# THE EFFECT OF HEMICELLULOSES ON THE MECHANICAL PROPERTIES OF INDIVIDUAL PULP FIBERS

A thesis submitted by

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TABLE OF CONTENTS

# SUMMARY

Recently, several theories have been presented which relate the mechanical properties of paper to the mechanical properties of the component fibers. Although the literature is replete with studies of paper properties, relatively little is known about the individual fiber properties. The purpose of this investigation was to study the effect of the hemicellulose content of the fiber on the individual fibers' mechanical properties and the interaction of chemical content and drying the individual fibers under an external load. This study was concerned with the holocellulose summerwood fibers of two growth rings of a longleaf pine tree. The hemicelluloses were selectively removed from the fiber by alkaline extraction.

It was shown that partial removal of hemicelluloses lowered the breaking stress, modulus of elasticity, yield point stress, and work-to-rupture (energy) of the fibers. Drying under load increased the breaking stress, modulus of elasticity, and yield point stress values. The modulus of elasticity values for both unextracted and extracted fibers nearly approached a common level when the fibers were dried under load. The work-to-rupture increased initially and then decreased when the fibers were dried under load. All values were based on the cross-sectional area of the cellulose portion of the fiber.

Data obtained from dry fibers subjected to cycled loads showed a decrease in tensile elastic recovery upon removal of hemicelluloses. The increase in modulus that accompanied dry straining also was proportional to the hemicellulose content.

Removal of the hemicelluloses increased the crystallinity of the fiber, indicating increased cellulose-cellulose bonding.

The interpretation of the data indicated that the removal of hemicelluloses from the fiber decreased the strength properties of the fiber by inhibition of internal stress redistribution. The relatively flexible hemicellulose-cellulose-hemicellulose bond was replaced by a more rigid cellulose-cellulose bond.

The sudden extension upon drying of the fiber which was noted by Jentzen also occurred in all fiber groups in this study. Removal of hemicellulose, however, decreased this extension.

Alkaline degradation, mercerization, and chemically-induced physical swelling were investigated as possible side effects caused by alkaline extraction. The investigation revealed that all side effects were negligible and that the effect of removal of hemicellulose was a true effect.

Enough fibers (roughly 25-30) were tested in each fiber group to ensure a statistically significant average.

# INTRODUCTION

Much work, particularly in the past few years, has been done to increase our understanding of the response of paper to applied stresses. Van den Akker (1) and several other workers in this field have presented theories which relate the mechanical properties of the sheet to the individual fibers' mechanical properties. However, much less is known about the mechanical properties of the individual pulp fibers.

Jentzen (2) did some pioneering work in this field by investigating the effects of drying individual pulp fibers under an axial tensile load on the mechanical properties of those fibers, and on the structural changes which take place in the fiber. The results of his work indicate that a large part of the differences in the directional mechanical properties of paper may be attributable to the change in the load-elongation characteristics of the individual fiber caused by drying under load.

The effect of the fibers' chemical composition on their mechanical properties has only been partially investigated (3,4) and the effect of the interaction between chemical composition and drying conditions on the mechanical properties of individual fibers has never been investigated. Since it is a well-known fact that each of the various commercial pulping processes has its specific influence on chemical composition of the pulp fibers as well as on the properties of the paper sheet produced from the pulp, these effects warrant a detailed investigation.

# OBJECTIVES

The objectives of this thesis are to determine the effect that the presence of hemicelluloses in the wood pulp fiber has on the mechanical properties of individual pulp fibers, to determine the effect on these mechanical properties of drying individual pulp fibers of varying hemicellulose content under an axia tensile load, and to determine the structural changes which occur in the fiber upon removal of the hemicelluloses.

# HISTORICAL REVIEW

The purpose of this review of the existing literature is to: (1) familiarize the reader with existing knowledge about the internal structure of fibers, in particular pulp fibers, and (2) inform the reader about scientific studies directly concerned with the subject of this thesis.

