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Doctor's Dissertation

A Critical Study of Certain Phases of the Structure and Behavior of Pulp Fibers

by T. Alfred Howells

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A Critical Study of Certain Phases of the Structure and Behavior of Pulp Fibers

A Thesis submitted by

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Chapter I.

INTRODUCTION.

During the past several years a new theory of cellulose structure has come from the Boyce-Thompson Institute. According to their results there are present in the cytoplasm of young cotton fibers ellipsoidal particles, about 1.5 microns long by 1.1 microns in diameter, covered with a thin layer of a pectic cementing material. When these particles were isolated mechanically or by extraction with pectic solvents, they were identified as cellulose. It was suggested that these particles, instead of the micelles previously suggested, would explain x-ray and swelling behavior. Crystalline properties were ascribed to the cellulose particles, colloidal behavior to the cementing material.

Isolated particles failed to show the high viscosity in cuprammonium hydroxide characteristic of cellulose, but the material extracted did produce viscosity. It was claimed that the particles did not dissolve in cuprammonium hydroxide, settling to the bottom of the flask when the viscosity due to cementing material was not too high. Since the viscosity of solutions of cellulose or of its derivatives has been shown to be a valuable criterion of the condition of the cellulose, such observations would necessitate considerable revision of present theories of

the behavior of celluloses. It is the purpose of the present study to determine whether this work can be substantiated in its various details and the inferences involved, using wood pulp as the source of raw material.

Chapter II.

HISTORICAL REVIEW.

Cellulose in the form of cotton and as derived from wood has been the subject of a great deal of investigation and this work has been adequately reviewed at various times (1-8). In cotton, cellulose occurs in a quite high degree of purity, being accompanied by small amounts of ash, pectin, fats and waxes. In wood it is usually accompanied by varying amounts of lignin and of other carbohydrates.

The molecular structure of cellulose is now generally accepted to be that of long chains of cellobiose residues. These chains are of such length that colloidal properties, quite different from those of cellobiose, result. The values for the length of the chain, as found by various investigators, vary considerably. These variations were probably due not only to the intrinsic difficulty of the techniques involved but also to actual differences in the raw materials and in the amounts of degradation taking place in those raw materials. Kraemer and Lansing (4) have reviewed this work and found considerable variation. Cotton in general yielded values higher than those of wood cellulose. The latter seemed to have fractions of greater variation in size. These values varied from very low figures for some wood celluloses to over 500,000 for native cotton cellulose.

Clark and Sisson (5), in a review of the x-ray behavior of cellulose, stated that such studies show natural cellulose fibers, bacterial membranes, and regenerated cellulose to have a truly crystalline constituent which must be identified as cellulose. Ordinarily there is little or no evidence of any gel-like or amorphous matrix. By analogy with metal wires, cellulose fibers must consist of small crystallites in preferred orientation. Diffraction data prove that cellulose must be built from small crystalline particles of some type. This had been shown by the large molecular weight and by swelling and reaction phenomena. Nageli in 1858 advanced a theory of micelles in colloidal material. This has been largely applied to cellulose. By certain extrapolations and the application of special equations a micellar length of 500-600 Angstroms and a cross-section of 50-60 Angstroms was calculated. By the use of very long x-rays, interferences for very large spacings were observed.

Farr and Hakerson (6) have isolated uniform cellulose particles 1.8 by 1.1 microns, which give Debye-Scherrer rings compatible with these particles being considered as single true crystals. It was suggested that these particles, rather than the theoretical micelles, are the true crystalline units. A molecule could have as a maximum length the visually measured length of the crystallite (1.8 microns). This would correspond to a

molecular weight of the order of half a million. This value seems to be further verified by Staudinger's (7) latest viscosity measurements and Kraemer's (8) ultra-centrifuge values on native cotton cellulose. However, determination of the molecular weight of these particles by Kraemer and Lansing (8) gave a value of only 40,000.

The smallest elements of the fiber which can be seen with certainty under the microscope are fibrillae sections, about 0.8 microns long and 0.3 - 0.8 microns in diameter. Various terms have been given to these sections. It is assumed that the fibrillae represent rows of micelles, a great number of which compose the fiber. It is frequently assumed that the fibrillae are arranged in layers (lamellae) and that the lignin and non-cellulosic carbohydrates are imbedded between these layers. This assumption is based larrely on the striated appearance of the fiber under certain conditions. Seifriz and Heck (9), by means of a micro-manipulator, pulled fibers apart into fibrils. They found the primary fibrils (about 1.4 microns in diameter) to be composed of secondary fibrils (0.1 - 0.3 microns).

The middle lamella is the chief dividing line between cells. It is now believed to originate between the halves of the split cell-plate, being the membrane first formed after cell-division. Most botanists differentiated the middle lamella by its refractive character, differential staining, or solubility in macerating agents (10). Dippel

(11) showed that the refractive layer consists of three distinct layers, namely, two anisotropic layers and an intervening isotropic layer.

The most active zone in the tree is the cambium. In this zone, the cells have the power of division, the cells thus formed later being differentiated into various types of tissue. The cell-wall formed in the cambium zone is called the cambial wall. Kerr and Bailey (10) found the "middle lamella" of mature xylem to consist of two lignified anisotropic cambial walls and the intervening truly isotropic layer of lignified material. The cambial wall persists as a non-cellulose residue after treatment of delignified wood with cuprammonium hydroxide but is soluble after treatment with polyuronide solvents. The polyuronides of the middle lamella seem to be of a pectic nature, while those of the secondary wall are hemicellulosic. Kerr and Bailey's data indicate that the walls of the cambial initials contain cellulose and are anisotropic, retaining these properties during tissue differentiation. They delignified wood with chlorine and ammonia without macerating it. Then, by use of a polyuronide solvent, the wood was macerated (separated into fibers).

The residue of the so-called middle lamella left after treatment with 72 per cent sulphuric acid consists of at least three layers, namely, the two cambial walls of adjoining cells and the intercellular material. By treatment

of wood with chlorine and hot sodium sulphite (which will dissolve both lignin and pectic compounds), only a part of the so-called middle lamella dissolves (the truly isotropic intercellular material). The cellulose-containing cambial walls persist and adhere to the layers of secondary thickening.

Bixler (18) cut microtome sections of several kinds of wood, cooked these under typical commercial cooking conditions, and examined the cooked sections. He found that the cambial walls persisted through the cooking and bleaching processes. In cross-section the cambial walls were very bright between crossed Nicols in comparison to the secondary wall. In longitudinal section, the cambial walls were dark and the secondary wall bright. When sections were treated with cuprammonium hydroxide or strong sulphuric acid, the secondary wall swelled but the cambial wall did not. Drastic sulphite cooking or drastic hypochlorite bleaching seemed to weaken the cambial wall, since it no longer restricted the swelling of the secondary wall. Alkaline cooking or chlorine bleaching did not have this effect.

A detailed discussion of the theories of fiber structure advanced by various investigators need not be given here but several of the outstanding ones will be mentioned. Bailey and Kerr (15) attribute some of the discrepancies in these theories to the differences in raw

materials used. They believe that no set pattern can be developed which will satisfactorily describe the structure of fibers differing as much as do, for example, the monocotyledonous fibers of bamboo, the libriform fibers of elm, the tracheids of spruce, and the seed-hair of cotton.

The seed-hair of the cotton plant is usually considered to be a single cell. Upon treatment of the cotton fiber with cuprammonium hydroxide Matthews (14) distinguished four parts. The main cell-wall, probably almost pure cellulose, is least resistant to solvent action. The external cuticle, possibly of modified cellulose, is more resistant. The wall of the central canal is still more resistant and the annular ligatures are most resistant of all. The fiber assumes a bead-like appearance, like a distended tube tied at intervals. Some considered these constrictions, or ligatures, as part of the cuticle, and explained their formation by the fiber swelling so considerably as to rupture the undisturbed cuticle in a weak place. The remaining cuticle then rolls or draws together into annular bands.

Balls (15) demonstrated that swollen cotton hairs have a layered structure with some twenty to thirty lamellae in the mature fiber. By the use of statistical methods, Balls claimed that one lamella is deposited each day during the period of secondary wall deposition. These lamellae were accordingly named daily growth rings. They were found to average 0.4 microns in width.

Georgi (16) has confirmed Hailé's work on growth rings as actual structural units. They appear to persist regardless of the treatment, since they are present in raw cotton, purified alpha-cellulose, nitro-cotton, fibrous cellulose acetate, and throughout cellulose etherification.

Kerr (17) found the secondary wall of the cotton hair to be a complex and coherent matrix, the appearance of layering in swollen fibers being due to a structural differentiation of the cellulose into an alternation of compact, strongly birefringent zones with more porous, comparatively isotropic layers. During the period of secondary wall deposition two lamellae, one compact and one more porous, are deposited every twenty-four hours, the two lamellae together constituting one growth ring. These growth rings show considerable variation in width and in the density of the more porous lamella. Variations in the density of the porous lamellae were correlated with changes in the temperature at night, a lowering of the temperature favoring a greater differentiation from the compact zone. The width of growth rings of cotton grown in North Carolina was 0.3 - 0.35 microns, while the value for cotton grown in Massachusetts was only 0.12 microns.

Anderson (18) found that the micelles in the cellulose wall of the young fiber are grouped into thread-like fibrils oriented at right angles to the axis, unifer m

over the entire primary wall. The first evidence of wall thickening is the appearance of delicate branching cellulose threads running spirally around the inner surface. The direction reverses frequently. Within 24 hours a second layer is laid down. This continues for 25 days or more. Lamellae can be produced by varying either the light or the temperature. No cellulose particles were found in the cytoplasm and no evidence supporting the existence of basic units of visible size cemented together by pectic material.

According to Liditke (19), the framework of the fiber is a system of skins enclosing the carbohydrates. After the middle lamella, largely lignin, has been removed in the process of pulping, the outside of the cell is the primary lamella, a thin skin invisible in cross-section due to its narrowness. Since it is not removed with the lignin of the middle lamella it is of different nature. It is thought to be more similar to lignin than to cellulose on the basis of some staining reactions, especially with alcoholic phloroglucinol hydrochloride. The secondary wall is divided into layers by skins of this same material, and these layers are divided into spiral strips by radial skins, the direction of the spirals alternating in adjacent layers. The strips are made up of fibrils, which are further sub-divided into fibril-sections by cross-lying skin layers, about 0.2 - 0.5 microns in length. These are

the smallest elements encased in skin of which Lüdtke claims knowledge. If it is assumed that the next smaller units are also encased, more skin substance would be required than the few per cent which he found.

One of the most controversial parts of Lüdtke's theory is the existence of cross-elements. These are supposed to be disc-shaped or thread-like masses of skin substance extending through the secondary wall transversely to the long axis of the fiber at fairly regular intervals, depending on the kind of fiber and varying from five to eighty microns. When fibers are swollen with cuprammonium hydroxide, the solvent enters the fiber wall through the primary lamella and partly dissolves the polymeric carbohydrates. Since the membrane is semi-permeable, the large copper-cellulose complex can not pass back through it and an osmotic cell is formed. As a result, the fiber swells to an extent depending on the condition of the membrane. Since the membrane is restricted at the cross-elements, it can not swell in these places and the familiar ballooning results. Lüdtke shows photographs in which some fibers have a telescopic appearance which he attributes to a cleavage of the various layers at the cross-elements.

Sakostschikoff (20) and Sakostschikoff and Tumarkin (21, 22) claim to have isolated cross-elements by treatment with strong sulphuric acid followed by dilution with water. He found average yields of up to 0.5 per cent

for raw cotton, 0.07 - 0.18 per cent for purified cotton, 0.7 per cent for unbleached kendyr, 1.3 per cent for unbleached pulp, and 0.07 - 0.00 per cent for bleached pulp. Haller (23) refuses to believe this evidence and maintains the particles obtained are parts of the cuticle which have been shoved together in swelling.

When cellulose was dissolved out of wood by sulphuric acid, Freudenberg (24, 25) found that a study of the lignin mesh under polarized light showed the presence of elongated hollow spaces. Largely on the basis of this phenomenon, he developed a theory of fiber structure in which micelle series are imbedded in a matrix of lignin and hemicellulose. The micelle series are about 600 Angstroms thick and are built up of micelles held together by secondary valences and a growing together of their ends. The series are arranged parallel in one layer and encircle the fiber at an angle of about 20 degrees to the fiber axis. Adjacent layers spiral in opposite directions. In the primary wall (outside the thick secondary wall), the micelle series make an angle of about 70 degrees with the fiber axis.

Ritter (26) found it possible to dissect fibers into various units. On alternate swelling and shrinking, layers became visible. If the whole fiber is used, each layer is an enclosed capsule. If short sections are used, the inner layer tubes may be pushed out. Ritter believed

the outer layers to be composed of windings transverse to the fiber axis and the inner layers to be composed of spirals all going in the same direction around the axis of the fiber and at an angle from it varying from zero to thirty degrees. He admits that it would be possible to get striations on a homogeneous outer coat by folding back of the outer coat. However, it is unlikely that these striations would be as uniform as is actually the case. It would also be impossible to get helical windings such as are sometimes observed.

As evidence against Lüdtke's cross-elements, Ritter mentions the appearance of fibrils passing through constrictions which Lüdtke would call cross-elements. Since cross-elements are supposed to occur at intervals of 40 to 60 microns, no fibril should be longer than this. Ritter has isolated fibrils and bundles of fibrils 230 microns long. The latter attributes the seemingly abrupt transverse fractures in fibers to slip-planes or places weakened by pits.

By treating stock, which had been highly refined to remove lignin, with dissecting agents such as sulphuric and phosphoric acids, the fiber separates into long slender fibrils. These fibrils readily break down under further treatment to fusiform bodies, which are spindle-shaped. Under more drastic treatment these further break down to spherical units, about 0.45 microns in diameter in the

swollen condition. Between crossed Nicols, their diffractive properties indicate random crystalline orientation, contrary to the preferred crystalline arrangement in the fusiforms. It therefore seems that the units were slightly elongated before separation and had parallel crystalline arrangement but in the process of separation were converted to spherical shapes with random orientation.

Carpenter and Lewis (27) showed that in a very raw cook of Jack Pine there was still a sheath of lignin left on the fiber. When such a fiber is treated with cuprammonium hydroxide it swells to a relatively slight extent, the lignin sheath sometimes separating in various forms. In a normal cook, this lignin layer has been dissolved and the secondary wall, of cellulose, is surrounded by an elastic, semi-permeable membrane. Either as a part of this layer or wrapped around it at right angles to the fiber axis are structures which may be separated into narrow bands or even threads; these are more resistant to cuprammonium hydroxide than is the secondary wall. Fibers from such a cook exhibit the normal bead-like ballooning in cuprammonium hydroxide, the semi-permeable membrane forming an osmotic cell. The more or less continuous nature of the transverse windings is visible. In over-cooked or overbleached fibers the outer membrane has been modified so that fibrillation results instead of ballooning.

In subsequent work, Lewis and Smith (28) have studied the effect of cupraammonium hydroxide on treated fibers by means of cine-photomicrographs. When fibers are degraded by heat, the primary membrane becomes either hard and brittle or more readily soluble in cupraammonium hydroxide. Ballooning does not result nor are the windings visible. The cellulose swells and dissolves. Fibers treated with concentrated nitric acid and potassium chlorate fibrillated with only faint suggestions of places where balloons might otherwise have formed. These fibrils on further treatment break down to give Ritter's fusiform bodies. No transverse windings were visible. Overbleached fibers swelled in cupraammonium hydroxide without ballooning. The transverse windings were visible, indicating that these windings alone are not sufficient to cause ballooning.

Lewis believes that at certain places the windings of the primary lamella appear to have fused together in such a manner as to form a non-elastic loop of a single thread or a band of several threads width; these are more resistant to the solvent action of cupraammonium hydroxide and to mechanical treatment than is the cellulose in the secondary wall. When normal fibers are swollen with cupraammonium hydroxide, the semi-permeable membrane swells due to the fact that the cellulose-copper complex can not diffuse back through it. The non-elastic loops or bands in the primary lamella resist the swelling action of

cuprammonium hydroxide, and, in fibers which are photographed when dissolving in cuprammonium hydroxide, it is apparent that the passage of the swelling agent through the walls of the fibers is building up a pressure within the fiber which is caused inpart by the restraining or choking effect of the loops and in part by the resistance to swelling of the primary lamella. Ultimately the pressure exceeds the strength of the primary lamellar loop, and the contents of the end portion of the fiber may be seen being expelled through the now open end. This continues and the fiber dissolves to the next point of constriction farther along the fiber. At the weaker portions in the transverse windings the membrane may be pushed through the windings in the characteristic balloons. The windings are then pushed apart and bunch together in the locality of the constricting loops. Such restricting bands behave in part as do Hadding's cross-elements but in no sense does the fusion penetrate into the secondary wall.

