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Reasons for Increase in
Paper Strength when Beater Adhesives are Used

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AN INVESTIGATION OF THE REASONS FOR INCREASE IN
PAPER STRENGTH WHEN BEATER ADHESIVES ARE USED

A thesis submitted by

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TABLE OF CONTENTS

INTRODUCTION	1
HISTORICAL REVIEW	3
PRESENTATION OF PROBLEM	20
PREPARATION OF RAW MATERIALS	21
West Coast Bleached Sulfite Pulp	21
Purified Locust Bean Gum	21
Locust Bean Gum Stock Solution	22
INVESTIGATION OF EXPERIMENTAL PROCEDURES	24
Determination of Locust Bean Gum Content of Paper	24
Introduction	24
Proposed New Galactose Method	25
Theory	25
Important Considerations	26
Paper Partition Chromatography	27
Study of the Sugar Units Present in Pulp and Locust Bean Gum	28
Removal of Locust Bean Gum from Pulp by Hydrolysis with Sulfurous Acid	32
Possible Destruction of Galactose	35
Reproducibility of Results	37
Complete Description of the Galactose Method in Final Form	41
Preparation, Sampling, and Hydrolysis	41
Recovery of Sugars	42
Separation of the Sugars	43
Determination of the Sugars	44

Measurement of Bonded Area of Papers Containing Locust Bean Gum	47
Introduction	47
Procedure	49
Results and Discussion	55
Measurement of the Specific Surface of Pulps Containing Locust Bean Gum	61
Procedure	61
Results	62
GENERAL EXPERIMENTAL AND TESTING PROCEDURES	64
Procedures Dealing with Locust Bean Gum	64
Determination of Locust Bean Gum Content of Paper	64
Determination of Concentration of Locust Bean Gum Dispersions	64
Determination of Viscosity of Locust Bean Gum Dispersions	64
Pulp Treatment and Sheet Preparation	64
Pulp Refining	64
Treatment of Pulps with Locust Bean Gum	65
Freeness Testing	65
Specific Surface Testing	65
Sheet Preparation	66
Variation of Formation	66
Variation of Wet Pressure	66
Paper Testing	67
Formation	67

Bonded Area	67
Bonding Strength	68
Zero-Span Tensile Test	70
Load-Elongation	70
Other Tests	70
PRELIMINARY INVESTIGATIONS	71
Effect of Time of Testing upon the Strength Properties of Handsheets	71
Introduction	71
Procedure	71
Results and Discussion	73
Effect of Locust Bean Gum Viscosity upon Strength Properties of Handsheets	75
Introduction	75
Procedure	76
Results and Discussion	78
INVESTIGATION OF THE REASONS FOR STRENGTH INCREASE WHEN BEATER ADHESIVES ARE USED	81
Introduction	81
Procedure	84
Presentation of Data	87
Discussion of Results	89
SUMMARY OF CONCLUSIONS	110
LITERATURE CITED	112
APPENDIX	118

INTRODUCTION

Almost since the beginning of papermaking, man has added nonfibrous materials to pulp suspensions in an attempt to improve some quality of the paper. A wide variety of materials, ranging from clays, rosin, and alum to naturally occurring gums, starch, and synthetic wet strength agents, have been used. Some of these materials are used primarily to alter the surface properties of paper, whereas others are used to bring about changes in strength properties.

A number of years ago, Hunter (1) revealed that Hibiscus manihot, a naturally occurring high polymeric gum, was used in Japanese papers to obtain good formation with long fibered pulps. Since that time many high polymeric gums have been tested as beater adhesives and a number of them have been shown to bring about startling increases in paper strength. The first and most obvious advantage of such beater adhesives is that they are able to produce the same effects upon the strength properties of paper as would be produced by beating or refining. Thus a considerable saving in time and power expended in the beating operation could be effected by using a beater adhesive. It has been demonstrated that beater adhesives not only advance the effects of beating but they also bring about greater strength development than can be attained by beating alone.

Many suggestions have been made to explain the increase in strength resulting from the use of these adhesives, but no fundamental study has been made to determine the factors which actually contribute to such increase. The aim of the present investigation is to determine the factors which are of importance in bringing about this increase in strength. When

these factors are known, improvements in the technique of application of the adhesives may be possible and, perhaps, predictions can be made concerning the types of materials which will be most successful when used as adhesives.

HISTORICAL REVIEW

A great deal of the work which is to be described is concerned with the strength properties of handsheets and the effect of locust bean gum upon these properties. Therefore, it is considered desirable to include a discussion of the reasons for paper strength and the effects of beating pulp on strength development.

It should first be pointed out that the morphological characteristics of the fibers used for papermaking exert a considerable influence upon the strength properties. Clark (2) concluded that tearing strength is proportional to $L^{3/2}$, bursting strength is proportional to L , and tensile strength is proportional to $L^{1/2}$ where L is the weighted average fiber length. Brown (3) and de Montigny and Zborowski (4) also concluded that tearing strength is closely related to fiber length. Brown pointed out that different fiber length fractions are likely to be chemically different so that, in studies of the effect of fiber length, variations in fiber length should be produced by knife cutting. de Montigny and Zborowski were not able to find any simple relationship between fiber length and tensile strength or bursting strength. Jayme (5, 6), Selleger (7), and Muhlsteph (8) felt that other morphological characteristics are even more important than fiber length. They emphasize the importance of such characteristics as fiber length distribution, ratio of fiber length to fiber width, cell wall thickness, and fiber flexibility. A complete review of the literature dealing with the effect of morphological characteristics of fibers upon the strength properties of paper is beyond the

scope of this work. However, the above discussion serves to indicate some of the important factors involved.

The chemical constituents of cellulose fibers also affect their paper-making properties. Wood pulp fibers are composed chiefly of cellulose but, invariably, they also contain hemicelluloses and small amounts of lignin. Lignin is believed to be detrimental to paper strength, and Keeney (9) claimed that the presence of large quantities of lignin in semichemical pulps accounts for their poorer strength properties as compared with chlorited semichemical pulps. He believed that lignin inhibits the swelling of pulp fibers and makes the fibers less flexible. Cellulose itself is the basic unit of the fiber. Cellulose molecules are believed to make up microfibrils, fibrils, and fibers in turn. The fibrils and microfibrils of a fiber are held together from point to point along the fiber in crystalline areas frequently referred to as micelles. A fiber derives its strength from the primary valence forces holding the individual cellulose molecules together and the forces of crystallization holding adjacent cellulose molecules together.

The hemicelluloses, the other component of wood pulp fibers, are believed to play an important role in the development of paper strength. Years ago Cottrall (10) and Bell (11) recognized that pulps with high alpha-cellulose contents were difficult to beat and they attributed this to the absence of hemicelluloses. Cottrall considered hemicelluloses necessary for fibrillation and believed that they may possess adhesive properties. Mark (12) referred to "dextrins produced...during the beating

process". Cottrall (13) also made reference to the fact that rag pulps are difficult to beat and attributed this condition to a lack of hemicelluloses in cotton fibers. He further suggested that hemicelluloses in wood pulp fibers perform a plasticizing function during beating. Nordman (14) has shown that the specific surface of a pulp increases rapidly during the early part of the beating cycle. He believed that the first increase in specific surface is due to rapidly beaten hemicelluloses. He also noted that the increase in specific surface was accompanied by increased bonding--presumably the result of the presence of hemicelluloses. Klingstedt (15) observed that the materials in beta-cellulose are easily peptized by bases and suggested that they may also be easily hydrated during beating.

Ross (16) recently pointed out that it is not yet known what component of the hemicelluloses imparts the favorable influences upon beating. Bell (11) attributed the effect to both beta-cellulose and gamma-cellulose components and Cottrall (17) claimed that the strength of pulps decreases with decreasing gamma-cellulose content. Young and Rowland (18) measured dilatometric swelling and pentosan contents of pulps and claimed that there is a linear relationship between the two properties in the case of softwood pulps. Swelling in turn is believed to be related to the degree of beating.

Several investigations (19-21) have been reported in which successive removal of hemicelluloses from pulps have been carried out. These studies succeeded in demonstrating that the presence of hemicelluloses enhances the strength properties of the pulps. Obermanns (22) found that, when

hemicelluloses were added to pulps, beating was more rapid and the strength properties of the pulps were improved. March (20), on the other hand, did not find any marked improvement in strength properties when hemicelluloses were added to pulp.

Although it is fairly certain that the hemicelluloses are important in papermaking, it is now recognized (16) that the manner in which the hemicelluloses content of a pulp is reached (i.e., method of cooking, bleaching, etc.) is probably more important than the actual content of hemicelluloses.

It has been pointed out that the individual fiber derives its strength from the primary valence forces holding the individual cellulose molecules together and the forces of crystallization holding adjacent cellulose molecules together. However, it has long been recognized that the strength of a sheet of paper is not limited merely by the strength of the individual fiber but also by the strength of the bonds holding the individual fibers together. The nature of these bonds has been the subject of a great deal of discussion. Strachan (23) felt that fibrillation produced by beating gave rise to strength in paper through mechanical intertwining of fibrils. However, Cottrall (24) has pointed out that wetted sheets (even those made from well-beaten pulps) lose their strength almost completely. So-called unbonded sheets (57) which are formed from water but have the water replaced successively by acetone and butanol before drying are found to be extremely weak. Sheets which are formed from water, frozen, and dried by sublimation of the ice are likewise very weak (25).

It has also been noted (26) that the viscoelastic properties of paper indicate that the intertwining of fibers is not an important factor in the strength of paper. Clark (27) found that, when two wetted sheets of viscose cellophane were placed together, pressed, and dried, the sheets stuck together firmly. This experiment indicated strongly that other forces than mere mechanical entanglement are involved in the bonding of one cellulose surface to another. In spite of all this evidence against the importance of mechanical bonding, Wilson (28) has recently published an article in which he claims that the "sole source of strength lies in the crimping of fibers one over another."

It has been conclusively established that the type of bonds which contribute greatly to paper strength are hydrogen bonds formed by the mutual attraction of the polar hydroxyl groups of cellulose. Bletzinger (29) has shown that acetylation of cotton fibers decreases the strength properties of sheets produced from the fibers. Acetylation covers the polar hydroxyl groups which participate in hydrogen bonding. A very lightly acetylated pulp has improved strength properties presumably because of the opening up of the fiber structure, thus making more hydroxyl groups accessible. Deacetylation of the pulps produced fibers which gave sheets with strength properties similar to the original pulp. Aiken (30) and Harrison (31) have confirmed and amplified the work of Bletzinger. Furthermore, Ellis and Bath (32) stated that infrared absorption data support the theory that the hydroxyl groups of cellulose are bonded together by hydrogen bonds or bridges. As a result of these studies, there can no longer be any doubt that the hydroxyl groups of cellulose are responsible for bonding

together of cellulosic fibers. Mark (33) summarized the different types of bonding in paper: Mechanical bonds produced by entanglement contribute very little to strength; hydrogen bonds are of primary importance to sheet strength; other polar bonds occur to a limited extent but do not contribute significantly to strength; finally, primary valence bonds hold the individual molecules within the fibers together.

The effect of beating or refining upon pulp has been a field of great speculation. Several theories have been evolved with varying amounts of theoretical support. Cross and Bevan, Schwalbe, and others believed that beating brings about a true chemical combination of water and cellulose to form a hydrated cellulose. This belief brought about the use of the term hydration which is so frequently used in discussions of beating. Strachan (34) concluded that no definite crystalline hydrate of cellulose was formed because there was no break in the curve of moisture content plotted against time of drying for either beaten or unbeaten pulps. Campbell (35-38) demonstrated by very careful experiments that the curves of vapor pressure plotted against moisture content of unbeaten and beaten pulps were the same (within a small experimental error). Thus, he concluded that no change in the degree of hydration of the pulps was produced by beating. Any change in hydration would cause a change in the equilibrium moisture content of a pulp for a given vapor pressure. Seborg and Stamm (39) have also pointed out that there is no difference between the electrical conductivity-moisture content relationships for beaten and unbeaten pulps. These authors do not claim that cellulose is not hydrated but they do assert that beating does not bring about any change in the degree of hydration.

Bell (40) and Cottrall (24) have pointed out that the quantity of water required to form a monomolecular layer (of hydrate) on the surface of pulp fibers is so small that it probably could not be detected by moisture content measurements.

A number of other pieces of evidence have been presented which also support the theory that beating does not affect the degree of hydration of pulp. There is no change in the x-ray pattern of cellulose during beating (38). Curran and co-workers (41) found that the only effect of beating on the chemical properties of pulp was an increase in the rate of hydrolysis. This difference is ascribed to a physical alteration. Kress and Bialkowsky (42) found no appreciable changes in chemical properties as a result of beating. Cottrall (24) pointed out that, although a beaten pulp loses its water more slowly than an unbeaten pulp, the equilibrium amount of water held by either pulp under a given pressure is the same. In view of the evidence presented, it is difficult to see how any appreciable amount of true hydration can occur during beating. Furthermore, if such hydration did occur, it would be very difficult to explain why it brought about such pronounced changes in the strength properties of the pulps but had little or no effect upon so many other physical and chemical properties of the pulp.

Another effect of beating which has received a great deal of consideration is fibrillation. Both Strachan (23, 43) and Campbell (36-38, 44) are convinced that fibrillation is one of the essential actions of beating. Cottrall (10) pointed out that regenerated cellulose could not be beaten

and ascribed the cause to lack of fibrillation. Cottrall (24) also made the point that any method producing a greater area of perfect contact between fibers will increase the strength properties. Fibrillation, he asserted, is one method of attaining this end.

On the other hand, there is evidence that fibrillation is not so important for paper strength. Nakano (45) made sheets from silk and asbestos fibers. These fibers split up into fibrils when beaten but the sheets formed from them are extremely weak. Edge (46) has beaten fibers in toluene and obtained a high degree of fibrillation. Sheets (made from water suspensions) comprised of these fibers showed little or no strength development. Harrison (47) and Gallay (48) have both emphasized the fact that an appreciable amount of strength development is obtained during the early part of the beating cycle, whereas no fibrillation is visible even under a high-power microscope. Campbell and Cottrall recognized that visible or external fibrillation is not the only important effect of beating, and Campbell emphasized that internal fibrillation is probably even more important than external fibrillation. The terms internal fibrillation, flexibilization, and loosening-up of the internal structure have all been applied to the phenomenon. The internal fibrillation produces a more flexible fiber which is capable of much better bonding than an unbeaten fiber for reasons to be discussed shortly.

It has been thoroughly established that pulp must be beaten in a liquid which swells the pulp. Kress and Bialkowsky (42) measured the degree of swelling and found that the swelling power of the medium used

for beating correlated with the degree of beating obtained. Jayme (6, 49) has concluded that any influence leading to decreased swelling is detrimental to strength. Lyne and Gallay (50) cited other evidences of the importance of swelling. Gallay (48) has discussed the methods of measuring swelling of pulp fibers; he claims that swelling is the most important single factor in bringing about strength increases. Campbell (35-38) also emphasized the importance of swelling. He points out that swelling is probably due to the attraction of hydroxyl groups in water to the hydroxyl groups in cellulose. If cellulose were a short chain material or if the hydroxyl groups of cellulose had a much greater affinity for water than cellulose, cellulose would completely dissolve in water. Campbell believed that swelling is a state of partial or limited solubility. When pulp is swollen by water the structure of the fiber is loosened up and fibrillation (internal and external) occurs upon beating.

Cellulose as present in pulp fibers is in a partly crystalline and a partly amorphous state. Water can easily enter into the amorphous portions and produce swelling. However, the crystalline portions resist the entry of water (if this were not the case, cellulose fibers could easily be disintegrated in water). In reviewing the subject Gallay (48) pointed out that pulp fibers are so crystalline that only a small amount of swelling occurs. He concluded that beating produces disruption of crystalline areas so that further swelling is possible. Campbell (37) proposed that the crystalline portions of fibers are held together by forces of varying magnitude depending upon the orientation of the individual molecules in a crystalline area. Where the orientation is poor, the forces are weak and

the crystalline structure is readily destroyed by the entry of water alone. Other crystalline areas are stronger and are disrupted by the action of the beater. Still other areas contain molecules so well oriented that not even beating will disrupt the structure.

Campbell (35-38) expressed the opinion that the amorphous portion, as well as the surfaces of the crystalline portions, are in a state of partial solution. Upon removal of water by drying, the surfaces tend to crystallize and reunite. If the orientation of the molecules is favorable, a strong crystalline area can be formed. Campbell asserted that fibrillation is the conversion of internal surfaces to external surfaces. One important aspect of fibrillation is that much greater bonding between adjacent fibers is possible by formation of strong crystalline areas from formerly amorphous and weak crystalline areas.

When water-swollen pulp fibers are beaten and fibrillated, a simultaneous increase in the surface of the fibers occurs. The increase in surface of the fibers is primarily important because it represents an increase in the potential bonding of the fibers. According to Campbell, the increase in surface represents an increase in the potential of crystalline cellulose when the fibers are dried.

Harrison (47) disagreed with Campbell on the question of the formation of a crystalline structure upon drying. He favored the view that, instead of having a condition of partial solution of cellulose, a colloiddally active surface is formed which tends to coalesce upon drying so that the fibers or fiber elements are held together by "surface cohesion."

Strachan (34, 43) originally proposed the existence of a colloidal film on pulp fibers. He noted changes in surface conductivity, in electrokinetic streaming potential, and in the adsorption of electropositive precipitates during the beating process. It has also been claimed (51) that the bonding strength of fibers increases linearly with increasing alumina adsorption, dye adsorption, and alkali binding capacity. Dixon (52) concluded from his studies of the hydrophilic nature of pulp that the predominant factor causing fibrils to bond was this hydrophilic character. He found that substances which increased the hydrophilic character of the pulp also increased the strength properties and, conversely, those which decreased the hydrophilic nature caused lower sheet strength. Clark (27) observed that wetted sheets of viscose cellophane placed together seemed to form a "mucilage of some kind" as they were drying. As previously mentioned, the cellophane sheets became strongly bonded together after pressing and drying. Mark has referred to dextrine produced during beating which "perform the function of sticking together the individual fibrillae." Bell (40) also made reference to a colloidal surface film of "cement-like" substance between fibers. Steenberg (53) referred to swollen cellulose molecules acting as a "glue." He pointed out that most high polymers have sticky or tacky properties only in limited chain-length regions. Molecules longer or shorter than this limited range do not possess these properties. The inference is, of course, that the hemicelluloses are very closely associated with formation of the mucilage or colloidal film.

It was previously mentioned that one of the important actions of beating is considered to be an internal fibrillation or flexibilizing of the fiber. The action is brought about when amorphous and poorly oriented crystalline portions of the fibers are subjected to the action of the beater. When more flexible fibers are produced, there is a tendency toward better matting of the fibers when a sheet is formed. The flexibility of the fibers also aids greatly during the drying process. According to Campbell (35-38, 44) the individual fibers and fibrils are drawn together during the drying process by the forces of surface tension. These surface tension forces bring the fiber surfaces into sufficiently intimate contact to permit the formation of bonds which give rise to sheet strength. The forces which resist the pull of surface tension are dependent upon the stiffness or flexibility of the fiber. Thus, it can be seen that flexibilizing of the fibers during beating is very important if a strong, well-bonded sheet is desired. From the standpoint of flexibility, the external fibrillation is also of great importance. Not only is more surface produced by external fibrillation but the size of the parent fibers is diminished. Fibrils of even much smaller diameters are also produced by fibrillation. As a consequence, the finer fiber elements do not resist bending as strongly because the dimensions (and, consequently, their flexural rigidities) are smaller. Therefore, surface tension can promote more bonding because of greater flexibility and of greater surface.

The fact that surface tension forces are required to promote bonding has been vividly demonstrated by Van den Akker (25). Wet handsheets which were frozen and dried by sublimation possessed little strength because of

the limited extent of bonding in the absence of the surface tension forces. Both Stamm (54) and Campbell have pointed out that the magnitude of the surface tension stresses, especially where fine fibrils are involved, is enormous (i.e., 150 to 200 atmospheres). Campbell (38) proposed that the normal state of the fibers is the wet, swollen state and that dried fibers are under stress because surface tension forces have produced bending of the fibers during the drying process. The fibers are then bonded so that the entire structure is being stressed from within. Campbell based his proposal upon sorption studies which revealed a definite relationship between the volume of liquid sorbed and the internal liquid tension corresponding to the vapor pressure involved, using several alcohols and water.

When the forces of surface tension act upon the fibers in a sheet, the fibers are drawn together and bonded to an extent dependent upon the flexibility or rigidity of the fibers. The more the fibers are drawn together the greater is the density of the sheet produced. Some authors have attached a great deal of significance to sheet density (apparent density or solid fraction). Clark (54) claimed that the apparent density is "accurately linearly proportional to the logarithm of the amount of beating." Doughty (55) stated that strength development during beating is due to a change in the fiber surface conditions and to an increase in solid fraction. An increase in solid fraction can also be produced by wet pressing. Dry pressing does not appreciably alter the solid fraction because the bonded fibers return to their normal positions after release of the pressure. However, pressing wet fibers improves the contact of fiber

surfaces and increases the amount of bonding and the solid fraction when the sheet is dried.

The effect of beating or wet pressing on the improvement of bonding has been followed by optical means. The specific scattering coefficient of a material is dependent upon the surface available for light scattering. It has been noted that wet pressing causes a decrease in the specific scattering coefficient which indicates that less surface is available for light scattering or that more of the surface is bonded (56). Parsons (57) found that the specific scattering coefficient was directly related to surface area. He proposed the determination of bonded area by comparison of the specific scattering coefficients of bonded and unbonded sheets. The unbonded sheets (dried from butanol) gave the scattering coefficient of the total fiber surface; the bonded sheets gave the scattering coefficient of the area not bonded. By difference the bonded area was measured. Modifications in Parsons' procedure have been made and are reported in the literature (21, 58). Recently, Nordman (14) has confirmed the fact that the specific scattering coefficient of pulp decreases as beating proceeds.

