bedplate. At various intervals during the beating, handsheets were formed and tested according to the methods specified below in the section "Handsheet Preparation and Testing." The results obtained from this beater evaluation were as shown in Table I.

TABLE I

BEATER EVALUATION DATA

Beating Time, min.	5	20	35	50	65
Freeness cc., S-R.	850	800	695	550	430
Basis Weight, lbs. 25x40/500	47.6	46.6	47.0	47.7	47.0
Apparent Density	14.5	15.4	15.8	16.0	16.3
Bursting Strength, points/100 lbs.	87.3	125.5	140.7	140.1	134.8
Tensile Strength, lbs.	12.5	18.0	19.4	20.1	20.6
Stretch, %	3.45	3.82	3.45	3.45	3.92
Fold, M.I.T.	376	2861	3199	3643	4255
Tear Factor	1.24	0.89	0.81	0.74	0.72
Opacity, %	65.8	57.4	53.8	50.8	44.6

Water

Throughout this work distilled water was used to reduce the possibility of any unintentional contamination of the pulp during the experimentation. On the few occasions when it was found necessary to use distilled water which contained no carbon dioxide, the water was boiled and then cooled out of contact with air.

EQUIPMENT

All the mechanical treatment of the pulp was carried out in a British disintegrator, a standard piece of equipment described in TAPPI Standard T 205 m-40. This apparatus was used because it was found by experimentation and microscopic observation to develop strength in pulp without altering the fiber length and with the production of a minimum of fibrillation.

The freeness tester used in this work was a self-lifting type Schopper-Riegler tester. Freeness tests were made in the usual way using 2.0 grams of ovendry stock in a liter of water at 20° C.

PROCEDURES

Beating of Pulp

Beating conditions were held constant throughout the investigation. In each case an amount of the wet lap pulp equivalent to 90 grams of ovendry pulp was torn up and charged into the British disintegrator with such an amount of distilled water as would give a total of two liters of water. The temperature of the water was measured and the disintegrator allowed to run for a predetermined length of time. At the end of the beating, the temperature of the pulp suspension was taken, the revolution counter read (the gear connecting this counter to the shaft had a gear ratio of 25:1), and the disintegrator emptied using, in most cases, one liter of distilled water for washing. The freeness of the beaten pulp was usually determined at the time the handsheets were made for strength testing.

Handsheet Preparation and Testing

All handsheets prepared from the pulp were made on the British standard sheet machine according to TAPPI Standard T 205 m-40. Except where indicated in the section "Results and Conclusions" all sheets were pressed as specified in this method. For pressing of the sheets under higher pressure, a larger Valley Iron Works hydraulic press was used rather than the usual hydraulic press. The sheets were air dried and then conditioned overnight in a humidity room at 65 per cent relative humidity and 70° F.

The sheets were tested for the various strength properties and for opacity by the following methods:

Test	TAPPI Method	Institute Method
Apparent Density	T 411 m-36	505
Tensile Strength	T 404 m-36	511
Bursting Strength	T 403 m-36	510
Folding Strength (M.I.T. Tester)	T 423 m-36 (Apparatus 2)	513-B
Tearing Strength	T 414 m-40	512
Opacity	T 425 m-35	518

Alumina Adsorption Test

Direct measurement of the zeta potential of pulp by any one of the several methods known is quite difficult and time consuming; the results usually obtained are not entirely reliable. In order to avoid these and many other difficulties, it was deemed advisable to develop some test which would serve as an indirect indication of the zeta potential or electrostatic activity of the fiber surface.

It is known that the cellulose fiber has a negative charge against water; the potential caused by this charge is called the zeta potential of the fiber. If a positively charged colloidal sol is added to a fiber suspension, the colloidal particles tend to be adsorbed onto the fiber surfaces and neutralize the negative charge on the fiber. It is obvious that the greater the charge on the fiber (i.e., the greater the zeta potential of the fiber), the more colloidal particles (of constant positive charge per particle) are adsorbed. Therefore, the amount of such a colloidal material adsorbed by a given quantity of pulp may be taken as an indication of the zeta potential.

Because positive ions can be adsorbed onto an electronegative surface (and thus reduce the charge) as well as electropositive colloidal particles, it is necessary, for such a test as this, to use a colloidal sol which is as nearly electrolyte-free as possible (naturally there must be a small amount of electrolyte present to peptize and stabilize the colloid). For the test developed, an electrolyte-free, electropositive alumina sol was prepared. Pure alumina (Al_2O_3) was made from C. P. aluminum sulfate by the method of Willstätter and Kraut (51), with a few modifications as noted below. The aluminum sulfate was dissolved in warm water and poured into warm ammonia solution to precipitate the alumina. The precipitate was digested for 1/2 hr. at a temperature of 55° to 60° C., and for 48 hrs. at the boiling temperature (the flask being fitted with a condenser). Because the condenser used failed to condense the ammonia boiled off, some 200 cc. of 28 per cent ammonia were added to the flask in small portions during the 48-hr. digestion period. After the precipitate was thoroughly digested, it was washed by

decantation, as specified by Willstätter and Kraut, three times with water, once with ammonia, and then with water until the pH of the decanted liquid failed to show any further change.

The pure alumina was then peptized with a small amount of HCl as suggested by Zsigmondy and Bonnell (52); it was found that the amount of acid they suggested was insufficient. The alumina sol prepared for this work was peptized with one equivalent of HCl for each 100 equivalents of $Al(OH)_3$. This gave a sol which was peptized only by considerable stirring and was quite turbid in appearance (indicating a large colloidal particle size). It was noted that, in the addition of acid to peptize the sol, it was necessary to use very dilute (less than 0.1 M) acid to obtain the proper results.

Such a sol as this cannot be exactly reproduced with reference to electrostatic conditions; therefore, the whole amount to be used throughout the investigation had to be made at one time to prevent the introduction of unmeasurable variables in this way. At the time it was used, the sol contained 0.3226 per cent of Al_2O_3.

Using the sol so prepared, the following test was developed to determine the alumina adsorption of pulp:

A portion of the pulp suspension containing 2.5 grams of ovendry pulp was weighed out. To 50 cc. (equivalent to 0.1613 grams of Al_2O_3) of the alumina sol in a 400-cc. beaker was added sufficient water so that the total volume of liquid after the addition of the pulp suspension would be 300 cc. The pulp suspension was then added

and the mixture thoroughly stirred. This was allowed to stand for 1 hr. and the pulp was separated from the liquid with suction on a Büchner funnel, the pulp forming its own filter pad. The first small portion of the filtrate was discarded because it contained a small amount of fiber. The rest of the filtrate passing through was not poured back through the pulp pad. The pulp pad was dried and weighed. An aliquot portion of the filtrate (200 cc. in every case) was then tested for its alumina content. For this test the sol was boiled with 10 cc. of concentrated HCl for 5 min. to dissolve the colloidal particles and prevent foaming. The alumina was then precipitated by the addition of ammonia to a change in color of methyl red indicator added to the solution. The precipitate was allowed to settle, filtered on ashless filter paper, ashed in a porcelain crucible, and weighed in a ground glass-stoppered weighing bottle. By a simple calculation the amount of alumina adsorbed by 2.5 grams of the pulp was determined. The results have been expressed in this work as the percentage adsorbed of the alumina used in the test. It is to be noted that these results are empirical as they are dependent upon the conditions as specified.

A sample calculation is given below:

Test on pulp beaten one hour.

Test	1.	2.
Pulp pad (less adsorbed Al_2O_3), g.	2.46	2.45
Crucible and ash, g.	18.6204	18.4948
Crucible, g.	18.5511	18.3849
Ash, g.	0.0693	0.0599
Ash from pulp*, g.	0.0012	0.0012
Al_2O_3 in aliquot, g.	0.0681	0.0587
Aliquot portion, cc.	200	200
Al_2O_3 used for test, g.	0.1613	0.1613
Al_2O_3 unadsorbed, g.	0.1022	0.1071
Al_2O_3 adsorbed, g.	0.0591	0.0542
Alumina adsorption, %	37.2	36.8

*As obtained in test with no Al_2O_3 added.

Because the reaction involved in this test is colloidal rather than stoichiometric and because the amounts of alumina used were quite small, an accuracy better than 5 per cent of the value obtained cannot be expected; however, the differences obtained by the alumina adsorption test for different conditions of beating are much greater than this, so it is assumed that the trend of results are indicative and reliable.