When a fiber is beaten, the transversely wound outer lamella is gradually beaten off, forming a portion of the so-called fibrillation commonly observed in beaten stock. In a bleached Mitscherlich pulp beaten to a Schopper-Riegler freeness of 180 cc., most of the outer layer seemed to have been removed except for a few of the loops or rings mentioned above. When treated with cuprammonium hydroxide, some ballooning resulted with these rings

forming the constrictions but the balloons were no longer spherical but might be described as elongated ellipsoids. In the same pulp beaten to a freeness of 80 cc., there was no ballooning, the fiber swelling continuously down the fiber axis and dissolving with neither ballooning nor fibrillation.

In a specially purified pulp with an alpha-cellulose content of over 99 per cent, two layers were visible. The outer one seemed to be shoved together into rings by the balloons. When these balloons dispersed, the rings spread out forming a sleeve. At other places, the outer layer appeared to turn back on itself, in effect turning inside out.

Bailey and Kerr (18) investigated a large number of different plants and found structural patterns of different types, radial, concentric, and combination. After removing non-cellulosic material there was a firm coherent matrix left. This matrix contained lamellae made up of heterogeneous complexes grading down to the limits of microscopic visibility. The dark lamellae contained a low ratio of birefringent complexes and the lighter lamellae contained a high ratio of the birefringent complexes and a low one of the isotropic ones. Cotton showed concentric patterns which seemed to be of the same type as those of the tracheids. Both contained layers of two optically different types: the one being strongly

birefringent, denser and containing more cellulose than the comparatively isotropic, more porous, one. In cotton these effects can not be due to non-cellulosic material since the small amount present is practically all in the cuticle.

If tracheids are treated with 72 per cent sulphuric acid, a coherent structure is left with a pattern just the reverse of that of the cellulose. In the more heavily lignified zones, the birefringent and comparatively isotropic parts persist in the lignin residues; in the less intensely lignified parts, the birefringent layers leave no structure. In longitudinal section, the residues of the heavily lignified parts exhibit conspicuous red double refraction; the residues in the less lignified parts do not. This means there are sub-microscopic differences.

In Bailey and Kerr's picture of fiber structure, the central layer of normal tracheids is composed in all cases of a complex and firmly coherent matrix of cellulose with elongated, intercommunicating interstices in which lignin and other non-celluloses may be deposited. This cellulosic matrix is composed of anastomosing elongated complexes which are oriented parallel to the long axis of the cell or in helical arrangement. These elongated complexes, of two different types, determine the striated appearance and the cleavage planes. Fibrils are simply

heterogeneous shredded parts of the original, continuous, coherent matrix. The inner and outer layers probably have similar structures but with the complexes oriented more nearly at right angles to the fiber axis.

When fibers are swelled, the cellulose expands at right angles to the fibrillar axis. The laterally expanding central layer splits the tenuous, longitudinally expanding outer layer into a series of constricting rings and helical bands, bulging outward between them. The controlling factor is the difference in orientation. If the orientation does not change in successive layers but there are films of non-cellulose present, all the layers swell together.

Bailey and Kerr mention five visible types of concentricities:

1. Segregation of two optically different aggregates of cellulose into concentric patterns.

2. Abrupt changes in the form or texture of the structural pattern.

3. Changes in orientation of the elongated birefringent complexes of the structural pattern.

4. Varying intensities of lignification or differences in the distribution of the non-celluloses.

5. Alternations of cellulose and non-cellulose.

Most tracheary cells and fibers exhibit type three usually with one or more of the other types.

Bailey and Kerr (13) explain the fact that Lüdtke (19) obtained telescopic appearances in fibers by the fact that he did a great deal of his work on bamboo. The anisotropic layers of such monocotyledonous fibers are frequently separated by non-cellulose films. These would be removed in purification, permitting the appearance of the different layers. Ritter (26) used the libriform fibers of the elm for much of his work. These are often of the "gelatinous" type, frequently characterized by having cellulose and non-cellulose lamellae.

Many investigators have visualized the secondary wall as being composed of visible units held together by non-cellulosic material. Bailey and Kerr found no evidence in untreated or carefully swollen fibers of discrete entities of cellulose which might be liberated by dissolving the non-cellulose. During the production of fibrils the matrix is shredded and disrupted. They found that by proper treatment of lignin residues, fragments resembling fibrils and dermatosomes could be obtained. When cotton was treated with solvents of non-cellulosic materials in such a way that degradation of the cellulose did not result, the pattern was not affected.

Farr and Wakeman (6) found in young cellulose fibers particles of uniform size, separate or in bead-like strands. These particles were ellipsoidal in shape, doubly

refractive, having an index of refraction lengthwise of 1.565 and crosswise of 1.530. When the proteins of the cytoplasm were removed by a short alkali treatment, the particles gave a clear cellulose blue with iodine and sulphuric acid. The particles appeared to be covered by a thin layer of pectic material. This was identified by its non-double refraction, solubility in alkali and staining with ruthenium red.

When the fiber is five or six days old, the limiting membrane is no longer entirely pectic but has gained a thin layer of fibrils. Farr and Bokerson advanced the theory that single chains of their particles go to make up fibrils. In the center of the cell, there were separate particles or short strands of them; nearer the cell wall the chains were longer. Particles could be mechanically isolated from the moist fibers of unopened bolls. Pectic solvents were required for separation of mature dried fibers.

A. J. Bailey (29) beat wood pulp and cotton and found that the ultimate products of beating were "cylindricoids" (fragments of the fiber roughly cylindrical in shape and measuring 3 - 4 microns in height and in diameter), finer fragments, and a clear gel. Overbeating in a ball mill by as much as sixty times commercial beating indicated that pulp could not be reduced to a homogeneous gelatinous mass. The gelatinous fraction approached a limiting value

which was estimated as about half the original pulp.

In agreement with other investigators, Bailey believed the fiber to be made up of fibrils oriented at a small angle to the longitudinal axis of the fiber in the inner lamellae and at practically right angles in the outer ones. Comminution in water causes softening, swelling, and disintegration. The fibrils appear to have a commonly recurring diameter of about 3-4 microns. As they are liberated there appears a more chemically active hydrogel which seems to function as a matrix. Unit fibrils disintegrate into cylindricoids and finer fragments. He suggested that the uniformity of height of these cylindricoids could be explained by the occurrence at one spot of the ends of enough micelles to form a weak place. Bailey's theory agrees with those of Ldditke (19) and of Freudenberg (24, 25) in some respects, with the addition that Bailey believed the matrix to be cellulosic since it occurred in cotton. Cylindricoids were thought to differ from the gel in having longer molecules.

A. J. Bailey (29) criticized the findings of Farr (6) in several respects. Farr had claimed that pectic solvents, absence of double refraction, and staining with ruthenium red indicated a pectic substance cementing ellipsoids and fibrils together. Ritter (30), Harlow (31), and Scarth, Gibbs, and Spier (32) had shown independently that pectic solvents and ruthenium red were unreliable. Bailey

claimed that the minimum thickness of section, of birefringence of 0.035 (as in Farr's cellulose particles), which could show observable anisotropy would be 6-7 microns. Smaller particles could give polarisation colors of such a low first order gray as to be indistinguishable from the darkness of minimum luminosity. This was checked experimentally, unit fibrils and cylindricoids (3-4 microns in diameter) failing to exhibit any anisotropy, while aggregates of unit fibrils which were two unit fibrils in thickness (6-8 microns) showed a very faint anisotropy.

Farr and Bokerson (35) isolated particles by treatment of cotton with concentrated hydrochloric acid at room temperature for periods of from thirty minutes to five days. With increasing time of treatment the fiber membrane was destroyed, the fibers showed cross-ruptures, the fibrils and particles became more evident, and finally the fiber separated into a mass of particles. The separated particles showed blue upon treatment with iodine-sulphuric acid, being very sensitive to swelling by the acid. In polarized light they were clearly doubly refractive.

Farr and Sisson (24) found that these separated particles gave a typical Debye-Scherrer ring for cellulose, similar to the powder diagram obtained by cutting cotton fibers into small fragments and pressing them into a pellet. It was suggested that the micelles frequently assumed on the basis of x-ray and swelling data might in reality be

these cellulose particles. Their size (1.8 by 1.1 microns) would still explain x-ray phenomena. The particles might be further sub-divided into smaller crystalline masses.

In an attempt to correlate these conflicting theories and data, Sisson (35, 36) advanced a compromise theory of secondary structure similar to that proposed by Zwicky for inorganic crystals. Since chemical reactions, density, energy content, and x-ray diffraction lines are about the same for all purified cellulose fibers, the molecular structure and unit cell must always be the same. These may be referred to as the primary structure. Since the practical physical properties, such as tensile strength, elasticity, swelling, and shrinkage, vary considerably, there must be differences in the configuration of the crystallites, their orientation in the fiber, and their association with other amorphous or non-cellulosic materials. The concept of a secondary structure superimposed on the primary structure would be a compromise. It would assume a more or less continuous structure, the crystalline regularity being intercepted by well-defined crevices occupied by non-crystalline material, serving as boundaries for the crystalline aggregates. The principal crevices would run parallel to the cellulose chains.

Since much of the knowledge of fiber structure has been a comparatively recent development, early theories of the mechanism of physical properties of cellulose made

no allowance for differences in structure. For example, the earliest theories of the mechanism of hydration were based on the formation of a cellulose hydrate which acted as a cementing material to bind the fibers together.

Since the curve of water vapor pressure against moisture content was shown to be a smooth curve and not step-wise as for hydrated salts, Strachan (37) argued that "hydration" could not be true chemical hydration but must rather be imbibition. He believed the layers of fibrillae to be porous, allowing water to penetrate, and causing the fiber to swell. During beating the outer layer was loosened, permitting fibrillation and easier access of water. In light beating, only the surface would be affected and a strong opaque paper would be obtained. In hard beating, the whole fiber would be fibrillated, softened, and bruised, resulting in a greaseproof type of paper. The strength was believed due to entanglement of fibrils, even of sub-microscopic ones.

Kress and Bialkowsky (38) showed that there was no appreciable change in the chemical constants during beating, except a slight drop in cuprammonium viscosity and an increased ease of hydrolysis, explainable by a greater degree of subdivision. Dye adsorption did not increase on beating, showing that the total surface did not increase, even though, through physical changes caused by beating, there was apparently an increased depth of color.

When pulp was beaten in various liquids, it was found that the ease of beating correlated with the swelling power of these liquids. The liquids which promoted the beating action most were those having hydroxyl or potential hydroxyl groups and a high specific inductance capacity.

Bell (39) favored Ldithe's concept of fiber structure. He believed that linkages between fibers are through a chain of orientated water molecules. In the unbeaten fiber something prevents this linkage occurring. This "something" is suggested to be the Ldithe membrane. These membranes are non-cellulosic and non-swelling. When they are broken in beating, cellulose to cellulose contact can take place.

Campbell (40) compared the curves of vapor pressure against moisture content for beaten and unbeaten pulp. Since the curves were identical it was concluded that beating caused no change in the degree of hydration, whatever the nature of such hydration. He advanced a theory of "partial solubility" of cellulose. When crystals of simple materials, such as sugar, dissolve the sugar molecules on the surface of the crystal surround themselves with water and are no longer bound in position by the attraction of the other sugar molecules. As soon as some molecules are dissolved, there is a tendency for molecules to be redeposited on the crystal. In cellulose a molecule of upwards of 100 glucose units is concerned.

Campbell postulated that individual units might be surrounded by an atmosphere of water molecules and, in a sense, be considered as dissolved. It would be very unlikely that all the units of a molecule would be so surrounded at the same time and therefore true solution of cellulose would not take place. When some part of a long chain "dissolved" it would enjoy a greater degree of freedom and might become attached to a neighboring crystal, if the latter were close enough. Such a theory would explain the results found by Kress and Bialkowsky (38), since liquids with a number of hydroxyl groups might be expected to have the greatest solvent action.

Campbell believed that the crystals were not separate and discrete particles but were united by branching of long chains from one crystal to another. During plant growth cellulose is deposited in the presence of a great deal of water. The cellulose structure, although strongly bonded, would be without strain. On removal of the water by evaporation strains would be set up and could be relieved only by the return of the water. When pulp is swollen in water these strains are relieved by the dissolving of the weak bonds.

Doughty (41) found that very little beating transforms the fiber so that, at equal solid fraction produced by wet pressing, the strength is independent of further beating. He divided beating into two parts. In one,

the strength increases due to actual changes in the surface condition of the fiber. In the other, increases are due purely to an increase of solid fraction dependent on increased shrinkage and, therefore, on decreased particle size. The second can be duplicated by wet pressing, while the first can not.

Campbell (40) conceived of beating effecting the same result in a different way. By mechanically flexing the swollen fiber, beating would cause breakage of some bonds which water would not dissolve by itself, causing greater flexibility and permitting greater compactness. As flexing proceeded, more bonds would be ruptured and finally fibrils would appear. Softening and fibrillation both permit greater possibilities of contact and hence greater strength. Subdivision of the fibers into fibrillae subdivides the water spaces into much smaller ones, thereby resulting in greater tension in the sheet during drying and consequently more compactness.

Clark (42) found that boiling (which largely destroyed the water of hydration) freed the beaten stock considerably but did not seriously affect the strength. He suggested that neither water of imbibition nor flexibility were as important as sometimes insisted. After prolonged soaking the pulp did not return to its low freeness before boiling. He believed that this indicated that the internal bonds of the fiber, broken by beating, were reunited without

causing great strain. Clark also investigated the adhesion between viscose strips. When strips are cleaned, wetted, placed together and allowed to dry, there is a definite adhesion. Since this can occur without rubbing, the effect can not be explained as entanglement of fibrillae. If the fibrillage theory be expanded to include crystallites partially broken away from the surface, this approximates Campbell's theory. From one viewpoint, these partially dissolved crystallites could be considered as the micilage assumed by earlier workers. Clark (42) believes that the small number of additional water molecules involved might easily escape detection by the rather crude chemical means employed in testing for a hydrate, and the small difference in moisture content for beaten and unbeaten pulp. He considered it significant that, although the evidence was slight and doubtful, it was all in favor of the existence of a hydrate.

Bailey (29) found that prolonged beating converted pulp into a gel, cylindricoids, and finer fragments. The gel was more easily hydrolyzed than the other material. He believed the gel to consist of short cellulose molecules, while the more resistant cylindricoids consisted of longer molecules. These results could be explained on the basis of partial solubility.

The theory of partial solubility can also be used to explain the well-known fact that the strength of pulps

and the rate of hydration decrease with an increase in the severity of digestion. In addition to the removal of non-cellulosic materials, purification would also result in the removal of the cellulose molecules of shorter length.

In wood, cellulose is accompanied by various amounts of other materials, principally lignin and hemicelluloses. Lignin is usually characterized by its staining properties, insolubility in 72 per cent sulphuric acid and by its methoxyl content. Hemicelluloses have been defined as those constituents of the cell wall which are insoluble in hot water, soluble in dilute alkalis, and easily hydrolyzed by dilute acids. Since some yield uronic acids, Gaudlin and Schryver (43) have suggested calling these polyuronides, reserving the term hemicellulose for those yielding only simple sugars on hydrolysis. Small amounts of other substances, such as resins, mineral matter, and proteins are also found.

Pectic substances are present in considerable amounts in non-lignified tissues but in very small amounts in most lignified tissues. According to Buston (44), all pectic substances are derivatives of pectic acid, which is thought to be composed of one molecule of arabinose, one of galactose, and four of galacturonic acid. This would give a uronic acid anhydride content of 70.5 per cent and liberate 20 per cent furfural on hydrolysis with 12 per cent hydrochloric acid.

Pectic compounds are divided into four types: (1) protopectin, insoluble, probably associated with cellulose and converted into soluble pectin by hydrolysis; (2) pectin, the soluble methyl ester of pectic acid, liberated from the cell wall by gentle hydrolysis; (3) pectic acid, the insoluble acid material derived by complete de-esterification of pectin; (4) metapectic acid, soluble stages in the degradation of pectic acid to simple sugars and sugar acids. Pectic substances can be extracted with 0.5 per cent ammonium oxalate, water at 105° - 110° C., dilute acids or dilute alkalis. Pectins are not soluble in cuprammonium hydroxide. There is no stain specific for pectin. They are usually identified by a combination of staining and solubility reactions. Anderson (45) states that there are several per cent pectin material in wood but that other substances are deposited which protect the pectin from the action of pectic solvents.