In order to measure bonded area, Parsons needed an estimate of the surface area of the unbonded fibers. It has already been pointed out that the amount of surface area of fibers is important from the colloidal standpoint. Surface area is also important because it represents the limit of the potential bonding of fibers. The surface area or specific surface of fibers can be measured in several ways. Direct microscopic measurement

may be used. Other methods include Clark's silvering technique (59-62) and fluid permeability measurements (63-65). It is beyond the scope of this work to discuss these methods in detail, but it should be pointed out that water-permeability measurements (63-65) also afford an estimate of the degree of swelling and air-permeability measurements (66) permit estimation of bonded area. An investigation is now in progress to measure specific surface and bonded area by gas adsorption techniques (67).

In the introduction it was mentioned that many nonfibrous materials have been added to pulp in the beater in an attempt to improve the strength properties of the paper being made. Jayne and co-workers (68) have published an excellent review of the work in this field. The types of materials used to improve strength properties may be classed as synthetic wet-strength agents, cellulose derivatives, and naturally occurring polysaccharides. A discussion of the field of wet-strength agents is beyond the scope of this review. Although the present study is concerned solely with naturally occurring polysaccharides, the composition and action of cellulose derivatives is sufficiently similar to the other polysaccharide materials to be of interest here.

The two most widely used cellulose derivatives are methylcellulose and the sodium salt of carboxymethylcellulose. Both these materials are deflocculating agents and consequently bring about improvements in the formation of paper (69-71), as well as improvements in the strength properties of the final sheet (72-74). Horsey (74) stated that the addition of a material (such as carboxymethylcellulose) which contains many free hydroxyl

groups will increase the strength of paper by increasing bonding.

Starch is the oldest and still most widely used naturally occurring polysaccharide type of beater adhesive. Musser and Engel (73) have reported that soluble starch increases the breaking length of paper. Rowland (75, 76) emphasized the importance of adsorption of starch and considered the adhesive quality of the starch to be related to its content of polar hydroxyl groups. Casey (77) suggested that starch increases the extent of bonding by acting as a cementing agent between adjacent fibers.

Broadbent and Harrison (71) investigated many naturally occurring gums and found Hibiscus manihot and deacetylated karaya gum to be particularly effective as beater adhesives. They observed that these materials not only swelled to form gelatinous masses in water but also exhibited "ropiness." Other materials which have been particularly effective as beater adhesives are guar and locust bean gum. Swanson (78) believed that guar and locust bean gum are adsorbed by the fibers in the form of a highly swollen mucilage. He pointed out the improvement in formation obtained when these gums are used. He attributed the improvement to a hydrophilic layer on the pulp and a negative electrokinetic potential. The improvement in formation is accompanied by increases in bonded area and improved tensile strength. Le Compte (78A) has patented a method for making a paper fiber deflocculant from karaya gum. Wollwage (79) noted that deacetylated karaya gum reduced the flocculation tendency of pulp suspensions and Erspamer (69) correlated this effect with sheet formation.

Erspamer noted that locust bean gum was an especially powerful dispersing agent.

The above discussion has been presented to review the theories and evidence related to the strength of paper and the effect of naturally occurring polysaccharides upon the strength properties. It is felt that the review is adequate to cover the background material for the present study.

PRESENTATION OF PROBLEM

It has been pointed out in the introduction that many high polymeric materials are capable of enhancing the strength properties of paper. Perhaps the most exhaustive work yet carried out in this field has been reported by Swanson (78). In his study it was shown that both locust bean gum and guar were effective in bringing about increases in paper strength. The effect of locust bean gum was particularly pronounced with long fibered pulps. Locust bean gum seemed to be superior to guar gum in the improvement of formation of handsheets. In order to avoid repetitious work, it was felt that a single pulp and a single adhesive should be used. On the basis of Swanson's work, locust bean gum and a coniferous sulfite pulp were selected.

It has already been stated that a great number of suggestions have been put forward to explain the effects produced by beater adhesives. Up until the present time, however, no fundamental investigations have been carried out to study the reasons for the strength increases produced by beater adhesives. The work herein reported covers such a study.

PREPARATION OF RAW MATERIALS

The two primary raw materials for this investigation were purified locust bean gum and West Coast bleached sulfite pulp.

WEST COAST BLEACHED SULFITE PULP

The determination of the physical characteristics of this pulp were carried out as part of the main investigation. Chemically, it is known that the pulp contains principally glucose with small amounts of mannose and xylose. Little or no arabinose and galactose are present. The actual source of the pulp was unknown, but if it is a typical West Coast bleached sulfite pulp, it is made principally from western hemlock with possibly a small amount of white fir.

The cut edges of the pulp were removed by tearing as recommended by Institute Method 411 (80).

PURIFIED LOCUST BEAN GUM

The locust bean gum for this work was purified according to a procedure described by Haug (81) for the purification of guar. The method used was as follows:

1. Forty-nine grams of finely divided impure locust bean gum were very slowly added to seven liters of vigorously agitated distilled water.
2. The dispersion was heated at a given rate with direct steam to 90°C. and maintained at that temperature for 20 minutes (constant agitation).
3. The hot dispersion was run through a Sharple's supercentrifuge rotating at 25,000 r.p.m. to remove undispersed materials.

4. After the centrifuged dispersion was cooled, it was poured slowly into 2.5 times its volume of vigorously stirred 95% ethanol.
5. The white stringy material obtained was filtered using a filter cloth on a Büchner funnel and squeezed free of excess ethanol by hand.
6. The material was then triturated thoroughly in a mortar with absolute ethanol and then filtered using filter paper on a Büchner funnel. A rubber dam was used to effect more complete removal of liquid during the filtration.
7. The trituration was repeated in absolute ether and the material was again filtered.
8. The sample was then allowed to stand in absolute ether for several hours to complete the dehydration. This procedure prevents hornification of the product.
9. The purified gum was filtered again and conditioned to air in a crystallizing dish in the humidity room for 3 to 4 hours.
10. The dried gum was finally screened to pass a number ten sieve. In this way large horny particles were removed. This step was later considered to be unnecessary.

LOCUST BEAN GUM STOCK SOLUTION

Dispersions of 0.5% locust bean gum in water were prepared by the following method. Five grams of gum were added to one liter of vigorously stirred distilled water. Stirring was continued while the mixture was heated to 85°C.; the dispersion was maintained at this temperature for ten minutes. Stray material and undispersed gum particles were removed by

filtering through a plug of glass wool. The filtered dispersion was stored in the refrigerator to inhibit microbiological attack.

It was at first thought that the screening procedure would eliminate formation of undispersed gum particles when the stock solution of gum was prepared. However, some gum still failed to go into solution presumably because of formation of a gel-like coating on the exterior of the particle which resisted the passage of water necessary for solution of the particle. Therefore, the hot gum solution was filtered through a plug of glass wool to remove undispersed material. The concentration of the gum solution was easily determined by evaporation of a weighed portion to dryness.

INVESTIGATION OF EXPERIMENTAL PROCEDURES

DETERMINATION OF LOCUST BEAN GUM CONTENT OF PAPER

INTRODUCTION

Up until the present time there have been available only two methods for the determination of the locust bean gum content of paper--the anthrone method and the viscometric method.

The anthrone procedure (82) makes use of the color reaction between anthrone in sulfuric acid solution and locust bean gum. The method is based upon the measurement of the gum content of a paper by determination of the gum not adsorbed by pulp from a solution of gum of known concentration. Although the method is a rapid one, it is indirect and, consequently, the gum content of the paper is determined by difference. An error in the amount of gum added or in the amount of gum not retained results in an error in the final value. Secondly, the method of mixing affects the test (83). Presumably, the temperature attained by the reaction mixture as a result of mixing the concentrated sulfuric acid with water affects the intensity of color produced.

Probably the greatest objection, however, is that anthrone is not a specific reagent for locust bean gum, but rather is a general carbohydrate color reagent (84) and, therefore, any carbohydrate material will affect the test. It is true that a control is run to cover this objection but it is felt that the presence of the gum may affect the filterability of the fine cellulosic particles. Actually, there is no assurance that all the gum itself will pass the filter or that only a

small constant amount of cellulosic material will pass. It is readily seen that these conditions are aggravated in the case of a beaten pulp where large quantities of fines are present. This causes a high control value and, consequently, casts more doubt on the accuracy of the results.

The second method is a viscometric one and, in general, suffers the same disadvantage as the anthrone method. It is indirect, it is not specific for locust bean gum, and inaccuracies are aggravated in the case of beaten pulps.

It was felt that a new and more reliable method for the determination of the locust bean gum content of paper should be sought. The theory of the new method and experimental results obtained are given below.

PROPOSED NEW GALACTOSE METHOD

Theory

Locust bean gum and pulp are composed ultimately of simple sugar units. The predominant simple sugar unit in pulp is glucose but others, such as mannose, xylose, arabinose, and galactose, may also be present; locust bean gum is composed solely of mannose and galactose units (85). When the contents of mannose or galactose of both the pulp and locust bean gum are known, the proportion of locust bean gum present in a pulp sample of known weight can be determined by analysis of the mannose or galactose content of the sample.

Important Considerations

Although the theory for the proposed new method is simple, there were a number of important considerations which had to be studied before a practical method could be evolved.

The amount of locust bean gum ordinarily present in pulp or paper samples is quite low--probably less than 3%. It was realized that only small quantities of simple sugars could be recovered from the locust bean gum present in a pulp sample. Thus, it was important that the sugar unit chosen for analysis (mannose or galactose) be present in locust bean gum in an appreciable amount; on the other hand, the pulp had to contain very small amounts or none at all of the chosen sugar.

In order to recover the simple sugars for analysis, it was essential that all the locust bean gum be dissolved and removed from the pulp residue by a hydrolytic treatment. Obviously, the method would not be quantitative unless complete removal of locust bean gum were accomplished. In addition, it was important that the hydrolytic technique bring about complete hydrolysis of the locust bean gum.

It was also recognized that it would be advantageous if the method of hydrolysis accomplished the separation of the sugars of the locust bean gum from at least the bulk of the sugar units present in the pulp. That is, a favorable method of hydrolysis would attack the pulp to a limited extent, whereas it would completely hydrolyze the locust bean gum. In this way, the problem of separation of the sugars could be greatly simplified.

It was also important that there should be no destruction of sugars during the hydrolysis or during the later steps necessary in the analysis. Finally, it was desirable that the time required for analysis of the samples be kept to a minimum.

Paper Partition Chromatography

The technique of paper partition chromatography has been used throughout this study, and therefore, it will be discussed briefly here. Paper partition chromatography was first employed for separation of amino acids (86) but was later extended to separation of sugars (87). Flood, Hirst, and Jones (88, 89) developed a quantitative method for the separation and determination of sugars using the technique of paper partition chromatography.

Although galactose may be determined in the presence of other sugars by conversion to mucic acid or by fermentation techniques, there is no doubt that the most rapid and reliable method is quantitative paper partition chromatography. The individual sugars can be readily separated and identified by means of paper partition chromatography and when the position of the sugars is known, the quantities present can also be determined.

The procedures of Flood, Hirst, and Jones were adapted for this work as outlined below. A portion of a sugar syrup was "spotted" or "drawn in a line" along a reference line on a strip of Whatman No. 1 filter paper. The strip was then placed in an irrigating tank containing a suitable solvent system with the top end of the strip dipping into the solution.

The solvent flowed over the paper by capillarity and eventually was siphoned off the lower end of the strip. The individual sugars moved down the paper strip at various rates. A separation of the sugars was obtained when a suitable solvent system was employed. The positions of the sugars were ascertained by spraying dried guide strips with a solution of aniline hydrogen phthalate. Spots were formed in the areas where sugars were present when these guide strips were dried in the oven. Using the guide strips, the position of the sugars in the main portion of the sheets was determined and the sheet was cut into portions containing the various sugars. The sugars were then individually eluted from the strips with water. The sugar solutions were oxidized with sodium periodate and the formic acid which was formed was titrated with alkali. Direct calculation of the amount of sugar present could be made from the amount of formic acid produced during the oxidation. However, it is common practice to add a known quantity of a given sugar to the mixture before spotting on the chromatogram, and then to determine the individual sugars by comparison with this known sugar. In the present work L-rhamnose was used as the reference sugar.

Study of the Sugar Units Present in the Pulp and the Locust Bean Gum

Samples of the pulp were hydrolyzed by two methods to determine the component sugars.

Complete hydrolysis was carried out with sulfuric acid. The pulp was treated with 72% sulfuric acid for 2 or 3 hours at 18°C. and the mixture was then diluted with water to an acid concentration of 3%. This mixture

was boiled for 4 hours, neutralized with barium carbonate, heated to boiling, and filtered. The filtrate, which contained the component simple sugars, was concentrated to a thin syrup. A sample was slurried with ethanol and clay [the clay was composed of 5 parts clay Florex XXX and one part of analytical grade Celite (90)] and chromatographed on a No. 3 column (length 230 mm., diameter 38 mm.), using a clay adsorbent and 95% ethanol developer. Appropriate cuts were taken on the effluent and each cut was evaporated to dryness. The extruded column was sectioned and eluted and the eluates were evaporated to dryness. Each fraction was moistened to form a thick syrup which was spotted on filter paper and subjected to paper partition chromatography using a pyridine-butanol-water (3:10:3) solvent system.

The data in Table I show the fractions taken from the chromatographic column.

TABLE I

	CHROMATOGRAPHIC FRACTIONS						
Fraction	1	2	3	4	5	6	7
"Filtrate," ml.	25	50	50	50	25	50	50

Fraction 8 was from the bottom of the column.

Fraction 9 was from the top of the column.

Paper partition chromatograms revealed large quantities of glucose in fractions 2 to 7. Xylose was found in fractions 2 and 3 and mannose was present in appreciable amounts in fractions 2 to 8. An extremely faint spot was found for galactose in fraction 7. This spot was scarcely visible

under ordinary light and showed only as a weak spot under ultraviolet light. In addition, fraction 7 contained a preponderance of glucose but this fraction was small in comparison with the others (especially fractions 4 and 5). Galactose was not found in any other fraction. From this experiment it was concluded that galactose was present in the pulp in very small amounts (less than 1%). On the other hand, the paper partition chromatograms showed that mannose was present in much larger amounts. It should also be noted that no rhamnose was found in the pulp.

The second hydrolytic technique used was treatment with sulfurous acid. Sulfurous acid hydrolysis for the study of sugars from polysaccharides is a relatively recent method (91) and has not as yet received widespread application. As will be pointed out, however, the method was found to be particularly suited to the present application and is a rapid method which can be successfully applied to relatively small samples.

Samples of the pulp were hydrolyzed with 3 to 5% sulfurous acid in a sealed Pyrex tube for 60 minutes at 135°C. The tube was opened and the contents were transferred to a fritted glass funnel and washed thoroughly to remove the sugars. The filtrate was neutralized with barium carbonate, concentrated, and filtered. The filtrate from this operation was taken to dryness and the yield of sugar was determined. The sugar was then moistened to form a thick syrup and was subjected to paper partition chromatography. Only a very weak spot (under ultraviolet light) was obtained for galactose, whereas mannose was present in an appreciable quantity. Again, no trace of rhamnose was found.

Locust bean gum was also hydrolyzed with sulfurous acid. The method was similar to that used for pulp, except that the initial filtration step was unnecessary. Paper partition chromatograms showed that both mannose and galactose were obtained from the gum in appreciable quantities but that no other sugars were present. At this point it was apparent that this method for the determination of locust bean gum content of paper should be based upon the galactose present in the system.

Quantitative determinations of the galactose obtained from pulp and from locust bean gum by sulfurous acid hydrolysis were next carried out. The sugars were determined by periodate oxidation (to be discussed in detail later). Tables II and III show the galactose content of the gum and of the pulp.

TABLE II

GALACTOSE CONTENT OF LOCUST BEAN GUM

Sample	Gum, g.	Galactose, g.	Galactose from Gum, %
1	0.0476	0.00911	18.6
2	0.0970	0.01375	13.8
3	0.1440	0.02070	13.9
4	0.1254	0.02235	17.2
5	0.0741	0.01529	20.0
6	0.1511	0.02705	17.4
7	0.0800	0.01390	16.9
8	0.0690	0.01100	15.5
9	0.1113	0.01950	17.0
10	0.1194	0.01289	10.5
11	0.0967	0.01390	13.9
12	0.1164	0.01436	11.9
13	0.1609	0.02910	17.5
14	0.1015	0.01620	15.5
15	0.0902	0.01636	17.6
Average			15.7

This average value was slightly lower than others reported in the literature--i.e., 16.5% (92), 16.5%, 17.5%, and 18.5% (93), and 20% (94).

Recently, Hirst and Jones (95) have reported values of 14.0% and 16.0%.

TABLE III

GALACTOSE CONTENT OF PULP

Sample	Pulp, g.	Galactose, g.	Galactose from Pulp, %
1	1.179	0.000096	0.0078
2	1.474	0.000241	0.0164
3	1.315	0.000143	0.0109
4	1.236	0.000193	0.0156
5	1.291	0.000177	0.0137
6	1.372	0.000206	0.0151
7	1.308	0.000143	0.0109
Average			0.0129

These quantitative data again demonstrated that galactose should be the sugar unit determined for this method. It was apparent that the amount of galactose removed from the pulp was sufficiently low so that only small control or blank values were required.

Removal of Locust Bean Gum From Pulp by Hydrolysis With Sulfurous Acid

Sulfurous acid hydrolyses of pulp, locust bean gum, and pulp treated with locust bean gum revealed qualitatively that sulfurous acid was capable of selectively separating the bulk of the gum as simple sugars from the bulk of the fibrous pulp. It remained to be shown whether or not the gum was quantitatively removed from the pulp. The following experiment was designed for this purpose.

Samples of untreated pulp and of pulp treated with locust bean gum were prepared. The pulp had previously been beaten 20 minutes in a laboratory Valley beater with a bedplate loading of 5500 grams. One specimen of each was subjected to sulfurous acid hydrolysis, the pulp residues were recovered and dried, and the hydrolyzates were subjected to paper partition chromatography. The pulp residues, as well as specimens of the original samples, were hydrolyzed with 72% sulfuric acid, as described previously, and the sugars were recovered and concentrated under vacuum. The sugars were then separated on a clay column using 95% ethanol developer and the various effluent cuts were spotted for paper partition chromatograms. The chromatograms were developed in the pyridine-butanol-water tank for 48 hours. The following evidence was obtained from a study of the paper partition chromatograms.

1. The sulfurous acid hydrolyzate of the pulp sample gave a very weak spot for galactose, and that of the pulp containing locust bean gum gave a strong spot for galactose.
2. No galactose was found in any of the fractions obtained from the sulfuric acid hydrolyzates of pulp residues which remained after hydrolysis with sulfurous acid.
3. The sample of the original pulp containing gum which was hydrolyzed with sulfuric acid (hydrolyzate chromatographed on clay column and fractions chromatographed on paper) showed a large spot for galactose from one fraction and a lighter spot from another fraction. In contrast, the untreated pulp sample (treated similarly) gave only a weak spot for galactose from one fraction and a questionable spot from

another fraction. The galactose spots from the untreated pulp sample were visible only under ultraviolet light.

These results demonstrated conclusively that sulfurous acid hydrolysis accomplished quantitative removal of the locust bean gum from the pulp.

Hydrolysis of locust bean gum samples for determination of galactose content was carried out with sulfurous acid (see Table II). The chromatograms of the hydrolyzates showed clearly that the only sugars present were mannose and galactose. No material was held at the upper part of the chromatogram (above the galactose) as would be the case if incomplete hydrolysis were encountered. Hydrolyses carried out on locust bean gum for short periods of time (using sulfurous acid) gave small visible spots in the disaccharide region. This incomplete hydrolysis did not occur under ordinary hydrolytic conditions. However, the fact that a disaccharide could be obtained indicated that mild hydrolysis of locust bean gum with sulfurous acid might be useful for structural studies.

It should be emphasized that, although the sulfurous acid hydrolysis accomplished rapid, complete hydrolysis of the gum, only a small amount of the pulp was hydrolyzed. For example, this method yielded 4 to 8% of the pulp sample as simple sugars. A small portion of the glucose was removed, together with most of the other sugars present in the pulp. Using this method, the major portion of the glucose in the pulp was not hydrolyzed, so that paper partition chromatography could be applied directly to the hydrolyzates. It should be mentioned that the pyridine-butanol-water (3:10:3) solvent system used for paper partition chromatography afforded

good separation of glucose and galactose--a pair of sugars separated only with difficulty (96). This placed additional emphasis on the desirability of minimizing the attack on the pulp during hydrolysis of the gum.

Possible Destruction of Galactose

If the proposed method were to be used as a quantitative analytical tool, it was important that there be little or no loss of galactose during the steps involved in the analysis. The only likely phases where such destruction might conceivably occur were during the hydrolysis and the recovery of the sugars. In order to test for possible destruction of galactose, the following experiments were carried out. Samples of galactose were subjected to the hydrolytic treatment and the amount of sugar which was recovered was determined gravimetrically. The results are given in Table IV.