In preliminary tests used to develop this method, it was shown that no appreciable change was obtained by allowing longer periods of adsorption than one hour. It was shown also that the higher alumina adsorption found for the beaten pulp was not at all attributable to the beaten pulp being "slower." This was proved both by the fact that

the alumina sol was fine enough to pass through an ordinary ashless filter paper and by the fact that considerable washing of the pulp pad (either by pouring large quantities of water through it or by removing the pad, stirring it up in water, and refiltering) did not appreciably alter the amount of alumina adsorbed.

It is assumed, therefore, that changes in the values obtained from this test are reliable indications of changes in the zeta potential of the pulp.

Dye Adsorption Test

In spite of numerous statements in the literature that beating does not alter the amount of dye adsorbed by pulp, it was deemed advisable to study this factor using a more refined technique developed in the laboratories of The Institute of Paper Chemistry. This test was as follows:

Into a 400-cc. beaker was measured 100 cc. of a 0.1 per cent solution of DuPont Purpurin 4B Conc. (a direct dye), a predetermined amount of water, and a portion of the pulp suspension equivalent to 3.0 grams of ovendry pulp. The amount of water added was that calculated to give a total volume of 300 cc. This mixture was stirred thoroughly and allowed to stand 24 hours. (In preliminary tests, it was shown that practically all adsorption of dye was complete after 16 hours.) At the end of the adsorption period the liquid was separated from the pulp pad by suction on a Buchner funnel. The pad was dried and weighed. The filtrate was tested for its dye content using a Cenco Photelometer

and an experimentally determined calibration curve.

The results were calculated much as were those from the alumina test and were expressed as the percentage dye adsorbed of that used for the test. It is to be noted that these results are empirical as they are dependent upon the experimental conditions specified.

A sample calculation is given below:

Test on unbeaten pulp

Test	1	2	3
Pulp pad (less adsorbed dye), g.	3.01	3.03	2.99
Photelometer reading (average)	32.6	32.6	32.5
Corresponding dye concentration, g./100 cc.	0.0205	0.0205	0.0206
Dye used for test, g.	0.1200	0.1200	0.1200
Dye unadsorbed, g.	0.0615	0.0615	0.0618
Dye adsorbed, g.	0.0585	0.0585	0.0582
Dye adsorption, %	48.6	48.3	48.6

Like the alumina test, this test involves colloidal rather than stoichiometric reactions; this test also uses rather small amounts of dye so that a probable error less than 5 per cent of the values found cannot be expected. Large differences for the different conditions were not found but it is felt that the trends shown are sufficiently reliable for the purpose at hand.

Unfortunately, the results of this test do not lend themselves to as definite an interpretation as do those of the alumina adsorption test but they should be of some value in light of the statement by Hall (33) that the oxidation of cellulose greatly reduces its adsorption of a direct dye.

Alkali Binding Tests

Dixson (17) used a modification of Down's (18) alkali binding test to study the effects of various treatments on the strength of sheets made from pulp. It was deemed advisable, for the purpose at hand, to alter this testing procedure in such a way that four times as much pulp was used per test, a larger amount of alkali (the optimum amount determined by trial) was added, and the titrations were carried out potentiometrically using a Cameron pH meter with a glass electrode.

Both Dixson and Downs used only sodium hydroxide for their alkali binding tests. In fairly concentrated solutions, sodium hydroxide is a good swelling agent for cellulose fibers, so that an alkali adsorption test with even dilute sodium hydroxide could hardly be considered a test for adsorption on the fiber surfaces only. In order to minimize internal adsorption, a similar alkali binding test was developed using triethanolamine (a fairly strong alkali with a large molecule) in place of caustic soda. Preliminary experiments showed that the amount of triethanolamine adsorbed was constant for any period of adsorption above 20 minutes, whereas the amount of caustic soda adsorbed increased with time, although slowly, up to 18 hours (as long as the test was continued); therefore, it was concluded that

triethanolamine was not internally absorbed whereas caustic soda was.

The procedure used for this test was as follows:

To the proper amount of a dilute solution (CO_2-free) of either alkali (equivalent to 0.23 grams of caustic soda or to 0.14 grams of triethanolamine) in a 600-cc. beaker was added carbon dioxide-free distilled water and an amount of the pulp suspension being tested equivalent to 20.0 grams of ovendry pulp. The amount of water used was just sufficient to give a total volume of liquid equal to 420 cc. The mixture was stirred thoroughly and allowed to stand 1 hour. At the end of this period, the liquid was separated from the pulp by suction on a Büchner funnel, the pulp acting as its own filter mat. The first portion of the filtrate was discarded, the rest was not poured back through the pulp mat after it had passed through once. The pulp pad was dried and weighed. An aliquot portion of the filtrate (25 cc. in the NaOH test, 100 cc. in the triethanolamine test) was titrated potentiometrically with 0.010 N HCl using a glass electrode and a Cameron pH meter. Because of certain buffering materials which were removed from the pulp during the test, it was necessary to take 5.0 as the end point pH for all titrations in the NaOH test. The end point in the triethanolamine test occurred at the pH of 5.0. By titrating water in which pulp had been soaked (no alkali added), the proper corrections to be made in each titration for acidic materials dissolved out of the pulp were determined.

The calculation of the results of this test were made much as they were for the alumina and dye adsorption tests. The results

are expressed as the percentage alkali adsorbed of that used for the test. It is to be noted that this test is empirical and thus the results are dependent upon the conditions as specified.

A sample calculation is given below:

Alkali used	NaOH	Triethanolamine
Pulp pad (less adsorbed alkali), g.	20.85	21.72
Aliquot portion titrated, cc.	25	100
Volume 0.010 N HCl used for titration (cor.), cc.	24.09	15.14
Alkali used for test, g.	0.2248	0.1432
Alkali unadsorbed, g.	0.1540	0.1138
Alkali adsorbed, g.	0.0708	0.0294
Alkali binding, %	30.17	15.9

Normally, two tests were made with each alkali for each pulp treatment. Because the nature of this test was such that accurate results could not be obtained and because the differences found for most of the treatments were relatively small, it is felt that the results from this test, per se, are of little value, but the fact that alkali binding results check those shown by the alumina adsorption test may be taken as corroboration of the significance of the latter test.

Fiber-Bond Strength Test

There are numerous fundamental objections to the ordinary handsheet physical strength testing methods for evaluating the magnitude of the forces involved in bonding individual fibers together. Fundamental

measurements of this property are impossible because of such unmeasurable and uncontrollable variables as the formation of the sheets, the nature of the actual area tested, and the several fundamental stresses empirically applied in any one standard physical test, and because of such other difficulty controlled variables as the apparent density of the sheet and the exact conditions of testing (humidity as well as operation of the testing mechanism).

In an attempt to arrive at a more fundamental method for the evaluation of fiber-to-fiber bond strength, many ideas were tried. Finally one method was chosen which, although embodying certain fundamental objections, was considered much more nearly a direct measure of fiber-to-fiber bond forces than is handsheet physical strength testing. This test was applied to fibers as follows:

From a fiber suspension of 0.2 to 0.4 per cent consistency, fiber bundles were formed by slowly drawing out of the suspension a dissecting needle, the end of which had been bent to form a very small hook. Microscopic observation showed that this forms bundles in which the fibers are all aligned parallel to the length of the bundle. The needles were then hung in the air until the bundles were dry. By observing these bundles under a microscope fitted with an eyepiece micrometer, the diameters at the points of most probable failure (minimum diameter along the length to be tested) were measured. In every case, the diameter recorded was the average of the measurements along the two principle axes perpendicular to the length of the fiber bundle. Each bundle was then tested for the force in grams required to produce rupture. This test was carried out with a Schopper dead-weight tensile

tester adjusted for the slowest possible rate of application of the load and with no weight on the indicator arm. A calibration curve was prepared to convert readings to actual grams of force. The jaws of the tester were set for the minimum sample length, 10 mm. Microscopic observations showed that under all conditions involved in this work the ruptures of the bundles occurred due to failure of the fiber-to-fiber bonds rather than to failure of the fibers themselves in tension.

Results calculated from the test data are expressed as the force per unit cross section area (grams per $mm.^2$) required to rupture the bundle.