Hemicelluloses can be separated on one basis into hexosans, pentosans, mixed polysaccharides, and uronic acids. Hawley and Norman (46) based a separation on the isolation of Cross and Bevan cellulose, those present in Cross and Bevan cellulose not containing uronic acids, and those rendered soluble by the treatment frequently containing uronic acids.

Hägglund (47) based a differentiation on the ease of hydrolysis. No sharp boundary could be set. He used a

sulphite cook for separation. He found it impossible to get a residue of pure cellulose, since certain parts of the hemicellulose dissolved at the same rate as that at which the cellulose was hydrolyzed. In the easily hydrolyzed portion he found mannose, glucose, galactose, fructose, xylose, and uronic acid. The presence of fructose has been questioned by some investigators. In the difficultly hydrolyzed part (based on lignin-, ash- and ether extract-free pulp) he found 87 per cent cellulose, 6 per cent mannan, 4.5 per cent xylan, and 2.5 per cent levulan.

Hägglund and Prosse (48) cooked wood with sodium bisulphite, bleached the pulp, and subjected it to an alpha treatment, analyzing the bleached pulp and alpha residue for constituent sugars. Uronic acids were not found in the bleached pulp. About 6 per cent xylan and 3-6 per cent mannan were found in three samples of the bleached pulp. Small amounts of levulan were found in each of the bleached pulps and small amounts of galactan in two of the samples. Alpha treatments removed all the xylan and galactan in all samples and all the mannan in two samples. A small amount of the latter was left in the third sample. Small amounts of levulan remained after the alpha treatment.

Kurth and Ritter (49) treated wood with chlorine and alcohol-pyridine to obtain the total carbohydrate fraction. By hydrolysis of this material with one per cent sulphuric acid, they obtained a residue similar to Cross

and Bevan cellulose. In the hydrolyzed material they found mannan, glucosan, galactan, araban, xylan, uronic acid anhydride, volatile acids, and a methoxyl content.

Roth (50) extracted pulps with alkali in various ways to lower the pentosan content. He found it very difficult to remove the last one per cent of pentosan. Pulp extracted with 8.7 per cent sodium hydroxide at 0° would not develop strength when beaten and the Schopper-Riegler freeness dropped only from 875 to 855 cc. Young and Rowland (51) found that for soft woods there was a linear relation between the pentosan content of the pulp and its swelling capacity. Krčma and Bialkowsky (52) had previously found a correlation between the swelling capacity and the ease of beating of the same pulp in different liquids. These results fall in line with observations previously made by various investigators, including Richter (53), Schwalbe (55), and Wenzl and Congehl (54), who had found that pulps purified by alkaline extraction were harder to beat. Schwalbe mentioned that over-cooking and overbleaching produced "slime-formers" at the expense of fiber strength.

In a comparison of two pulps of practically the same lignin and pentosan content, Jones and Rieth (56) found a correlation of strength with mannan content. When the two pulps were extracted with barium hydroxide, the loss in breaking length at equal beating time was proper-

tional to the mannan content. Addition of xylan or mannan increased the strength. Obermanns (86) found that over-bleaching rags at elevated temperatures to produce degradation decreased the beating time, strength, and viscosity, and increased the copper number. Addition of xylan or of beta-cellulose to rag or sulphite pulp increased the speed of hydration and strength up to a maximum. Schorger (87) observed that treatment with hydrochloric acid reduced the beating time if the treatment was not excessive. It is well known that acid treatment degrades cellulose, as shown by decreases of viscosity and increases of copper number. This is supposed to indicate a shortening of the cellulose molecule.

Farr and Peterson (88) isolated cellulose particles from cotton by treatment with concentrated hydrochloric acid, considered by her a good pectic solvent. Later she mentioned (6) that particles and cementing material were isolated for further analysis by use of "standard pectic solvents" without specifying what solvents were used. "The cellulose particles will account for the crystalline behavior and the cementing material for the colloidal behavior.....Many of the fiber reactions which have been designated in the past as cellulose degradation represent only membrane disintegration. The cellulose particles themselves remain apparently unharmed, in the form of a white powdery residue." (88)

Farr (39) observed "The behavior of cotton fibers in solutions of cuprammonium has been studied in the light of the previously demonstrated structure of the cellulose membrane. The two primary cell membrane components, the cellulose particles and the cementing material which holds them together were studied separately. The cellulose particles failed to produce viscosities more than appreciably higher than the viscosity of the cuprammonium solution itself. Highly viscous solutions were produced, however, when cementing material, from citric acid extractions, was added to the cuprammonium solution. Equal quantities of cotton fibers treated for increasing lengths of time with 1% potassium hydroxide or 0.5% ammonium oxalate produced decreasing viscosities in the same order, when added to cuprammonium. When small quantities of cotton fibers were added to excessive amounts of cuprammonium, the viscosity of the solution was low enough to permit the falling of the cellulose particles to the bottom of the flask. They were recovered and their size, shape, optical properties and microchemical properties were found to be unchanged. It may be concluded therefore, that the cellulose component of the plant cell membrane does not dissolve in cuprammonium to produce the viscosities commonly attributed to it, but that the cementing material which surrounds the particles is responsible for this much-discussed phenomenon." (Underscoring added by the writer of this paper.)

"In conclusion it must be emphasized that the data presented concerns cellulose membrane formation and not cellulose formation.....Nor have we any basis at present for applying these data to the presumably more complex lignified and suberized plant cell membranes."

In another place, Farr (60) states: "A microscopic examination of the mixture of cotton and cuprammonium hydroxide corroborates this chemical behavior. The particles are seen to be dispersed throughout the mixture. When removed from viscous matrix they are still doubly refractive and react in their characteristic fashion to sulphuric acid and iodine.

"When a single fiber is treated with cuprammonium hydroxide, the outer limiting membrane does not dissolve. The rapidly swelling inner layers of the membrane burst through this resistant covering in a series of balloon-like enlargements. The cellulose particles are not visible at this point in the reaction. If, however, the swollen fiber is carefully washed with either cuprammonium or ammonia alone, it becomes evident that the presence of the particles has been obscured by the swollen cementing material. This reaction, too, may be carried past the point of disappearance in polarized light by washing the treated fiber with more of the cuprammonium. The double refraction of the cellulose portion of the fiber then reappears....

"Among the many problems which we hope some day

to study in detail are those of the hygroscopic behavior of fibres and their reactions to dyes. From scattered observations we have the impression that the hygroscopic behavior of the fibre is primarily associated with the reactions of the cementing material to moisture, augmented by the fact that upon softening this material, the fibrils in the wall tend to straighten from their spiral positions in the lamellae. We believe also that in the various processes of dyeing we shall be able to differentiate between the reactions of the separable membrane constituents. These impressions must be carefully checked and the measurable factors which enter into these reactions determined."

These observations are, to say the least, rather surprising since investigators have thought for a long time that cellulose dissolved in cuprammonium hydroxide. Staudinger (61) believed the cellulose was dispersed as molecules in sufficiently dilute solutions, and determined the molecular weight by a measurement of viscosity. Kraemer and Lansing (8) also believed the cellulose was subdivided to a molecular dispersion. They converted cellulose to di- and tri-acetates and back to cellulose again and determined the molecular weights at different points by means of the ultra-centrifuge. The agreement demonstrated that the solute particle in the several kinds of solutions is a fixed entity that goes through chemical reactions unchanged in size, and since it seems highly unlikely that

any assembly of molecules bound together by Van der Waals's forces, cementing materials from the original cellulose, or any agencies other than primary valence forces could so behave, it is permissible to infer that the solute unit in solution is the chemical molecule."

McBain and Scott (62) and others disagree and believe that the forces of association are too great to permit determination of the molecular weight from the viscosity. They found they could obtain an increase of molecular weight of cellulose derivatives simply by physical means and concluded from this that association was the important factor.

Whatever the cause of viscosity; molecule length, association, or cementing material, it is recognized in practice as a valuable criterion of "degradation" of cellulose. Kubelich (63) found a correlation between the viscosity of rag half-stocks and the strength of the handsheets made from them. Bialkowsky (64) noted a correlation of viscosity with the folding endurance of sheets. Gibbons and Ridge (65) found that the viscosity correlated with the tensile strength of single fibers under widely varying conditions of treatment with acid and oxidizing agents. McGregor (66) degraded rag, alpha, and Mitscherlich pulps by means of heat, bleach, and acid and found a correlation of the viscosity with the amount of degradation and with the folding endurance.

The sensitivity of cellulose to acids was early recognized and the name hydrocellulose was given to cellulose so modified. Dorée (87) gives various methods of preparation by treatment with acids in various ways and describes the work of Birtwell, Clibbens, and Geake (88)who prepared a series of hydrocelluloses under different conditions and determined their properties. Farr (88) has suggested that many fiber reactions designated in the past as cellulose degradation were in reality membrane disintegration, the cellulose particles remaining unharmed. It is hard to believe that cellulose would be unharmed by concentrated hydrochloric acid, when fuming hydrochloric acid will readily dissolve it and dilute acids will hydrolyze lower polysaccharides readily. It would also be difficult to explain the relation between copper number, viscosity, and strength of cellulose modified by acids, as found by Birtwell, Clibbens, and Geake (88). On the basis of previous work on viscosity, it is not so surprising that "cellulose particles" isolated by treatment with concentrated hydrochloric acid (if they were so isolated) failed to increase the viscosity of cuprammonium hydroxide appreciably.

It would be more surprising if such particles could be isolated by means of dilute alkali treatment, since a prolonged alkali boil is recommended as a preparation for standard cellulose from raw cotton by the Div-

ision of Cellulose Chemistry of the American Chemical Society (49). Other workers (54) have found that alkaline treatments lower the viscosity of cellulose very little or even raise it.

Farr (70) has stated: "..that the wood fiber- the young wood cell- is built up by means of cellulose particles layer upon layer." On this basis it does not seem probable that cellulose in the wood fiber would have a fundamentally different structure than that in cotton. It hardly seems possible however that any material of a pectic nature could survive the pulping and bleaching processes. Since wood pulp shows no signs of disintegrating or being modified in such a way as to become insoluble in cuprammonium hydroxide, the possibility is suggested that the cementing material is of a different nature. Ritter (26), by means of strong acids, has dissected wood fibers into small particles and the presence of a membrane has been suggested by Lüdtke (19).

Sakostschikoff (80, 81, 82) claimed to have isolated cross-elements from wood fibers and from cotton. As mentioned above, these cross-elements are assumed to have the same composition as the membrane material of Lüdtke. Cross elements were obtained both by the action of sulphuric acid and by centrifuging cuprammonium solutions of cotton. Lewis and Brauns (71) found that certain wood pulps contained a fraction which was insoluble in

cuprammonium hydroxide. A yield of 1.36 per cent was obtained from one pulp and a much smaller yield from a specially purified high-alpha pulp. The insoluble fraction separated as a copper compound containing 30-32 per cent copper oxide. Upon acidifying, a gray precipitate and a green-blue solution were formed. The latter was dialyzed and precipitated by absolute alcohol. A product was then obtained with an ash content of only 0.46 per cent, and negative uronic acid and methoxyl tests. A combustion analysis showed 44.37 per cent carbon and 6.25 per cent hydrogen as compared with 44.44 per cent carbon and 6.17 per cent hydrogen for cellulose. Upon hydrolysis with 42 per cent hydrochloric acid a yield of 97 per cent reducing sugars was obtained, of which about 55 per cent was pentosan. Mannose and galactose were absent.

Chapter XXI.

PRESENTATION OF THE PROBLEM.

It is readily apparent that there is still no general agreement as to the structure of the cell wall. The majority of investigators favor theories involving the occurrence in the cell wall of more or less discrete particles imbedded in a matrix, or surrounded by a membrane. The nature of this membrane varies. Liddle believes it to be similar to lignin. Frendenberg assumes a micelle series imbedded in lignin and hemicellulose. A. J. Bailey believes the matrix to be cellulose, since he found evidence of it in surgical cotton. Farr believes how particles are coated by pectic material. Lewis believes that there is a membrane, at least around the whole fiber if not also in the cell wall, which consists mostly of carbohydrates. I. W. Bailey and Kerr believe that the cell wall is a continuous, coherent matrix, having zones varying in density, in orientation, and sometimes in composition.

Contrary to the usual beliefs, Farr stated that cellulose did not dissolve in cuprammonium hydroxide. She found by separation of the particles and the cementing material that the viscosity was due, not to the cellulose, but to the cementing material. The cellulose particles seemed to remain unchanged by various methods of separation, not being affected by concentrated hydrochloric acid or by

cuprammonium hydroxide. She believed that many fiber reactions frequently referred to as cellulose degradation were in reality nothing but membrane disintegration.

It has been repeatedly demonstrated that the viscosity of solutions of cellulose or of cellulose derivatives has a great practical value in indicating the behavior to be expected in industrial processes. If these statements by Farr are correct, the cementing material must be of much greater technical significance than has hitherto been believed, and the practical properties of the fiber must be closely correlated with the nature of these cementing substances.

It is the purpose of this study to determine to what extent the chemical and physical properties of wood pulp fibers are related to a hypothetical pectic cementing substance.

Chapter IV.

PRESENTATION OF DATA.

A. The System: Cellulose-Cuprammonium Hydroxide.

1. Introduction.

The system formed when cellulose dissolves in cuprammonium hydroxide is too complex to be discussed here. It is known that certain limitations are placedupon its solvent power. Joyner (72) found that the solubility of cellulose was independent of the viscosity produced and depended on the amount of copper present, if sufficient ammonia was also present. He found that one gram of copper dissolved about 2.3 grams of cellulose, corresponding to about one molecule of copper per glucose unit. At low copper concentrations, the cellulose would not dissolve but if more concentrated solutions were prepared, they could be diluted to the same low concentration with ammonium hydroxide without the cellulose precipitating. He noted that high copper concentrations, especially with a low ammonia concentration, caused the cellulose to gelatinize and that it then dissolved very slowly.

2. Materials.

Unless otherwise noted, a bleached Mitscherlich pulp was used in the following tests. It had an alcohol-benzene solubility of one per cent and a lignin content of

less than 0.1 per cent. A few tests were also run on other types of cellulosic material. One was a commercial bleached kraft, another was a specially purified pulp. The latter had an alpha-cellulose content of 99.1 per cent, pentosan content of 0.7 per cent and an ash content of 0.077 per cent. One test was also made on a few fibers of raw cotton. These were taken from a single boll which had been picked for some time and was quite dry.

3. Viscosity.

a. The Effect of Various Cupric Solvents on the Viscosity of the Extracted Pulps.- Small samples of the bleached Mitscherlich and bleached kraft pulps were extracted at one per cent consistency in two-liter Erlenmeyer flasks placed in a constant-temperature oil bath. At the end of the extraction period, the contents of the flask were filtered on filter paper, washed well with hot distilled water, and air-dried. After drying, the pulp was shredded, the moisture content determined, and the viscosity determined in triplicate by TAPPI Standard T 206 m. There was one exception to this procedure. Samples of bleached Mitscherlich and of bleached kraft pulp were moistened with water to about 50 per cent, heated in Erlenmeyer flasks for 18 hours at 95° and allowed to air-dry, without removing any material, to observe the effect of heat in

the presence of water, as distinguished from this effect plus extraction.

Table I.

The Effect of Extraction with Acetic Solvents on the Viscosity of the Extracted Pulps

Treatment No.	Solvent	Concn. (%)	Temp. °C.	Time hrs.	Yield of Extraction %	Mitsch. Viscosity of pulp (centipoises)	Mich. Kraft Viscosity of pulp (centipoises)
1	Blank	-	-	-	-	32.8	11.5
2	Heat	-	95	18	-	28.4	9.8
3	Water	-	95	18	-	27.5	-
4	Ammonium Oxalate	0.5	75	1	-	28.1	10.6
5	Ammonium Oxalate	0.5	75	15	-	30.4	9.8
6	Ammonium Oxalate	0.5	95	18	93.7	28.6	-
7	Ammonium Oxalate	5.0	95	21	-	29.0	9.3
8	Hydrochloric Acid	0.01 N	95	18	97.7	9.5	-
9	Sulphuric Acid	1.0	95	1	98.3	15.6	-
10	Sulphuric Acid	1.0	95	18	95.1	7.2	-
11	Sodium Hydroxide	0.05	95	18	-	27.2	-
12	Sodium Hydroxide	1.0	95	1	99.0	26.1	-
13	Sodium Hydroxide	1.0	95	18	79.6	20.5	-

As a check on the change of chemical constants which might have accompanied the very considerable drop in viscosity shown by the acid-treated samples, alpha-, beta-, and gamma-cellulose, and copper number were determined on the bleached Mitscherlich pulp treated according to extraction no. 8, 0.01 N hydrochloric acid. The results are given in Table II.