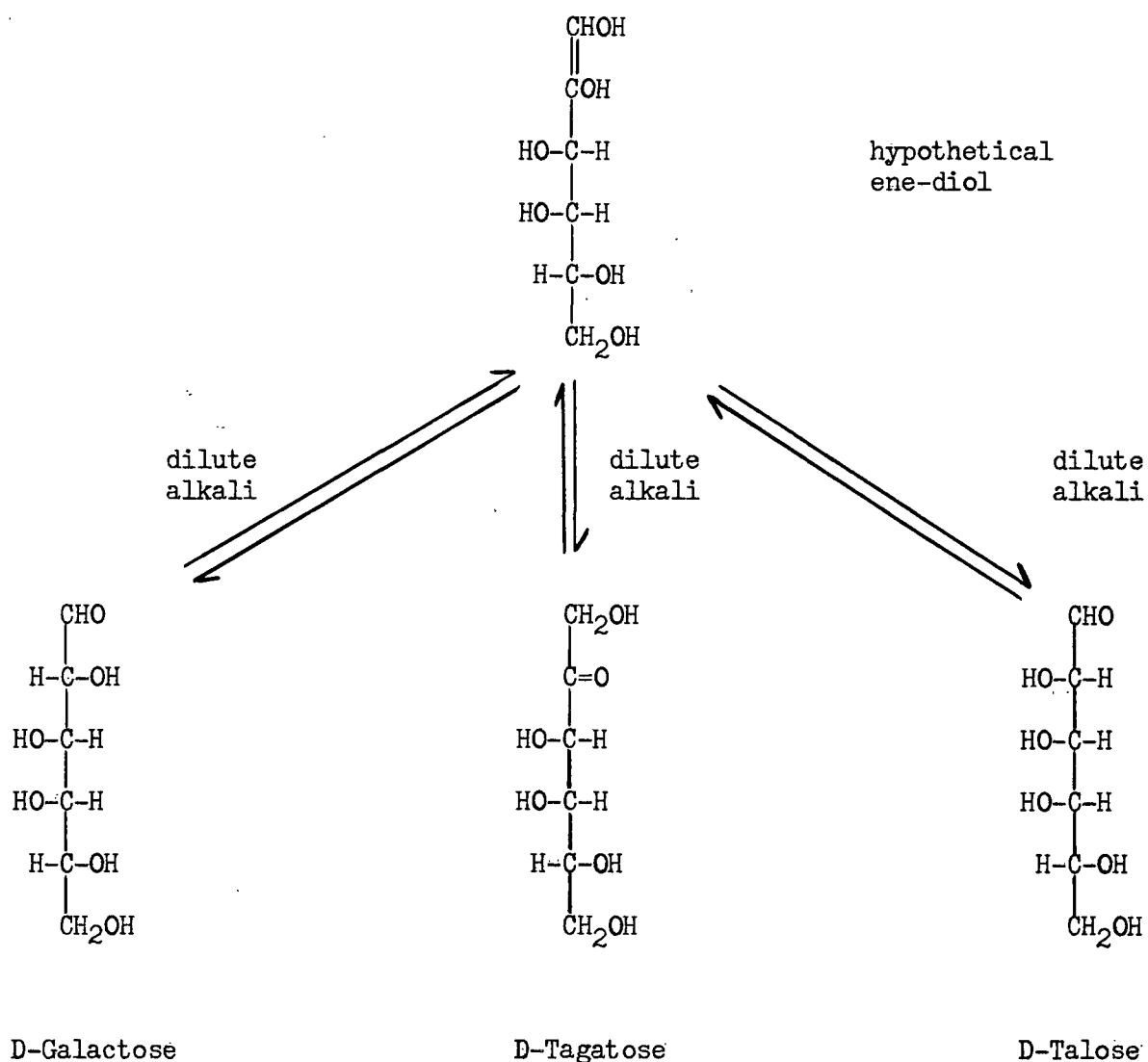
TABLE IV

APPARENT RECOVERY OF GALACTOSE FROM HYDROLYTIC TREATMENT

Sample	1	2	3
Galactose used, g.	0.1387	0.2426	0.4068
Sugars recovered, g.	0.1415	0.2413	0.4129
Difference	+2.0%	-0.5%	+1.5%

Obviously, there can be no appreciable loss of galactose as a result of the hydrolytic treatment. The small errors encountered could easily be due to moisture, presence of barium carbonate in the filtrate after neutralization (a step in the recovery of the sugars to be discussed later), and small mechanical losses of sugar in transfer.

It was also suggested that the barium carbonate used in the recovery of the sugars (if used in excess) might make the sugar solution sufficiently alkaline to permit epimerization. Epimerization of D-galactose would produce D-talose and possibly the ketose, D-tagatose.



Samples of galactose were subjected to treatment with barium carbonate and with dilute sodium hydroxide. The samples were concentrated and spotted on chromatograms along with appropriate reference sugars. After development

and spraying, the chromatograms indicated that a limited amount of epimerization had occurred. Quantitative determination showed that the loss of galactose in the presence of barium carbonate amounted to only 3.5%. In some cases, it appeared that even less epimerization occurred. Although the loss of galactose due to epimerization was measurable, it will later be shown that the extent of epimerization encountered is not significant when compared with the accuracy of the method as a whole.

At this point it was felt that the development of the new method was complete. It has been shown that:

- (1) Galactose was the suitable sugar for analysis.
- (2) Locust bean gum was quantitatively removed from pulp and was completely hydrolyzed by treatment with sulfurous acid, whereas only limited hydrolysis of the pulp occurred.
- (3) No appreciable destruction of galactose occurred throughout the steps involved in the determination.

Evaluation of the method was undertaken after the development was completed. This phase of the work is covered in the following section.

Reproducibility of Results

It was desirable to know the precision which could be expected from the new method. First, however, the precision of the paper partition chromatography-periodate oxidation technique was determined. In order to study this, a mixture of glucose, galactose, and rhamnose was used. In this way the problem of separation of glucose and galactose was encountered just as it would be with a sugar mixture obtained from the hydrolysis of a

pulp sample which contained locust bean gum. In order to allow complete separation of glucose and galactose, the rhamnose portion of the chromatogram was removed after two days, whereas the glucose and galactose were run for four days. The percentages of the three sugars determined are given in Table V. Approximately 10 mg. of sugar mixture were used for each chromatogram.

TABLE V
REPRODUCIBILITY OF PAPER PARTITION-PERIODATE TECHNIQUE

Sample	Galactose, %	Rhamnose, %	Glucose, %
1	29.0	33.8	37.2
2	27.7	34.3	38.0
3	28.3	32.6	39.1
4	28.9	35.0	36.1
5	27.3	36.0	36.7
6	26.6	36.4	37.0
7	27.3	37.4	35.3
8	24.6	37.5	37.9
9	27.4	37.3	35.3
10	26.3	38.5	35.2
Average	27.3	35.9	36.8
High	29.0	38.5	39.1
Low	24.6	32.6	35.2

It will be noted that, for a given sugar, the variation between sample values amounts to no more than 6% (based on total sugar).

Two sets of samples were prepared for the study of the reproducibility of results for the galactose method as a whole. Both sets were made from a single pulp suspension treated with approximately 5% locust bean gum. The pulp used was West Coast bleached sulfite beaten for 40 minutes in the

laboratory Valley beater with a bedplate loading of 5500 grams. The freeness of the pulp was 645 cc. Schopper-Riegler.

The first set of samples (A) consisted of 2-gram sheets prepared on a British sheet mold, using the normal procedure. The second set (B) was prepared on a 80-mm. Büchner funnel equipped with a wire mesh; the filtrate from the first pass was recirculated in order to retain the fines in the pad. Two-gram sheets were again prepared.

The sheets in each set were cut into small squares and samples were drawn at random. The samples were hydrolyzed, neutralized, concentrated, etc. as described later. After rhamnose was added and paper partition chromatograms were run, the sugars were determined by periodate oxidation. The results in Table VI show the analyses for gum content of the various samples.

The galactose method clearly distinguished between the two groups of samples whose locust bean gum contents differed by only 0.37%. According to statistical theory (Student's "t" test), it is practically impossible that the "A" samples had the same gum content as the "B" samples.

It is particularly interesting, but not at all surprising, that these two sets of samples have different gum contents. One would expect the fine cellulosic material to have a greater adsorptive surface than the long-fibered material. Therefore, the samples prepared with recirculation of the filtrate should have a higher gum content (as was the case). It is also to be pointed out that these two sets of pulp samples were prepared from a

TABLE VI

REPRODUCIBILITY OF GALACTOSE METHOD

Sample	Weight, g.	Galactose, g.	Gum, g.	Gum, %
A-1	1.646	0.00290	0.01848	1.12
A-2	1.614	0.00281	0.01790	1.11
A-3	1.737	0.00326	0.02072	1.19
A-4	1.617	0.00296	0.01888	1.17
A-5	1.663	0.00345	0.02200	1.32
Average				1.18
High				1.32
Low				1.11
B-1	1.803	0.00410	0.02612	1.45
B-2	1.952	0.00549	0.03495	1.79
B-3	1.794	0.00407	0.02590	1.44
B-4	1.922	0.00428	0.02725	1.42
B-5	1.741	0.00413	0.02630	1.51
B-6	1.646	0.00443	0.02822	1.71
Average				1.55
High				1.79
Low				1.42

common pulp-gum slurry. The galactose method, using the paper samples, differentiated clearly between the two samples, whereas they would have been considered as identical in gum content if analyzed by the anthrone or by the viscometric method which use the pulp slurry for samples.

In summary, it is felt that the newly developed galactose method possess several advantages over the anthrone and viscometric methods.

1. The galactose method measures the gum content of paper samples. This is not the same quantity as the gum adsorbed by a pulp from a gum dispersion which is measured by the anthrone and viscometric methods.
2. The galactose method is a direct method, whereas the anthrone and viscometric methods are indirect.
3. The galactose method is specific for locust bean gum (or the sugar unit

determined), whereas the anthrone and viscometric methods are not.

4. It is doubtful that the degree of beating (or physical nature) of the pulp has any effect upon the galactose method.

COMPLETE DESCRIPTION OF THE GALACTOSE METHOD IN FINAL FORM

The following description covers the method which was used in the previous section dealing with precision and for all the determinations of locust bean gum content which follow. The steps involved in the procedure may be outlined as given below:

- (1) Preparation, sampling, and hydrolysis
- (2) Recovery of sugars
- (3) Separation of sugars
- (4) Determination of sugars

Preparation, Sampling, and Hydrolysis

The preparation of samples will not ordinarily be required because the method will be used to determine the locust bean gum content of prepared papers. In much of the preceding work a wire mesh was used to prepare sample sheets so that the normal sheetmaking procedure would be imitated.

Any method of sampling which supplies random representative samples will be satisfactory. Where two or more specimens of the same sample are used, it is considered good practice to cut the paper sample into small squares and to draw specimens at random.

Each sample may be individually oven dried at 105°C. or a separate moisture sample may be taken. Approximately two grams of oven-dry material

are weighed on an analytical balance to the nearest milligram. The sample is transferred to a reaction tube of 16-mm. Pyrex glass tubing which has been sealed at one end. The contents of the tube are well covered with a solution of sulfurous acid made by diluting one part of an aqueous solution of sulfur dioxide saturated at room temperature with one part of water, and the tube is sealed.

The hydrolysis is carried out by heating the contents of the tube to 135°C. for 60 to 90 minutes. A convenient arrangement is to immerse the tube in a bath of boiling xylene which affords automatic temperature regulation. The equipment used here consisted of a large vertical copper cylinder equipped with a water condenser and containing copper tubes into which the glass reaction tubes could be placed. Originally, a reaction time of 60 minutes was used but it was later felt that, for this work, a period of 75 to 80 minutes was preferable in order to insure complete hydrolysis of the locust bean gum. Small amounts of disaccharide material were found occasionally from 60-minute hydrolyses of locust bean gum.

When the reaction period is complete, the samples are removed from the bath and allowed to cool before recovery of the sugars.

Recovery of Sugars

The reaction tubes are opened by carefully breaking off the tops. The contents are transferred quantitatively to a fritted glass funnel and the filtrate is collected. The pulp residue should be broken up and thoroughly washed to insure complete removal of sugars. The filtrate containing the sugars in dilute solution is then concentrated and neutralized. Caution at

this point of the operation is emphasized, for the sugars are easily burned.

The filtrate containing the sugars is heated on a steam bath under a stream of air to aid evaporation. Barium carbonate is added to the hot solution to neutralize the excess sulfurous acid, as well as the small amount of sulfuric acid inevitably formed. Although the volume should be reduced to a few milliliters, the sample should not be taken to dryness at this point because of the danger of burning.

A small amount of analytical grade Celite is next added to the neutralized concentrated sugar solution. The solution is filtered through a small cotton-asbestos filter (which has been washed with water prior to filtration) and the filtrate containing the sugars is collected. Again, washing is advised to insure a quantitative recovery of the sugars. At this point in the operation a known amount of a reference sugar (rhamnose was used) is added to the sugars. Quantitative handling of the sugars is not required beyond this point until the final step (elution and oxidation). The entire sugar solution is next concentrated to a thin syrup for the separation of the sugars.

Separation of the Sugars

Separation of the sugars is accomplished by paper partition chromatography. The sugar syrup is laid down in a thin line across the paper strip from a fine, strong capillary tube. Whatman No. 1 filter paper (4 by 24-inches) is used. The paper strip is irrigated in a tank with a pyridine-butanol-water system (3:10:3) for 44 to 48 hours. At the end of this period, the strip is dried and thin guide strips are cut from both edges.

The guide strips are sprayed with a solution of aniline hydrogen phthalate (in butanol saturated with water) and placed in the oven for several minutes. Spots are formed where sugars are present and these serve to locate the corresponding sugars in the main portion of the strips. The rhamnose which moves rapidly will invariably be found near the bottom of the strip at the end of the first development period. The portion of the main strip which contains rhamnose is then cut off and the upper part of the strip is returned to the chromatographic tank for another 44 to 48 hours. In this way the rhamnose is easily separated and recovered in two days, whereas the galactose and glucose are allowed four days of treatment. This procedure has been found satisfactory since it gives good separations of glucose and galactose. Such separations frequently were not possible with two days' development. At the end of the second development period, a second set of guide strips are sprayed and the portion of the main sheet containing the galactose is cut out. A blank or control specimen containing no sugar is also cut out. The portions which have been cut out contain the sugars to be oxidized for quantitative determination. Care should be taken that the samples represent corresponding portions of the width of the original chromatogram.

Determination of the Sugars

The sugars are recovered from the paper portions by the process of elution (97, 98). One end of the small paper sample is held between the ends of two microscope slides. The slides in turn dip into a Petri dish filled with water so that, by capillary action, water is fed to the top of

of the paper sample. Water slowly flows down the paper, flushing the sugars with it. It has been established that the sugars follow the water interface very closely. When the water reaches the bottom of the strip a small portion containing the sugar is cut off with scissors and allowed to fall into another Petri dish. This strip is then carefully transferred with forceps to a ground-glass stoppered reaction tube. The implements and Petri dish are rinsed and the rinsings are added to the tube so that quantitative transfer of the sugar is effected.

One ml. of 0.25 molar sodium periodate is added to the reaction tube and the tube is stoppered. The mixture is heated on the steam bath for ten minutes. The stopper is removed and the tube is cooled under a cold water tap. Three drops of Methyl red indicator and 0.5 ml. of ethylene glycol are added and the tube is allowed to stand a few minutes for reaction of the ethylene glycol with the excess sodium periodate. The formic acid which is produced by periodate oxidation of the sugar is then titrated with very dilute alkali (0.001 to 0.005 N). The blank or control strip, the galactose strip, and the rhamnose strip are titrated in this manner. The relative amounts of galactose and rhamnose are found by subtracting the blank titration. The percentage of gum in a paper sample can be calculated by the following formula:

$$\text{Percentage gum} = \frac{\left[\frac{(G - B)}{(R - B)(1.14)} \right] (r)(100)}{\left[\frac{g}{100} \right] (s)}$$

where G = ml. for galactose,

B = ml. for blank,

R = ml. for rhamnose,

r = weight of rhamnose added (g.),

g = percentage galactose from gum, and

s = weight of sample (g.)

1.14 = conversion factor for rhamnose to be equivalent to a
normal hexose sugar by periodate oxidation.

MEASUREMENT OF BONDED AREA OF PAPERS CONTAINING LOCUST BEAN GUM

INTRODUCTION

One of the measurements which was expected to be particularly interesting in the studies which follow was that of bonded area. At the present time, the best available method for measuring bonded area is a modification of the procedure of Parsons (57). Unbonded sheets are produced by replacing the water in a sheet successively with acetone and butanol or benzene so that the sheet is not dried from water but from a liquid with a low affinity for cellulose and hydroxyl groups. Therefore, hydrogen bonding is kept to a minimum and the sheet produced is essentially unbonded. Since the sheet is unbonded, all its surface is available for scattering of light. On the other hand, a sheet dried from water has an appreciable portion of its surface bonded and, therefore, not available for light scattering. Thus, by a comparison of specific scattering coefficients of bonded and unbonded sheets, the portion of the area which is not available for scattering and is considered to be bonded can be determined.

It was suggested that locust bean gum deposited upon the fibers might affect the scattering coefficients of the fibers. If this were the case, any attempt to measure bonded area through use of the specific scattering coefficient would be in error. Therefore, it was important to know whether or not the presence of locust bean gum on the fiber surface affected the scattering coefficient and the magnitude of any effect under study.

A preliminary experiment was carried out in which unbonded sheets were made by forming the sheets from acetone and replacing the acetone with benzene. Various amounts of locust bean gum were added to the pulp in acetone suspension. The gum was in a finely divided form. In this way a mechanical mixture of gum and pulp was obtained in an unbonded form. It is emphasized that the gum was not adsorbed on the fiber but was present simply in mechanical mixture. The specific scattering coefficients of these sheets are given in the Table VII.

TABLE VII
SPECIFIC SCATTERING COEFFICIENTS OF GUM-PULP MIXTURE

Sample	Basis Weight, g./sq. cm.	Gum Added,* %	Specific Scattering Coefficient (s)	
1	0.072	0.0	279	
2	0.130	0.0	272	276
3	0.088	0.5	295	
4	0.160	0.5	285	290
5	0.084	2.0	286	
6	0.156	2.0	280	283
7	0.100	5.0	296	
8	0.176	5.0	299	298
9	0.108	20.0	349	
10	0.212	20.0	357	353

*Based on pulp

The results of this preliminary experiment indicated that locust bean gum might well have affected the scattering coefficient of a sheet. It was felt that the form of the locust bean gum in a sheet (i.e., smooth film, fine particles, irregular contour, etc.) would undoubtedly affect the

scattering coefficient, since it would affect the surface available for light scattering. The manner in which the sheet was treated before drying could affect the nature of the surface. For instance, the gum in a sheet dried from water might be present as a smooth film, whereas the gum present in a sheet treated with acetone and benzene before drying might be present in a precipitated form.

The bonded area measurement required determination of the specific scattering coefficients of both bonded and unbonded sheets and, therefore, it was necessary to determine the effect of locust bean gum on the scattering coefficients of fibers treated with water and of fibers treated with acetone-benzene. The procedure used for this experiment is given below.

PROCEDURE

In order to avoid any effect on the scattering coefficient resulting from variations in the degree of bonding or unbonding, it was decided that completely unbonded fibers would be used. In order to obtain completely unbonded fibers dried from water, it was almost essential that these fibers be dried in such a manner that there be little or no contact between the fibers during the drying process. Several possible methods, such as spray drying from dilute suspension, drying of fibers in a bed of inert material, and drying the fibers from a dilute suspension on a piece of filter paper, were considered. In view of the time requirements and some preliminary tests, the last method was chosen. The filter paper used for the experiment had to be colored so that the desired white fibers would be visible against the background. Upon dyeing filter papers with blue, black, and

red dyes, it was found that the fibers were most easily seen against the red background.

A number of Whatman No. 1 filter papers were dyed with Pontamine Fast Scarlet 4BS (a direct dye). The procedures outlined in Table VIII were used in an attempt to prevent subsequent bleeding of the dye from the filter papers to the white fibers.

TABLE VIII
DYE TREATMENTS OF FILTER PAPERS

Filter papers to be used for fibers-

Treatment	Dried from Water	Washed Successively with Acetone and Benzene
1	dye bath	dye bath
2	water bath	water bath
3	$\text{Al}_2(\text{SO}_4)_3$ -NaCl bath	acetone bath
4	dry	benzene bath
5	water bath	acetone bath
6	dry	water bath
7	-----	$\text{Al}_2(\text{SO}_4)_3$ -NaCl bath
8	-----	dry
9	-----	water bath
10	-----	acetone bath
11	-----	benzene bath
12	-----	dry

The fibers used in the experiment were prepared as follows. A sample of West Coast bleached sulfite pulp was soaked for 4 hours and then beaten for 35 minutes in the laboratory Valley beater with a bedplate loading of 5500 grams. The freeness of the pulp at the end of the run was 590 cc. Schopper-Riegler. The entire charge of pulp was then passed through a

Bauer-McNett classifier and the long-fibered fraction (retained on a 20-mesh screen) was collected. From 360 grams of pulp charged to the beater, 87 grams were recovered as the long-fibered fraction. Fractionation of the pulp was carried out to produce a more homogeneous material for the experiments. It was felt that the long-fibered fraction would be the only fraction easily recovered for scattering coefficient measurements.

Known amounts of fiber and locust bean gum were added to water so that a suspension of 0.50% consistency resulted. Agitation was supplied, and sufficient time was allowed for equilibrium adsorption of locust bean gum on the fibers. Small portions (10 to 15 ml.) of each suspension were diluted to one liter and filtered on a Büchner funnel, using the filter papers which had been dyed red. Light suction was applied during filtration. In this way, a large number of fibers were laid down so that contact with neighboring fibers was very limited. One set of fibers prepared in this manner was dried without further treatment. A second set was prepared in the same manner except that, before drying, a sheet of dry white filter paper (Whatman No. 1) was placed over the wet red filter paper containing the "individual" fibers while the red filter paper was still in the Büchner funnel. A watch glass was placed on top of the white filter paper and acetone was poured into the watch glass and allowed to overflow onto the filter paper. In this way the fibers which had been laid down with a minimum of contact were washed with acetone without disturbing the distribution or position of the fibers. Three washings with acetone and three washings with benzene were made, using a total of 500 ml. of each reagent. The watch glass and white filter paper were then removed, and the

red filter paper containing the washed fibers was allowed to dry.

The remaining fiber suspension from each sample was formed into pads on a Büchner funnel using a wire mesh. These pads were then analyzed for their locust bean gum content using the galactose method.

The individually dried fibers were next removed from the red filter papers with forceps (using a low-power dissecting microscope). Any fibers which appeared to be bonded to others over an appreciable area were discarded. The fibers which were removed were placed in a small tube of approximately 10 mm. diameter and, when sufficient fibers were collected, they were compacted into a small sheet using a glass rod of appropriate size. A sheet of Ethocel had been placed under the open end of the tube to receive the fibers. The pad of fibers was held against the Ethocel film by means of narrow strips of scotch tape placed at the edges of the sheet. A second sheet of Ethocel was placed over the fragile pad of fibers to protect it when it was not being tested.