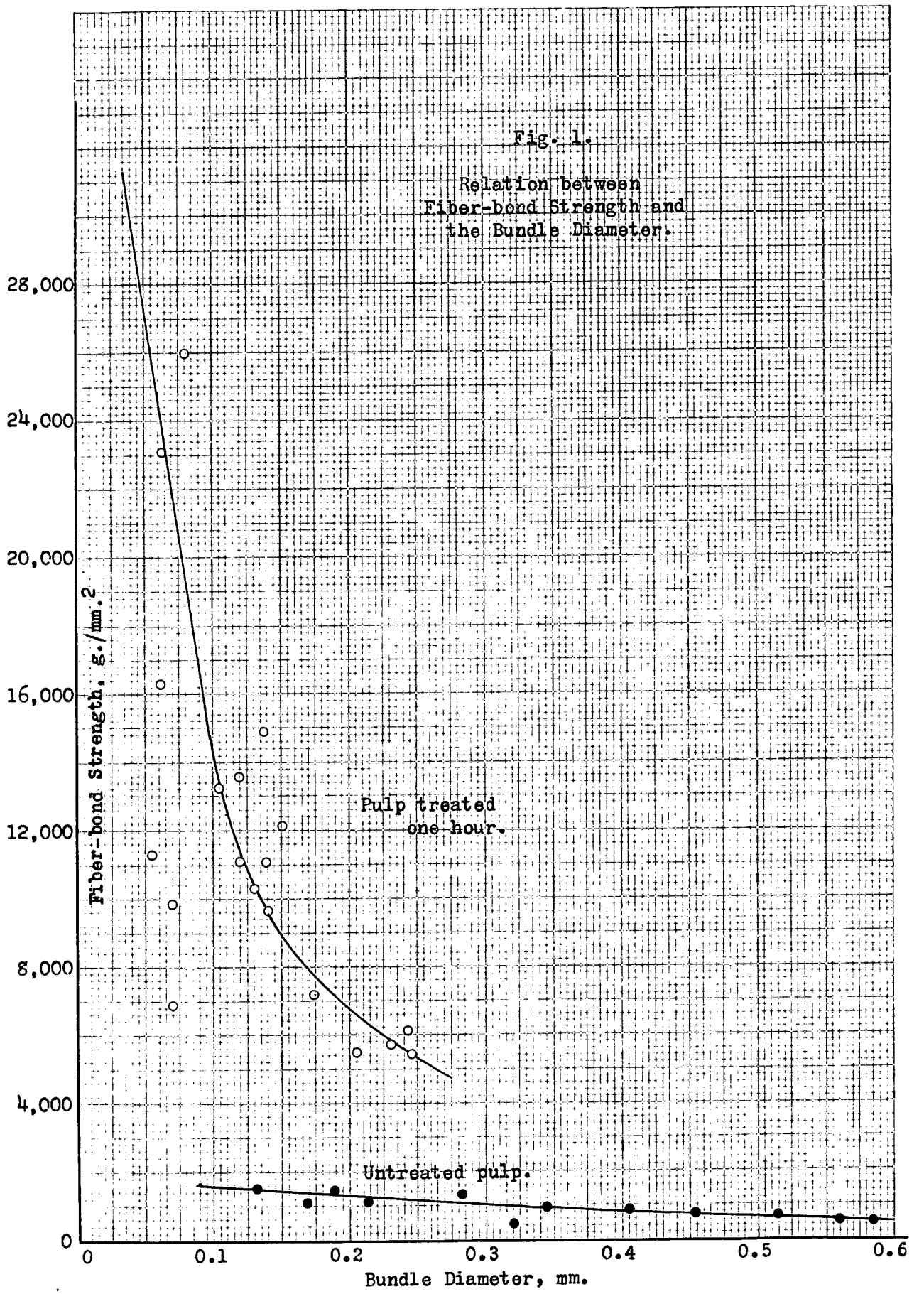
Sample calculations are given below:

Pulp	Bundle No.	Bundle Diameter mm.	Bundle Cross Section Area $mm.^2$	Rupture Force gms.	Fiber-Bond Strength $gms./mm.^2$
Unbeaten	1	0.133	0.01385	22	1588
	2	0.168	0.02215	25	1130
	3	0.190	0.02830	42	1483
Beaten 1 hr.	1	0.1058	0.00878	116	13,200
	2	0.1182	0.0110	122	11,090
	3	0.1198	0.01125	153	13,600

In nearly all cases, twenty-four fiber bundles were formed and tested for each condition of beating. Numerous difficulties were encountered in determining fiber bundle diameters. Because the most likely error is in the direction of too high a reading, unusually low fiber-bond strength values were considered insignificant.

As is shown in the typical plots of results (Fig. 1), the fiber-bond strength decreases markedly and regularly with an increase in the bundle diameter. From a fundamental consideration of the conditions involved, one would expect the bond strength to rise with an increase in the diameter of the bundle because in the larger bundles a larger percentage of the fibers are completely surrounded by other fibers and, hence, by fiber bonds, than is the case in a smaller bundle. That this trend does not occur in practice can be explained only by the fact that fiber flexural stresses develop upon drying before the fiber-bond forces develop to their maximum value. Fiber flexural stresses are, of course, cumulative throughout the bundle whereas fiber-to-fiber bond forces are not. The result is that, as the bundle becomes larger, the cumulative fiber flexural stresses developed during the drying become greater, whereas the actual fiber-to-fiber bond strength remains constant. Therefore, in the larger bundles there is a stronger tendency for the flexural stresses to rupture the bond forces during the drying and therefore fewer bond forces per fiber are left in the dry bundle. Another effect of this action is to cause voids to form in the bundles; this results in a decrease in the number of fibers per unit cross section area. Obviously both of these actions have the effect of decreasing the rupture force per unit cross section area and, therefore, explain the unusual trend found.

It is entirely possible that a given cross section area of a bundle of unbeaten fibers would not contain the same number of fibers as an equal section of beaten fibers, but trends in the results of the fiber-bond test correspond quite closely to trends in strength tests;


Fig. 1.
Relation between
Fiber-bond Strength and
the Bundle Diameter.
28,000
24,000
20,000
16,000
12,000
8,000
4,000
0
Fiber-bond Strength, g./mm.2
Pulp treated
one hour.
Untreated pulp.
0
0.1
0.2
0.3
0.4
0.5
0.6
Bundle Diameter, mm.

therefore, it is assumed that the comparison suggested is reliable.

In view of the effect of fiber stiffness forces, it was deemed advisable to evaluate the fiber-bond strength test in terms of the fiber-bond strength at a given diameter of bundle. Such values were obtained directly from graphs similar to those shown in Fig. 1. Because of the nature of the test, the size of the bundles formed, and the types of correlations obtained, it is thought that the most reliable conclusions may be obtained by considering the values for 0.1 mm. diameter bundles as the most indicative of the fiber-bond strength.

DATA AND RESULTS

The Effect on Strength and Fiber Surface Properties of Treating Pulp in the British Disintegrator.

In this experiment, 90-gram batches of wet lap pulp were beaten in distilled water for various intervals of time, each batch being tested immediately after the beating for alumina adsorption, dye adsorption, fiber-bond strength, and handsheet strength. Subsequently, other 90-gram batches were beaten in CO_2-free distilled water for the same intervals of time and tested for alkali binding with both sodium hydroxide and triethanolamine. The averaged results of these tests are given in Table II. In Fig. 2, the fiber-bond strength data are plotted as functions of the alumina adsorption test data. In Fig. 3, certain of the handsheet strength properties are plotted as functions of the alumina adsorption test data. In Fig. 4, the dye adsorption test data and the alkali binding test data (both alkalies) are plotted against the alumina adsorption test data.

It was found, as is shown in the accompanying photomicrographs (Fig. 5), that some fibrillation is developed during the mechanical treatment in the British disintegrator. It is considered quite probable, however, that the total increase in alumina adsorption cannot be attributed solely to a simple increase in the fiber surface area resulting from this fibrillation or from fibrillation invisible under the microscope.