Due to their commercial importance, many investigations have been conducted on various properties of cotton and wood pulp fibers. The majority of studies on mechanical properties of fibers have been concerned with cotton fibers and only recently have the individual wood pulp fiber's mechanical properties come under closer scrutiny. There are many similarities between cotton and wood pulp fibers, and it would be of interest to compare the two kinds of fibers.

## INTERNAL STRUCTURE OF CELLULOSIC FIBERS

### MOLECULAR STRUCTURE

Cotton fibers are composed principally of cellulose while wood pulp fibers contain four chemical groups: cellulose, hemicellulose, lignin, and a miscellaneous group which includes pectinaceous material, inorganic compounds, etc. The organic compounds are normally present as short and long-chain polymers.

Cellulose, the major constituent, consists of long, linear chains of glucose anhydride units linked together by beta-1,4 glycosidic bonds. The hemicelluloses are generally combinations of sugars: mannose, xylose, arabinose, galactose, and glucose. The most prevalent hemicellulose polymer chains are 4-O-methylglucuronoarabinoxylan (softwoods; no arabinose in hardwoods) and glucomannan. The hemicellulose polymer chains also have internal linkages of some type of glycosidic bond.

Pulp fibers are polycrystalline materials, due to the fact that cellulose is partially crystalline. Crystallization is favored by rigid chains; the tendency of the hydroxyl groups to form hydrogen bonds; and the geometric arrangement of the atoms within the glucose unit, which allows a closely packed structure. The hemicelluloses with their branching form a less-ordered structure than the glucose units and therefore do not tend to crystallize. With a few exceptions, natural cellulosic fibers have a cellulose I crystal lattice structure. This lattice structure is schematically represented by the well-known monoclinic unit cell of Meyer and Misch.

Three kinds of forces are in existence in the cellulose unit cell. Along the cellulose chain, the glucose units are held together by the 1,4-glycosidic primary valence bonds. Between cellulose chains, hydrogen bonds undoubtedly occur where oxygen atoms exist and the separation between atoms is within the required 2.5 A. Van der Waal's forces must also exist where the separation is within 3-4 A. The approximate disassociation energy of these bonds is respectively: 80, 5, and 3 kcal./mole.

The fiber is not wholly crystalline. Exclusive of the amorphous hemicellulose fraction of the fiber, which will be discussed later, the cellulosic porti is divided into crystalline and amorphous regions. It is generally agreed that these regions are not well defined but, rather, the transition is gradual from crystalline to amorphous, i.e., there are varying degrees of lateral order.

There are two principal theories that attempt to explain the crystalline structure of the cellulosic fiber in the light of existing knowledge. The olde fringed micelle theory (5) states that the micelles or crystalline regions alte nate with the less-ordered amorphous regions and, within broad limits, there i no connection between the length of the crystalline regions and the molecular length.

The newer theory, proposed by Hearle (6,7) suggests that the crystalline regions are continous "fringed fibrils" composed of molecules diverging from the fibril at different positions along its length. Jentzen (2,8) felt that his data best supported the fringed fibrillar theory.

There is also a third theory with new experimental evidence backing it. This concerns the folding of the cellulose molecule upon itself in the crystalline regions. Lindenmeyer (9) and Tønnesen and Ellefsen (10) have discussed this possibility in cellulose molecules. Tønnesen and Ellefsen can account for many properties of cellulose with this model, except for the strength of the cellulose fibril. Manley (11) obtained data supporting the chain-folding hypothesis. In his particular model, the basic structural element in plant cell walls is a filament 35-A. wide, consisting of a ribbon wound as a tight helix. Within this unit the cellulose molecules assume folded conformations. The microfibrils themselves exist in ordered arrays in the cell wall, according to his theory.

Manley's work was with a single crystal of a cellulose derivative. Dolmetsch (12) noted that when cellulose is formed "freely" in the substrate by individual cells, it can follow its "own laws of crystallization" but when it is formed with cellular tissues, its freedom is spatially limited. The influence of living cells causes the deviation of complicated and important structural systems, such as the primary and secondary layers, fibrillar orientation, and various lamellar structures. Thus, internal structures that may occur in a single crystal may not occur in a complicated cellulosic fiber.