Table II.

Change of Chemical Constants of Acid-Treated Pulp.

	Original	Acid-Treated
Yield (%)	-	97.7
Alpha-Cellulose (%)	82.6	79.9
Beta- Cellulose (%)	4.7	5.2
Gamma-Cellulose (%)	12.7	14.9
Loss of Alpha-Cellulose (%)	-	4.5
Copper Number	2.66	3.06
Viscosity	32.8	9.6

Since Farr found that large amounts of material could be extracted from cotton fibers by ammonium oxalate and that these extracted fibers showed almost no viscosity in cuprammonium hydroxide, a test was also run on cotton. The fibers were separated from the seeds and part of the mature fibers extracted with 0.5 per cent ammonium oxalate at 75° for 15 hours, washed in hot distilled water, and

air-dried. The viscosity was determined on both the extracted and unextracted samples by the standard method, with the exception that only one-half the specified weight was used, making a 0.5 per cent consistency. This was done because the regular 1.0 per cent consistency was so viscous it would not flow through the viscosity tube. After extraction the viscosity was found to have changed from 36 to 48, an increase rather than a decrease but probably within experimental error, since this series did not check as well as previous ones had.

A commercially purified pulp was also extracted. This pulp had been purified to a high degree, as shown by Table III.

Table III.

Chemical Analysis of Specially Purified Pulp.

Alpha-cellulose	99.1 per cent
Pentosans	0.7 " "
Ash	0.077" "
Copper Number	0.049

It appears that any cementing material of a pectic nature would surely have been removed in the process of bringing this pulp to such a high degree of purity. When it was extracted with 0.5 per cent ammonium oxalate at 95° for 18 hours, it was found that the viscosity had dropped from 48.1 to 36.6. This represents a percentage decrease

about the same as that found on treatment of the bleached Mitscherlich pulp, either with ammonium oxalate or with water.

b. The Effect on the Viscosity of the Addition of Pectin to Cuprammonium Hydroxide.- If the viscosity of solutions of cellulosic materials in cuprammonium hydroxide is due to the effect of highly viscous pectic material, it should be possible to change the viscosity of cuprammonium hydroxide very appreciably by the addition of varying amounts of pectic materials. Since only a small amount of pectin is known to be present in cellulose fibers, correspondingly small amounts of pectin were used in these tests. Two types of pectin were used. One was Eastman Kodak Co. Lemon Pectin, prepared by citric acid extraction; the other was Certo, a commercial pectin solution. Amounts of the dry pectin corresponding to various concentrations were placed in regular viscosity tubes and treated as in TAPPI Standard Method T 206 m. To avoid the effect of dehydration of the pectin, the commercial solution was also used. In these tests, the total solid content of the Certo was determined and amounts corresponding to various concentrations were used, adjusting by the addition of distilled water so that the concentration of the cuprammonium hydroxide would be constant throughout the test. Samples of this were tested, both with and without the presence of bleached Mitscherlich

pulp. When pulp and Certo were used together, it was found necessary to disperse for 60 hours instead of the usual 15 hours. A test was also made to determine whether the system Certo-cuprammonium hydroxide was appreciably changed by increasing the concentration of copper. Cuprammonium hydroxide as prepared according to the recommended practice of the American Chemical Society (73) was used. This contains 30 grams copper, 165 grams ammonia and 10 grams sucrose per liter, as compared to 15 grams copper, 200 grams ammonia and 2 grams sucrose per liter in the TAPPI Standard cuprammonium hydroxide.

Table IV.

The Effect of the Addition of Pectin to Cuprammonium Hydroxide.

Kind of Cuprammonium Hydroxide	Concn. of Pulp %	Kind of Pectin	Concn. of Pectin %	Viscosity Centi-poises
TAPPI	0.00	Lemon	0.00	1.35
"	0.00	"	0.001	1.36
"	0.00	"	0.01	1.38
"	0.00	"	0.1	1.40
"	0.00	Certo	0.00	1.34
"	0.00	"	0.05	1.39
"	0.00	"	0.1	1.54
"	1.00	"	0.00	35.4
"	1.00	"	0.10	35.8
A.C.S.	0.00	"	0.00	1.40
"	0.00	"	0.05	1.39
"	0.00	"	0.10	1.41

4. Swelling Behavior.

The behavior of certain of the pulps extracted for viscosity determinations and determination of the fraction insoluble in cuprammonium hydroxide was studied in graduated strengths of cuprammonium hydroxide. TAPPI cuprammonium hydroxide was diluted with various amounts of distilled water, the percentage subsequently referred to being the amount of TAPPI cuprammonium hydroxide present in the dilute solution. A few fibers of the pulp being studied were mounted in water on a microscope slide, covered with a cover glass, and adjusted on the stage of a microscope. Beginning with 10 per cent cuprammonium hydroxide (one part TAPPI cuprammonium hydroxide to nine parts of water), cuprammonium was added at one side of the cover glass and drawn off at the other by means of paper toweling. When the effects at one concentration had been observed, the next stronger solution was used.

The pulps treated with heat, hot water, ammonium oxalate, and alkali all swelled at the same concentration of cuprammonium hydroxide (25 per cent TAPPI) and with the same type of swelling as did the original pulp. The slight differences observed were probably due to variations within the same pulp. Pulp number 9 (Table I), treated with one per cent sulphuric acid for one hour, showed only a faint suggestion of ballooning, without true balloons being formed. The helical windings became visible, the fiber swelled and

started to dissolve. With 18 hours acid treatment (pulp number 10), fibrillation resulted at a lower concentration (20 per cent) than that at which ballooning took place in the untreated pulp (25 per cent). The size of the fibrils was not uniform. With increasing strength of cuprammonium hydroxide, the fibrils dispersed, leaving a gelatinous, almost invisible mass which in turn was further dispersed by stronger cuprammonium hydroxide.

5. Solubility in Cuprammonium Hydroxide.

a. Settling under Gravity.- For this series of tests the pulps prepared for viscosity determination were used. Only part of the pulps prepared by treatment of the bleached Mitscherlich pulp were used. The details of the treatment are given with the results in Table V. One gram each of the various pulps were extracted with alcohol-benzene, washed with hot water, dried and dispersed in 100 cc. cuprammonium hydroxide of TAPPI strength with the sugar omitted. The dispersion was carried out in glass tubes 35 cm. long and 1.8 cm. in diameter with 2 regular viscosity wedges, the tubes being rotated on the viscosity wheel for at least 24 hours. A 70 cc. test tube was then filled with the dispersion, stoppered, wrapped to exclude light, and placed in an upright position in the refrigerator. To avoid any possibility of the viscosity being too high to permit settling, 10 cc. of the one per cent dis-

persion was diluted to 70 cc. with distilled water, mixed, and allowed to stand in the refrigerator. At the end of five weeks, the tubes were examined and an estimation made of the amount settled. The sediment from the dilute dispersion was so slight that no quantitative estimation could be made. The results of the other tests are given in Table V. The figures refer to the approximate number of cc. of material which settled out under the influence of gravity from 70 cc. of a one per cent dispersion.

Table V.

The Separation, by Settling, of Material Insoluble in Cuprammonium Hydroxide.

Treatment No.	Extracting Agent	Concn. %	Temp. °C.	Time hrs.	cc. Settled from 70 cc. of 1% dispersion
1	Blank	-	-	-	1.5
2	Heat	-	95	18	0.8
3	Water	-	95	18	0.8
6	Ammonium Oxalate	0.5	95	18	1. and some unsettled
8	Hydrochloric Acid	0.01 N	95	18	0.5
10	Sulphuric Acid	1.0	95	18	Trace
11	Sodium Hydroxide	0.05	95	18	Unsettled
13	Sodium Hydroxide	1.00	95	18	Trace

b. Quantitative Determinations.- A determination was made of the fraction of the bleached Mitscherlich pulp which was insoluble in cuprammonium hydroxide. Unless otherwise stated, cuprammonium hydroxide of the strength specified by TAPPI Standard T 206 m, omitting the sugar, is used. In each case a weighed sample of shredded pulp of known moisture content was dispersed in cuprammonium hydroxide, centrifuged at 3000 r.p.m. for 10 minutes, and the clear liquid decanted off. Fresh cuprammonium hydroxide was then added, the settled material dispersed in it by means of a motor-driven stirrer passing through a stopper. After standing at least several hours, the dispersion was centrifuged as before and the treatment repeated until no more cellulose was dissolved. In making this test, it is necessary to leave the cuprammonium hydroxide-insoluble material dispersed in cuprammonium hydroxide over-night before centrifuging, then decant and acidify the clear liquid, and again allow it to stand over-night. If no precipitate of cellulose has separated out at the end of this period, the centrifuged material is considered free of cellulose. After washing free of cellulose, the material was then washed in the same way with 1:1 ammonium hydroxide until the clear liquid removed only slight amounts of blue color. The material was then filtered on a Gooch crucible, washed with alcohol and ether, and dried at 105° to constant weight. The Gooch crucible was then heated in the muffle furnace at about 750° C. to

constant weight. From these weights, the ash-free yield was calculated.

Several modifications were made to improve the accuracy of the method. In the first trial, 4.0 grams of shredded pulp was dispersed in a bottle with 400 cc. of cuprammonium hydroxide and the insoluble fraction collected by centrifuging and decanting off the clear liquid. It was feared that the mechanical difficulty of collecting all the material and of transferring it from one vessel to another introduced errors; therefore 1.0 gram samples were dispersed in the centrifuge jars to avoid transference of the dispersion. However, in these, the weight of final product was so slight that errors and losses caused large percentage errors. It was also feared that all the resins were not removed; to remove this possibility, the samples were extracted with alcohol-benzene in a Soxhlet extractor for 8 hours, washed with hot water, and dried before dispersing. For the last series, 10 grams of pulp were tumbled in 500 cc. of cuprammonium hydroxide for 2 days, diluted to one liter with distilled water, well mixed and collected by centrifuging, then washed as in the other tests. One large sample, 80 grams, not extracted with alcohol-benzene, was dispersed at three per cent consistency, diluted to one per cent, mixed, collected by centrifuging, washed in the usual way and dried in a vacuum desiccator over concentrated sulphuric acid for analysis. A micro-ash determination was made

and the ash-free yield calculated.

In order to determine the effect on the per cent insoluble in cuprammonium hydroxide of treatment with pectic solvents, samples of bleached Mitscherlich pulp were extracted for 18 hours at 95° C. with 1.0 per cent sulphuric acid, 1.0 per cent sodium hydroxide, and 0.5 per cent ammonium oxalate. These pulps were then washed, dried and extracted with alcohol-benzene as in the regular determination.

Table VI.

Determination of Cuprammonium Hydroxide-Insolubility

Sample	Size of Sample g.	Ash-free Yield %
Bleached sulphite	4.0	1.08
" "	2.0	0.75
" "	1.0	2.19
" "	1.0	1.98
" "	1.0	1.82
" "	30.0	2.73
Ammonium Oxalate extracted	1.0	1.91
" " "	1.0	1.99
Hot Water extracted	1.0	0.6
" " "	1.0	0.9
Alcohol-benzene extracted	10.0	0.92
" " "	10.0	1.38
" " "	10.0	1.37
Acid extracted, followed by alcohol-benzene	10.0	0.16
	10.0	0.17
Alkali extracted, followed by alcohol-benzene	10.0	0.04
	10.0	0.09
Ammonium oxalate extracted followed by alcohol-benzene	10.0	1.60
	10.0	1.74

c. The Nature of the Insoluble Fraction.- As described before, a large sample of 30 grams of the bleached Kitscherlich pulp was dispersed at three per cent consistency, diluted to one per cent, collected by centrifuging, washed free of cellulose with cupramonium hydroxide, the excess copper washed out with ammonium hydroxide, and the material then washed with alcohol and ether, and dried over concentrated sulphuric acid in a vacuum desiccator. This dry material was weighed for yield and a sample of 1.5 grams taken out for analysis. When an attempt was made to use this dry material for a micro-ash determination, it was found to be very hygroscopic. The remainder of the material was allowed to come to equilibrium with the moisture of the air and the moisture content calculated from the increase of weight. Ash was then determined on this material by a micro-method and calculated to the dry basis.

The 1.5 gram sample was treated with 42 per cent hydrochloric acid, allowed to stand several hours, diluted, and allowed to stand over-night. The insoluble material was coagulated by digesting at 80°, filtered on a Gooch crucible, and weighed. Copper was removed from the filtrate with hydrogen sulphide, the solution decolorized with carbon, filtered, and concentrated under vacuum at 35° C. The residual hydrochloric acid was neutralized with sodium hydroxide so that the solution was acid to litmus but neutral to Congo Red, and the solution diluted to about

5 per cent. Samples were removed and treated with phenylhydrazine and acetic acid to test for mannose. After six hours in the refrigerator with occasional scratching of the test tubes, no phenylhydrazone had separated, indicating the absence of mannose. After two days, a small amount of yellow, gummy material had separated.

The remainder of the hydrolyzed sample was diluted to about two per cent and mixed with an equal volume of yeast extract. The total reducing sugar was determined on this mixture by a micro-modification of Allihn's method (74) developed and tested by Dr. E. F. Kurth, of the staff of the Institute of Paper Chemistry. In this method, 10 cc. each of the Allihn copper sulphate and alkaline tartrate are mixed with 20 cc. distilled water and brought to a boil. The boiling mixture is then poured into 2 cc. of a one per cent sugar solution diluted to 10 cc. with distilled water, and boiled for exactly 2 minutes. The solution is then filtered on asbestos without diluting, washed, and the cuprous oxide determined volumetrically by titration with sodium thiosulphate according to the method of the Association of Official Agricultural Chemists (75).

Since the yeast extract had a reducing value of zero, the total reducing sugar could be calculated. Ten cc. samples were then placed in small calibrated tubes, sterilized at 15 pounds pressure for 15 minutes and inoculated for selective fermentation. Two tubes were inoculated

with mixed Saccharomyces cerevisiae, which ferments all hexoses. Two other tubes were inoculated with Torula dattila, which ferments all hexoses except galactose. These organisms had been tested and found satisfactory. After fermenting at 28° for 6 days, samples were withdrawn, boiled to expel aldehydes formed during fermentation, and the residual reducing sugar determined. Considering all the residual sugars as pentoses, the relative percentages of pentose, glucose, and galactose were then calculated.

Table VII.

The Nature of the Fraction Insoluble in Cuprammonium Hydroxide.

Total yield (on original pulp)	5.05%
Moisture content of isolated material at equilibrium with the atmosphere	5.2 %
Ash content (on dry basis)	15 %
Fraction insoluble in acid (on dry basis)	3 %
Total reducing sugar (on dry basis)	82 %
Composition of reducing sugar	
Mannose	0 %
Glucose	82 %
Galactose	3 %
Pentoses	15 %

B. The Effect of Extraction of Bleached Mitscherlich Pulp with Hot Water and with Ammonium Oxalate.

1. Method of Extraction.

The same bleached Mitscherlich pulp was used for this series of tests. Its alcohol-benzene solubility was one per cent and its lignin content less than 0.1 per cent. Two different series of tests were run. In the first set, designated as Series A, 100 grams of air-dried pulp were extracted with 1500 cc. of the extracting agent in two-liter Erlenmeyer flasks placed in a constant-temperature oil bath, held at 95° C. At the end of 10 hours, the contents of the flasks were strained off on a cloth and washed well with distilled water. Six such samples were combined in a 10 gallon crock and thoroughly mixed at about two per cent consistency with a Lightnin mixer. The pulp was then strained off on a cloth, squeezed, and spread out to air-dry.