TABLE II

THE EFFECT OF TREATING PULP IN THE BRITISH DISINTEGRATOR ON ITS FIBER SURFACE PROPERTIES AND SHEET STRENGTH

Period of treatment, hrs.	0	1/4	1/2	1	1-1/2
Freeness, cc. S-R.	813	805	762	735	700
Revolutions of disintegrator (x25)	0	1824	3718	7285	10884
Temperature Increase, °C.	0	8	15	26	35
Alumina adsorption, %	8.6	25.3	34.1	37.0	48.9
Dye adsorption, %	48.5	51.3	56.5	58.3	57.5
Alkali binding, %					
Sodium hydroxide	30.0	29.6	33.8	32.3	33.7
Triethanolamine	19.7	28.0	29.9	26.6	30.5
Fiber-bond strength, g./mm.^{2}					
Diameter					
0.10 mm.	1600	7000	12,200	14,400	17,900
0.15 mm.	1500	4800	8,100	9,000	10,300
0.20 mm.	1350	3900	6,150	6,800	8,200
0.25 mm.	1200	3300	-	5,400	-
Handsheet properties					
Basis weight, lbs.	48.0	47.0	47.0	47.0	48.8
Apparent density	13.88	14.55	14.92	15.12	15.25
Bursting strength points/100 lbs.	56.4	102.1	113.0	115.3	122.1
Tensile, lbs.	8.9	14.3	14.4	14.3	14.9
Stretch, %	3.6	4.8	4.6	5.3	5.2
Fold, M.I.T.	63	789	1315	1276	1509
Tear Factor	1.37	1.26	1.23	1.15	1.05

Fig. 2.

Relation between
Fiber-bond Strength and
Alumina Adsorption of Pulp

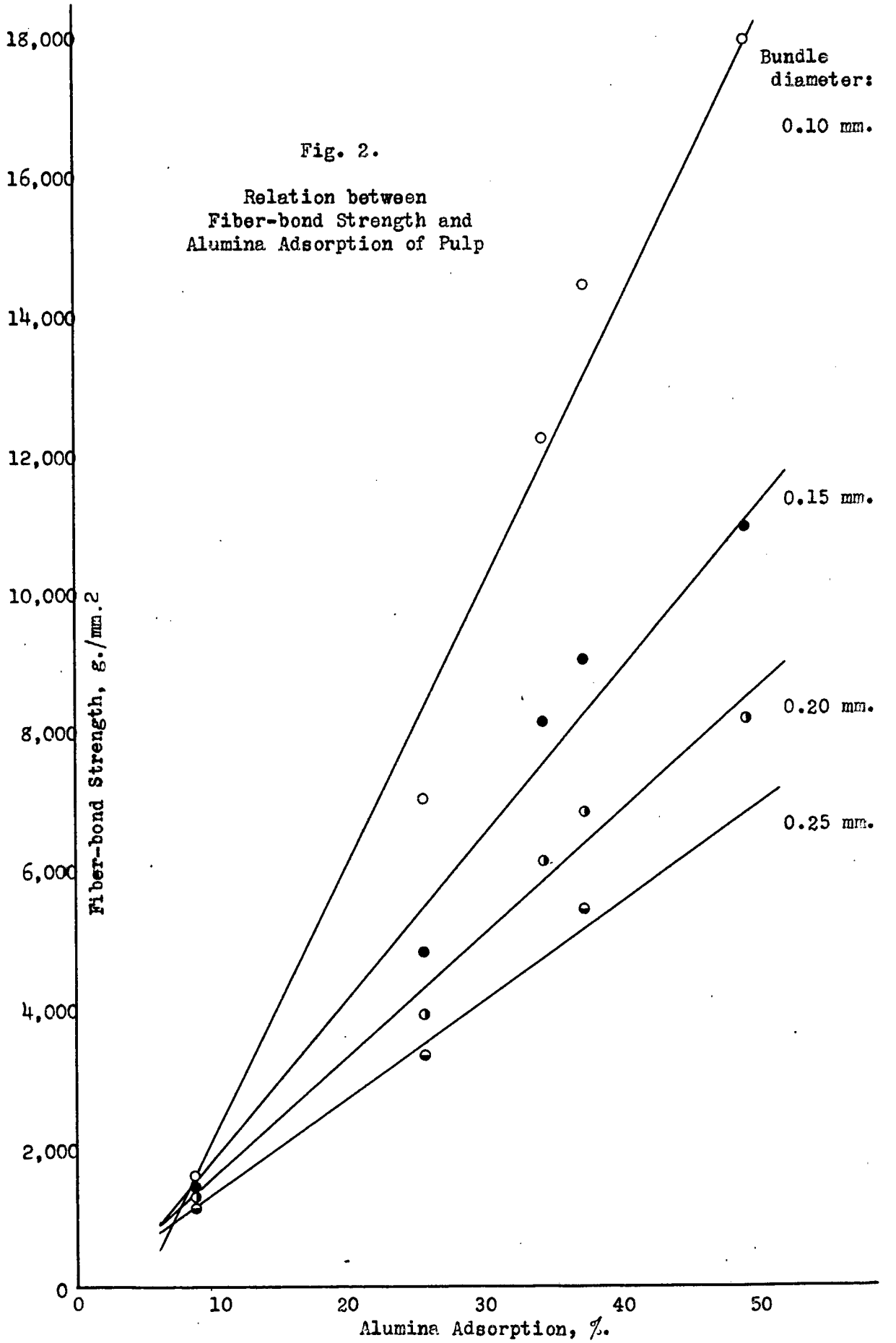


Fig. 3.

Relation between Various Sheet Strength Properties and Alumina Adsorption of Pulp.

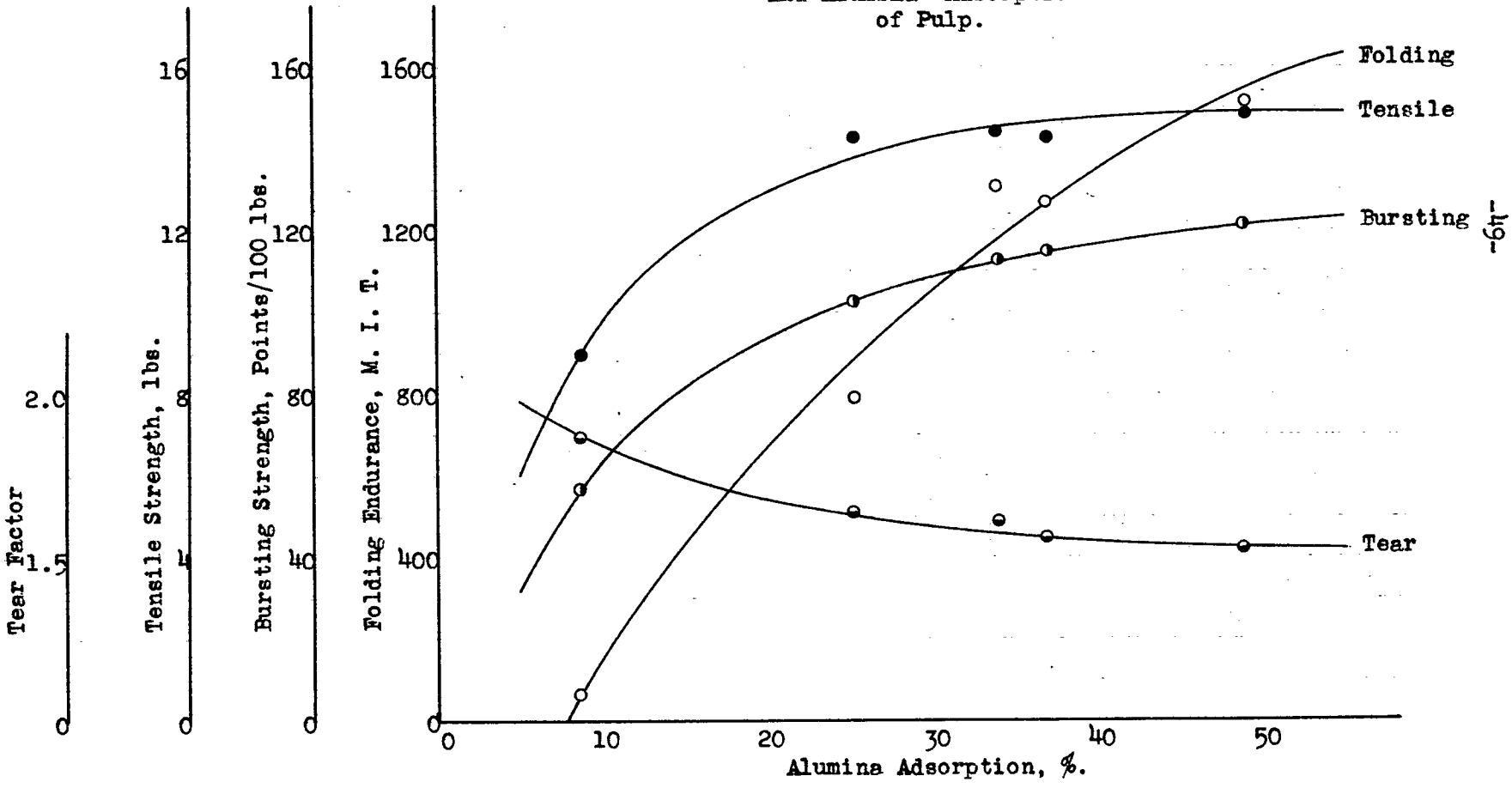


Fig. 4.