Several years ago Adrian (99) developed a method for evaluating the opacifying properties of pigments. In the process of this work he formed films of pigments on Ethocel sheeting for study of the optical properties of the films. In order to determine the scattering coefficients of the pigments, Adrian found it necessary to have a chart peculiar to the backing which was used. Using several grades of commercial paper, Adrian determined the reflectances of (1) paper backed by magnesium carbonate, (2) paper backed by Ethocel and magnesium carbonate, (3) an opaque pad of paper, (4) paper backed by Ethocel and a black body, and (5) paper backed by a

black body. With the aid of the Kubelka and Munk theory (100) the necessary calculations were made and a suitable chart was prepared. The chart can be used to determine the scattering coefficient of a sample backed with Ethocel if the reflectances of sample-Ethocel-magnesium carbonate and sample-Ethocel-black body are determined.

Adrian's technique was used in this study to determine the scattering coefficients of the unbonded samples because it was found that the samples were too fragile to be tested in an unsupported state. His chart has been extended to cover an additional area used for determining the scattering coefficients of several samples in the present work. These data are found in the Appendix.

Because of the fact that the fiber specimens were in the form of such small sheets, the General Electric Recording Spectrophotometer (GERS) could not be used for the measurement of reflectances without making some alteration in the procedure. The so-called narrow-beam technique was used. Optical lenses (+10 diopter) were placed at both entrance portals of the integrating sphere of the GERS, using special brass holders. In order to eliminate stray light from contributing significantly to the reflectance, masks of black velour paper with openings 4 by 7 mm. were used at both sample positions on the integrating sphere. These openings were approximately 1/8 inch greater in both dimensions than the light beam so that translucency effects were of a minor order, if present at all. The size of the light source image used for illumination of the samples was decreased by blocking out the lower half of slit no. 1 of the GERS. A sheet of

aluminum foil served to block out the desired portion of the beam. The intensity of the light source was increased so that adequate sensitivity could be obtained. A GERS curve of one of the samples indicated that measurements could be made satisfactorily at 600 mmu. (600 mmu. is in the range covered by Adrian's chart). As indicated above, measurements of reflectance of the sample backed with Ethocel and magnesium carbonate, and Ethocel and a black body, respectively, were made so that the Adrian chart could be used.

In order to determine the specific scattering coefficient of the samples, the basis weight had to be determined. It was realized that the sheets which were prepared were not perfectly uniform. The greatest variations existed near the edge of the sheets because of the wall effects present when the sheets were formed. Therefore, it was decided that the optical measurements should be performed over areas not including the edges of the sheets. In all cases attempts were made to use a central portion of the sample with a diameter of approximately 6.5 mm. The basis weight sample was then taken as nearly as possible from this same section of the sheet. A steel punch with a hardened tip was used to cut the basis weight sample. The tool was held securely in an arbor press, perpendicular to the base. A smooth hard piece of thermosetting resin board was placed on the base and the sample with the protective Ethocel sheets was placed on the board. Pressure was then applied to cut out the sample. The sample was pushed out of the punch by a glass rod. The protective Ethocel disks were removed and the fibers were weighed on a microbalance.

The area of the specimens was determined by microscopic measurement of test portions cut out by the same punch. Low-power binoculars were used with eyepieces of 10 X magnification and objectives of 0.7 X magnification. The eyepiece micrometer was calibrated against a precision-marked machinist's rule.

Thus, it will be seen that the necessary and appropriate measurements have been taken so that the scattering coefficient and basis weight can be calculated. From these data, the specific scattering coefficients (\underline{s}) (101) of the various sheets can be determined.

RESULTS AND DISCUSSION

The locust bean gum contents of the fibers as determined by the galactose method are given below in Table IX. Analyses were run in triplicate.

TABLE IX
LOCUST BEAN GUM (LBG) CONTENTS OF
SCATTERING COEFFICIENT SAMPLES

Sample	Dried from water	acetone- benzene	LBG Added, %	LBG Adsorbed, %	Corrected LBG Adsorbed, %
1	x		0.00	0.104	0.069
2	x		1.16	0.83	0.72
3	x		4.62	1.19	1.50
4	x		11.57	1.84	1.71
5		x	0.00	0.082	0.100
6		x	1.17	0.83	0.64
7		x	4.70	1.12	1.54
8		x	11.78	1.68	1.52
					0.009
					0.091*
					0.77
					1.28
					1.87
					0.00
					0.68
					1.19
					1.78
					0.00
					0.65
					1.27
					1.61

*A control value of $\left[\frac{0.091 + 0.083}{2} \right] = 0.09\%$ is used.

The control value represents the galactose content of the pulp.

It will be seen that the control value was small in comparison with the gum contents involved. The amount of gum adsorbed by the fiber increased steadily with an increase in the amount of gum added. However, the ratio of gum adsorbed to gum added decreased steadily with increases in the amount of gum added. These results are in qualitative agreement with the results of similar experiments (78) using the anthrone technique, but the galactose method gave much lower absolute values of gum adsorbed than did the anthrone method.

The measurements of the diameter made on the basis weight samples are shown in Table X.

TABLE X

MICROSCOPIC MEASUREMENT OF DIAMETER

Calibration of Eyepiece Micrometer

Length Measured,* mm.					Eyepiece Micrometer Divisions				
6	6	6	6	6	94	93	94	94	93
"	"	"	"	"	94	94	94	94	93
"	"	"	"	"	94	93	94	93	94
"	"	"	"	"	94	95	94	95	94
Average 6					93.85				

1 scale division = 0.0640 mm.

*a different 6-mm. interval was used for each measurement

Measurement of Diameter of Punched Sample

Diameter of Sample (4 samples), scale divisions				
106	107	107	106	
107	107	108	106	
106	106	107	106	
106	106	106	105	

Average = 106.4 divisions

sample diameter = 0.682 cm.

sample area = 0.365 sq. cm.

Table XI shows values determined for scattering coefficients. The samples are numbered to correspond with those shown in Table IX.

TABLE XI
SCATTERING COEFFICIENTS OF UNBONDED
SAMPLES CONTAINING LOCUST BEAN GUM

Sample	<u>sw</u>		Weight, mg.			<u>s</u>	
1	1.01	1.16	1.334	1.571		276	269
2	1.17	1.22	1.531	1.615		278	276
3	0.98	1.09	1.348	1.548		266	257
4	1.14	0.80	0.79	1.392	1.246	1.144	291 234 252
5	2.08	1.33	1.657	1.045		458	465
6	2.32	2.53	1.694	1.777		499	520
7	2.24	2.13	1.696	1.693		482	459
8	2.99	2.52	1.990	1.720		549	535

Samples 1 to 4 dried from water

Samples 5 to 8 dried from acetone-benzene

The data from the experiment are summarized in Table XII.

TABLE XII
SUMMARY OF EXPERIMENT

Sample	Dried from		Gum	Gum	Specific Scattering Coefficient (<u>s</u>)
	water	acetone- benzene	Added, %	Adsorbed, %	
1	x		0.00	0.00	273
2	x		1.16	0.68	277
3	x		4.62	1.19	262
4	x		11.57	1.78	259
5		x	0.00	0.00	462
6		x	1.17	0.65	510
7		x	4.70	1.27	471
8		x	11.78	1.61	542

There are several interesting points to be brought out in connection with this experiment. It will be seen that the magnitudes of the specific scattering coefficients of water-dried fibers and acetone-benzene-dried fibers were quite different. It is emphasized that all the samples used were essentially completely unbonded, so that the difference in scattering coefficients was caused by some other factor. It would seem plausible to expect that the fibers dried from water would have a smaller surface area available for light scattering than those dried from acetone-benzene. That is, fibers dried from water would have fine fibrils drawn back to the parent fiber and cell pores closed up, whereas those dried from benzene would be essentially in the same condition as the wet fibers. Consequently, the fibers dried from water would be expected to have a smaller specific scattering coefficient. It can be seen by comparison of the specific scattering coefficients of sample 1 and sample 5 that approximately 60% of the surface of a water-dried fiber is unbonded; the remaining 40% is bonded. This is a measure of the intrafiber bonding which would exist in paper made from fibers of sample 1.

Observation of the fibers under a high-power microscope (200 X) revealed no obvious difference in the extent of fibrillation of the two types of fibers. This does not mean, however, that the extent of submicroscopic fibrillation was the same in both cases. The latter could have an appreciable effect upon the total surface and, thus, upon the specific scattering coefficient. When the two sets of fibers were viewed under a high-power microscope using dark-field illumination, it was noticed that the fibers dried from acetone-benzene displayed noticeably greater opalescence than

those dried from water. Thus, it seems probable that very fine fibrils and tiny cell pores were available for light scattering in the fibers dried from acetone-benzene; these would account for the higher specific scattering coefficients.

A second interesting point was the variation of specific scattering coefficients among the acetone-benzene-dried fibers. Analysis of variance showed that the values obtained were significantly different (at 1% level). However, there was no steady trend of the scattering coefficients with a change in gum content. It was suspected that the manner in which the gum particles were precipitated on the fiber surfaces had a large influence upon the specific scattering coefficient. If precipitation were rapid and fine particles were formed, greater surfaces would be available for light scattering. Unfortunately, the precipitation process is not easily controlled, so that identical precipitation conditions could not be assured. It should be pointed out, however, that the specific scattering coefficients of all the samples containing gum were larger than that of the sample containing no gum. This fact further indicates that the gum was precipitated in some form (presumably fine particles) which gave rise to a larger surface for light scattering.

The third and most important part of the results was concerned with the fibers dried from water. Although there appeared to be a slight trend toward decreasing specific scattering coefficient with increasing gum content, analysis of variance revealed that this was far from significant when compared with the variation within the sample. Thus, the assumption that

all the samples came from the same population could not be invalidated and it is concluded that the presence of locust bean gum upon fibers dried from water had no effect upon the specific scattering coefficients of such fibers. As a result, the bonded area measurements as proposed by Parsons (57) and Ratliff (21) could be used without application of correction factors. The implication of the results was that the gum dried upon the fiber surface in a thin smooth film in optical contact with the fiber when the fiber containing gum was dried from water. In this way, a fiber containing locust bean gum could have essentially the same surface available for light scattering as a similar fiber containing no gum.

As a result of these studies, the following procedure was advised for determination of bonded area. The specific scattering coefficients of all bonded sheets of a particular series (with various gum contents) would be measured. Unbonded sheets (containing no gum) of the same series would be prepared for measurement of specific scattering coefficient. The bonded area of all bonded sheets would be determined by comparison of specific scattering coefficients with that of the unbonded sheet containing no gum. This procedure assumed only that the presence of locust bean gum had no effect upon the specific surface of a pulp.

MEASUREMENT OF THE SPECIFIC SURFACE OF PULPS CONTAINING LOCUST BEAN GUM

PROCEDURE

Although several methods were available for the measurement of the specific surface of pulp fibers, the silvering technique was the only suitable method for this work in view of the time and/or equipment required by the other methods. The method was originally developed by Clark (59) but has received additional study by McEwen (60) and Browning (61). The most recent modifications are embodied in a proposed TAPPI method (62) and these modifications were adopted in the present work.

Keeney (9) has shown that the specific surface of the various fractions of a beaten pulp increases greatly as the particle size decreases. He showed that settled fines and centrifuged fines have specific surface areas of 100,000 to 400,000 square centimeters per gram as compared with whole pulp specific surface areas of 25,000 to 45,000 square centimeters per gram.

The fact that fine cellulosic particles had such high values of specific surface raised the question of whether locust bean gum as a colloidal dispersion might not also have an enormous surface. If the gum did have a large surface area its presence with a pulp would undoubtedly affect the value obtained for the specific surface even though only small amounts of gum were present.

An experiment was designed to determine the specific surface of a locust bean gum dispersion and to show the effect of added locust bean gum upon the specific surface of pulps with various degrees of beating. One

per cent locust bean gum was added in each case. The pulp was beaten in the laboratory Valley beater with a bedplate loading of 5500 grams.

RESULTS

The locust bean suspension was found to have a specific surface of 215 sq. cm./g. The results of the experiment with pulps of different freenesses are shown in Table XIII.

TABLE XIII
SPECIFIC SURFACES OF PULPS WITH VARIOUS DEGREES
OF BEATING (WITH AND WITHOUT GUM)

Sample	Beating Time, min.	Freeness, cc. S.-R.	Gum Added, %	Specific Surface, sq. cm./g. measured			Average
1	0	915	0.0	6800	8600	8830	8100
2	0		1.0	8980	8340	7450	8400
3	15	860	0.0	11120	11120	11290	11500
4	15		1.0	11190	10860	12110	11600
5	30	730	0.0	12500	14030	16000	14200
6	30		1.0	14570	13580		14100
7	45	595	0.0	15250	13620	14310	14400
8	45		1.0	18300	17550	17950	17900
9	60	420	0.0	17970	17170		17500
10	60		1.0	20200	18590		19300

As will readily be seen, the locust bean gum suspension had an extremely low (essentially negligible) apparent specific surface. The data in Table XIII showed a remarkable agreement between the specific surface values of pulp alone and pulp plus added locust bean gum for the first three beating intervals. The agreement was at least to some extent fortuitous as was seen by comparison of variations within and between samples. However, there appeared to be a difference for the two samples during the last two beating intervals. Whether or not a real difference exists is open to some question

because of the large variations involved for so few samples.

The conclusions from this experiment are listed below.

1. Locust bean gum suspensions have no appreciable surface of their own as measured by the silvering technique.
2. The presence of locust bean gum has no effect upon the measurement of specific surface in the cases of unbeaten, lightly beaten, or moderately beaten pulps.
3. The presence of locust bean gum in more highly beaten pulps has an uncertain effect upon the specific surface as measured by the silvering technique. It would appear that the gum causes higher values of specific surface.

In view of the results obtained from the experiment, it was decided that the specific surface measurements would be confined to pulps not treated with locust bean gum.

GENERAL EXPERIMENTAL AND TESTING PROCEDURES

PROCEDURES DEALING WITH LOCUST BEAN GUM

DETERMINATION OF LOCUST BEAN GUM CONTENT OF PAPER

The procedure for the determination of the locust bean gum content of paper by the newly developed galactose method has been presented in a previous section.

DETERMINATION OF CONCENTRATION OF LOCUST BEAN GUM DISPERSIONS

A sample of the dispersion (approximately 10 ml.) was pipetted onto a tared 3-inch watch glass and weighed on an analytical balance. The sample was then evaporated to dryness on a steam bath and placed in an oven at 105°C. for five to ten minutes to remove moisture. It was next cooled in a desiccator and weighed on an analytical balance. The concentration was expressed as percentage by weight.

DETERMINATION OF VISCOSITY OF LOCUST BEAN GUM DISPERSIONS

The viscosity of samples of locust bean gum dispersions (approximately 0.5%) was determined in a constant temperature bath ($25 \pm 0.01^\circ\text{C}.$) using an Ostwald-Fenske viscometer No. 400. The same viscometer was used for all determinations. The results were expressed in seconds (time of flow). The flow time for water was 1 to 2 seconds.

PULP TREATMENT AND SHEET PREPARATION

PULP REFINING

All pulps were beaten in the laboratory Valley beater as described in Institute Method 403. The beating intervals used were arbitrary and, in

most cases, the entire charge of the beater was removed when the desired degree of beating was obtained.

TREATMENT OF PULPS WITH LOCUST BEAN GUM

When pulps were treated with locust bean gum, the gum was added after the beating had been completed and prior to freeness testing and sheetmaking. Weighed portions of locust bean gum stock solution of accurately known concentration were added to the pulps and at least one hour was allowed for attainment of equilibrium adsorption of the gum by pulp before sheet preparation.

FREENESS TESTING

The Schopper freeness tester was used as described in Institute Method 414. The freeness of samples with and without added locust bean gum was determined. The results were expressed as cc. S.-R.

SPECIFIC SURFACE TESTING

The specific surface was determined by the silvering method according to the proposed revision of TAPPI method T 226 sm (62). In this method a continuous film of metallic silver is deposited on the surfaces of fibers and fibrils by virtue of their reducing properties. The deposited silver is capable of catalytically decomposing a dilute solution of hydrogen peroxide. By comparison of the amount of hydrogen peroxide decomposed by silvered fibers with the amount decomposed by silvered cellophane of known surface area (obtained from a calibration chart), the surface area of the fibers is determined. In this study, the specific surface was determined

only on pulps containing no locust bean gum. The results were expressed in square centimeters per gram.

SHEET PREPARATION

Preparation of handsheets was carried out according to Institute Method 411 using the British sheet mold. The only modification in the procedure was that, for standard conditions, a 15-second interval was allowed between removal of the perforated stirrer and opening of the drain (instead of 10 seconds recommended in the procedure). Other variations in the sheetmaking and pressing operations were made in certain cases and are discussed below. However, unless specifically mentioned, the standard conditions were used.

VARIATION OF FORMATION

In part of the work to follow the formation of handsheets has been purposely varied by variation of sheetmaking conditions. These variations are listed below in tabular form. Procedure C was the standard procedure.

Procedure	Depth of Stock, cm.	Volume of Stock, ml.	Flocculation Time, sec.
A	5	1000	30
B	10	2000	20
C	35	7000	15
D	35	7000	0

VARIATION OF WET PRESSURE

The standard condition of wet pressing is given in Institute Method 411; 50 pounds per square inch pressure is used. Two pressings are used; the first is for five minutes and the second is for two minutes. For special sheets, the following pressures will be used.

Designation	First Pressing, p.s.i.	Second Pressing, p.s.i.
15 p.s.i. wet pressing	15	15
200 p.s.i. wet pressing	50	200
1000 p.s.i. wet pressing	50	1000

PAPER TESTING

FORMATION

Formation was measured on the Thwing formation tester. The procedure is described in Institute Method 525. The design and principle of the instrument have been discussed in the literature (102-104). The instrument consists of a pair of glass plates mounted on a vertical shaft. The paper sample is held between these plates. Above the plates is a light source on a separate mounting and below the plates is a photoelectric cell on the same mounting as the light source. The glass plates rotate and the light source and photocell oscillate so that the specimen is thoroughly scanned. The transmitted light received by the photocell is a measure of the regularity of the structure of the paper. By means of appropriate electrical systems, the fluctuation in transparency is compared with the average transparency to give a measure of formation. It will be seen that the basis weight is not involved in the measurement.

BONDED AREA

Bonded area was measured by the optical method. The method was developed by Parsons (57) but has since been modified (21, 58). In principle, the method makes use of the fact that the specific scattering coefficient of pulp fibers is proportional to the surface area of the fibers. Bonded and unbonded sheets are prepared and their specific

scattering coefficients are determined. When the surface area of the unbonded fibers is determined, the area corresponding to the scattering coefficient of the unbonded sheet becomes known. The scattering coefficient of the bonded sheet corresponds to the area of that sheet contributing to scattering; the difference between the two areas is considered to be the bonded area. The method assumes that the area of optical contact is also the area of bonding. The results were expressed as square centimeters per gram (specific bonded area) and as percentage bonded area.

The preparation of unbonded sheets is carried out as follows. A handsheet is prepared from water in the normal fashion. Instead of couching the wet sheet from the wire, a piece of 18.5-cm. Whatman No. 1 filter paper is placed over the sheet and the cylinder is returned to the vertical position. Three 500-ml. portions of acetone are passed through the sheet to replace the water. Three 500-ml. portions of benzene are then passed through the sheet to remove the acetone. After removing the filter paper, the sheet is covered with a blotter and rubbed very lightly. The sheet is carefully removed from the wire while still moist with benzene and is allowed to dry. Drying the fibers from a nonpolar liquid such as benzene leaves them in an essentially unbonded condition. The use of benzene in place of butanol has been advocated by Keeney (9) and was adopted for this work.

BONDING STRENGTH

The bonding strength was determined with the aid of the recently developed bonding strength tester (105, 106). In this test a steel wheel

with a finely ground surface is coated with a film of oil and made to roll over a paper surface. The oil-coated wheel, carrying a known load, is made to roll over the paper surface with a known acceleration by controlling the acceleration of the paper-carrying wheel.

When the wheel rolls over the paper strip, it carries with it a film of oil. As the wheel moves away from the paper, a tensile stress is applied to the oil film at the trailing nip. The oil film, because of its viscosity, resists this stress and exerts corresponding forces upon the oil-coated wheel and the paper surface. As the rate of separation of the oil-carrying wheel and the paper surface is increased, the force exerted by the oil film is increased and, at some critical rate of separation, this force becomes great enough to cause breaking of the bonds in the paper and rupture of the strip occurs. The velocity of the wheel relative to the paper surface at this instant is called the critical velocity. It has been found that the product of the critical velocity and the viscosity of the oil is constant for a given bonding strength.

The oil films used were polyisobutylene with various viscosities (various degrees of polymerization). The film thickness was 0.0010 inch. The load per linear inch of contact was 130 pounds. A new modification of the method, known as prefilming (107), was used in order to eliminate the effects of surface roughness. With this technique, the specimen was coated with a film of high-viscosity polyisobutylene before the test was run. The results were expressed as kilopoise-centimeters per second.

ZERO-SPAN TENSILE TEST

The zero-span tensile strength was determined according to Institute Method 527, using a set of jaws of more recent design (108). The new set of jaws was constructed so that a desired clamping load could be applied to the specimen. A clamping load of 360 pounds on each jaw was used. The speed of the tester was 3.0 inches per minute. The results are expressed as pounds per 1.5-inch width per 100 pounds basis weight.

LOAD-ELONGATION TEST

The Baldwin-Southwark universal tester was used for this work. The instrument and the procedure of operation have been described (109) and consequently will not be covered here. A new set of jaws recently obtained from the Instron Engineering Corporation greatly facilitated lining up the specimen and were used in this study. Specimens 1.5 inches wide were tested with a 2-inch jaw span. A constant rate of elongation of 0.10 inch per minute was used. Specimens were stressed to failure and the ultimate tensile strength and elongation were noted. The tensile strength was expressed as pounds per 1.5-inch width per 100 pounds basis weight. The elongation was expressed as percentage elongation.

OTHER TESTS

The other tests which were run need no discussion and are covered by Institute Methods (80). They are listed below.