In Series B, the pulp was extracted in a 10 gallon milk can at about two per cent consistency. The pulp was agitated with a Lightnin mixer kept running about 20 per cent of the total extraction time. The milk can was placed inside a larger can into which a steam line was run. In this way a temperature of about 98° was maintained in the pulp suspension. At the end of 10 hours the pulp was strained off on a cloth, washed with distilled water to remove the oxalate, and finally with tap water. Extractions VI and VII

were made as outlined, the former with distilled water and the latter with 0.5 per cent ammonium oxalate. Extraction IX was made using three short extraction periods totalling 10 hours instead of the one long period, washing the pulp between periods, and redispersing in fresh ammonium oxalate.

In extraction VIII, an attempt was made to determine the effect of heat treatment alone as distinguished from this effect plus extraction. For this purpose, the same weight of pulp (600 grams) was moistened with water and placed in a container, which was in turn placed in a hot water bath. The pulp was mixed occasionally and at the end of 10 hours spread out to dry.

2. Yields.

Yields were not determined on the extractions of Series A. In Series B, the pulp used was carefully weighed, sampled for moisture, extracted, air-dried, weighed, and again sampled for moisture. Ash determinations were made on the oven-dry moisture samples and the yields calculated to the oven-dry, ash-free basis, since the ammonium oxalate-extracted pulps were found to have an appreciable ash content, no doubt due to the pulp being washed with calcium-containing tap water before the oxalate was completely removed with distilled water. This ash content persisted, even after the pulps were redispersed in water and rewashed.

Table VIII.

Oven-dry, Ash-free Yields, Series B.

Extraction Number	Type of Treatment	Ash Content Per Cent	Ash-free Yield Per Cent
VI	Hot Water Extraction	0.24	99.2
VII	Ammonium Oxalate Extraction	3.4	98.7
VIII	Heat in Presence of Water	0.26	100.
IX	Repeated Ammonium Oxalate Extraction	1.2	96.9

5. Chemical Analysis.

Chemical tests were made on the pulps prepared in Series A and B by the standard methods. Alpha-cellulose was run according to TAPPI Standard Method T 203 m and calculated to the ash-free basis. Gamma-cellulose was run by oxidation with potassium dichromate and concentrated sulphuric acid by Institute Standard Method 425. Beta-cellulose was calculated by the difference between the sum of the alpha-cellulose and gamma-cellulose and 100. Pentosans were determined by distillation with 12 per cent hydrochloric acid and precipitation with phloroglucin, according to Institute Standard Method 424, followed by extraction with alcohol. Copper numbers were determined according to TAPPI Standard Method T 430 m and cuprammonium viscosity by T 206 m.

Table IX.

Chemical Analysis, Series A and B

Pulp No.	Extract used	Ash %	Cellulose Alpha %	Cellulose Beta %	Cellulose Gamma %	Pento-sans %	Copper Number	Viscosity Centi-Poises
-	Blank	0.35	82.6	4.7	12.7	7.0	2.69	30.8
IV	Hot Water	0.20	82.9	4.0	13.1	6.3	2.46	27.3
V	Ammonium Oxalate	0.49	82.1	4.4	13.5	6.8	2.35	28.7
VI	Hot Water	0.24	82.6	3.8	13.6	6.3	2.43	24.7
VII	Ammonium Oxalate	3.4	82.0	4.1	13.9	5.7	2.35	24.8
VIII	Heat Only	0.26	83.5	3.5	14.0	6.4	2.49	28.3
IX	Repeated Ammonium Oxalate	1.2	82.9	3.7	13.4	6.8	2.38	29.3

4. The Nature of the Extract.

The same bleached Hitscherlich pulp was extracted at 95° for 15 hours, the filtrate collected and evaporated under vacuum at 35° to 250 cc. A similar extraction was made with 0.5 per cent ammonium oxalate, one-half of the filtrate concentrated and the other half treated with lime to remove the oxalate, filtered, and concentrated to 250 cc.

Total solids were determined by evaporation and drying at 105° to constant weight. Ash was determined on the same sample by ignition in the muffle furnace. The total reducing sugar was determined by boiling in 3 per cent sulphuric acid in an oil bath for 6 hours, neutralising

with calcium carbonate, filtering, and determining the reducing sugar on the filtrate by Koch and Ruhsam's modification (78) of Allihn's method. Since all the material was not rendered soluble by this hydrolysis, the insoluble material was filtered off previous to neutralization and weighed. Aliquot samples were evaporated to dryness in a vacuum desiccator and used for lignin determinations according to Institute Standard Method 13. Pentosans were determined by hydrochloric acid distillation (Institute Standard Method 424), followed by extraction of the furfural phloroglucide with alcohol. Liquid samples were used and the concentration of the acid adjusted accordingly. Uronic acid anhydride was determined from the carbon dioxide evolution when boiled with 12 per cent hydrochloric acid, according to a modification of a micro-method devised by Burkhart, Baur and Link (77). Results were calculated on the basis of total solids and also on the basis of the original pulp. A comparison of the two types of extracts is given in Table X.

5. Strength Characteristics.

A weight of air-dry pulp equivalent to 360 grams of oven-dry pulp was weighed out and soaked in water at 25° for 30 minutes. It was then furnished to a 1½ pound Valley beater with enough additional water to make 23 liters in all, slushed for 10 minutes, and then 6500 grams plus a

Table X.

The Nature of Hot Water and Ammonium Oxalate Extracts

	% of Total Solids		% of Original Pulp	
	Hot Water	Ammonium Oxalate	Hot Water	Ammonium Oxalate
Total solids	-	-	1.06	1.01
Ash content	17	18	0.18	0.18
Reducing sugar	46	40	0.48	0.40
Dilute acid insoluble	4	3	0.04	0.03
Lignin	1	4	0.01	0.04
Pentosan	28	34*	0.29	0.34*
Uronic acid anhydride	6	8	0.06	0.08

* All tests except this one were made on the filtrate after removal of the oxalate.

balancing weight added to the bed-plate arm. Samples were removed at 5 minutes after adding the weights and every 10 minutes thereafter. Freeness was determined with a Schopper-Riegler freeness tester, using a sample equivalent to 2.0 grams oven-dry pulp, recording the flow from the side arm and correcting to 20° C. Sheets were made according to TAPPI Standard Method T 205 m, conditioned over-night, and tested for basis weight, caliper, bursting strength, tearing strength, tensile strength, and fold.

The bursting strength was calculated to per cent points per pound by dividing the actual burst in pounds per square inch by the basis weight in pounds for a ream

of 500 sheets 25 by 40 inches, and multiplying by 100. Tearing strength was converted to a tear factor by dividing the actual recorded tear of 8 sheets by 8, multiplying by 16, dividing by the basis weight, and multiplying by 100. Apparent density was calculated by dividing the basis weight in pounds by the caliper in points (thousandths of an inch). The results of the fold determination were so erratic that no significant differences could be found between the various treated pulps, all of which were lower than the original pulp. In Table XI, representative values have been selected for comparison. Detailed results can be found in the Appendix.

Table XI.

Strength Characteristics, Series A

Pulp Number	-	IV	V
Treatment	Blank	Hot Water	Ammonium Oxalate
Time to 400 freeness (min.)	104	121	139
Maximum burst (% pts./lb.)	114	108	102
Tear factor at 90 minutes	165	159	153
Tear factor at 400 freeness	85	83	80
Maximum breaking length (yards)	9570	8990	8600
Apparent density at 400 freeness (lbs./pt.)	16.4	15.7	15.7

It was found that the beater used for Series A changed in calibration quite rapidly. When the second series was ready to be run, the beater had changed so that it required a much longer time to beat a stock to the required freeness. The beater was sharpened and several stocks beaten in it before the series was started. As a check on the amount of change in the beater, the untreated pulp was beaten first then pulps VI, VII, VIII, and IX, followed by another sample of the untreated pulp, all runs being made under the same conditions and the beater being used for nothing else during the series. The conditions were the same as for Series A, except that only 5 minutes was allowed for slushing and only 4500 grams was used on the bed-plate instead of 8500 grams.

Table XII.

Strength Characteristics, Series B.

Pulp Number	-	VI	VII	VIII	IX	-
Treatment	Original	Hot Water	Ammonium Oxalate	Heat Only	Repeated Ammonium Oxalate	Original
Time to 400 freeness (minutes)	62	67	65	80	90	84
Maximum burst (% pts./lb.)	110	112	104	109	99	112
Tear factor at 20 minutes	122	135	138	147	136	139
Tear factor at 400 freeness	83	89	91	93	93	88
Maximum breaking length (yards)	9160	9120	8310	8910	7970	9090
Apparent density at 400 freeness	16.8	16.6	16.8	16.3	15.9	17.0

Chapter V.

DISCUSSION OF RESULTS.

It can readily be seen from Table I that pectic solvents, with the exception of acids, have no effect on the viscosity of wood pulps. While each test did show a slight drop from that of the original pulp, this can be charged to the effect of heat in the presence of water. It is possible that the increase of viscosity above that of the water-extracted pulp when treated with alkali is significant. If so, it can be explained by the removal of the more degraded material, thereby resulting in a greater concentration of the less degraded part.

The acid did lower the viscosity but this is no new observation. The question involved here is whether the decrease is due to chemical degradation (probably hydrolysis of the hemi-acetal linkage), dissociation, or to a disintegration of a membrane material. If the latter is true, assuming as did Farr that there is practically no change in the cellulose itself, then we should not expect an appreciable change in the chemical analysis of the pulp, since the membrane is assumed to make up only a few per cent of the total weight.

If we examine the chemical constants given in Table II for one of the pulps treated with acid, we find that the copper number was increased. The change, while

appreciable, is not so great that it could not be explained by a change of membrane material. The loss of alpha-cellulose is easily explained on the usual basis of degradation; that is, by lowering the resistance to solution of a certain percentage of the cellulose molecules below the threshold fixed by the conditions of the determination.

On the basis of Farr's theory, the change is not so readily explained. The membrane material might be assumed to be insoluble in the alpha-cellulose determination and rendered soluble by the acid treatment. In that case, if the cellulose is assumed to remain unchanged, the membrane substance must compose at least 4.5 per cent of the fiber. Since, even in wood pulps, higher viscosities are obtained than that of the original pulp used in these tests, we must assume that the membrane makes up a large part of the fiber or that the material is of a different nature in different pulps. If cotton is considered, very much higher viscosities are obtained.

The results of several special extractions are also given. The changes can hardly be called significant. In the case of the raw cotton, the viscosity under standard conditions of one per cent consistency was so viscous that it would not flow through the viscosity tube. Accordingly, only one-half this amount was used. Due to the nature of the material it was harder to handle than the shredded wood pulps and the probable error is greater. The pulp purified

to an alpha-cellulose content of over 99 per cent and a pentosan content of less than one per cent showed only about the same percentage decrease in viscosity as the other pulps, supporting the belief that this drop is due to degradation of the cellulose rather than to removal of cementing material.

In this connection, Kraemer's determination of the molecular weight of Farr's particles may be mentioned. Although molecular weights of over 500,000 have been obtained for native cotton cellulose, Kraemer obtained only 40,000 for these particles. It appears from evidence discussed above that cellulose in cuprammonium hydroxide is present in the molecular form. A molecule of length corresponding to the size of the ellipsoidal particles would have a molecular weight of about 500,000. But since, actually, these particles have a molecular weight of only 40,000, we are forced to conclude that the cellulose molecule has been subdivided, or degraded.

Even if the nature of the cementing material were known, it is questionable whether it could be added to pulp in such a way as to approximate the natural state. However, Farr has stated that cementing material extracted by citric acid, when added to cuprammonium hydroxide, considerably increased its viscosity. In the present results, in Table IV, slight increases are noted, for example by the addition of 0.1 per cent Certo, but this amount represents 10 per

cent of the weight of cellulose usually used. When it is remembered that a 1 per cent solution of cotton cellulose in cuprammonium hydroxide can have a viscosity well above several hundred, it is obvious that pectin would have to make up a very considerable portion of the fiber to account for these viscosities. As before mentioned, no claim is made that the addition of pectin in this manner duplicates its occurrence in the native fiber. It is possible that the treatment of the pectin in a different manner might raise the viscosity.

The swelling characteristics of cellulose fibers in cuprammonium hydroxide are usually explained by theories similar to that of Lewis, mentioned above (p. 15-6). He assumes the formation of an osmotic cell, the outer membrane of the cell constituting a semi-permeable membrane. Cuprammonium hydroxide diffuses through this membrane and combines with the cellulose but the cellulose-copper complex can not diffuse back. Consequently an osmotic pressure is built up which expands the fiber. Since the fiber appears to be restricted at certain places, this expansion takes on the familiar bead-like formation.

On the basis of Farr's theory, since the cellulose particles themselves are not affected by cuprammonium hydroxide, the swelling must be due to an interaction of the cuprammonium hydroxide and the cementing material. Treatment with pectic solvents should remove this cementing

material and thereby prevent swelling. The results here are similar to those on viscosity, all extracting agents except acid being without effect.

Farr obtained almost quantitative yields of cellulose recovered from cuprammonium solution as particles. Since the viscosity is supposed to prevent particles from settling out under ordinary conditions, extracting the cementing material should permit the cellulose to settle more readily. Although previous tests had shown these extractions to be without effect on viscosity, dispersions of these pulps in TAPPI cuprammonium hydroxide were allowed to stand. What little sediment did settle out was decreased rather than increased by these treatments.

Farr (60) believed that the cementing material swelled when fibers were treated with cuprammonium hydroxide and that this swollen cementing material masked the cellulose particles so that they could not be seen. When fibers were treated on a microscope slide with cuprammonium hydroxide and then the swollen cementing material washed out with fresh cuprammonium hydroxide, she said the cellulose particles were clearly visible. In the present work, even centrifuging of one per cent solutions failed to separate any appreciable amount of material, the highest yield after removal of resins being less than two per cent, a value more nearly corresponding to the amount of membrane material supposed to be present.

Farr (79) said: "It is not an easy thing to obtain this reaction with a cotton fiber. The tendency is to wash the entire fiber mass from the field. I would not like to tell you about the difficulties which we have before we learned how to treat the fiber just enough to cause them to disappear and reappear." This statement suggests that perhaps the reason Farr found cellulose particles not soluble in cuprammonium hydroxide was because she varied the conditions so as to keep the cellulose from dissolving. The fact that cellulose can be reprecipitated from cuprammonium hydroxide is not new; the copper-silk industry is based upon it.

The conditions necessary for solution of cellulose by cuprammonium hydroxide have been studied by various investigators. Joyner (78) noted that one gram of copper would dissolve approximately 2.5 grams of cellulose. Eagle (78) observed that after 4-5 days, a cuprammonium-cellulose solution kept saturated with ammonia became much less viscous and gave rise to a bulky, amorphous, pale-blue precipitate. If the ammonia pressure was reduced, the precipitate quickly dissolved. In the results being considered here (Table VI), the material was treated with cuprammonium hydroxide until there was no further solvent action.

One possible explanation for Farr's reported visibility of particles in cuprammonium hydroxide can be based on Kerr and Bailey's (13) concept of cell-wall

structure. They believe the cell-wall is made up of zones differing in density, orientation, and sometimes in composition. It is reasonable to suppose that zones of cellulose differing only in density would differ also in their susceptibility to the solvent action of cuprammonium hydroxide. If solvent of just the right concentration were used, it is conceivable that these weaker zones might be dissolved, causing ballooning and giving the cuprammonium hydroxide a viscous character. If this material is washed out with weak cuprammonium hydroxide or with ammonium hydroxide, the more resistant parts would be left as fibrils or other shreds of the original coherent matrix of cellulose.

Even allowing for the large errors apparently possible in the determination, it appears from Table VI that extraction with alcohol-benzene reduces the insoluble fraction. Whether this is due entirely to the removal of resins or whether the insoluble fraction is so changed by the extraction as to become soluble is a question whose answer is not apparent. Lewis has observed that the action of heat will render the primary lamella either more brittle or less resistant to the solvent action of cuprammonium hydroxide. It is possible that a similar effect is taking place here. Probably the result is a combination of this effect and the removal of resins.

If the two determinations made are considered approximately correct, it appears that hot water treatment

reduces the amount insoluble in cuprammonium hydroxide. The action of ammonium oxalate appears interesting, since it seems to cause a slight increase rather than to decrease the insoluble fraction, even as much as does hot water. Part of this effect may be due to the formation of insoluble oxalates by reaction of the ammonium oxalate with the calcium of the ash, or by retention of the ammonium oxalate in the fiber and its reaction later with the cuprammonium hydroxide. The presence of either of these oxalates would not be entirely accounted for by the ash determination, since both would break down to oxides.