## MICROSCOPIC STRUCTURE

On the microscopic scale, the fiber basically is composed of structural elements called fibrils. Frey-Wyssling (13) further defines these elements according to size as elementary fibrils, microfibrils, and macrofibrils. Their sizes, respectively, are 30 by 100 A., 250 by 250 A., and 4000 by 4000 A.

Thompson (14) has obtained electron micrographs of holofibers showing an apparent spiral arrangement of the elementary fibrils. His interpretation indicates a solid-wound ropelike helical structure for this fibril.

Ohad and Mejzler (15,16) recently have done some model studies on the internal structure of cellulose microfibrils, including a "probabalistic model" representing the structure of an ideal cellulose microfibril.

On a grosser scale, the fiber has a lamellated structure. Both cotton and wood pulp fibers contain this same basic structure, although there are broad variations between the two kinds of fibers. The principal layers of both fibers are called P, $S_1$, $S_2$, and $S_3$ layers.

The natural architectural arrangement of the cotton fiber is that of concentric layers (17) of cellulose encased in a skin or primary wall (P). The secondary wall consists of concentric rings of cellulose, whose number is directly equal to the age of the fiber in days. The total thickness of a lamella is approximately 0.1 micron; a single lamella is roughly five microfibrils thick. The separation of single microfibrils from a lamella sheet is difficult (18), indicating that cohesion of the fibrils is relatively great.

The thin primary wall of wood pulp fiber consists of an irregular network of microfibrils. In its native state, this network is very loose, and can easily undergo plastic deformation. The cell wall grows inward, but can expand in its early stage of formation.

The $S_1$ layer is called the transition layer because its structure is intermediate between the structures of the primary wall and the secondary wall. The microfibrils run relatively parallel to each other at an angle of about 50° to the fiber axis. Electron microscope studies have shown that the $S_1$ layer consists of two or more lamellae with a crossed fibrillar structure. The large angle which the microfibrils make with the fiber axis in the $S_1$ layer is responsible for its strong double refraction in transverse sections through the wood (19).

In the $S_2$ layer, the microfibrils are closely parallel and run in a steep helix, forming an angle of 10 to 20° to the fiber axis. The $S_2$ layer forms the bulk of the cross section of the fiber, particularly in summerwood fibers.

In the tertiary layer of the cell wall, the $S_3$ layer, the microfibrillar spiral angle is large, and thus this layer, like the $S_1$ layer is also birefringent in transverse sections. The microfibrils are not as parallel as in the $S_2$ layer and their angle with the fiber axis is much greater than in the secondary layer. The contact between $S_1$ and $S_2$ and between $S_2$ and $S_3$ is usually very loose (19).

Frey-Wyssling (13) noted that the walls of the fiber, particularly the secondary wall, grow by apposition, and therefore appear to be lamellated. In the secondary wall lamella, the microfibrils of cellulose are in a densely packed parallel arrangement. They touch one another laterally, fuse, lose their individuality, and form characteristic fasciations.

There are two major differences between the internal structure of cotton and wood pulp fibers. One difference is that in cotton, the fibrillar spiral reverses itself at various points along the fiber axis.

Wakeham and Spicer (20) studied the structural reversals in cotton fibers and found that these reversals were a preferred location of breaks when the fibers were ruptured in tension. The fractures were studied with a polarizing microscope.

The cellulose in the region of the reversals appeared to be more highly crystalline than the cellulose between the reversals. Swelling in 18% NaOH reduced the percentage of breaks at the reversals and increased the strength of the fibers. Treatment of the fibers with formaldehyde, or hydrochloric acid also reduced the percentage of breaks at the reversals but lowered the strength of the fiber.