Test	Institute Method
Basis weight (25 x 40--500)	411
Bursting strength	510
Tearing strength	512

PRELIMINARY INVESTIGATIONS

EFFECT OF TIME OF TESTING UPON THE STRENGTH PROPERTIES OF HANDSHEETS

INTRODUCTION

It has been said that the strength properties of machine-made papers are dependent upon the time elapsed between drying and testing. The object of this section of the work was to determine whether or not such an effect was present in the case of handsheets and, if so, the magnitude of the effect.

PROCEDURE

West Coast bleached sulfite pulp was beaten for 20 minutes in a laboratory Valley beater using a bedplate loading of 5500 grams. Portions of the pulp were treated with various quantities of locust bean gum and handsheets were prepared. Seventy-five handsheets of each variety were prepared. Fifty of these sheets were used for tensile, burst, and tear testing, and the remaining 25 were used for bonding strength V.V.P. testing. Several batches of pulp were used for the experiment but, for any given run, a single pulp was used. The beating time (20 minutes) and freeness (865 to 870 cc. S.-R.) were the same for all the batches.

Four distinctions were made with reference to gum added. These were:

- (1) No gum added,
- (2) 2% gum added,
- (3) 5% gum added, and
- (4) 5% gum added, sheets water washed.

The amount of gum added was based upon the pulp used. The third and fourth classifications differ only in that water washing of the sheets was carried out in group four. The procedure was similar to that used in preparing unbonded sheets. A sheet of filter paper was placed over the wet, freshly formed sheet on the sheet mold and fresh water (three washings of 500 cc. each) was drawn through the sheet. This was done in an attempt to remove gum which was loosely held in the large capillary structure of the sheet. It was noticed that the sheets which were washed were thin near the edges, so that the basis weight of these samples and strength factors based on the basis weight may be misleading. However, the results within the group are comparable.

The times from start of drying to testing were approximately 12 hours, 36 hours, 84 hours, 132 hours, and 300 hours. All handsheets within a single group (50 for tensile, burst, and tear; 25 for V.V.P.) were randomized, using a table of random numbers before arranging into time-for-testing groups. Table XIV illustrates the batches of pulp used, the amount of gum added, and the time of testing for various groups.

TABLE XIV
TESTING SCHEDULE

Tests	Pulp	Gum Groups	Testing Times, hrs.				
T,T,B	A	1	13-1/2	36-1/2	84-1/4	132-1/2	348
T,T,B	A	2	12	36	90	132-1/4	324-1/2
T,T,B	B	3	14	42	84-1/4	136-1/2	373-1/2
T,T,B	B	4	10-1/4	38	80-1/4	132-1/2	369-1/2
VVP	C	1	21	45	93	141	309
VVP	C	2	21	45	93	141	309
VVP	C	3	21	45	93	141	309
VVP	C	4	21	45	93	141	309

RESULTS AND DISCUSSION

The results have been summarized and appear below in Table XV. For each entry, 20 burst, 10 tensile, 5 tear, or 5 V.V.P. tests were made.

TABLE XV
DRYING-TO-TESTING-TIME STUDY

Gum Group No. 1 (0.0% gum added)

Time, days	Tear Factor	Burst Factor	Tensile* Factor	VVP, kilopoise-cm./sec.
0.5	1.61	61.6	0.208	195.9
1.5	1.58	60.9	0.211	197.1
3.5	1.65	61.2	0.212	192.9
5.5	1.61	58.9	0.202	183.6
12.5	1.60	56.2	0.211	179.1

*Expressed here as lbs./100 lbs. basis weight (15 cm. width)

TABLE XV (continued)

DRYING-TO-TESTING-TIME STUDY

Gum Group No. 2 (2.0% gum added)

Time, days	Tear Factor	Burst Factor	Tensile* Factor	VVP, kilopoise-cm./sec.
0.5	1.33	92.1	0.285	667.4
1.5	1.29	93.5	0.278	685.9
3.5	1.29	83.4	0.286	622.6
5.5	1.28	89.4	0.281	656.9
12.5	1.31	89.1	0.286	678.8

Gum Group No. 3 (5.0% gum added)

Time, days	Tear Factor	Burst Factor	Tensile* Factor	VVP, kilopoise-cm./sec.
0.5	1.23	96.6	0.288	782.3
1.5	1.22	97.9	0.296	789.9
3.5	1.15	97.1	0.287	690.8
5.5	1.18	98.8	0.294	880.1
12.5	1.15	99.2	0.289	782.0

Gum Group No. 4 (5.0% gum added, water washing)

Time, days	Tear Factor	Burst Factor	Tensile* Factor	VVP, kilopoise-cm./sec.
0.5	1.35	101.5	0.314	740.1
1.5	1.29	98.8	0.315	774.0
3.5	1.31	101.4	0.309	707.8
5.5	1.25	100.0	0.309	866.3
12.5	1.30	99.1	0.305	777.7

*Expressed here as lbs./100 lbs. basis weight (15 cm. width)

It was apparent from the above results that there was no significant trend or difference in the strength properties of the various time samples. Therefore, future testing could be carried out at any time from 0.5 to 12.5 days after the start of drying without fear of changing strength

properties. There was no reason to believe that the strength properties would change after 12.5 days.

Comparison of the samples with and without gum showed clearly that the gum imparted strength properties to the sheet similar to those which would be expected with additional beating of the pulp. Comparison of the samples with 2% gum added and those with 5% gum added was not advisable because different batches of pulp were used for these sets of sheets. Comparison of the V.V.P. values for the two pulps with 5% gum added gave reason to suspect that the washing procedure had little effect other than causing an unevenness in the sheet basis weight. Actually, it would appear that very little gum would be held in the capillaries of the sheet because of the very high dilution used in the sheetmaking process.

EFFECT OF LOCUST BEAN GUM VISCOSITY UPON STRENGTH PROPERTIES OF HANDSHEETS

INTRODUCTION

Very early in the investigative work it was noticed that the viscosity of a locust bean gum dispersion (0.5%) dropped regularly from day to day, even when stored in the refrigerator. This effect is shown by Table XVI. The drop in viscosity indicated that degradation of the gum was taking place and that the average degree of polymerization was being decreased. The mechanism of this reaction was not known and no attempt was made to study it, but it was believed that the action was principally micro-biological in nature. However, if the stock solution of the gum were to be stored for any period of time, appreciable degradation would occur which could affect the strength properties of paper made with the gum. Thus, a

TABLE XVI

GUM VISCOSITY-TIME RELATIONSHIP

Elapsed days	Viscosity, sec.	Elapsed days	Viscosity, sec.
0	140.4	7	108.7
1	130.3	9	104.8
2	123.7	13	97.2
3	120.2	19	87.8
4	118.6	25	69.2
5	114.5	31	23.1*

*Colonies of micro-organisms were visible in the gum solution when this test was made.

Flow time for water = 1 to 2 seconds.

section of the program was devoted to a study of the effect of the viscosity of locust bean gum upon the strength properties of papers made with the gum samples.

PROCEDURE

The experimental work was divided into two portions. Initially, the experiment was performed using a lightly beaten pulp. The first part of the experiment was set up in such a way that only two batches of pulp and a single starting locust bean gum solution were used.

One large batch of gum solution was prepared so that the concentration of all viscosity samples would be identical. The solution was divided into eight different portions and the initial viscosity of each of these portions was checked and found to be substantially the same. Two samples were then stored at each of four different temperatures--3°C., 25°C., 37°C., and 60°C.--in order to produce different rates of degradation. The

viscosities of one set of samples were measured at the end of 2 and 3 days and portions of these samples were used at those times for handsheet preparation. One batch of pulp was used with these samples. The viscosities of the other set were measured at the end of 4 and 5 days and the second batch of pulp was used with these samples. The pulps were beaten for 20 minutes in the laboratory Valley beater with a bedplate loading of 5500 grams. The freeness was 860 cc. S.-R. Two per cent locust bean gum was used for all sheets.

Fifteen handsheets were prepared for each gum sample; five were used for V.V.P. testing and the other ten were used for tensile, tear, and burst testing. The samples were randomized before testing.

The second part of the experiment was carried out using one batch of pulp beaten for 40 minutes in the laboratory Valley beater with a bedplate loading of 5500 grams. The freeness was 655 cc. S.-R. A single gum suspension was again used. This part of the experiment was undertaken because it was pointed out that the pulps used in the first part of the experiment were very lightly beaten and that the extent of adsorption of gum was probably small. Conceivably, selective adsorption of higher D.P. material could have occurred. In this way all the paper samples would have contained the same small amount of high D.P. locust bean gum and no difference in strength properties would be expected.

The procedure for the second part of the experiment was similar to that in the first part. However, because of the similarities obtained for

the tensile, tear, and burst tests, the bonding strengths of the sheets were not determined. The strength characteristics of the untreated pulps were measured in this section of the experiment.

RESULTS AND DISCUSSION

The summary of the results of the first part of the experiment are shown in Table XVII.

TABLE XVII
GUM VISCOSITY-PAPER STRENGTH RELATIONSHIP

Sample	Viscosity, sec.	Tear Factor	Burst Factor	Tensile* Factor	VVP, kilopoise-cm./sec.
1	125.5	1.43	75.8	0.232	369.3
2	127.7	1.47	73.9	0.224	338.6
3	127.3	1.50	79.1	0.236	376.9
4	94.2	1.52	81.5	0.256	399.7
5	119.1	1.53	82.0	0.240	415.3
6	87.5	1.50	77.9	0.246	369.2
7	120.0	1.55	82.6	0.256	379.5
8	87.3	1.61	85.0	0.256	387.0
9	117.1	1.82	74.9	0.240	299.1
10	45.6	1.81	76.5	0.241	293.4
11	9.1	1.87	78.1	0.246	312.0
12	83.4	1.87	76.6	0.240	321.8
13	112.3	1.96	75.0	0.252	312.9
14	8.0	1.81	80.5	0.254	300.4
15	2.2	1.92	68.9	0.227	229.5
16	79.5	1.71	76.0	0.244	303.6

*Expressed as lb./100 lb. basis weight (15-cm. width)

Samples 1 to 8 were made with one batch of pulp and samples 9 to 16 were made with a second batch of pulp.

It was seen that there were no significant differences in the strength properties of the various samples regardless of viscosity of the gum with

the exception of sample 15. The viscosity of the locust bean gum employed in samples 11 and 14 was very low, but the strength properties of these samples were comparable with those of high-viscosity samples. Therefore, it was concluded that the viscosity of the gum had no effect on the strength properties of the paper unless the viscosity of the gum was extremely low. It is to be pointed out that the viscosity of gum stored in the refrigerator under normal conditions for 31 days did not drop nearly to the level where any effect on strength properties would occur.

The results of the second part of the experiment are shown in Table XVIII. Samples A and B contained no locust bean gum. All other samples had 2% gum added to the pulp.

TABLE XVIII

EFFECT OF LOCUST BEAN VISCOSITY ON
STRENGTH PROPERTIES OF HANDSHEETS

Sample	Temp., °C.	Storage, days	Viscosity, sec.	Tear Factor	Burst Factor	Tensile* Factor
A	----	2 (pulp)	-----	2.25	85.2	0.299
B	----	5 (pulp)	-----	2.36	81.7	0.301
1	3	2	132.9	1.80	107.8	0.360
2	25	2	130.9	1.82	107.8	0.352
3	37	2	127.2	1.79	110.5	0.363
4	3	3	130.1	1.85	110.2	0.373
5	25	3	125.4	1.92	108.6	0.373
6	3	4	126.1	1.82	111.1	0.364
7	37	7	40.4	1.71	112.7	0.362
8	37, 25, 37	4, 1, 2	40.4	1.73	112.0	0.387
9	37	3	26.6	1.78	110.6	0.369
10	25, 37	4, 3	10.0	1.76	112.2	0.394

*Expressed as lb./100 lb. basis weight (15-cm. width).

It was apparent from Table XVIII that the change in viscosity of the locust bean gum had no appreciable effect upon the tear factor and burst factor for handsheets containing gum. Examination of the tensile strengths revealed that samples 8 and 10 (low-viscosity samples) had greater tensile strengths than the sheets prepared with high-viscosity gum samples. Although these two samples (8 and 10) seemed to have appreciably greater tensile strengths than the other samples, it is to be pointed out that samples 7 and 9 (also made with low-viscosity gum samples) had tensile strengths comparable with the other samples in the series. Therefore, it seemed logical to conclude that the decreases in locust bean gum viscosity observed were not associated with the strength properties of handsheets made from pulps containing the gum. Any effect (in the range studied) would appear to have been in the same direction as additional beating of the pulp. These results were in agreement with the results of the first part of the experiment.

Comparison of samples A and B with the samples containing locust bean gum revealed the magnitude of the effect of locust bean gum upon the strength properties of the handsheets.

INVESTIGATION OF THE REASONS FOR STRENGTH INCREASE WHEN BEATER ADHESIVES ARE USED

INTRODUCTION

The primary object of the program of study was to investigate the reasons for the increase in paper strength when beater adhesives were used. The work which has been reported in the earlier portions of the thesis was devoted to laying a sound foundation for this study.

The major portion of the historical review was devoted to a coverage of the literature concerned with beating, bonding, and the strength characteristics of paper. As a conclusion of that section, it may be said that the strength of a sheet of paper is primarily dependent upon the following four factors:

- (1) the strength of the fibers,
- (2) the strength of the bonds,
- (3) the number of bonds, and
- (4) the formation (distribution of fibers and bonds).

It is felt that beater adhesives bring about an increase in strength by affecting one or more of these factors. The object of this portion of the program was to investigate the effect of locust bean gum upon each of the factors contributing to paper strength and to relate any effect to its consequent effect upon the strength properties of the paper. It was immediately recognized that a test would be required to measure each of the factors involved. It would indeed have been difficult to obtain an absolute measure of each factor; however, methods of testing were available which gave satisfactory estimates.

The zero-span tensile test was used for estimation of the strength of the fibers. It was known that the zero-span tensile strength was affected by bonding (58). However, after the initial stages of beating there are only small changes in this property. Thus, it was felt that the test would be reliable for comparison of the strength of fibers which had been moderately beaten. The comparison made was between pulps containing various amounts of locust bean gum.

The strength of the bonds was measured by the new bonding strength tester discussed in an earlier section. The quantity measured was the strength of an aggregate of bonds and not the strength of the individual bonds. The strength of the individual bonds was believed to be more nearly related to one of the following quantities:

- (1) bonding strength/specific bonded area;
- (2) bonding strength/percentage of bonded area

These quantities were intended to represent the total bonding strength divided by the number of bonds or the actual strength of an individual bond.

The optical method for determining bonded area was used as a measure of the number of bonds. Actually, the method gives a measure of the area in optical contact. It is believed that the distances of separation of surfaces involved for optical contact and for bonding are of different orders of magnitude. If optical contact involves distances of, say $1/10$ of the wavelength of light, the distance of separation would be 500 Angstrom units as compared with 5 Angstrom units for hydrogen bonding.

Therefore, the optical method can hardly measure the true bonded area but it can measure a quantity which is related to the true bonded area. This is probably the case, for one would not expect two surfaces to be in optical contact unless bonding were involved. Throughout these studies it was assumed that the area of optical contact was proportional to the bonded area.

Formation was measured by the Thwing formation tester. It was felt that this instrument gave a better measure of the quantity desired than any of the other tests used to measure the factors contributing to paper strength.

In addition to selecting tests to measure the factors contributing to paper strength, it was also necessary to determine the strength properties of the paper. These were measured by the following tests:

- (1) bursting strength,
- (2) tearing strength, and
- (3) load-elongation properties (tensile and elongation).

Since the gum probably produces an effect upon more than one factor, it is necessary to determine the effect of changes in the individual factors upon paper strength in the absence of locust bean gum.

Changes in formation and bonded area were readily produced (independently) by variation of sheetmaking conditions and by variation of wet pressing conditions. The effect of changes in these two factors upon paper strength were studied as part of the present investigation. Thus,

comparison of changes in strength properties produced by the gum with those produced by changes in formation (or bonded area) in the absence of gum would reveal the importance of any change in formation (or bonded area) produced by the gum. That is, a given change in formation would produce a given change in strength properties (in the absence of gum), and only a corresponding change in strength properties could be attributed to the change in formation produced by the gum. Any other change in strength properties must have been due to a change in one of the other factors caused by the presence of the gum.

The strength of the fibers is not easily controlled or varied. For this study no attempt was made to produce any variation. The effect of the gum upon the fiber strength was studied at various beating intervals in order to determine whether or not any appreciable changes were produced by the gum.

The variations of formation and bonded area were compounded so that the bonding strengths of sheets with and without gum could be compared at similar levels of bonded area and formation. In this manner the effect of the gum upon the bonding strength could be ascertained. Comparison of the effect of changes in bonding strength upon the strength properties of sheets with and without gum would indicate the importance of any changes produced in bonding strength by the gum.

PROCEDURE

West Coast bleached sulfite pulp was soaked overnight, disintegrated in the Williams disintegrator, and broken up in the laboratory Valley

beater for five minutes with no load upon the bedplate prior to beating. Each charge to the beater consisted of 360 grams of ovendry pulp. The pulp was beaten for the desired beating interval and then dropped from the beater. The beating intervals used were as follows: 0, 20, 35, 50, and 65 min. One batch of pulp was sufficient for each of the 0, 20, and 65-minute intervals. However, three batches were required for the 35 and 50-minute intervals. The three batches were beaten successively and combined in both cases.

Locust bean gum (as 0.5% stock solution) was next added to appropriate portions of pulps from each beating interval. The quantities used were as follows: 0, 0.5, 2.0, and 5.0%. The gum-pulp mixture was agitated and allowed to stand at least one hour for attainment of equilibrium adsorption. Freeness measurements were then made, using appropriate quantities of the slurries. The remaining pulp was diluted to a suitable consistency for sheetmaking (approximately 800 ml.). The sheetmaking and wet pressing conditions have been covered in an earlier section. The variations in sheetmaking and wet pressing conditions were compounded so that 16 sets of sheets (without gum) were produced for each of the 35 and 50-minute beating intervals.

Each set of sheets produced contained 20 handsheets. All sheets were randomized before testing. Eight sheets were used for bonding strength testing; the remaining 12 were used for optical and strength testing. The sheets containing locust bean gum were saved (after testing was completed) for analysis of the gum content by the galactose method. In addition to

these handsheets, one sheet was prepared from each beating interval for measurement of specific surface. These sheets were prepared in the normal manner, so that the specific surface would represent the surface of the fibers actually present in the sheet and not those of the pulp before sheetmaking.

The design of the experiment is shown schematically in Table XIX. Each possible combination for any given beating time was used.

TABLE XIX
EXPERIMENTAL DESIGN

Beating Time, min.	Gum Added, %				Formation Condition							
0	0	0.5	2.0	5.0	C				50			
20	0	0.5	2.0	5.0	C				50			
35	0	0.5	2.0	5.0	A	B	C	D	15	50	200	1000
					C				50			
50	0	0.5	2.0	5.0	A	B	C	D	15	50	200	1000
					C				50			
65	0	0.5	2.0	5.0	C				50			

The different tests used have been covered previously. The testing schedule is shown below.

1. S.-R. freeness--on each beating interval and each quantity of locust bean gum added
2. Specific surface--on each beating interval
3. Gum content--on each interval and each quantity of locust bean gum added
4. Bonded area--unbonded sheets--each beating interval and each formation value (no gum); bonded sheets--each individual sample

5. Zero-span tensile--on each beating interval and each quantity of locust bean gum added
6. Formation--on each beating interval, each quantity of locust bean gum added, and each formation condition
7. Bonding strength--each individual sample
8. Bursting strength--each individual sample
9. Tear strength--each individual sample
10. Load-elongation (tensile and stretch)--each individual sample

The number of tests of each type carried out were as follows.

Test	Number of Readings or Tests Made
S.-R. freeness	3
Specific surface	4
Gum content	4
Bonded area	12
Zero-span tensile	8
Formation	12
Bonding strength	8
Bursting strength	16
Tear strength	8
Load-elongation	8

PRESENTATION OF DATA

The data obtained from the experiment have been summarized in Table XX. The graphs which follow are based entirely on the data from Table XX.