The action of alkali and acid on the insoluble fraction is interesting when considered in connection with the swelling behavior. It might be supposed that the cuprammonium hydroxide-insoluble fraction could be identified as the part of the fiber responsible for the constrictions in ballooning. Lewis (79) has observed that dark-field photographs of a fiber, even after standing for three days in cuprammonium hydroxide, show the form of the swollen fiber. He believed this due to the membrane immediately beneath the transverse windings of the primary lamella on the outside of the fiber. This membrane would thus seem to be insoluble in cuprammonium hydroxide.

When the pulp is treated with acid, whatever causes the constrictions is so modified that ballooning no longer takes place. This correlates with the decrease

in the cuprammonium hydroxide-insoluble portion. However, when the pulp is extracted with alkali, the insoluble portion is reduced practically to zero, although ballooning is not affected. This does not mean that the insoluble portion is not connected with the constricting elements. In the determination of the insoluble portion, strong cuprammonium hydroxide is used and the solvent action is allowed to go to completion. It is quite possible that various parts of the cell wall could differ in their resistance to the solvent action of cuprammonium hydroxide and yet the entire wall be completely soluble when stronger cuprammonium hydroxide is used. It does mean that the insoluble portion is not necessarily the same as the more resistant part of the cell wall and that determination of the insoluble fraction is not necessarily an index of swelling behavior.

In the sample of the cuprammonium hydroxide-insoluble material isolated for analysis, a higher yield was obtained than in any of the other tests. This sample was not extracted with alcohol-benzene, a fact which might partially account for the high value. The ash content (Table VII) is only about half that reported by Lewis and Brauns (71) in similar material isolated from West Coast bleached sulphite pulp. The acid-insoluble material would correspond to the gray precipitate reported by them upon acidification of the blue copper compound. This material was partially

soluble in ether and left a small amount of ash on ignition. One possible constituent might be the calcium or copper salt of resin acids.

The yield of sugar is considerably lower than their value but high enough to indicate that the material is largely carbohydrate. The value reported should be considered as a minimum, since losses due to degradation or handling will reduce it. In Table VII, reducing sugar is calculated on the basis of the copper compound. If corrected for ash and for acid-insoluble material, the yield would be 76 per cent as compared with 67 per cent reported by Lewis and Brauns. Differences are also observed in the analysis of the reducing sugars. Lewis and Brauns found no mannose or galactose present and about half the reducing sugar present as pentose. Since fermentation methods seldom are 100 per cent accurate, the reported 15 per cent pentose might be considered as a maximum, since it contains any unfermented hexoses. In view of the fact that a different raw material was used, a duplication of the results of Lewis and Brauns should not be expected.

Various writers have pointed out that pectin in wood may be protected from the action of pectic solvents by deposits of other materials. It seems very unlikely that any deposit of truly pectic material could survive the pulping and bleaching processes. On the other hand, there is no indication of commercial pulp having any tendency to

break down into cellulose particles. Ammonium oxalate appears to remove slightly more material than does hot water (Table VIII). The increase in the amount removed by repeated extractions with ammonium oxalate may be caused in part by mechanical losses, since the pulp was handled three times as much. Because cloth was used as the filtering medium, it is conceivable that a small amount might be lost each time. If this were the case, the fraction lost would not be representative of the pulp since it would consist of fine fragments.

The changes in chemical analysis shown in Table IX are not surprising. Even admitting the existence of particles and membranes, there should not be a great change in chemical analysis, since the cellulose particles are assumed to make up the greater part of the fiber and to remain practically unchanged. The gamma-cellulose fraction is increased in each case at the expense of the beta-cellulose, and in some cases at the expense of the alpha-cellulose. The net result appears to be a combination of purification and degradation. The decrease in copper number reflects the purification, which takes place by the extraction of the least resistant parts. The decrease in viscosity reflects the degradation, due to the hydrolytic action of heat in the presence of water.

In the analysis of the extracts it appears that there is no great difference between the hot water and the

ammonium oxalate extracts. What small differences do appear in Table X may or may not be significant, since the small amount of material and its nature were not conducive to great accuracy. The liquid samples were composed of material partly in solution and partly in suspension, the latter being brown, amorphous, and sticky. The small amount of uronic acid anhydride found may be due to formation of sugar acids from the sugars. Farr (80) found in her extracts 14 per cent carbon dioxide, corresponding to 56 per cent uronic acid anhydride, or to 79 per cent pectin. This value, compared with 88 per cent pectin in apple pectin and with about 90 per cent pectin in citrus pectin, indicated that her extracted material was very largely pectic in nature. By the same analogy, the material extracted in this case is not pectic in nature.

While an apparent change of the rate of hydration is obtained in Series A (Table XI) by extraction with ammonium oxalate, in view of the poor reproducibility of results shown by the beater in Series B (Table XII), the change can hardly be considered significantly greater than that caused by hot water alone. In Series B, there is again a slight trend toward a decrease in the speed of hydration but so slight as to be of doubtful significance. These slight changes can be explained on the basis of the purification of the pulp. Several investigators have shown that the removal of pentosans, hemicelluloses, beta-cellulose or

similar materials will decrease the speed of hydration. Slight decreases in the amount of beta-cellulose and of pentosans were shown by these pulps after extraction (Table IX). The slight decrease in the rate of hydration thus corresponds with the work of these investigators. These facts could be made to fit into almost any theory of fiber structure and strength development. The significant thing is that extraction with a standard peptic solvent did not greatly affect the physical character of the pulp.

Chapter VI.

SUMMARY AND CONCLUSIONS.

1. Pectic solvents, with the exception of acids, had no effect on the viscosity of wood pulps in cuprammonium hydroxide solution.

2. Acids lowered the viscosity but this change was accompanied by a degradation of the cellulose as evidenced by chemical analysis.

3. The addition of pectin to cuprammonium hydroxide and to solutions of cellulose in cuprammonium hydroxide did not appreciably change the viscosity.

4. The swelling behavior of the fibers in cuprammonium hydroxide was unchanged by pectic solvents, with the exception of those pulps treated with acid.

5. Wood cellulose, as such, could not be settled or centrifuged out of solution in cuprammonium hydroxide, except for a few per cent of insoluble material.

6. The amount of this insoluble material was not affected by ammonium oxalate extraction of the pulp, but was reduced practically to zero by acid or alkali treatment of the pulp.

7. The cuprammonium hydroxide-insoluble material was apparently a definite compound of copper with some material in the pulp, and was broken down by acidification.

8. The ash-free portion of this copper-compound

was largely carbohydrate in nature.

9. Extraction of wood pulp with ammonium oxalate, a standard pectic solvent, had no appreciably greater effect on the chemical and physical characteristics of the pulp than did extraction with hot water. These effects could be explained on the basis of purification of the pulp and could be made to fit into almost any theory of cellulose behavior.

10. The nature of the material extracted from wood pulp by hot water and by ammonium oxalate was essentially the same.

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APPENDIX

INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Freeness

Pulp Quality

Pulp Bleached Mitscherlich

Series A

at Max. Str.

at Max. Str.

Date

Beater Conditions

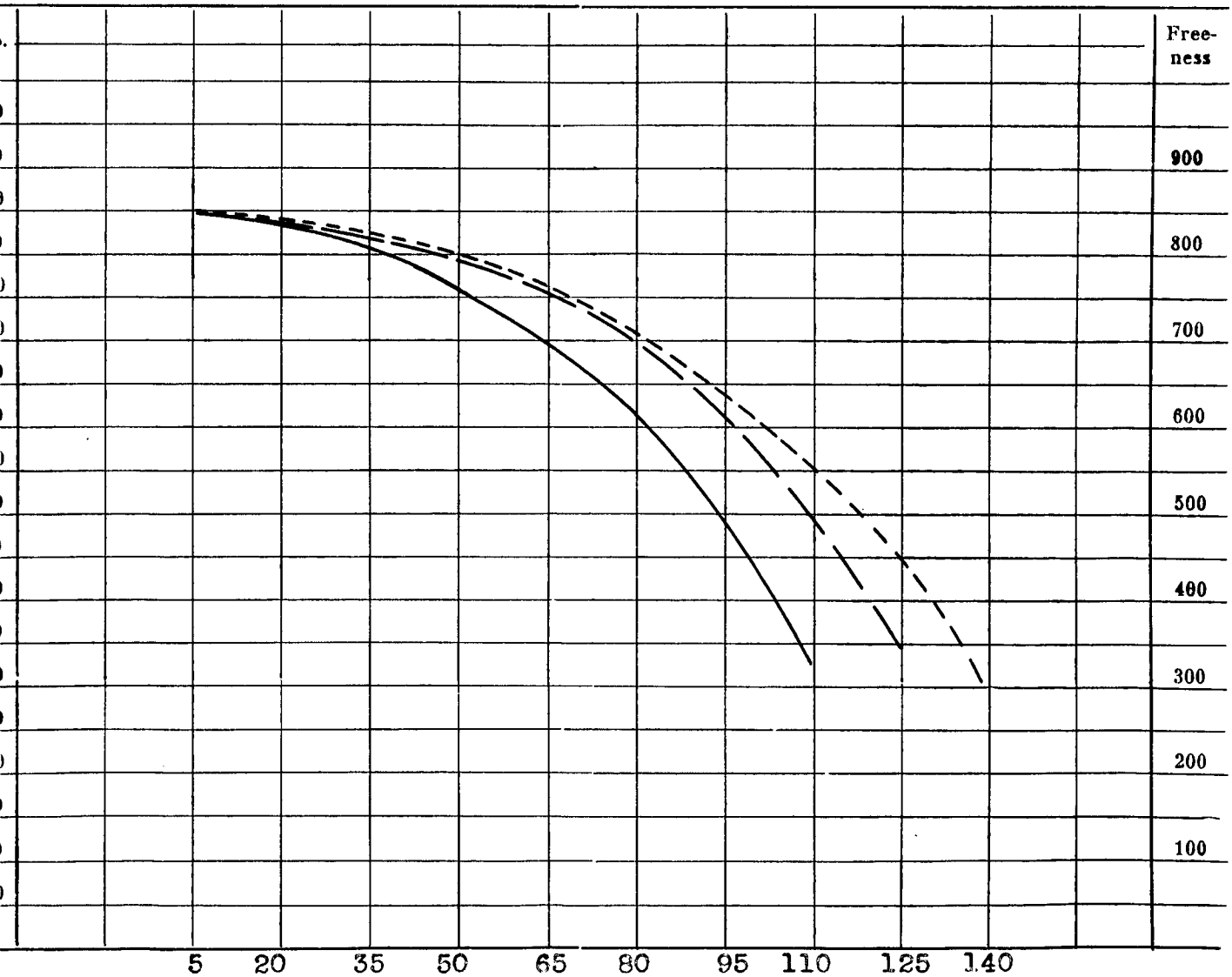
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 10 min. slushing

5500 grams on balanced bed-plate

——— Original pulp
- —— Extracted with hot water
------ Extracted with ammonium oxalate



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FOLD DATA

Time	Wt. of Sheet	DOUBLE FOLDS						Ave.	Basis Wt.	Fold Factor
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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
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INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Bursting Strength

Pulp Quality

Pulp Bleached Mitscherlich

Series A.

at Max. Str.

at Max. Str.

Date

Beater Conditions

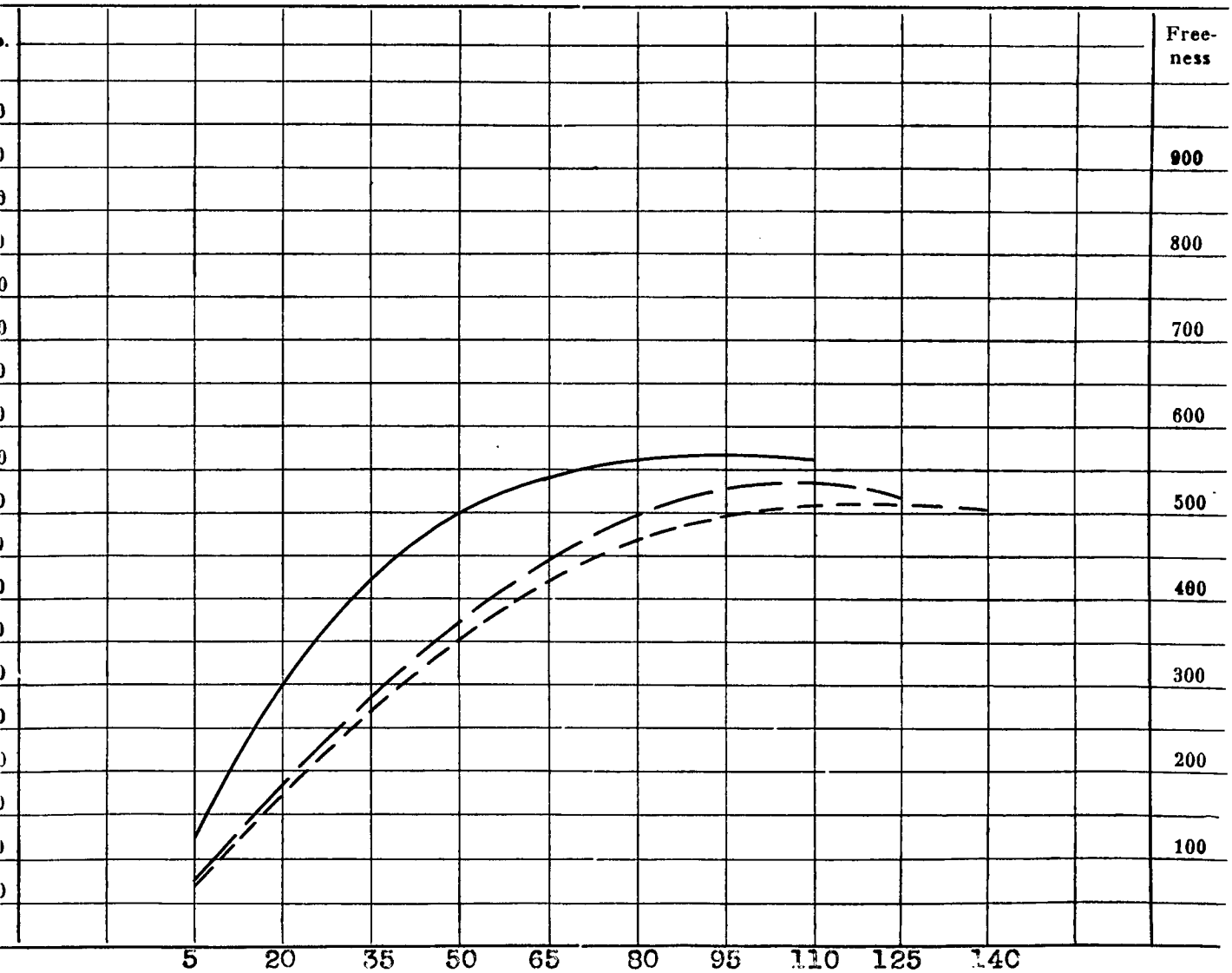
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 10 min. slushing

5500 grams on balanced bed-plate

——— Original pulp
- —— Extracted with hot water
- - - - - Extracted with ammonium oxalate



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TEAR DATA

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INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Tear Factor

Pulp Quality

Pulp Bleached Mitscherlich

Series A.

at Max. Str.

at Max. Str.