The Relation of Dye Adsorption and Alkali Binding with Alumina Adsorption in Pulp.

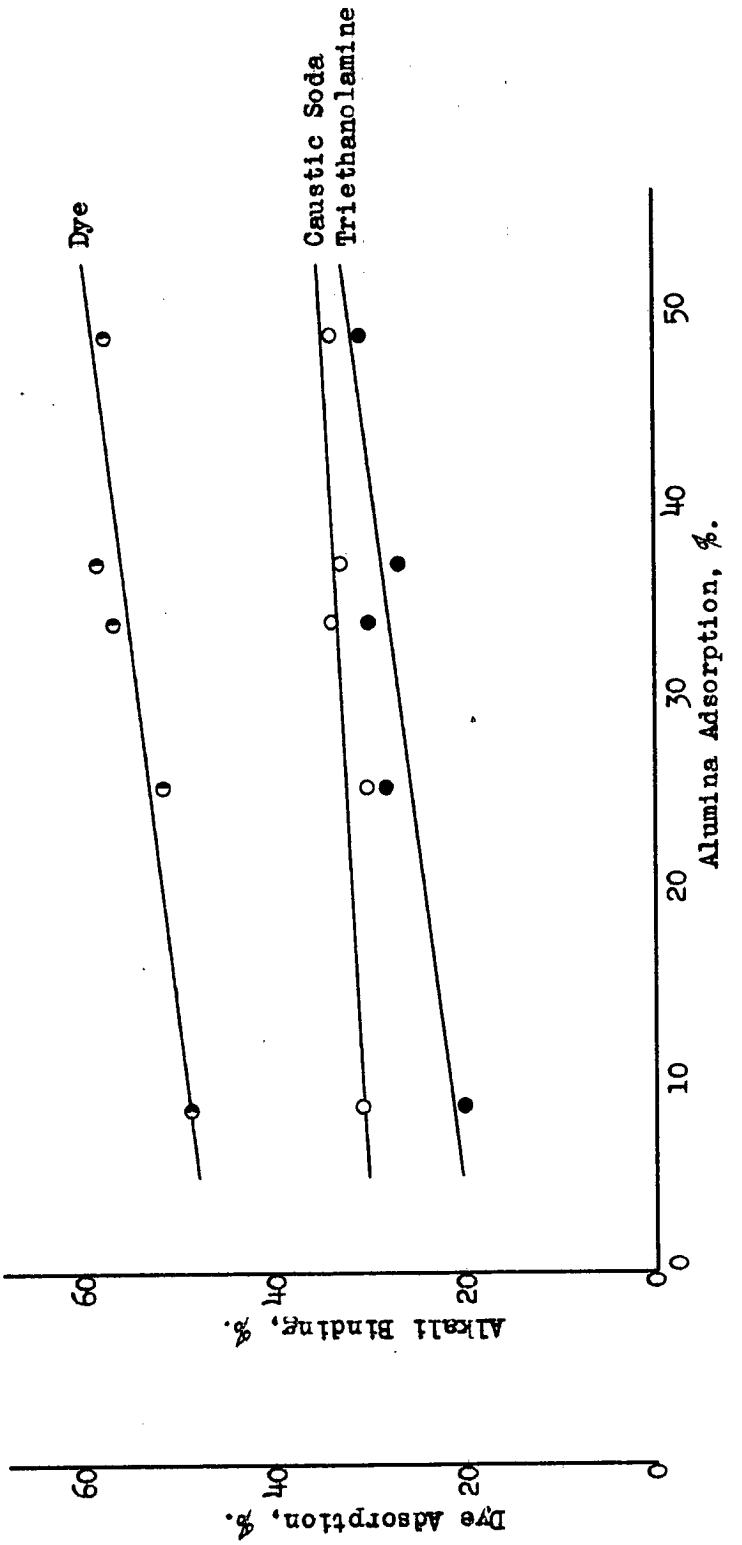
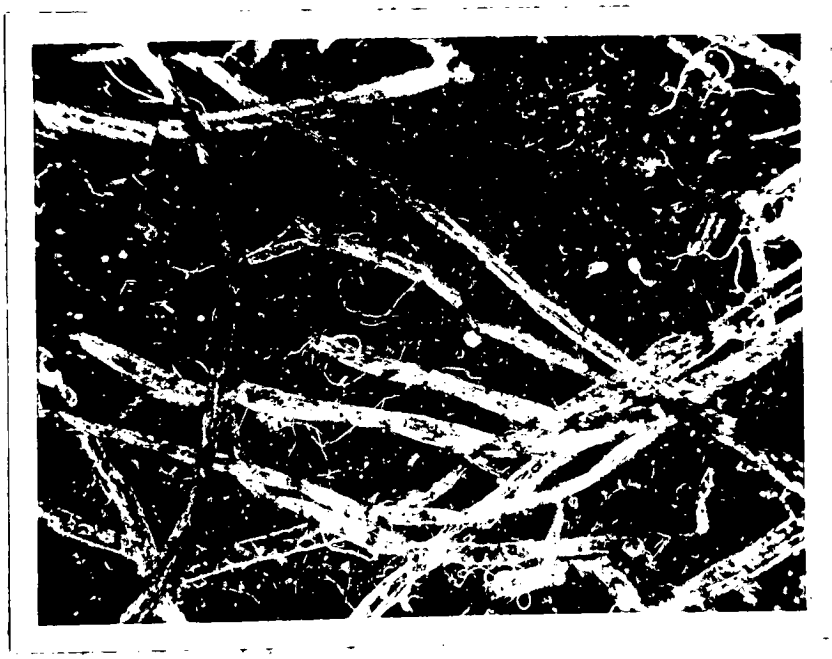


Fig. 5

Darkfield Photomicrographs
of Pulp Fibers.
(100x magnification)



A. Untreated.



B. Treated 1½ hours in the
British disintegrator.

In the first place, it is inconceivable that the increase in fibrillation shown in the photomicrograph in Fib. 5B (as compared with that indicated in Fig. 5A) could result in a 6-fold increase in surface area. Furthermore, if fibrillation is the only factor involved in alumina adsorption and bond strength development, then the extrapolation of the 10-cm, bundle diameter curve in Fig. 2 to the abscissa (zero fiber bonding) would indicate the alumina adsorption of the surface of pulp which has not been fibrillated. It is very difficult to imagine that this surface area could be increased some 10-fold (to correspond to the 10-fold increase in alumina adsorption from this extrapolated value to the maximum value found) with only the amount of fibrillation shown in the photomicrograph in Fig. 5B, or even to this plus any reasonable amount of invisible fibrillation.

In a mathematical study of fibrillation, calculations were made of the increase in surface area caused by various hypothetical changes on the surface of a cylinder. It was shown that, if the whole area of a cylinder were covered with small spheres, the ratio of the area of the cylinder and the spheres to that of the cylinder alone would be $1+\pi$ to 1 or approximately 4. If the whole area of this cylinder were covered with very small cylinders projecting out from the large cylinder, then the surface area could be changed to produce any ratio depending upon the length of the small cylinders. In fact, it is readily shown that the small cylinders would not have to be very long to give a 10-fold increase in total area if their diameters were very small as compared with the dimensions of the large cylinder and if these small cylinders were closely packed on the surface of the large

cylinder. When, however, a condition approximating that which might be expected upon fibrillation—i.e., one in which the small cylinders projecting from the sides of the large cylinder were closely packed in the transverse direction but separated in the axial direction by a distance equal to their lengths—was studied, it was shown that the maximum ratio of total area to initial area was $1+\pi$ to 1 or approximately 4. This maximum occurs when the diameters of the small cylinders are negligible as compared with their length. If, however, these small cylinders were replaced by small columns, the cross sections of which were squares, the ratio of total area to initial area would be 5.