The following comment is to be made in connection with the bonding strength testing. An improper prefilming technique was used for samples 1 to 5, so that these results are to be regarded with suspicion. Most of the other bonding strength tests were made using a prefilm of Vistax No. 4 (polyisobutylene) film 0.0010 inch thick. Test film thicknesses were also

TABLE XX
SUMMARY OF EXPERIMENTS

Sample Number	Heating Time (minutes)	Locust Bean Gum Added (%)	Sheet Forming Condition	Wet Pressing Condition (psi)	Freeze (cc. S.R.)	Specific Surface (sq. cm./gr.)	Locust Bean Gum Content (%)	Basis Weight (lb./ream) (25 x 40-500)	Thwing Formation Number	Bonded Area (%)	Bonded Area (sq. cm./gr.)	Bonding Strength (kilopoise-cm./sec.)	Zero-Span Tensile Strength (lb./100 lbs.) (1.5 in. width)	Bursting Strength (psi./100 lbs.)	Tear Factor (gr. per sheet/100 lbs.)	Tensile Strength (lb./100 lbs.) (1.5 in. width)	Elongation (%)
1	0	0.0	C	50	900	7630		44.1	35.9	21.5	1640	(48)	0.932	18.1	1.03	0.079	2.0
2	0	0.5	C	50	895		0.16	44.3	60.4	23.2	1770	(120)	1.023	18.1	1.40	0.156	2.6
3	0	2.0	C	50	905		0.76	45.7	63.4	25.0	1910	(176)	0.923	18.6	1.97	0.171	3.3
4	0	5.0	C	50	905		0.59	46.1	61.0	24.0	1830	(147)	1.013	19.5	1.96	0.186	3.5
5	20	0.0	C	50	810	10500		47.4	40.2	62.4	6550	(312)	1.312	69.4	1.39	0.633	5.3
6	20	0.5	C	50	790		0.44	46.2	48.7	44.2	6730	574	1.387	90.9	1.19	0.755	6.2
7	20	2.0	C	50	740		1.52	45.8	54.7	66.3	6960	833	1.465	95.6	1.06	0.825	6.8
8	20	5.0	C	50	720		1.90	45.4	51.6	68.8	7220	1022	1.486	102.6	0.99	0.828	6.6
9	35	0.5	C	50	590		0.56	44.8	36.8	78.5	9700	719	1.333	94.0	0.93	0.788	6.8
10	35	2.0	C	50	465		1.49	41.5	41.5	80.3	9910	1088	1.430	108.9	0.88	0.876	6.8
11	35	5.0	C	50	380		2.27	46.1	36.1	83.2	10270	1818	1.440	111.9	0.86	0.902	6.9
12	35	0.0	A	15				46.2		69.0	8510	240		56.7	1.29	0.556	4.0
13	35	0.0	A	50				47.2	21.9	73.3	9040	235		60.2	1.16	0.587	4.2
14	35	0.0	A	200				46.4		75.6	9330	262		65.3	1.14	0.672	4.5
15	35	0.0	A	1000				47.4		82.8	10200	414		69.6	1.02	0.722	4.8
16	35	0.0	B	15				45.3		71.7	8840	240		66.0	1.20	0.638	4.4
17	35	0.0	B	50				46.3	23.0	74.7	9210	235		70.0	1.16	0.672	4.6
18	35	0.0	B	200				46.1		77.0	9500	261		70.3	1.16	0.703	4.8
19	35	0.0	B	1000				45.8		83.0	10220	357		76.0	0.99	0.723	4.7
20	35	0.0	C	15				47.3		73.1	9020	230		74.8	1.21	0.641	5.9
21	35	0.0	C	50	570	12370		45.7	32.9	76.0	9370	238	1.372	78.6	1.10	0.695	5.6
22	35	0.0	C	200				46.1		78.0	9620	228		79.6	1.11	0.779	5.9
23	35	0.0	C	1000				46.9		83.9	10320	390		81.7	0.94	0.729	5.9
24	35	0.0	D	15				47.3		72.2	8910	233		78.6	1.16	0.719	6.0
25	35	0.0	D	50				47.7	42.0	74.6	9200	234		84.1	1.07	0.725	6.2
26	35	0.0	D	200				47.4		77.7	9590	270		85.9	1.04	0.757	6.2
27	35	0.0	D	1000				45.4		83.5	10310	364		91.0	1.02	0.797	6.2
28	50	0.5	C	50	510		0.54	45.0	26.5	86.5	12490	901	1.431	92.9	0.83	0.813	6.2
29	50	2.0	C	50	365		2.04	45.3	29.5	84.4	12770	1584	1.355	106.4	0.79	0.914	6.8
30	50	5.0	C	50	265		3.04	46.3	24.3	91.5	13210	1959+	1.307	116.6	0.75	0.933	6.9
31	50	0.0	A	15				45.8		82.0	11850	435		69.9	1.03	0.703	5.0
32	50	0.0	A	50				46.0	17.5	84.8	12240	452		72.0	0.97	0.707	4.5
33	50	0.0	A	200				45.7		84.8	12240	458		74.4	1.02	0.698	4.5
34	50	0.0	A	1000				45.6		88.9	12820	578		71.9	0.87	0.700	4.6
35	50	0.0	B	15				45.2		83.6	12080	405		69.2	0.97	0.706	4.4
36	50	0.0	B	50				44.3	18.6	84.5	12220	415		71.1	0.93	0.697	4.6
37	50	0.0	B	200				44.9		86.3	12470	464		76.2	0.93	0.771	5.3
38	50	0.0	B	1000				44.3		88.9	12820	579		74.9	0.80	0.761	4.9
39	50	0.0	C	15				43.8		82.7	11940	390		78.1	0.91	0.758	5.7
40	50	0.0	C	50	410	14450		45.6	24.7	84.6	12220	443	1.250	79.4	0.92	0.757	5.8
41	50	0.0	C	200				42.7		85.4	12320	452		80.3	0.95	0.756	5.7
42	50	0.0	C	1000				43.0		88.4	12780	613		84.7	0.76	0.798	6.2
43	50	0.0	D	15				45.0		83.0	11990	399		84.0	0.92	0.827	6.5
44	50	0.0	D	50				45.0	26.9	85.1	12300	438		85.6	0.89	0.784	5.8
45	50	0.0	D	200				45.0		85.4	12320	435		88.2	0.85	0.820	6.1
46	50	0.0	D	1000				44.6		88.2	12730	567		89.5	0.78	0.812	5.9
47	65	0.0	C	50	320	16160		41.0	20.2	87.2	14090	616	1.280	80.5	0.84	0.790	6.0
48	65	0.5	C	50	380		0.80	41.2	23.9	88.4	14280	1041	1.267	86.2	0.75	0.840	6.1
49	65	2.0	C	50	285		1.68	42.8	23.0	90.1	14560	1773	1.213	107.9	0.72	0.799	5.7
50	65	5.0	C	50	225		3.37	48.5	19.2	92.7	14810	1938+	1.181	112.2	0.70	0.963	7.1

1. Sheet forming conditions

Volume of Stock (ml.)

Flocculation Time (sec.)

A	1000	30
B	2000	20
C	7000	15
D	7000	0

2. Improper prefilming

3. No failure of samples

0.0010 inch thick. However, samples 10, 11, 29, 30, 48, 49, and 50 had bonding strengths of such great magnitude that a test film of lower viscosity than the prefilm viscosity was no longer possible. Therefore Vistax No. 4 was used for both the test film and prefilm. The film thicknesses were reduced to 0.0004 and 0.0006 inch, respectively, for the prefilm and test film. This was done to avoid errors caused by too great a test film thickness. Samples 30 and 50 were too strong to be ruptured by even the Vistax No. 4 film.

It is also to be noted that, after wet pressing, some blotter paper adhered to the handsheets in the cases of samples 46 to 50. The effect may be reflected in optical measurements (bonded area and formation).

DISCUSSION OF RESULTS

The effects of beating and of locust bean gum upon the physical properties of the pulp are illustrated in Figures 1 and 2. It will be seen from Figure 1 that the specific surface of the pulp as determined by the silvering technique increased almost linearly with beating. This will at first seem contradictory to Clark's statement (110) that the specific surface of a pulp is proportional to the logarithm of the amount of beating. However, it is to be pointed out that the specific surface measurements made for this work were carried out on pulp which had been previously formed into handsheets and some of the short-fibred material was undoubtedly lost. On the other hand, Clark made his determinations on pulp taken directly from the beater. Thus, the two cases are not strictly comparable.

Figure 1 also shows the effect of locust bean gum and of beating upon the freeness of the pulp. It will be seen that large quantities of locust bean gum caused a decrease in the freeness of the pulp. This decrease in freeness corresponds to an increase in drainage time in the sheetmaking process.

The effect of the amount of locust bean gum added to a pulp and the degree of beating of the pulp upon the adsorption of locust bean gum are also shown in Figure 1. The data given represent the locust bean gum adsorbed by the fibers and retained during the sheetmaking procedure. It will be seen that greater adsorption is favored by larger additions of the gum and by higher degrees of beating of the pulp. The fact that increased beating favored adsorption of gum is attributed to the larger amount of surface available for adsorption in the case of the more highly beaten pulps. It will be seen that sample 48 had an apparent gum content of 0.80%, whereas only 0.50% gum was added. The reason for the discrepancy was found to be incomplete separation of glucose and galactose on these particular chromatograms. Hence, some glucose was present when the galactose was determined and the erroneous result was obtained. The values of 0.56% and 0.54% obtained for samples 9 and 28 are considered to be accurate within the experimental error.

The relationship between the bonding strength and the amount of locust bean gum adsorbed and retained by the sheet is also illustrated in Figure 1. The diagram shows the effect of the adsorbed gum for several beating intervals. As will be pointed out later, this chart shows that

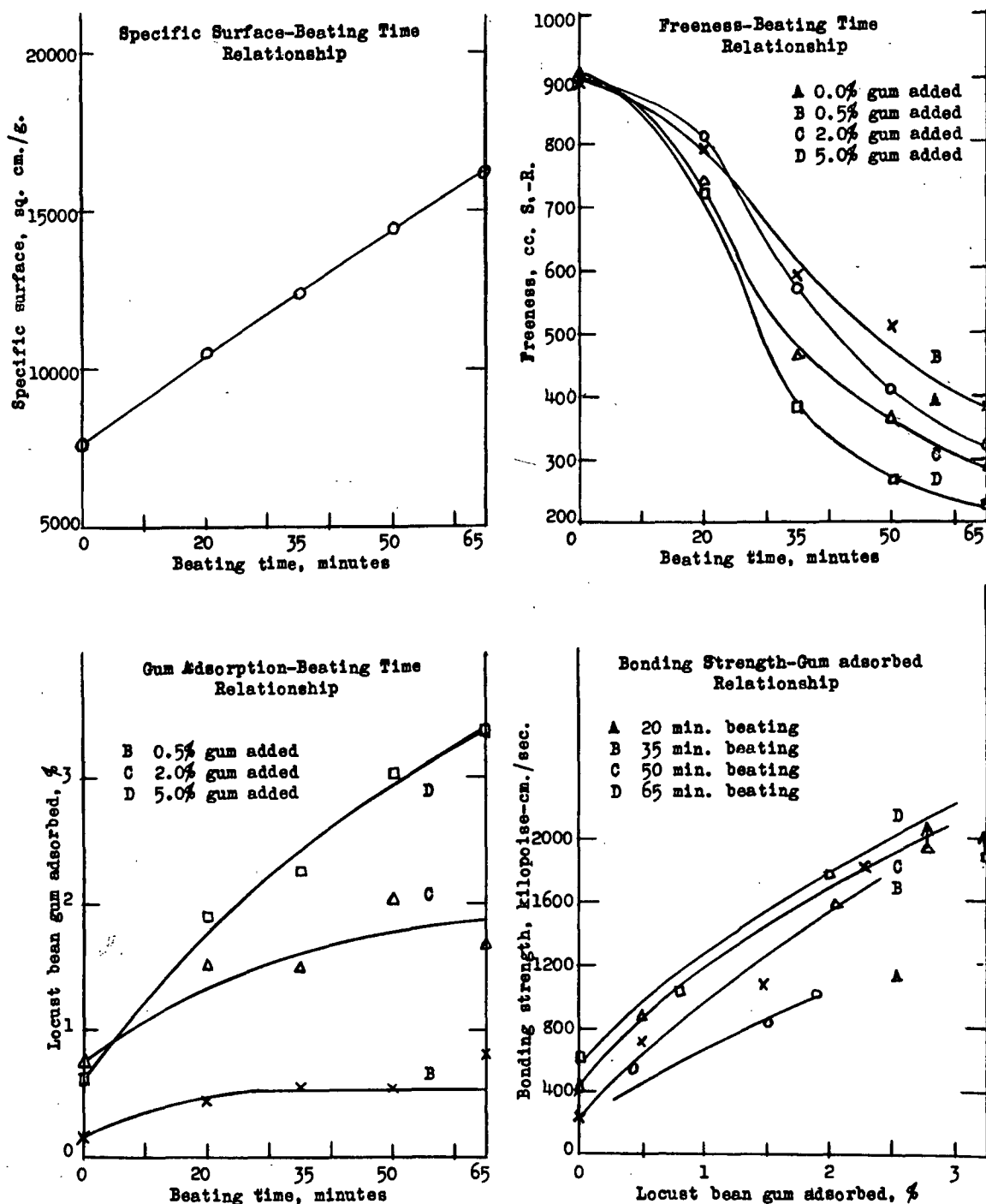


Figure 1

the locust bean gum content of a paper has a very marked influence upon its bonding strength. Papers containing larger amounts of gum have much greater bonding strengths. The independent effect of increased beating is also shown and is discussed in detail later.

Figure 2 illustrates the effect of beating and of locust bean gum upon the strength properties of the pulp. These data are in close agreement with the work already reported by Swanson (78) and need no further discussion.

The effects of beating and of locust bean gum upon the factors which contribute to paper strength are illustrated in Figure 3. It can be seen that an improvement in formation was obtained with a small amount of beating. However, as beating was continued the formation value of the paper decreased. This effect is believed to be due to an increase in the time available for flocculation of the fibers in the sheet mold because of the slower drainage (lower freeness) of more highly beaten pulps. The effect of locust bean gum upon the formation is most pronounced at the early stages of beating where great improvements were obtained. It can be seen that the formation values of the sheets made with 5.0% gum were quite poor during the later stages of beating. The poor formation was due in part to slow drainage, but also in part to the fact that small portions of the blotters adhered to these specimens.

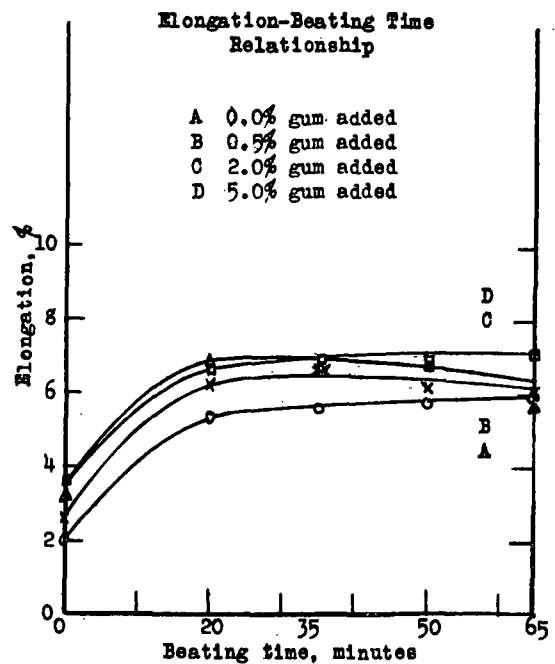
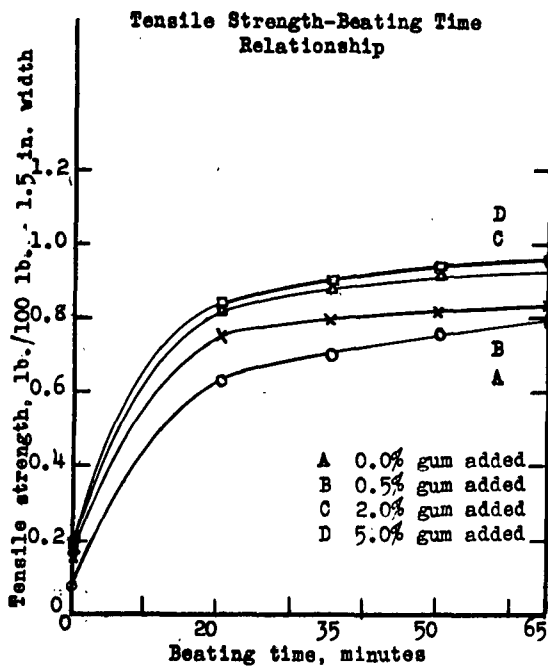
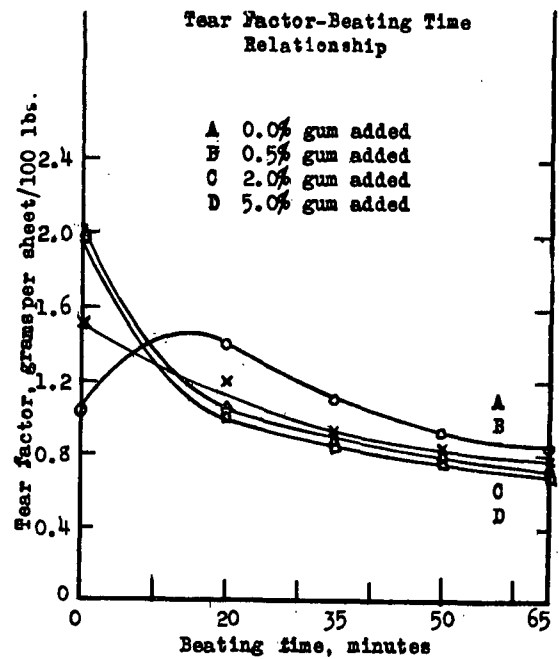
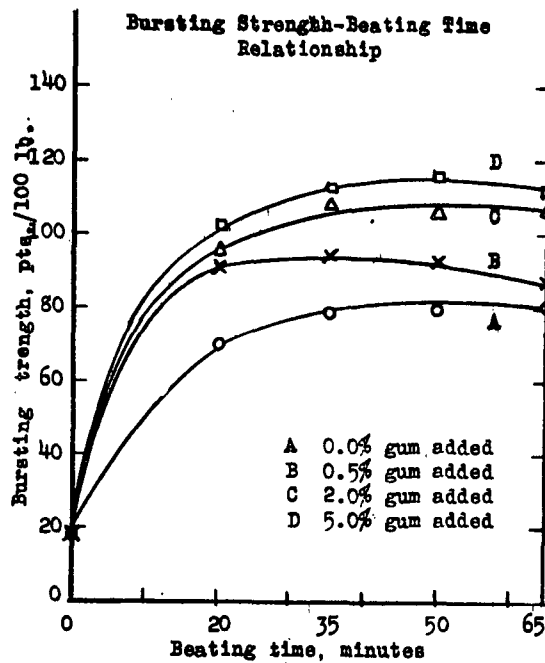


Figure 2

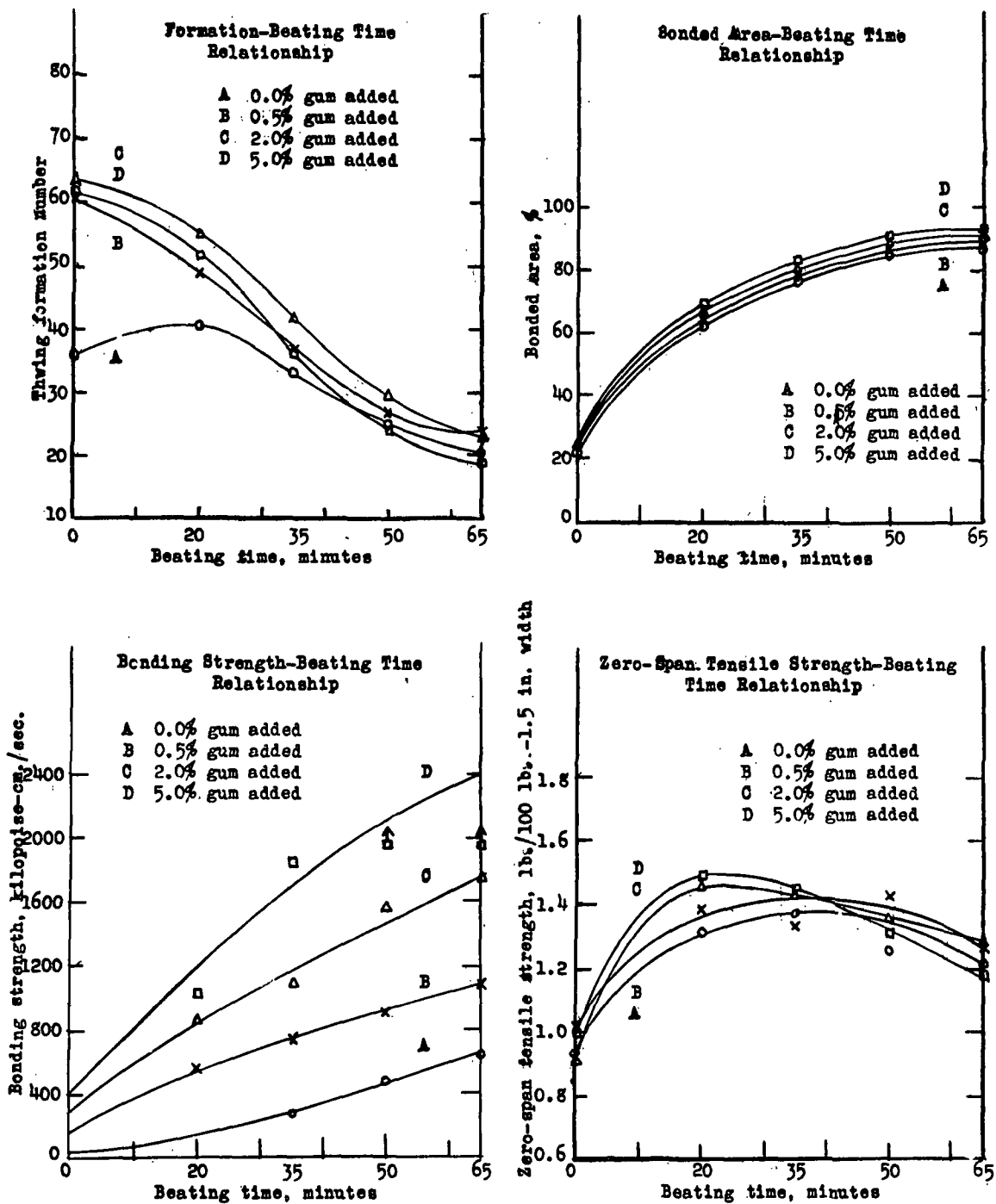


Figure 3

Beating caused a regular increase in the percentage of area bonded. The data confirm the work discussed in the Historical Review. It can be seen that the presence of locust bean gum produces small regular increases in the percentage of bonded area. Since it has been shown that the presence of adsorbed locust bean gum does not affect the specific scattering coefficient, it can safely be said that locust bean gum brings about an increase in the number of bonds.

Examination of the effect of beating upon the bonding strength of paper showed an increase in bonding strength as beating proceeded. The increase was greater than the corresponding increase in bonded area (either percentage bonded area or specific bonded area). The increase represents an increase in the actual strength of the bonds. It would appear that stronger bonds were formed because of greater opportunity for orientation of cellulose chains during bonding or that the beaten fibers were sufficiently more flexible and a less stressed structure was formed upon drying. Nordman and co-workers (111), using a different technique, found no change in the strength of bonds with beating.

The effect of locust bean gum upon bonding strength was very pronounced. The use of even so small an amount as 0.5% locust bean gum doubled the bonding strength. Comparison of the changes brought about in bonding strength by the gum with changes in the other factors affecting paper strength would lead immediately to the belief that the principal function of the gum was to increase the strength of the bonds. However, no such conclusion would be justified unless it could be shown that changes in

bonded area and formation have a small effect upon paper strength (as compared with the effect of locust bean gum).