Date

Beater Conditions

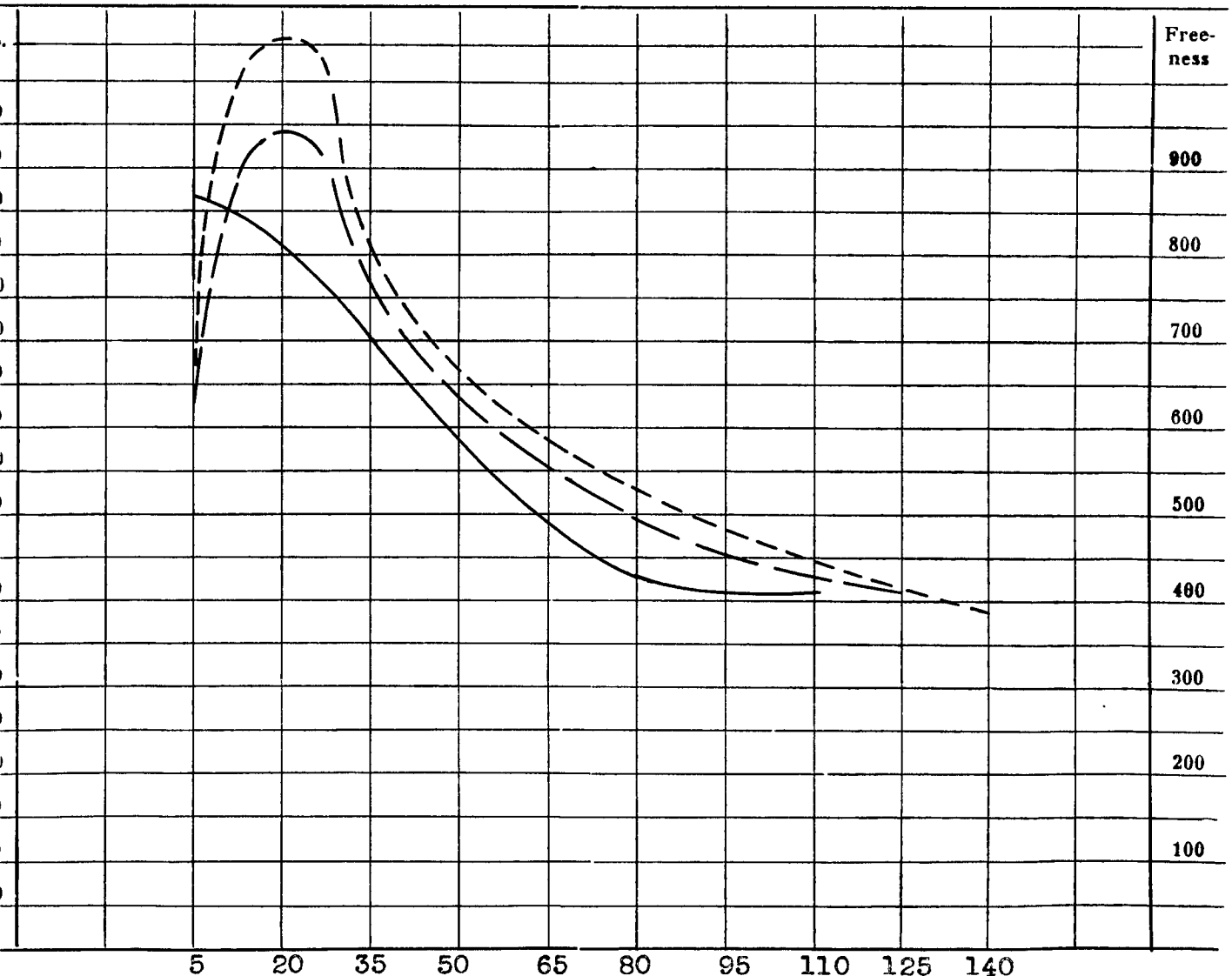
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 10 min. slushing

5500 grams on balanced bed-plate

———Original pulp
– – ———Extracted with hot water
------Extracted with ammonium oxalate



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FOLD DATA

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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
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INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Breaking Length

Pulp Quality

Pulp Bleached Mitscherlich

Series A.

at Max. Str.

at Max. Str.

Date

Beater Conditions

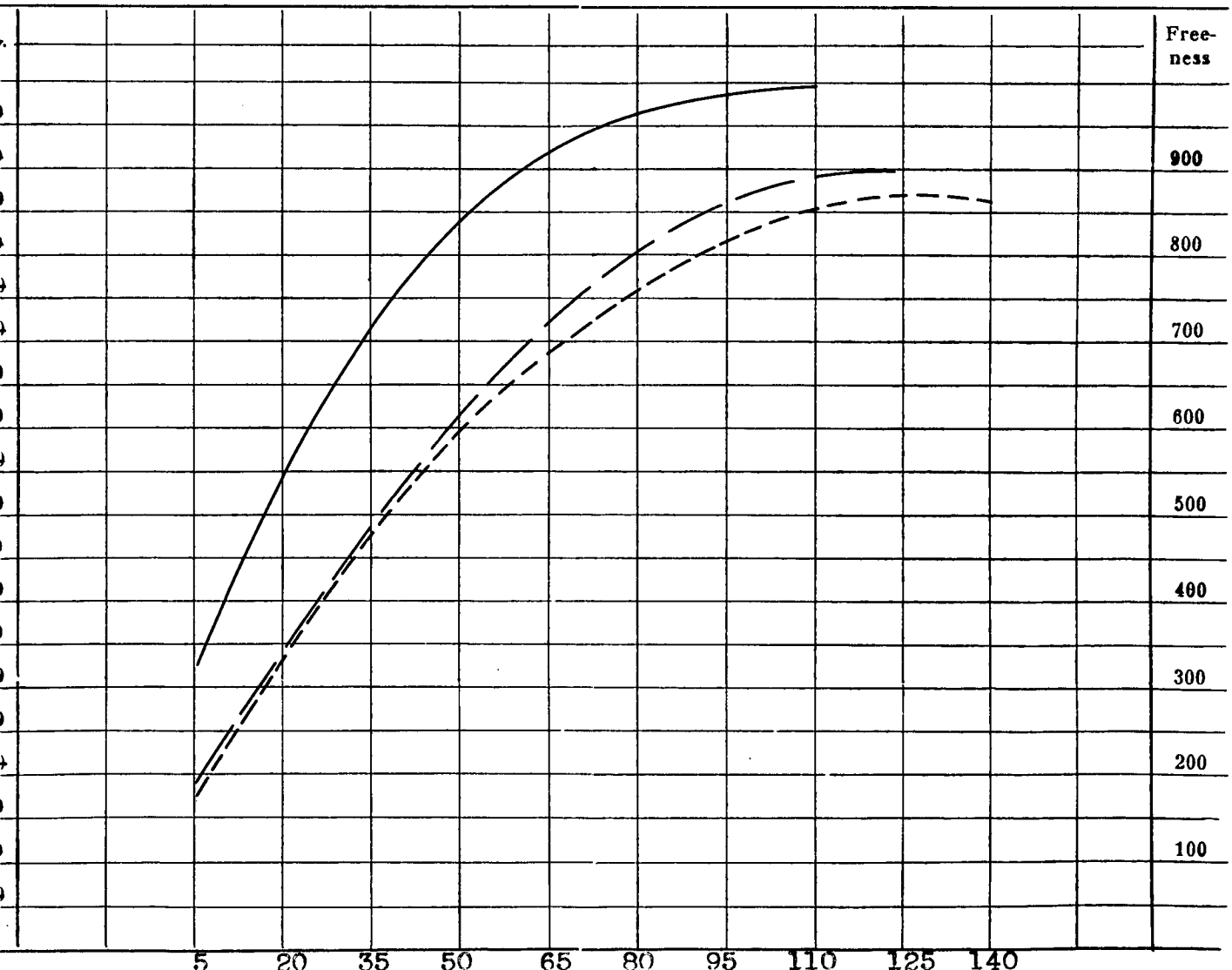
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 10 min. slushing

5500 grams on balanced bed-plate

——— Original pulp
- ——— Extracted with hot water
- - - - - Extracted with ammonium oxalate



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FOLD DATA

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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
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INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Apparent Density

Pulp Quality

Pulp Bleached Mitscherlich

Series A.

at Max. Str.

at Max. Str.

Date

Beater Conditions

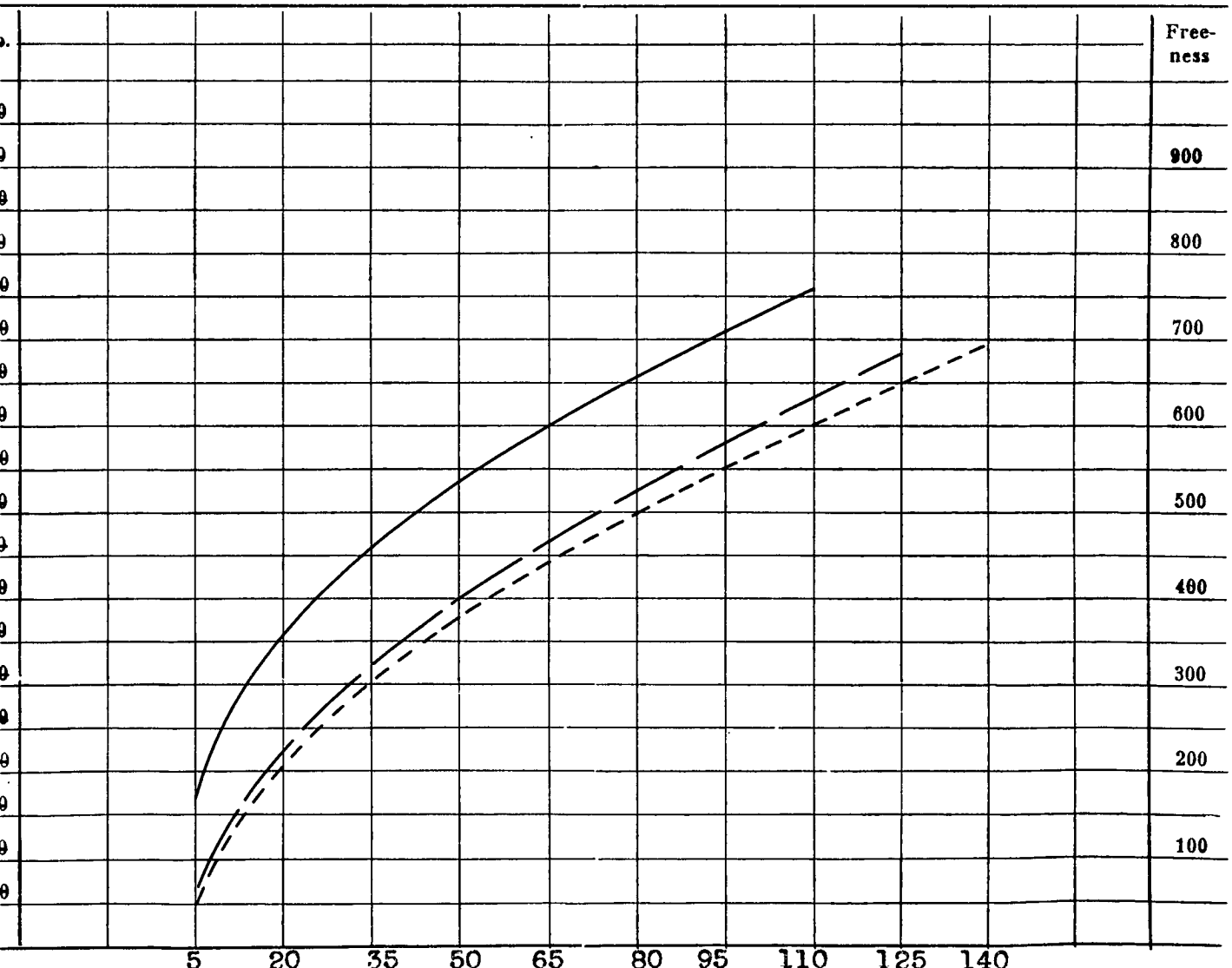
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 10 min. slushing

5500 grams on balanced bed-plate

——— Original pulp
- ——— Extracted with hot water
- - - - - Extracted with ammonium oxalate



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FOLD DATA

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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
		1	2	3	4	5				
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INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Freeness

Pulp Quality

Pulp Bleached Mitscherlich

Series B.

at Max. Str.

at Max. Str.

Date

Beater Conditions

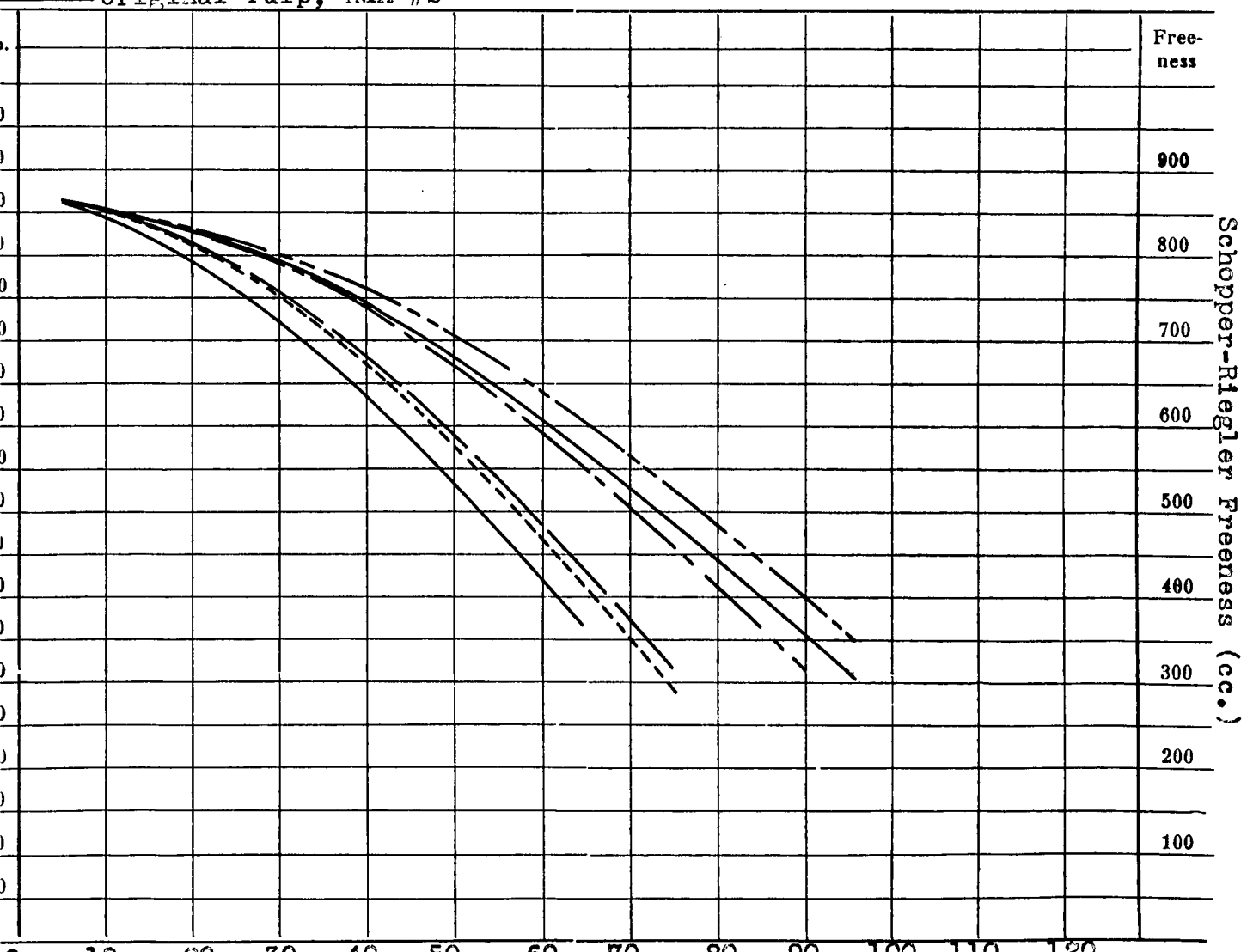
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30' soaking, 5' slushing

4500 grams on balanced bed-plate

——— Original Pulp, Run #1
– – —— Extracted with Water, VI
– – – – – Extracted with Ammonium Oxalate, VII
– – – —— Treated with Heat, VIII
– – – —— Extracted 3 times with Ammonium Oxalate, IX
——— Original Pulp, Run #2



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FOLD DATA

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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
		1	2	3	4	5				

INSTITUTE OF PAPER CHEMISTRY Bursting Strength
APPLETON, WISCONSIN

Pulp Quality

Pulp Bleached Mitscherlich

Series B.

at Max. Str.

at Max. Str.