Wakeham and Spicer felt that breakage occurred at the reversal locations because of internal stresses at those points. They said, "If the cellulose structure in the region of the reversals is under an internal stress, swelling the cellulose would permit the relaxation and removal of these internal stresses and eliminate the cause of preferential breaks at the reversal, for the 18% (breaks) obtained with caustic swollen fibers is not much greater than the theoretical 15% based on a chance involvement."

Later, Wakeham, Radhakrishnan, and Viswanathan (21) obtained x-ray pictures of reversal and nonreversal areas and found higher crystallinity in the reversal areas.

In considering these data, one must recall that 18% NaOH solution is of mercerizing strength, and that this drastically changes the fiber's internal structure. However, the same increase in strength upon swelling in caustic of strength less than that of mercerization was found by this writer and by Schuber (22).

The other major difference between the structure of the cotton fiber and th wood pulp fiber is that the wood pulp fiber contains hemicelluloses. Meier (19) felt that the hemicelluloses may lie between the cellulosic microfibrils either as an amorphous or as a crystalline granular material, or they may form their o microfibrils which may or may not have crystalline regions. Most workers feel, however, that the hemicelluloses for the most part are amorphous material, surrounding the more crystalline fibrils. Frey-Wyssling (13) stated that the elementary fibrils seem to be ideally crystallized, but that the spaces between them are filled partly with paracrystalline cellulose and partly with noncellulosic material, which can be removed by alkali treatment.

## LOCATION OF THE HEMICELLULOSES IN THE CELLULOSE STRUCTURE

No scientific work has been performed which directly locates the hemicelluloses in the microstructure of the wood pulp fiber. Meier (23) indirectly located the hemicelluloses in the cell-wall layers, on a gross scale, by studying pine fibers in different stages of maturation. His work was based on the apparently valid assumption that when a layer of sugars or polysaccharides is laid down in the growing cell wall, the layer remains unchanged as successive layers are placed over it. Since the middle lamella and primary wall are formed first, and the other walls are added later, analysis of fibers in different stages of maturation will yield a rough estimate of sugar concentration in the different cell layers (Table I). Meier's work, of course, yielded no information as to the microlocation of the xylans and glucomannans in the P, $S_1$, $S_2$, and $S_3$ layers.

### TABLE I

### SUGAR CONTENT IN DIFFERENT CELL LAYERS OF PINEWOOD (19,23)

| Sugar | M + P | $S_1$ | $S_2$ Outer Part | $S_2$ Inner Part + $S_3$ |
|---|---|---|---|---|
| Galactan | 20.1 | 5.2 | 1.6 | 3.2 |
| Cellulose | 35.5 | 61.5 | 66.5 | 47.5 |
| Glucomannan | 7.7 | 16.9 | 24.6 | 27.2 |
| Arabinan | 29.4 | 0.6 | 0.0 | 2.4 |
| Glucurono-arabinoxylan | 7.3 | 15.7 | 7.4 | 19.4 |

Sultze (24) isolated the middle lamella and the primary wall from quaking aspenwood (*Populus tremuloides*) and found this portion consisted of arabinose, galactose, and pectic material including galacturonic acid.

Nearly all of the experimental work on the location of the hemicellulose fractions in the fiber's internal network is based on extraction data. The principal basis for using the data of this work is the assumption that the relative differences in ease of extraction of the various hemicellulose components are caused by their different locations in the fiber network. Extraction work by Hamilton and Quimby (25), Leopold (26) and others (27-31) has lent credence to the belief that the arabans and galactans are mainly located in the exterior layers of the fiber with the pectic material, while the xylans appear to be in the interior of the fiber, probably interspersed between the fibrils, or possibl on a grosser scale between the lamellae. The mannans, principally in the form of glucomannan polymer, appear mainly to be associated intimately with the cellulose fibrils.

Most of the arabans and galactans are easily removed in dilute caustic (Tables II and III) while removal of the xylans requires stronger caustic solutions. Removal of glucomannans requires even stronger concentrations of caustic with the addition of complexing agents such as boric acid.