The effect of beating upon zero-span tensile strength is also shown in Figure 3. It can be seen that zero-span tensile strength reaches a maximum and then declines as beating proceeds. This is in agreement with earlier work with the zero-span tensile test (58). The initial increase is believed to be caused by the effect of bonding and the decrease is believed to be a result of actual weakening of the fiber caused by beating. Locust bean gum causes an additional increase in the zero-span tensile strength in the early stages of beating followed by a sharp decrease. The early increase is attributed to increased bonding. It would appear, as with other measures of strength, that the gum has the effect of advancing the action of beating. The strong decrease in zero-span tensile strength may be a result of this effect. The magnitude of the changes in zero-span tensile strength involved when locust bean gum was used was small. Thus, it seems reasonable to conclude that the great increases in strength properties brought about by locust bean gum are not due to any change in the strength of the fibers (caused by the gum).

Figures 4 and 5 show the various strength properties as functions of bonded area for several values of formation. Charts are given for both 35 and 50-minute beating intervals. From these charts, the effect of changes in bonded area or changes in formation upon the strength properties can be ascertained. The changes involved represent the independent effect of one factor upon the strength properties.

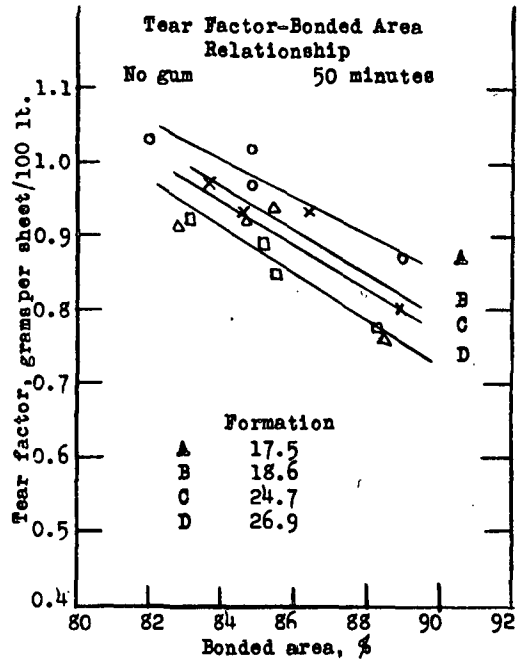
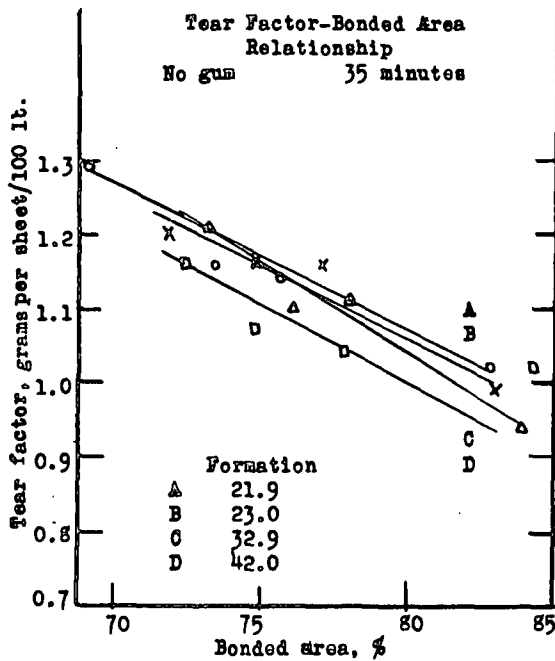
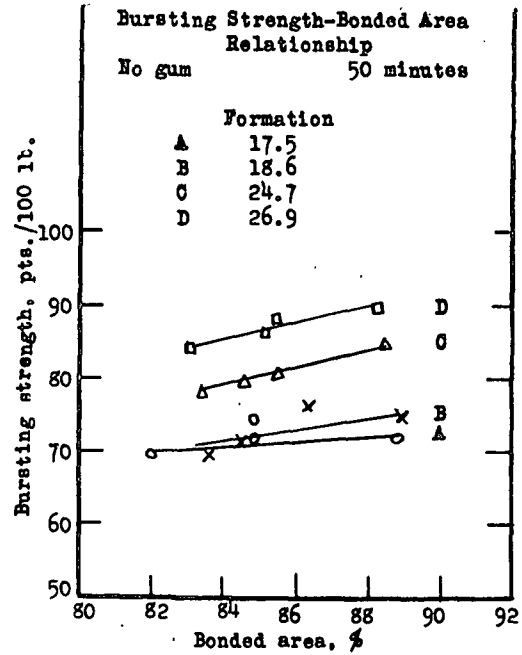
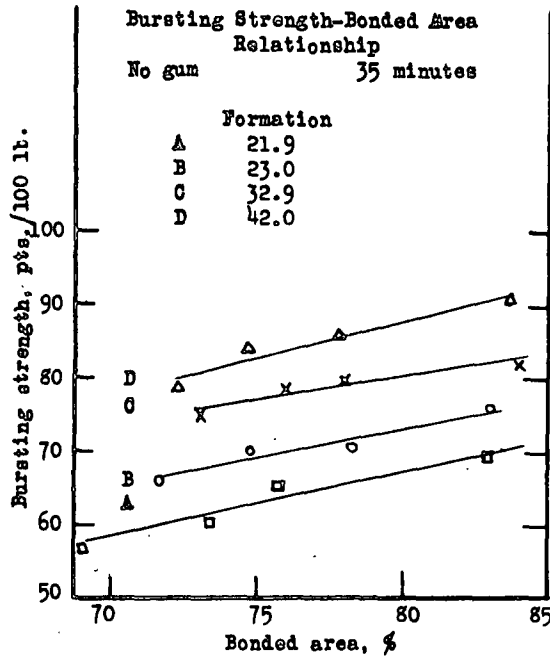


Figure 4

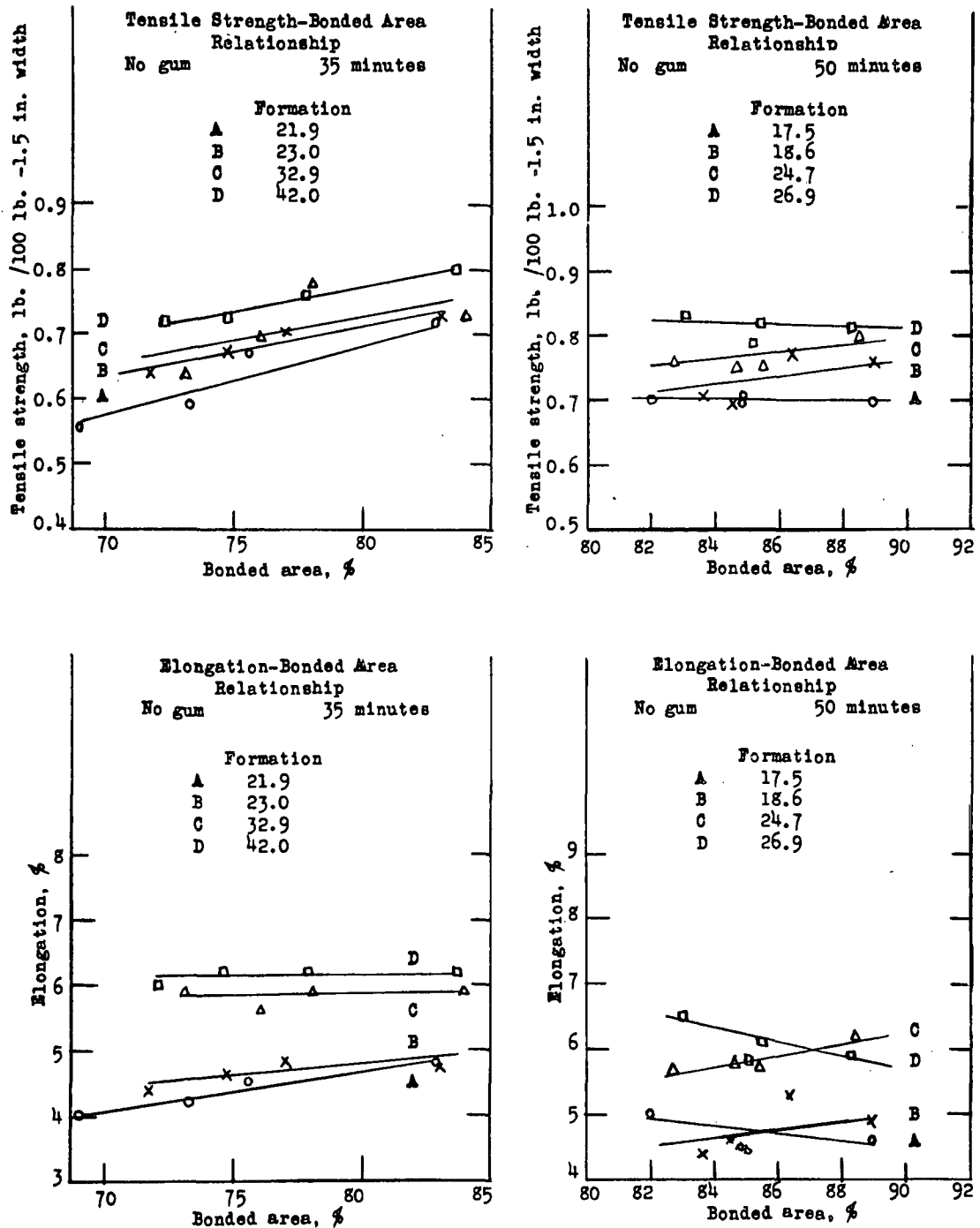


Figure 5

As would be expected from the theories of bonding, bursting strength and tensile strength are increased by increases in bonded area, whereas tearing strength decreases with increasing bonded area. The results confirm other work published in the literature (14, 112). Elongation would appear to be almost independent of bonded area. Bursting strength and tensile strength also show increases with improved formation. This is certainly to be expected because both tests are tests of the weakest parts of the paper. Improved formation produces a more uniform sheet which is less apt to have weak portions. The tearing strength appears to be a weaker function of formation. This is also to be expected because the tearing strength represents the average force required to tear the sheet and thus should not be greatly dependent upon formation. Higher values of elongation appear to be obtained with papers having better formation. The reason is probably that more uniform stresses (and corresponding strains) are produced when papers having high formation values are subjected to load-elongation testing.

Figures 6 to 9 show a comparison of the effect of locust bean gum upon strength properties with the independent effect of either bonded area or formation upon the strength properties. Again, 35 and 50-minute beating intervals are given. In each case, the line for "no gum added" was obtained from Figures 4 and 5. The line was so chosen that it passed through the "standard conditions, no gum added" point (i.e., sample 21 for 35 minutes of beating time and sample 40 for 50 minutes of beating time). The important aspect of these diagrams is the relative slopes of the "gum added" and "no gum added" lines. The slope in each case represents the

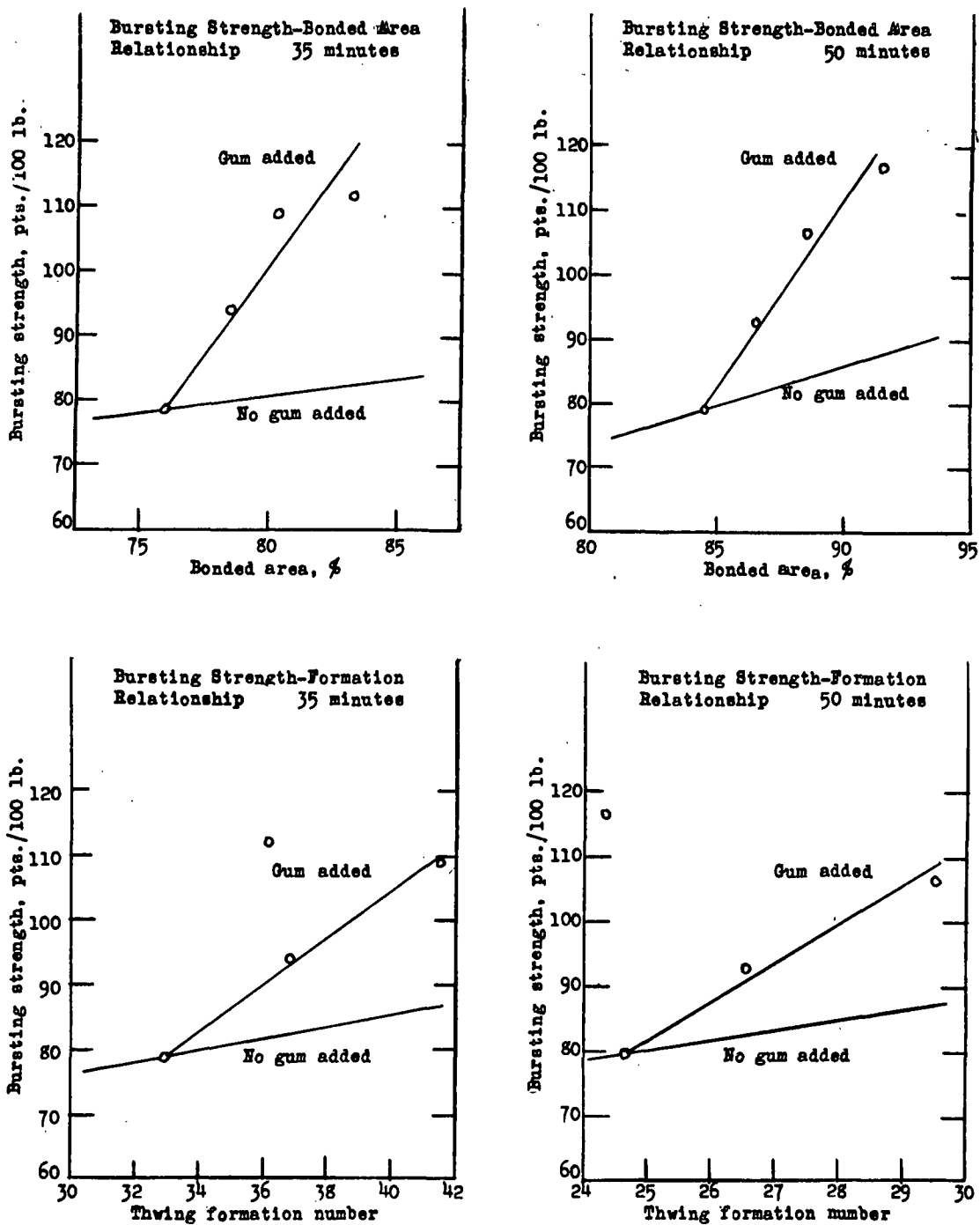


Figure 6

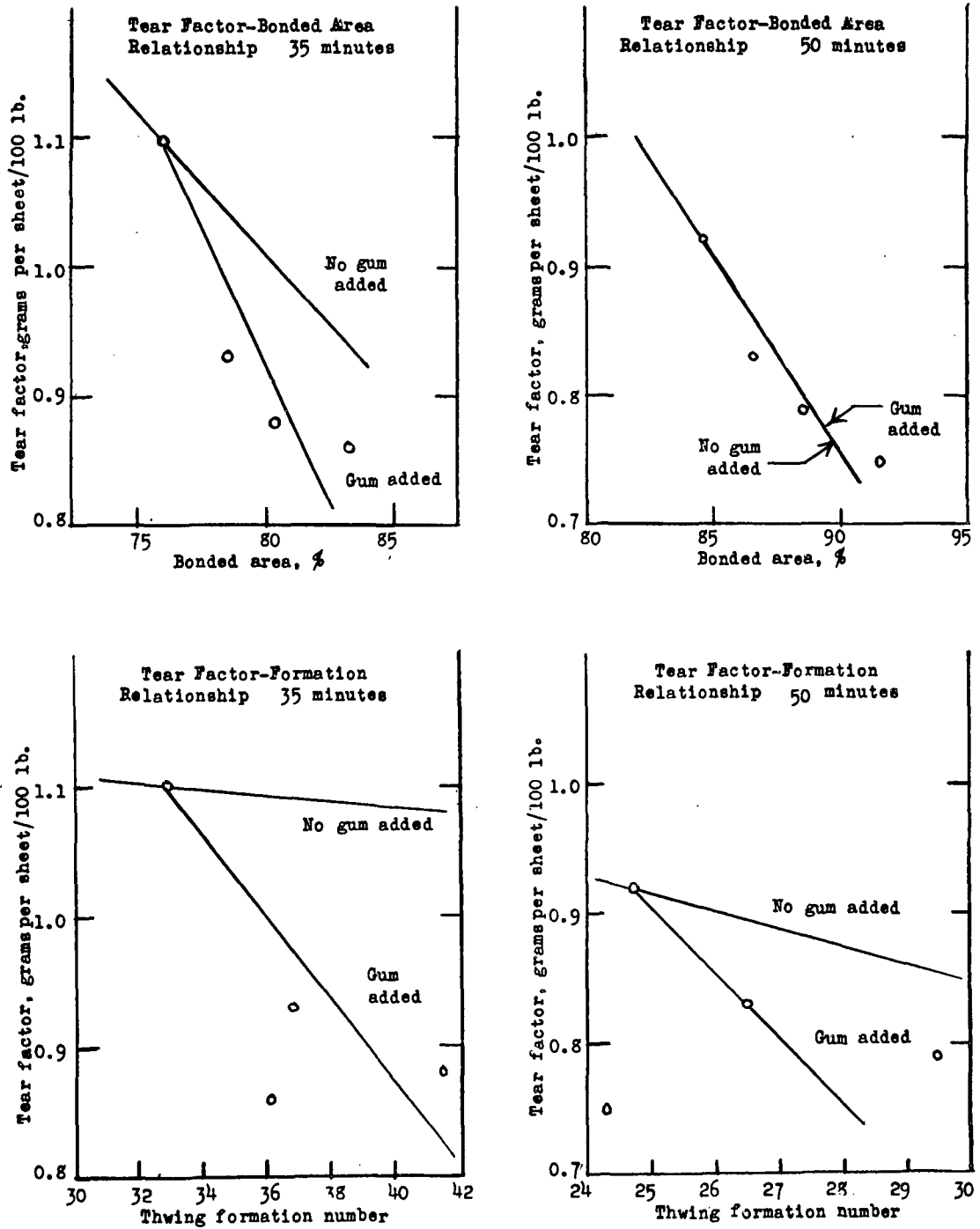


Figure 7

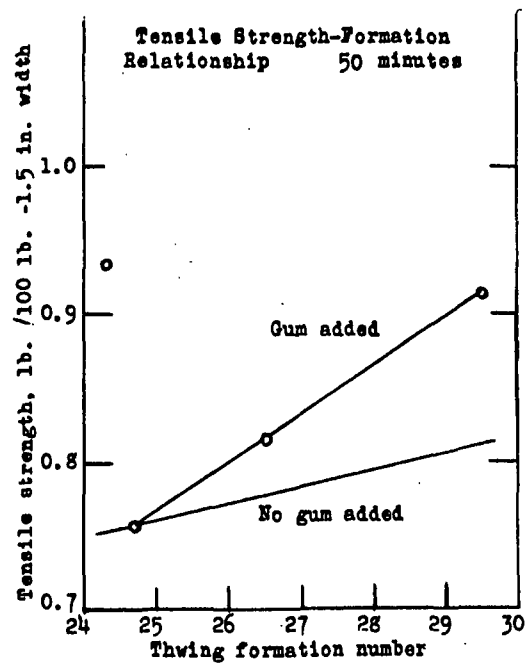
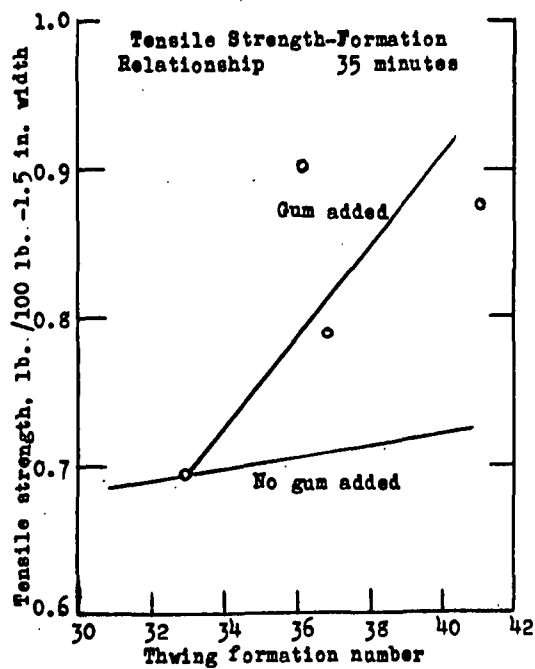
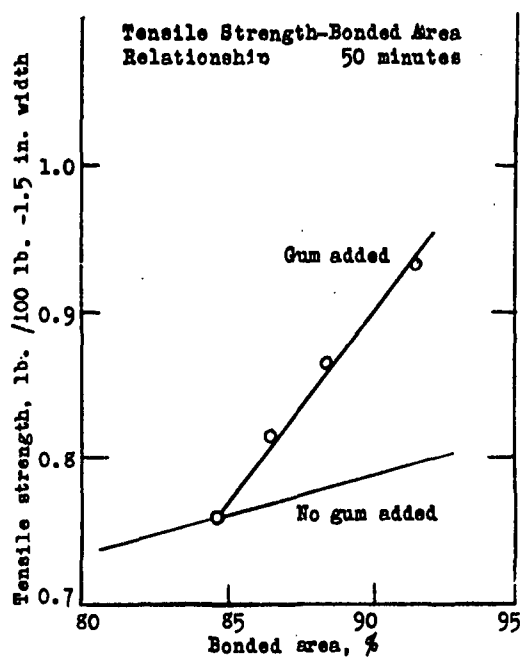
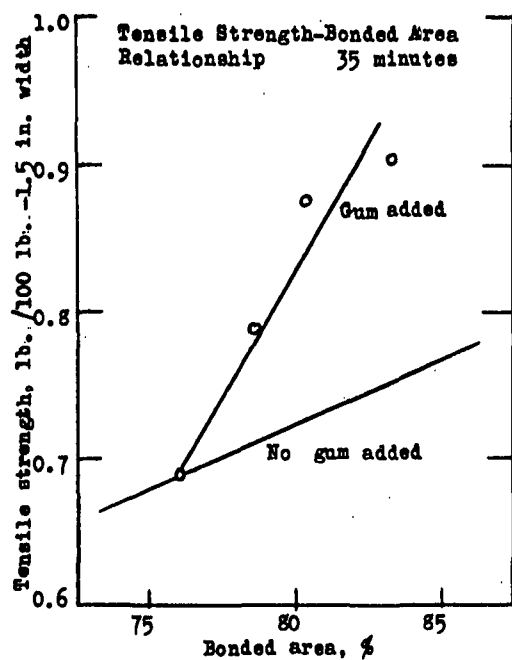