Date

Beater Conditions

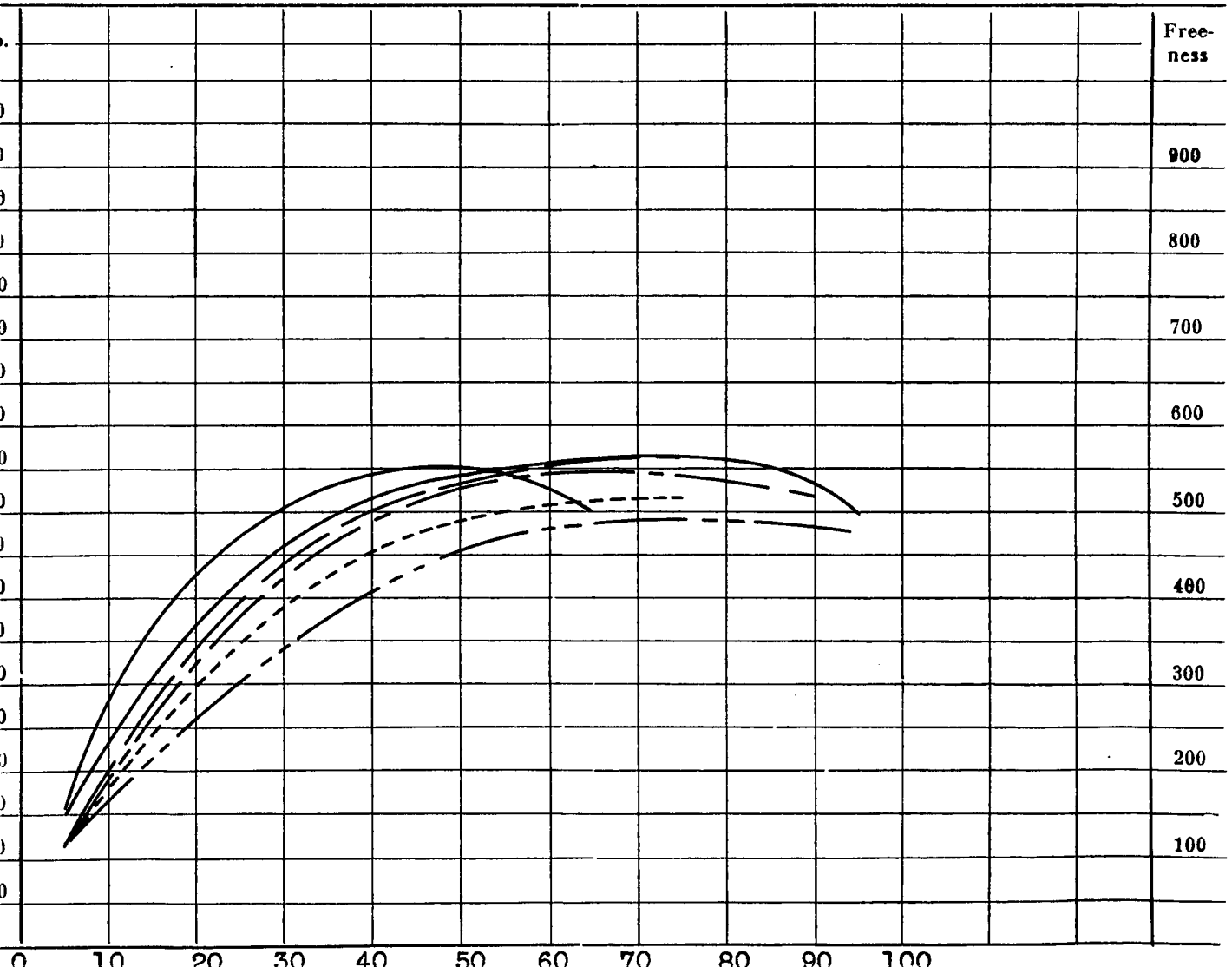
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 5 min. slushing

4500 grams on balanced bed-plate

———— Original pulp, Run #1
— ——— Extracted with water, VI
- - - - - - Extracted with ammonium oxalate, VII
- - ——— Treated with heat, VIII
- - ——— Extracted 3 times with ammonium oxalate, IX
———— Original pulp, Run #2



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FOLD DATA

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		1	2	3	4	5	6			

TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
		1	2	3	4	5				

INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Tear Factor

Pulp Quality

Pulp Bleached Mitscherlich

Series B.

at Max. Str.

at Max. Str.

Date

Beater Conditions

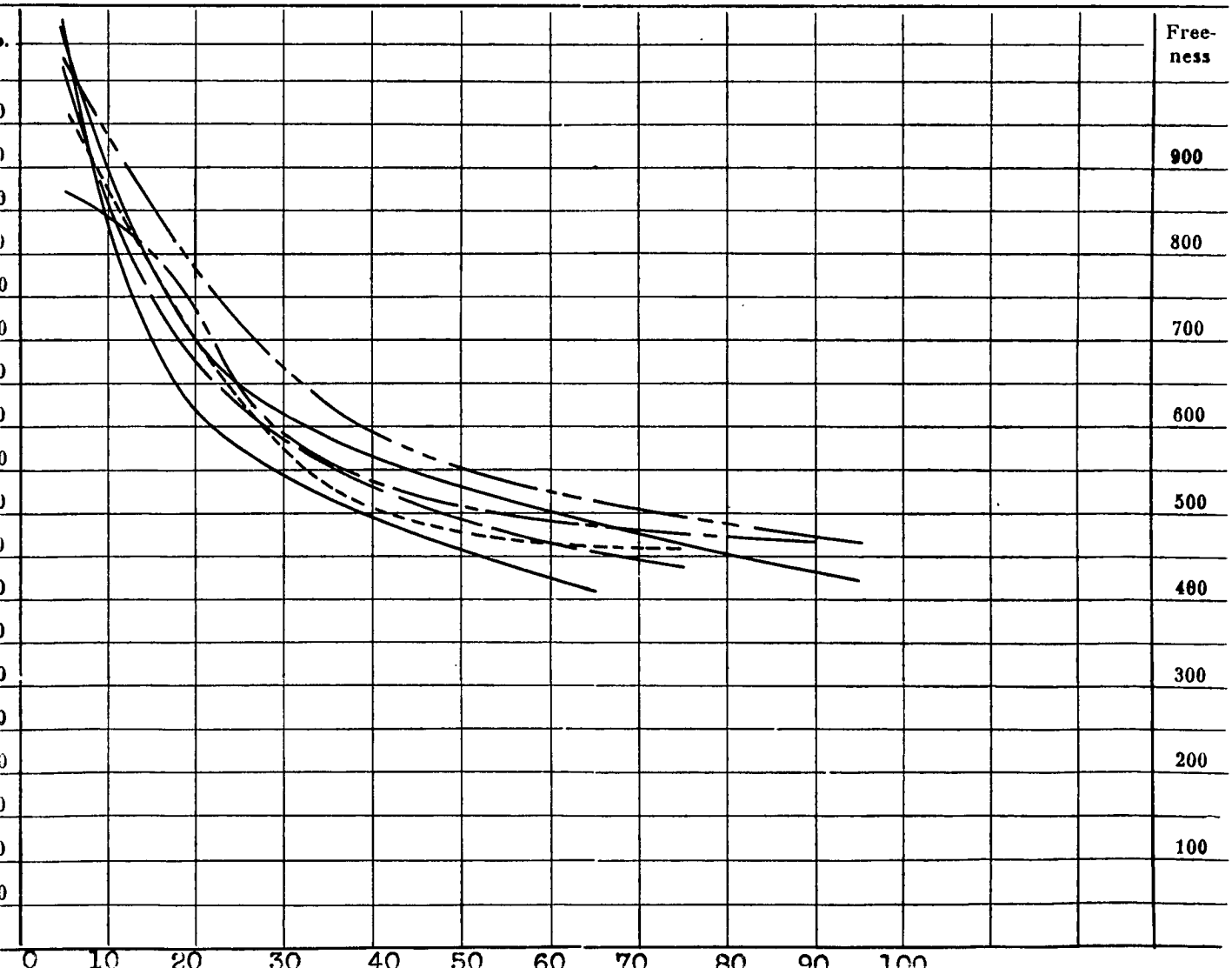
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 5 min. slushing

4500 grams on balanced bed-plate

———— Original pulp, Run #1
— ——— Extracted with water, VI
- - - - - Extracted with ammonium oxalate, VII
-- ——— Treated with heat, VIII
--- ——— Extracted 3 times with ammonium oxalate, IX
———— Original pulp, Run #2



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FOLD DATA

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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
		1	2	3	4	5				

INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

Breaking Length

Pulp Quality

Pulp Bleached Mitscherlich

Series B.

at Max. Str.

at Max. Str.

Date

Beater Conditions

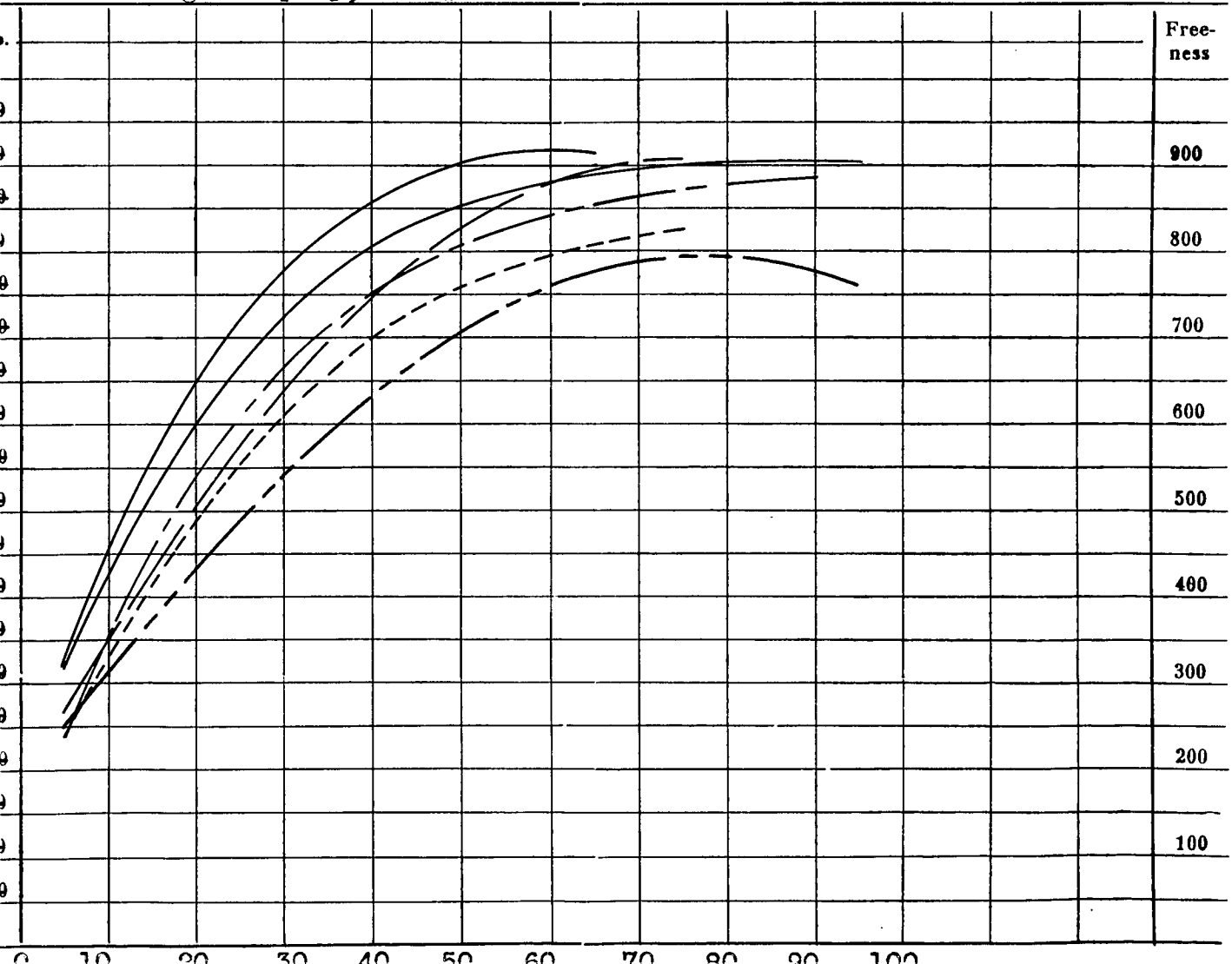
360 grams pulp (oven-dry basis)

23 liters water at 25° C.,

30 min. soaking, 5 min. slushing

4500 grams on balanced bed-plate

——— Original pulp, Run #1
— — — Extracted with water, VI
- - - - - - Extracted with ammonium oxalate, VII
— — — — Treated with heat, VIII
— - — - — Extracted 3 times with ammonium oxalate, IX
——— Original pulp, Run #2



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TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
		1	2	3	4	5				

INSTITUTE OF PAPER CHEMISTRY Apparent Density
APPLETON, WISCONSIN

Pulp Quality

Pulp Bleached Mitscherlich Series B.

Date

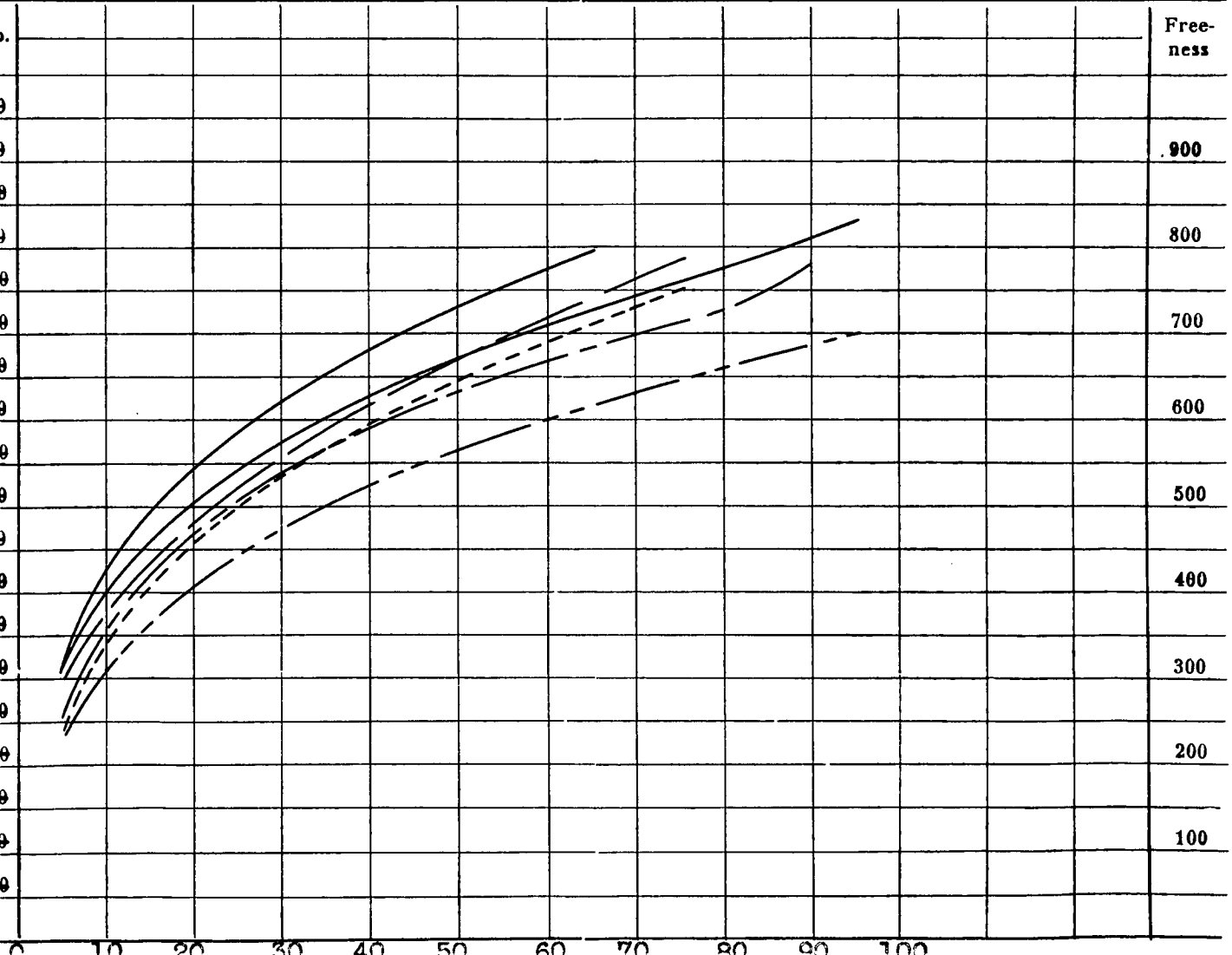
Beater Conditions

360 grams pulp (oven-dry basis)
23 liters water at 25° C.,
30 min. soaking, 5 min. slushing
4500 grams on balanced bed-plate

at Max. Str.

at Max. Str.

——— Original pulp, Run #1
— ——— Extracted with water
------- Extracted with ammonium oxalate, VII
- - ——— Treated with heat, VIII
- - - ——— Extracted 3 times with ammonium oxalate, IX
——— Original pulp, Run #2



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FOLD DATA

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		1	2	3	4	5	6			

TEAR DATA

Time	Wt. of Sheet	TEAR 16 SHEETS					Ave.	Basis Wt.	Tear Factor	
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