These last two hypothetical conditions are probably as close as one can come to calculating, from a theoretical standpoint, the increase in area realized through fibrillation. It seems improbable that complete fibrillation could occur over the whole outer surface of the fiber and virtually impossible that it could take place to any appreciable extent on layers below the outer layer. Therefore, it is quite unlikely, as judged from a theoretical standpoint, that sufficient fibrillation could be produced under the conditions involved in this work to account for a 10-fold increase in surface area. It is to be noted that such calculations as this would involve invisible fibrillation, as well as that which can be seen under the microscope.

In view of the straight-line relationship shown in Fig. 2, it seems necessary to assume that both fiber-bond strength and alumina adsorption must be attributed to the same fundamental cause. If, as the above discussion seems to prove, the whole of the alumina adsorption

cannot be attributed simply to an increase in fiber surface area, then the whole of fiber-bonding strength cannot be attributed to fibrillation, and some other factor must be introduced which will produce both results. An increase in fiber surface activity is the only other factor that seems to answer the requirements. In this connection it should be remembered that, as many investigators have shown (11,13,14,17,18,19), fibrillation alone cannot account for the development of strength in pulp.

In view of the above discussion, it must be assumed that at least a part of the development of fiber-bonding strength in pulp and a part of the increase in alumina adsorption of this pulp during the development of strength by treatment in the British disintegrator is to be attributed to some colloidal effect taking place on the surfaces of pulp fibers to produce a higher degree of fiber surface activity.

In subsequent portions of this work it is shown that certain treatments of the beaten fibers which could not conceivably alter the degree of fibrillation caused appreciable changes in fiber surface activity and corresponding changes in fiber-bonding strength. These data serve as supporting evidence to prove that the colloidal nature or condition of the fiber surface is a factor in controlling the fiber-bonding strength and sheet strength.

The findings of Doughty (17) relative to the effect of variations in apparent density on sheet strength might well explain the fact that the handsheet strength data do not show straight-line relationships with the alumina adsorption values. The data and graphs of the

results on the dye adsorption and alkali binding tests serve as additional proof that the effect causing the change in alumina adsorption is a surface effect, for neither dye adsorption nor alkali binding tests would show an increase if the alumina adsorption results were solely a matter of mechanical filtration. The previous evidence to prove that the alumina adsorption was not due to mechanical filtration was given in the discussion of the alumina adsorption test on page 35. Hence it must be concluded, as shown above, that the increase in alumina adsorption is attributable only to an increase in the total surface area and to an increase in the fiber surface activity.

The explanation offered for the results found in the above experiment is that, in the British disintegrator treatment of the pulp, the fibers are whipped around quite strongly and are caused to rub against the sides of the container, against the propeller and, mostly, against each other. This has the effect of both causing a small amount of fibrillation--i.e., small relative to the amount which would be obtained in a beater--and rubbing off of various materials present on the surfaces of the fiber. Naturally the effect of fibrillation would be to produce fiber surfaces which would need little if any of this rubbing to remove extraneous material. The removal of this material from the original fiber surfaces and the formation of the new fibril surfaces exposes the hydroxyl radicals on the fiber surface and thus makes them available for forming fiber bonds. The polar nature of the radicals thus exposed causes an increase in the zeta potential of the fiber and thus gives rise to an increase in the adsorption of alumina and, perhaps, dye and alkalies. However, the adsorption of the alkalies may also be, in part, the formation of a colloidal double layer on the fiber.

The Effect of Allowing Pulp to Stand after Beating.

A. Pulp Allowed to Stand in Water in which it was Beaten.

In order to investigate the effects normally found when pulp is allowed to stand after being beaten, two 90-gram batches of the wet lap pulp were beaten in the British disintegrator for 1-1/2 hours each. No special precautions were taken to prevent bacterial action; the pulp was charged into the disintegrator in the ordinary wet lap form and ordinary distilled water was used. The beaten pulp batches were removed from the disintegrator and mixed together without the use of the one liter of wash water. This pulp was tested immediately for alumina adsorption and dye adsorption. Fiber-bond strength bundles were then formed and handsheets were made for subsequent testing. The remaining pulp was allowed to stand (at 4.5 per cent consistency) for seven days when the above tests were repeated. The pulp left after this second testing was again allowed to stand; it was tested after standing an additional twenty-one days. The averages of the values found in the several tests are given in Table III.

B. Pulp Washed after Beating and then Allowed to Stand in Distilled Water.

In an attempt to determine a probable cause for the effects found above, two 90-gram batches of the wet lap pulp were beaten for 1-1/2 hours each in the British disintegrator. Immediately after the beating, each batch was washed according to the following procedure:

TABLE III

THE EFFECT OF ALLOWING PULP TO STAND IN THE WATER IN WHICH IT WAS BEATEN

Period of storage, days	0	7	28
Freeness, cc. S+R.	710	755	740
Alumina adsorption, %	40.2	40.7	45.0
Dye adsorption, %	55.0	73.3	65.0
Fiber-bond strength, g./mm.^{2}			
Diameter			
0.10 mm.	16,500	13,000	14,700
0.15 mm.	10,000	9,800	10,600
0.20 mm.	8,200	7,600	8,450
0.25 mm.	-	6,300	7,000
Handsheet properties			
Basis weight, lbs.	48.0	47.6	48.0
Apparent density	15.22	15.15	15.31
Bursting strength points/100 lbs.	118.2	112.6	116.0
Tensile, lbs.	15.3	14.4	15.1
Stretch, %	5.4	5.0	5.5
Fold, M.I.T.	1381	1445	1407
Tear factor	1.18	1.29	1.27
Opacity, %	61.1	60.6	61.3

a. The pulp was separated from the water in which it was beaten. This was done on a Büchner funnel by suction, the pulp forming its own filter mat.

b. One liter of distilled water was poured through the pulp pad formed.

c. The pulp pad was removed from the funnel and thoroughly stirred in two liters of distilled water. This suspension was poured back into the Büchner funnel and the pulp again separated from the water by suction.

d. One liter of distilled water was poured through the pulp pad formed.

Samples of water from each of the four washing steps were tested for their pH to determine if the washing was removing acidic material from the pulp. The pH testing was done with a glass electrode and a Cameron pH meter. The following results were obtained:

Water from step	pH
Distilled water	5.8
a	6.21
b	6.66
c	6.39
d	6.85

It was noted in carrying out this procedure that water Samples a and c both contained colloidal materials.

The pulp was then suspended in enough water to give a 3 per cent consistency and was tested for alumina adsorption and dye adsorption. Fiber bundles and handsheets were formed for subsequent testing. The remaining pulp was allowed to stand at 3 per cent consistency, and was

tested after an elapse of seven days and again after a total elapse of twenty-eight days by the same tests as were applied initially. The averaged data obtained are collected in Table IV.

The data obtained in this experiment show small but very interesting surface and strength changes with the periods of standing. Because the changes are not far outside the ranges of accuracy of the several tests, they could be considered as insignificant were it not for the fact that all trends agree so well. During the first seven days of pulp storage (either in the water in which it was beaten or in distilled water), all strength properties decrease except fold in A (the changes in which are well inside the range of probable error) and tear (which might be expected to rise with a decrease in other strength properties). This decrease in handsheet strength is paralleled by a drop in the fiber bond strength and a decrease in the alumina adsorption test. Over the same period it is seen that the freeness rises slightly and the dye adsorption markedly. The changes in handsheet opacity are deemed insignificant. It is of significance, however, that the strength properties, but not the surface activity properties, changed slightly less in the case of pulp stored in distilled water than that stored in the water in which it was beaten.