TABLE II

RETENTION OF SUGARS IN WOOD AFTER PULPING (32)

| | Yield, % | Glucan, % | Galactan, % | Mannan, % | Arabinan, % | Xyla %|
|---|---|---|---|---|---|---|
| Loblolly pine summerwood | 71.7 | 100 | 72 | 93 | 50 | 99 |

## TABLE III

### EXTRACTION OF LOBLOLLY PINE SUMMERWOOD (26)

| | Yield, % | Glucan, % | Galactan, % | Mannan, % | Arabinan, % | Xylan, % |
|---|---|---|---|---|---|---|
| Wood | 100 | 46.9[a] | 1.6 | 11.0 | 0.7 | 6.4 |
| Holo (peracetic) | 71.7 | 47.3 | 1.2 | 10.2 | 0.4 | 6.3 |
| DMSO | 70.7 | 47.7 | 1.1 | 9.2 | 0.1 | 6.2 |
| Hot water | 68.5 | 47.0 | 0.7 | 9.4 | 0.0 | 5.9 |
| 0.1N KOH | 64.5 | 46.3 | 0.0 | 9.2 | – | 5.8 |
| 0.4N KOH | 62.8 | 46.1 | – | 8.9 | – | 4.8 |
| 1.5N KOH | 57.3 | 46.5 | – | 9.0 | – | 0.9 |
| 1.5N KOH + 0.75 $H_3BO_3$ | 52.8 | 44.7 | – | 7.4 | – | 0.8 |
| 3.6N KOH + 0.75 $H_3BO_3$ | 51.7 | 44.2 | – | 6.0 | – | 0.5 |

[a] Percentages based on ovendry wood.

Much discussion exists in the literature as to whether the difference in ease of extraction between each of the hemicelluloses is a chemical or physical phenomenon.

There is much experimental work indicating that the reason for the differences in extractive ability of the various extractants is strictly of a chemical nature. It has been found that glucomannans isolated from softwoods are largely insoluble in aqueous potassium hydroxide but soluble in sodium hydroxide (33). This may be why, with alkaline solutions of moderate strength, sodium hydroxide is superior to potassium hydroxide for removing glucomannans from wood, as originally discovered by Hamilton and Quimby (25). Jones, Wise, and Jappe (34) were the first to notice that the extractive power of potassium hydroxide was substantially increased by the presence of boric acid. Timell (35) felt that t borate forms a complex with the 2,3-*cis*-hydroxyl groups of the mannose residues thus rendering the polymer more acidic and hence more soluble in alkali. Suppo ing the morphological approach, however, Hamilton and Quimby (25) found that mechanically disintegrated holocellulose or holocellulose which had been briefl hydrolyzed with acid could be almost completely freed from hemicelluloses by a subsequent extraction with alkali (down to 0.18% of the wood). The outer laye of the fiber wall were probably disrupted by these treatments and the fiber st ture was swollen much more easily. Lindberg and Meier (36) found that the res dual, resistant glucomannan in a holocellulose from Norway spruce, which had p viously been exhaustively extracted with alkali, could be removed after a mild acid hydrolysis or by dissolving the residue in cupriethylenediamine. Both treatments broke down the fiber structure.

Thompson and Kaustinen (37) froze a slurry of 10% sodium hydroxide and fibers and found that more glucomannan could be extracted this way. Evidentl the freezing disrupted the fiber somewhat, making the glucomannan more access As mentioned, Hamilton and Quimby found that sodium hydroxide was a better ex tractant for glucomannans than potassium hydroxide. Heuser and Bartunek (38) found that sodium hydroxide swelled cotton fibers to a greater degree than po sium hydroxide; hence, one can judge that the reason sodium hydroxide is the better extractant is that it can reach the more inaccessible regions. The he cellulose components least easily extracted must be located deep in the fiber microstructure, according to the physical theory of extraction.