Figure 8

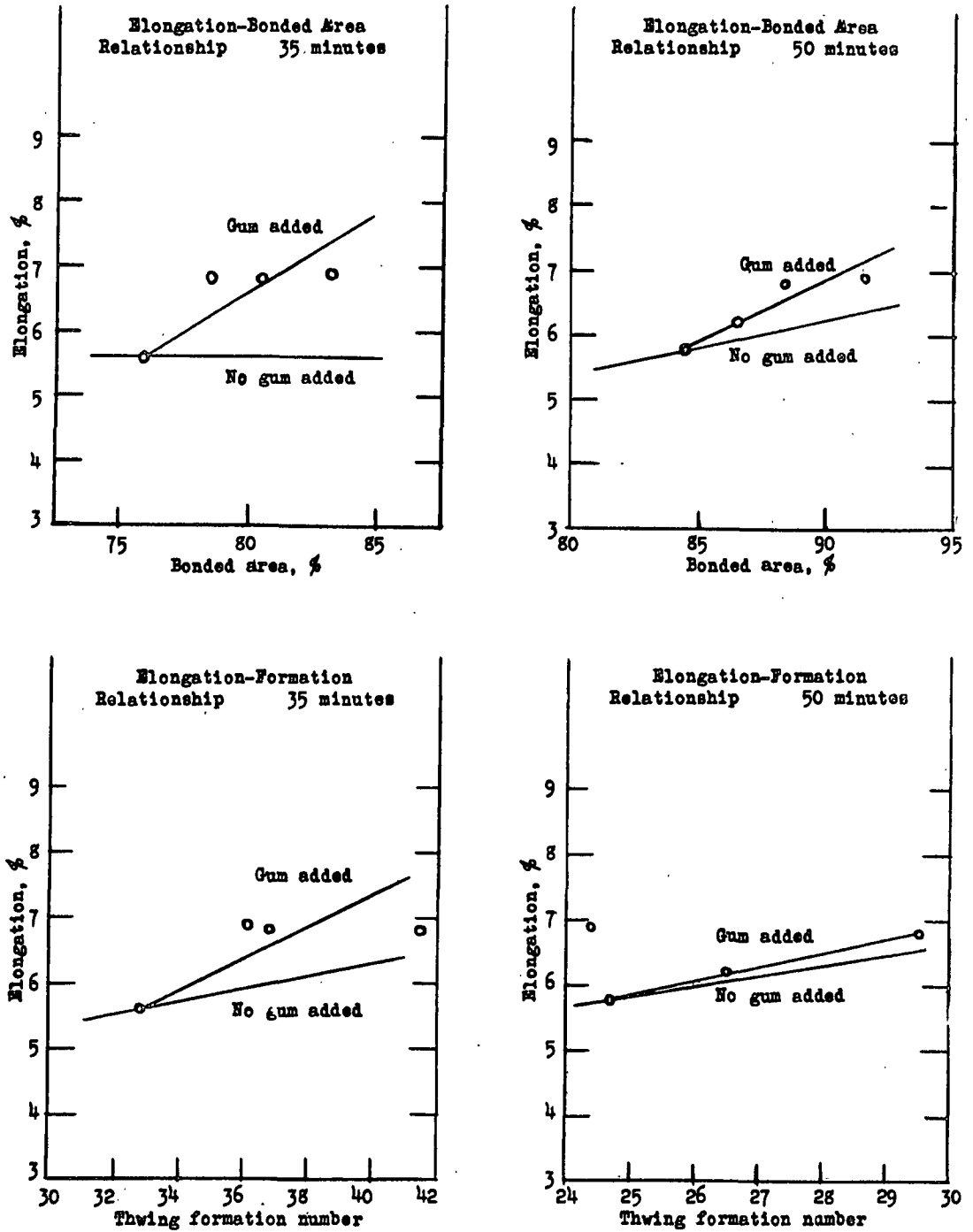


Figure 9

change in the strength property corresponding to a change in bonded area (or formation). For example, in Figure 6 it can be seen that a certain increase in bursting strength can be attributed to an increase in bonded area. Only if the lines of "gum added" and "no gum added" were coincident could it be said that the strength improvements brought about by locust bean gum were due solely to increases in bonded area. This is very obviously not the case. The diagram shows that only a small portion of the increase in strength properties brought about by locust bean gum can be attributed to an increase in bonded area. The same reasoning can be applied to all the diagrams in Figures 6 to 9.

Thus, it is shown that the improvements in bursting strength obtained with locust bean gum can be partially attributed to increases in bonded area and partially to improvements in formation. However, in both cases the contribution of these factors is small when compared with the total improvement produced by the gum. The same may be said for the contribution of these factors to tensile strength.

It can be seen that the decrease in tearing strength caused by the gum is due largely to the effect of increased bonded area. In accordance with the theory of the tear test, the presence of a large number of bonds can decrease the tearing strength by causing rupture of the fibers instead of separation of the intact fibers. Apparently, this is the effect being encountered here. The contribution of formation to the total change in tearing strength is small, as would be expected.

Locust bean gum brought about very mild improvements in elongation. The improvements obtained are seen to be more a result of improvement in formation than an increase in bonded area.

There was no method available for controlling and varying the bonding strength as formation and bonded area were controlled and varied. Therefore, a comparison was made of the bonding strength of sheets with and without locust bean gum added. Comparisons were made at the same values of formation and bonded area so that the effect of the gum upon the bonding strength could be isolated from the effects of changes in bonded area and formation.

The diagrams in Figure 10 show that bonding strength increases with increasing bonded area. The ratio of bonding strength to bonded area does not remain constant as previously mentioned. However, the variations involved are small. It would appear that bonding strength is nearly independent of formation. This is not surprising because the bonding strength test is essentially a test performed on the surface of the sheet rather than on the cross section of the sheet. The diagrams in the lower half of Figure 10 show that locust bean gum produces an enormous increase in bonding strength beyond that which can be attributed to any improvement in formation and increase in bonded area. The data shown in these diagrams present concrete evidence that locust bean gum brings about major increases in the strength of the bonds.

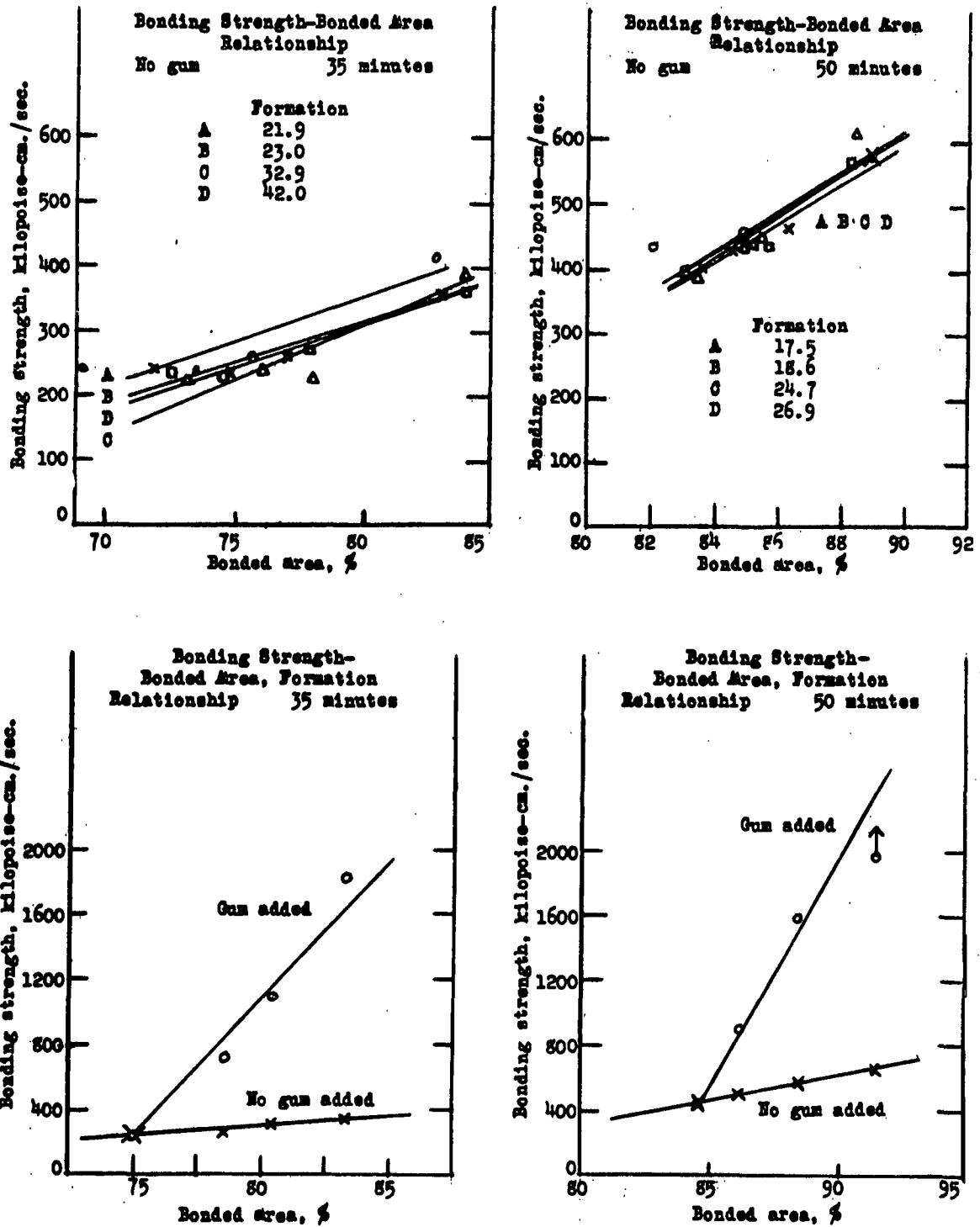


Figure 10

The question naturally arises as to why locust bean gum does not increase the strength properties of paper even more than it does if it can bring about such tremendous increases in bonding strength. A partial answer to this question can be found in Figure 11. Both diagrams show that the strength properties increase very rapidly with increases in bonding strength when no gum is added. However, at the higher values of the strength property there appears to be a tendency for the property to increase more slowly with increasing bonding strength. The points for the standard condition samples at various beating intervals show very slow increases in strength properties with increasing bonding strength. The rate of increase appears to approach that which is found when locust bean gum is used. The implication is that locust bean gum causes increases in strength properties which are comparable with those which might be obtained in the absence of the gum at similar values of bonding strength.

In summary, it has been demonstrated that locust bean gum increases paper strength by improving formation, by increasing the bonded area, and by increasing the strength of the bonds. The increase in the strength of the bonds is believed to be the greatest effect. From the relative slopes of lines in the various figures, the increases in strength properties have been estimated to be approximately as follows:

<u>Strength Increase due to</u>	<u>Contribution, %</u>
Increased bonded area	15
Improved formation	25
Increased bonding strength	60
Increased fiber strength	0

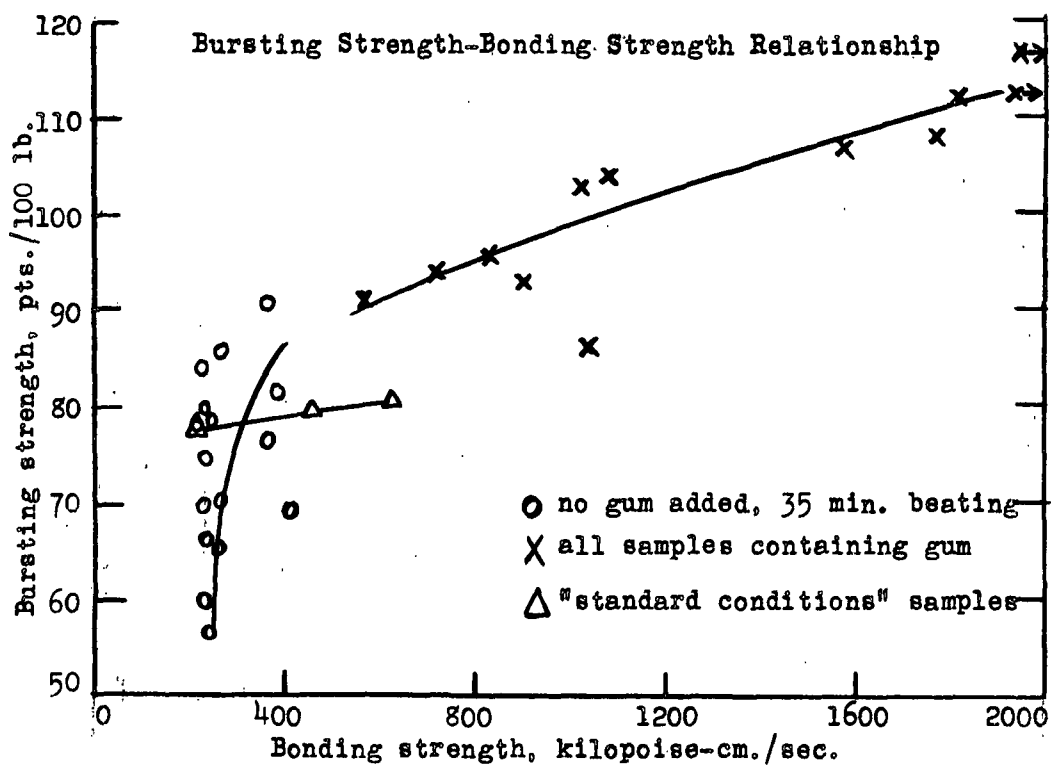
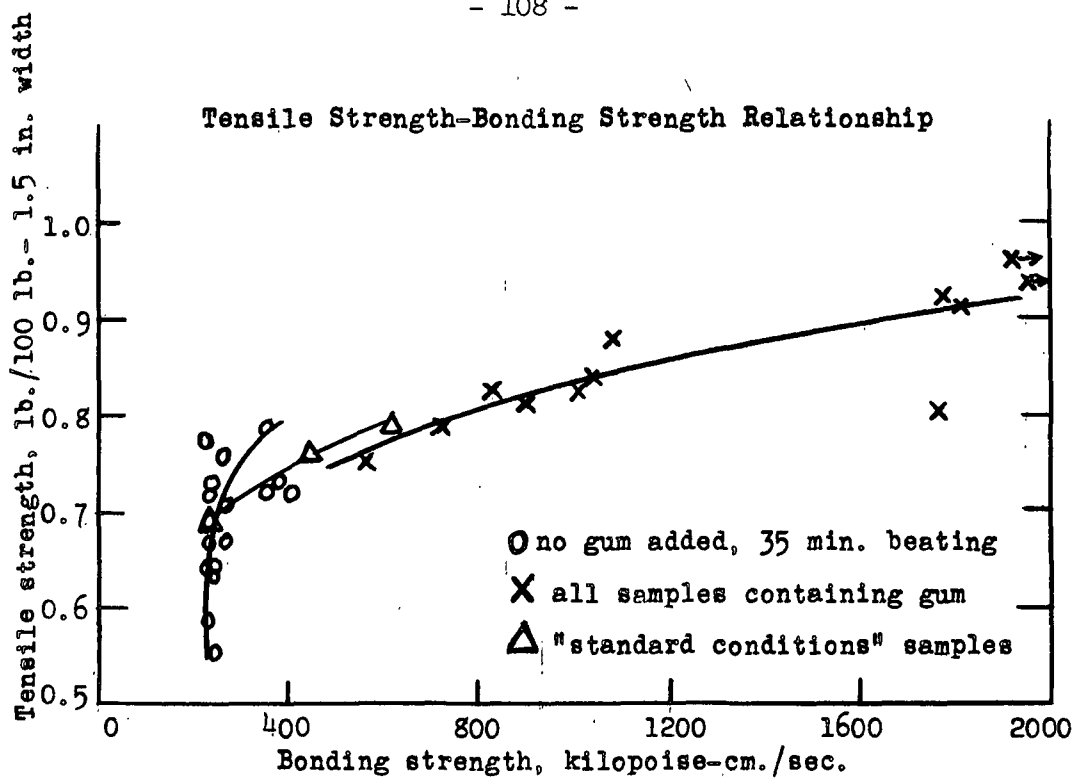


Figure 11

The increased bonding strength may be due to one of several factors. If there is truly an increase in the strength of the individual bonds, then it is probable that this strength increase is brought about by the formation of bonds involving the gum molecules. Such bonds would indeed be more flexible than bonds between two cellulose molecules which are rigidly held in the crystalline structure of the fibers. It is to be pointed out at this time that the chemical nature and some of the physical effects of hemicelluloses appear to be similar to those of locust bean gum and other polysaccharide beater adhesives. It is suggested that the hemicelluloses may also form stronger, more flexible bonds.

The remaining possibility is that the optical technique for measurement of bonded area does not give a true measure of this property because of the difference in distances involved for optical contact and hydrogen bonding. That is, there may be more bonds per unit bonded area (as measured by the optical method) when locust bean gum is present. It is felt that a gas adsorption method of measuring surface area (and, consequently, bonded and unbonded areas) would reveal whether or not such a condition exists because the distances involved with gas adsorption techniques are more nearly of the same order of magnitude as the distances involved in hydrogen bonding. The use of gas adsorption methods for the measurement of surface area of pulp fibers is currently under investigation by Haselton (67).

SUMMARY OF CONCLUSIONS

As a result of the studies which have been reported, the following conclusions are drawn:

1. Hydrolysis of pulp samples containing locust bean gum with 3 to 5% sulfurous acid at 135°C. for 80 minutes accomplishes complete removal and hydrolysis of the gum.
2. No appreciable destruction of galactose occurs during the hydrolysis or during the neutralization and concentration steps which follow.
3. The locust bean gum content of a pulp can be determined by acid hydrolysis. In the work reported, galactose was the sugar unit determined.
4. Fibers dried from water (without being bonded to other fibers) have a much lower value of specific scattering coefficient than corresponding fibers which have been treated successively with water, acetone, and benzene before drying. It is presumed that the fibers dried from water have small fiber elements drawn back to the parent fiber and cell pores closed up when the drying takes place so that less surface is available for light scattering.
5. The presence of locust bean gum upon the fibers dried from water had no detectable effect upon the scattering coefficient of the fibers. The implication was that the gum was adsorbed and dried as a smooth film in optical contact with the fiber surface.
6. Suspensions of locust bean gum have no appreciable surface as measured by the silvering technique. Locust bean gum has no effect upon the specific surface of unbeaten or moderately beaten pulps.

7. The time between drying and testing of handsheets has no effect upon their strength properties.
8. The viscosity of locust bean gum dispersions has no effect upon the strength properties of handsheets made from pulp and gum unless the viscosity of the gum is extremely low.
9. The quantity of locust bean gum adsorbed by pulp is a function of the amount of gum added and the degree of beating of the pulp. Retention is greater with larger amounts of added gum and with higher degrees of beating. Increases in bonding strength appear to be closely related to the percentage of locust bean gum adsorbed.
10. Locust bean gum brings about improvements in formation, increases in bonded area, and very large increases in bonding strength of handsheets.
11. Improved formation, increased bonded area, and increased bonding strength bring about increased strength properties of handsheets (except tear factor).
12. The strength improvement in paper brought about by locust bean gum has been shown to be due to increased bonded area, improved formation, and increased bonding strength. The relative contribution of these factors has been estimated to be as follows:

<u>Strength Increase due to</u>	<u>Contribution, %</u>
Increased bonded area	15
Improved formation	25
Increased bonding strength	60

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APPENDIX

EXTENSION OF ADRIAN'S CHART

$\frac{R_{\infty}}{R_{R_1}}$	$\frac{sW}{R_{R_1}} = 1.5$		$\frac{sW}{R_{R_1}} = 1.4$		$\frac{sW}{R_{R_1}} = 1.3$		$\frac{sW}{R_{R_1}} = 1.2$		$\frac{sW}{R_{R_1}} = 1.1$	
	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$
0.56	.630	.507	.639	.500	.649	-----	.659	.482	.671	.471
0.58	.655	.519	.663	.511	-----	.502	.682	.492	.694	.486
0.60	.678	.530	.686	.521	.695	.512	.705	.501	.715	.489
0.62	.701	.540	.708	.531	.717	.521	.726	.509	.736	.499
0.64	.723	.550	.730	.540	.738	.529	.746	.517	.755	.506
0.66	.743	.559	.750	.548	.757	.537	.765	.525	.773	.510
0.68	.763	.567	.769	.556	.776	.544	.783	.531	.790	.516
$\frac{R_{\infty}}{R_{R_1}}$	$\frac{sW}{R_{R_1}} = 1.0$		$\frac{sW}{R_{R_1}} = 0.9$		$\frac{sW}{R_{R_1}} = 0.8$		$\frac{sW}{R_{R_1}} = 0.7$		$\frac{sW}{R_{R_1}} = 0.6$	
	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$	$\frac{R_{R_1}}{R_{R_2}}$	$\frac{R_{R_2}}{R_{R_1}}$
0.56	.684	.459	.698	.444	-----	.428	.731	.408	-----	.386
0.58	.684	.467	.719	.452	.734	.434	.750	.414	.767	.391
0.60	.727	.474	.739	.459	.752	.440	.767	.419	.782	.395
0.62	.746	.482	.757	.465	.770	.446	.783	.424	.797	.399
0.64	-----	.488	.775	.471	.786	.451	-----	.428	.810	.403
0.66	.782	.494	.791	.476	.801	.455	.812	-----	.822	.406
0.68	.798	-----	.806	.481	.814	.460	.823	.436	.833	.408