During the subsequent three weeks of standing, it is seen that, in A, there was a partial regain in sheet strength with a corresponding regain in fiber bond strength and alumina adsorption and, in B, a complete regain in sheet strength and fiber bond strength but a slight drop in the alumina adsorption. During the same period, the dye ad-

TABLE IV

THE EFFECT OF ALLOWING PULP TO STAND IN DISTILLED WATER AFTER IT HAS BEEN BEATEN AND WASHED

Period of storage, days	0	7	28
Freeness, cc. S-R.	740	748	760
Alumina adsorption, %	41.9	31.6	28.5
Dye adsorption, %	46.2	63.9	54.9
Fiber-bond strength, g./mm.^{2}			
Diameter			
0.10 mm.	17,000	14,800	17,000
0.15 mm.	11,100	10,400	11,500
0.20 mm.	8,100	8,400	8,650
Handsheet properties			
Basis weight, lbs.	48.0	48.0	47.7
Apparent density	15.27	15.25	15.38
Bursting strength points/100 lbs.	119.8	114.1	120.5
Tensile, lbs.	15.15	14.58	15.12
Stretch, %	5.0	5.5	5.4
Fold, M.I.T.	1751	1424	1779
Tear factor	1.12	1.22	1.22
Opacity, %	60.6	60.8	61.6

sorption partially returns in both cases to its original value. The changes in freeness and opacity are considered insignificant.

From the data and trends obtained in A, it might be expected that the alumina adsorption for the 28-day period in B would rise considerably above that for the 7-day period. Actually it did not. The value shown is the average of the results from three tests, none of which was more than 2 per cent from the average. Although it does not seem likely, it is possible that the alumina sol had become slightly contaminated before this test was made in such a way as to cause the results to be much lower than they should. Since this was the last of the alumina sol, this possibility cannot be confirmed. It was quite impossible to check this value because none of the alumina sol was left and it would not be possible to prepare another alumina sol which would exactly match, in a colloidal sense, the one used. Except for this one value, all the data obtained in this experiment indicate that the change in fiber-to-fiber bonding strength is controlled by the same fundamental factor that causes the change in alumina adsorption—i.e., the zeta potential.

The behavior of the pulp strength and fiber surface properties during standing can be attributed only to contamination of the fiber surfaces. Such factors as bacterial action and loss of fibrillation produced during the beating cannot serve as explanations for they fail to account for the subsequent regain in sheet and fiber-bond strength. The contamination cannot be attributed, to any great extent, to the readsorption of material scraped from the fiber surface during beating

because almost as large strength drops are found when the pulp is washed and then stored in distilled water as when it is stored in the water in which it was beaten. Oxidation cannot be the factor causing the contamination because the dye adsorption increases with the strength drop [Hall (53) stated that oxidation of cellulose decreases its ability to adsorb direct dye] and because this mechanism would not explain the rise in strength found when longer periods of standing are involved.

In view of all these findings, it is concluded that the contamination of the fiber surface can be caused only by material removed from inside the fiber--reaching the surface by diffusion--and to a very slight extent by material adsorbed from the water in which the pulp is stored. The following is proposed as the mechanism for this reaction: Starting immediately after the pulp surface is cleaned, there is a tendency for various noncellulosic materials inside the fiber to diffuse outward to the surface. The rate of this diffusion is high at first but decreases as the amount of this material in the pulp is reduced. (It is to be remembered that only very small amounts of materials need be involved in such an action as this because of the effect that minute quantities of materials can have on colloidal behavior). As the material diffusing from the inside of the fibers collects on the fiber surface there is a tendency for it to diffuse from the fiber into the suspending medium. The rate of this diffusion is much slower than that occurring inside the fibers and will be controlled both by the concentration of material on the fiber surface and by that of the material in the water surrounding the fiber. Thus, the diffusion should be

slower from the fibers which are standing in the water in which they were beaten than from the fibers in the pulp which was washed after beating and then stored in distilled water. If such an effect does occur, it would explain why there is a greater regain in strength by the pulp stored in distilled water; however, the effect should also cause a corresponding rise in the alumina adsorption. No explanation can be given as to why this alumina adsorption does not increase.

By comparing the initial tests in Table III and Table IV, it is seen that washing the pulp after beating produces an appreciable change in the fiber surface without reducing the bond strength or the handsheet strength. Apparently the washing has removed from the pulp some material which possesses the ability of adsorbing alumina without correspondingly promoting fiber-to-fiber bond strength. The acidity and the colloidal nature of the wash water seem to support this theory. To show that the acidic materials in the wash water come from the pulp, a 90-gram batch of the wet lap pulp was beaten 1-1/2 hours and washed by the method outlined above. Similar acidity of the wash waters as found before was obtained. The pulp was then tested for its alkali binding power with the following results:

Alkali	Average Alkali Binding Value	
	Pulp Beaten and Washed	Pulp Beaten but not Washed*
Sodium hydroxide, %	29.7	33.7
Triethanol-amine, %	20.6	30.3

*Data taken from Table II.

Thus it is seen that washing the pulp has greatly reduced its alkali binding power--especially on the fiber surfaces, as shown by the triethanolamine test. Downs (54) showed that the alkali binding power of a pulp measures both colloidally adsorbed alkali and alkali reacting chemically with acidic materials in the pulp. Because of the acidity of the wash water, it may be assumed that this decrease in alkali binding is attributable to the removal of acidic materials from the pulp surface. The polar nature of these acidic materials is such that they assume a strong negative charge with regard to water; therefore, their removal will reduce the zeta potential of the fiber and thus the amount of alumina adsorbed. Because acidic materials such as those indicated in this discussion do not possess the same bond forming properties as do the hydroxyl groups on the cellulose and because their presence would tend to cover up the hydroxyls and reduce their effect, it could rationally be expected that the removal of such acidic materials would result in a slight increase in pulp strength. Both the handsheet strength data and the fiber-bond strength data indicate a slight increase in strength with washing. It is to be noted, however, that these increases in strength are not outside the range of accuracy of the test and, therefore, are not entirely conclusive.

The Effect of Drying of Pulp before Beating on its Surface Activity and Strength Properties after Beating.

It is well known in the industry that dry pulp, when beaten, does not produce as good sheet strength as wet lap pulp. As reasons for this, many proposals have been made: Nakano (45) claimed that there was an irreversible change of the colloidal state of the fiber surface.

Urquhart (21) postulated that, upon drying, adjacent hydroxyl groups mutually satisfied each other. De Bruyne (46) extended Urquhart's postulation by proposing that the "mutual satisfaction" was, at least in part, a reaction between the two hydroxyl groups to form an ether linkage, with the formation of a molecule of water. Finally, since drastic drying conditions cause an oxidation of cellulose, the strength loss might be attributed to an oxidation of the bond-producing hydroxyl groups on the fiber surface into acidic groups, which are incapable of producing fiber-to-fiber bonds.

It was thought that, by applying the various techniques used in the above experiments, one might be able to throw more light on this important problem. To this end, samples of ovendried pulp were prepared by drying the wet lap pulp in an oven at 105° C. for 24 hrs., and a sample of airdried pulp was prepared by drying a sample of the same pulp at room temperature (25° to 30° C.) and a relative humidity of approximately 15 per cent for 72 hrs.—i.e., to constant weight. Ninety grams of each of these samples were beaten in the British disintegrator for 1-1/2 hrs. Alumina adsorption and dye adsorption tests were made on the beaten pulps and fiber bundles and handsheets were formed for subsequent testing. On one sample of the beaten, ovendried pulp, alkali binding tests were made. The data obtained are as follows:

Alkali	Average Alkali Binding Values: Ovendried Pulp	Wet Lap* Pulp
Sodium hydroxide	47.1	33.7 %
Triethanol-amine	32.9	30.5 %

*Data taken from Table I.

It was noted that the handsheets formed from the pulp which had been dried before beating were quite bulky. To show that the low strength properties in these sheets were not due solely to the lack of sufficient fiber contacts, sheets were formed from the pulp and pressed under conditions different from those used in the standard procedure. In one case (h in Table V) a pressure of 200 lb./in.^{2} was applied for the standard time; in another case (g in Table V) a pressure of 200 lb./in.2 was applied for twice the standard time. The averaged results obtained in this experiment are given in Table V.

These data, compared with the data for wet lap pulp beaten to the same degree, show that the effect of the drying is to increase greatly the alumina and dye adsorption and to decrease greatly the strength. It appears, judging from the alumina adsorption, that the effect produced on the fiber surface properties is much the same irrespective of the degree or method of drying, whereas the effect on strength is much greater for the pulp which was completely oven-dried than for that which was air-dried to 5 per cent moisture content.