Nelson (39) followed the width of the 002 x-ray diffraction peak during traction of slash pine chlorite holocellulose with alkali. The drop in peak width was proportional to removal of mannan but bore no relation to removal of xylan. These results indicated that at least part of the mannans are located in close association with the cellulose, since its removal results in a higher degree of order. Nelson also felt that this agreed with the data on the differences in ease of alkali extractions of xylans and glucomannans, both sets of data indicating that the glucomannans are located more deeply inside the framework of the cellulose fibrils than the xylan.

The conclusion from the cited work is that ease of extraction depends on concentration and type of extraction solution and involves both physical and chemical phenomena; however, the data and the fiber wall sugar analysis strongly support the hypothesis that the hemicelluloses are located in the microstructure of the fiber.

## ASSOCIATION BETWEEN CELLULOSE AND THE HEMICELLULOSES

It is generally felt that fibrils are bonded to each other by hydrogen bonds. Frey-Wyssling (13) suggested that even if the hydrogen bonds are few, the length of the fibril is so great compared to the width that even a low density of hydrogen bonds will result in a greater strength than the covalent bonds in the cross section. He also stated "...of course, if there is hemicellulose left between the fibrils, much stronger lateral bonding results, exceeding many times the tensile strength of the elementary fibril."

On the other hand, Rånby (40) stated that the viscosity of cellulose is lower in polar solvents because, in these solvents, hydrogen bonds do not form between sugar units. In a like manner, he said, hemicellulose acts as a protective colloid and prevents solid aggregation (hydrogen bonding and cocrystallization) of the fibrils. He showed electron-micrographic evidence that dispersion into separate fibrils was easy if hemicellulose is present. He also found electron-microscopic evidence that the hemicellulose was dispersed between the cellulose fibrils through the whole fiber wall. Cotton fibrils, on the other hand, are difficult to separate (19).

The ease with which cellulose and glucomannan tend to associate is evident from recent investigations on acid sulfite cooking of wood. Annergren and Rydholm (41) found that if they pretreated the wood with alkali, the resulting acid sulfit pulp contained more mannose residues than after a one-stage cook. The O-acetyl groups in the native O-acetyl glucomannan were removed during the alkaline pretreatment. This evidently made it possible for the glucomannan to become adsorbe on the cellulose, and thus more resistant to acid hydrolysis. Glucomannan is structurally similar to the cellulose chain, making a glucomannan-cellulose association likely.

Frey-Wyssling (13) with similar reasoning felt that the major portion of xylan should have little ability to associate intimately with cellulose because of its position with respect to the fibrils and its frequently branched structure In like manner, this same inability to align must also occur between the galactoglucomannan (GGM) and the cellulose chain in the native fiber.

Timell (35) hypothesized that the relatively large number of galactose side chains in GGM probably prevent the macromolecules from aligning themselves with resulting formation of strong hydrogen bonds. This is indicated by the high solubility in water of GGM.

In summation, the highly branched hemicellulose polymers, e.g., 4-O-Me glucuronoxylan and GGM would seem to be unable to associate closely with the cellulose because they lack the uniformity and linearity required for close packing. The glucomannan polymer possesses more of this required linearity, and hence can associate more intimately with the cellulose chains. The differences between the types of hemicellulose in degree of packing with cellulose becomes significant in considering the effect of removal of these hemicelluloses on fiber strength. This is further covered in the section on Discussion of Results.

## FIBER STRENGTH VERSUS HEMICELLULOSE CONTENT

The only work on strength of individual fibers that has been related to the hemicellulose content of the fiber has been performed by Leopold and McIntosh, although other workers have suggested relationships from work with the zero-span test on commercial-type pulps (42,43). Leopold and McIntosh (3) prepared a peracetic holocellulose from loblolly pine chips. He extracted the delignified fibers with a series of extractants of increasing extractive ability (KOH, KOH + borate, NaOH). The degree of polymerization of his holocellulose, as determined by the nitrated holocellulose in ethyl acetate, was 2530. The degree of polymerization of the extracted residue continually decreased upon application of stronger extractants, although the change was not appreciable (10-15% over-all). However, one would expect the degree of polymerization to increase upon extraction because of the removal of lower D.P. materials, unless the cellulose itself was being degraded, which evidently happened in Leopold's case. The degradation can probably be attributed to his procedure, in which he extracted for 24 hours at room temperature and then again for seven hours with fresh reagent. Thompson (14) and Nelson and Schuerch (44) have stated that the adsorption of the caustic by the fiber is almost instantaneous, and all extractions that can occur at that particular concentration will occur in about one-half hour. After that, degradation predominates.