TABLE V

THE EFFECT OF DRYING OF [illegible] BEATING ON ITS SURFACE ACTIVITY AND STRENGTH PROPERTIES AFTER BEATING

Pulp	Wet Lap+	Oven-dried			Air-dried to 34.8%
Freeness, cc. S-R.	700	708			715
Alumina adsorption, %	48.9	68.6*			70.4
Dye adsorption, %	57.5	73.9			66.0
Fiber-bond strength, g./mm.^{2}					
Diameter					
0.10 mm.	17,900	6,700			13,200
0.15 mm.	10,900	4,400			8,800
0.20 mm.	8,200	3,200			6,250
0.25 mm.	-	2,450			4,500
Handsheet properties		a	b*+	c*+	
Basis weight, lbs.	48.8	47.9	48.1	48.0	47.0
Apparent density	15.25	12.84	15.10	15.05	14.58
Bursting strength points/100 lbs.	122.1	63.0	73.7	72.4	105.5
Tensile, lbs.	14.9	8.7	10.1	10.3	13.6
Stretch, %	5.2	4.6	4.3	4.6	5.1
Fold, M.I.T.	1509	37	72	73	990
Tear factor	1.05	1.46	1.07	1.12	1.32
Opacity, %	61.0	76.3	67.0	65.9	64.3

+Data from Table II except for opacity which was taken from Table III.
*This value was taken from data obtained on a check determination.
*Wet pressing of these sheets at high pressures.

From the data collected, it is evident that some change has taken place on the fiber surfaces involving, perhaps, the hydroxyl groups. The nature of this change is to produce a surface condition which, upon mechanical treatment, is more highly active electrostatically but which does not possess the property of producing fiber-to-fiber bonding.

If this change in the fiber surface is due to the formation of carboxyl (acid) or ether structures, the electrostatic potential set up around such a group might be sufficient to explain the unusually high alumina, dye, and alkali adsorption values found. It has been shown (49) that the presence of hydroxyl groups is necessary for the formation of fiber-to-fiber bonding forces. There is no evidence, however, either in the chemistry of cellulose or in that of analogous compounds that carboxyl groups or ether structures possess the powers of association usually exhibited by hydroxyl groups. It would not be expected, then, that either carboxyl groups or ether structures would produce bonding strength in any way comparable to that produced by hydroxyl groups. A recent paper by Mideal (47) seems to support this view.

If Hall's finding (53) that the oxidation of cellulose decreases its adsorptivity for direct dyes is applicable under these conditions, the dye adsorption test results may be considered as data opposing the oxidation theory.

No prediction can be made as to the nature of the electrostatic potential which would be set up around mutually associated

hydroxyl groups. It is reasonable, however, to expect that hydroxyl groups mutually satisfied would not be able, even after subsequent mechanical treatment, to associate with hydroxyl groups on other fibers to give rise to fiber-to-fiber bonding strength.

The Effect of Soaking Beaten and Washed Pulp in a Calcium Hydroxide Solution.

To illustrate the effect of the presence of a very small amount of fiber surface contamination on pulp strength, 90 grams (oven-dry) of wet lap pulp were beaten for 1-1/2 hrs., washed as described on page 58, and stored in a weak solution of calcium hydroxide. The pulp was at a consistency of 3 per cent during the storage and the amount of lime present was equivalent to 0.5 per cent of the weight of pulp; this gave a concentration of 0.15 grams of $Ca(OH)_2$ per liter of solution or a molarity of 0.00203. Before the addition of the lime, the pulp was tested for alumina adsorption and fiber bundles and handsheets were formed for subsequent testing. After the lime was added, the pulp was allowed to stand forty hours and again tested. Dye adsorption tests were not made because it was found that the lime affected the tinctorial power of the dye used. It is to be noted that the alumina used for this experiment was not the same as that used in previous work. However, this alumina was made by the same method, except that more acid was used in peptizing and stabilizing the colloid; therefore, the trend obtained in the results should be comparable to that which would have been shown had the original sol been used. The averaged values of the data obtained are given in Table VI.

TABLE VI

THE EFFECT OF SOAKING BEATEN AND WASHED PULP IN SODIUM HYDROXIDE SOLUTION

	Beaten and Washed Pulp	After 40 Hours Soaking
Freeness, cc. S-R.	680	700
Alumina adsorption*, %	23.3	96.6
Fiber-bond strength, g./mm.^{2}		
Diameter		
0.10 mm.	17,800	15,100
0.15 mm.	11,000	10,200
0.20 mm.	-	7,500
0.25 mm.	-	5,700
Handsheet properties		
Basis weight, lbs.	48.5	48.0
Apparent density	15.40	15.35
Bursting strength, points/100 lbs.	120.5	114.2
Tensile, lbs.	15.8	14.4
Stretch, %	5.8	5.1
Fold, M.I.T.	1869	1507
Tear factor	1.22	1.24
Opacity, %	61.3	62.3

*Not the same alumina sol as used in previous test.

The data show that the adsorption of the calcium hydroxide on the pulp fibers increased the alumina adsorption of the pulp but decreased its fiber-to-fiber bond strength. It was found, by ashing a sample of pulp separated from the lime solution as is done in the alumina test, that the pulp adsorbed about 0.35 per cent of its weight in lime during the soaking in the lime solution.

The explanation offered for the results obtained in this experiment is that the presence of calcium hydroxide on the surface of the fiber causes the formation of a double layer which possesses strong electronegative properties resulting in a high zeta potential, but the lime partly interferes with the effect of the hydroxyl radicals on the cellulose molecule to produce fiber-to-fiber bonding. That the presence of lime on the fiber surface might increase the fiber zeta potential is quite likely in view of certain data in the literature. Kanamaru (22) showed that both potassium chloride and sodium hydroxide in concentrations comparable to that of the lime in this experiment substantially increased the zeta potential of cellulose placed in the solution. Stamm (55) reports similar effects with various electrolytes at much lower concentrations.

SUMMARY AND CONCLUSIONS

Using the British disintegrator, which was found to produce fiber-to-fiber bonding strength and thus sheet strength by its mechanical action, an easy beating Mitscherlich sulfite pulp was treated for various periods of time and tested for strength and fiber surface properties. It was shown that, under these conditions, the alumina adsorption, dye adsorption, and alkali binding increase linearly with the development of bond strength. From a theoretical consideration, it was shown that the increase in adsorptive properties of the fibers is dependent at least in part on an increase in the fiber surface activity as a result of mechanical treatment. Since some increase in fibrillation occurred, it is thought likely that part of the strength development is attributable to it and that part of the increase in adsorptive properties is caused by the increase in surface area resulting from this fibrillation.

By studying both surface and strength effects produced when pulp was stored after mechanical treatment in the British disintegrator, both in the water in which it was treated and in distilled water, it was shown that there is a loss in strength and a decrease in alumina adsorption occurring in this pulp with storage attributable to materials diffusing from inside the fiber to the fiber surface and to a much smaller extent to materials adsorbed onto the fiber surfaces from the water in which the pulp is stored (when it is stored in the water in which it was mechanically treated). Longer storage permits some of this material concentrated on the fiber surface to diffuse from the

fiber surfaces into the suspending medium; this results in a partial recovery of the strength lost. Since simple storage cannot conceivably alter the degree of fibrillation, it is obvious that the changes in alumina adsorption must be measures of changes in fiber surface activity and that these activity changes must cause the changes in strength.

It was shown that the drying of pulp at either room or elevated temperature causes a fundamental change in the nature of the fiber surface which results in a decrease in the fiber-to-fiber bond strength that can be developed by the type of mechanical action used in this work. From the data collected, no conclusion could be drawn as to the mechanism of this surface change. It is proposed, however, that it is either the mutual association of adjacent hydroxyl groups, the formation of ether linkages by the condensation of these adjacent hydroxyl groups, or the oxidation of the primary hydroxyl group on the cellulose molecule.

Fibers which had been treated in the British disintegrator subsequently were allowed to adsorb a considerable portion of calcium hydroxide from a dilute solution. This artificial contamination caused a decrease in the fiber-bonding strength of the pulp.

From this investigation it is apparent that the minimum amount of mechanical action necessary to produce an increase in sheet strength will cause a slight degree of fibrillation and that, in studies of strength development, such slight increments in fibrillation must be taken into account. Nevertheless, the data presented with reference to fiber surface activity and fiber-to-fiber bond strength cannot be

fully accounted for on the basis of fibrillation alone; furthermore, the experiments carried out with fibers under conditions which could not conceivably alter the degree of fibrillation further substantiate the hypothesis that important changes in fiber surface activity and fiber-to-fiber bond strength occur independently of the fibrillation phenomenon.

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