Leopold, together with McIntosh (3), then determined the tensile strength of these individual fibers. Their procedure involved gluing the fibers between two paper tabs. The tabs were supported by Jeweler's chains and the axial tensile load was applied through these chains. Elimination of distortion through twisting of the fiber during application of the load was cited as an advantage by the investigators. The applied load was obtained by running water into a beaker which was attached to one chain. When the fiber broke, the beaker was weighed to determine the breaking load. This system, although quite simple, had the disadvantage of yielding only the breaking load, with no information obtained about strain, modulus of elasticity, etc.

The cross-sectional area was measured by embedding the fibers in cellulose acetate, microtoming them, and taking a picture of the cross section.

Leopold and McIntosh found a correlation between fiber strength and xylan content, the former being proportional to the latter. Fiber strength was plotted versus mannan content and D.P. but no correlation was apparent. However, this writer noticed an apparent correlation between D.P. and mannan content in the cited work, although McIntosh and Leopold did not mention it. This could be attributed to the location of the mannans next to the cellulose. The concentrations of extractants required to remove the mannans may also degrade the cellulose fiber.

Several criticisms of the above work can be made. The fibers were obtained from the tenth to twelfth growth rings of the tree section, and Wardrop (45) has shown that the fibers are not uniform in this range. Their means for determining cross-sectional area involved changing the environment of the fiber (organic solvents, etc.), shedding some doubt on the results. In spite of the fact that they supposedly had no appreciable stress at the glue line, 50% of the fiber breaks occurred at this point (compared to roughly 20% for work done on the I.P.C. Fiber Load-Elongation Apparatus). However, they used these results because they noted no significant difference between the average values for fibers broken at the glue line and those broken elsewhere. The final criticism would be the amount of degradation that appeared to occur because of the extraction procedure.

McIntosh (4) later performed the same mechanical test on loblolly-pine kraft fibers cooked to different yields. He further delignified with peracetic acid-sodium borohydride in order to separate the fibers. In contrast to the results previously mentioned, McIntosh stated that he found a correlation between mannan content and fiber strength for the kraft fibers. The following considerations cast some doubt on his results, however: (1) Apparently, his fiber population was not very homogeneous as evidenced by the extreme variance in cross-sectional area. (2) He used the peracetic acid-borohydride solution as needed, immersing each fiber group for different times without recording the amount or length of treatment time used. (3) He plotted strength *versus* yields and registered a general decrease in strength with decreasing yield for summerwood fibers. From this he determined an apparent correlation with mannan content, although this correlation was not apparent to the writer, and McIntosh did not list a graph showing this correlation.

## EFFECT ON FIBER MECHANICAL PROPERTIES OF DRYING UNDER EXTERNAL FORCE

Jentzen (2) recently completed an investigation of the effect of drying individual pulp fibers under an axial tensile load on the mechanical properties of the individual fibers and on the structural changes which take place in the fibers. He investigated chlorite holocellulose fibers prepared from longleaf pine. The load-elongation properties of both springwood and summerwood fibers were measured at several drying loads. To determine the structural changes in the fiber, Laue x-ray diffraction patterns were run on the individual fibers, and the crystallinity and crystallite orientation were measured.

He obtained the following results. The summerwood fibers showed a maximum increase of 37% in the tensile strength and 82% in the modulus of elasticity, while the ultimate elongation decreased 10% due to drying under load. His springwood fibers exhibited similar changes, except that the levels were two to four times greater.

He found that the never-dried and the once-dried-and-rewet summerwood fibers showed the same changes in mechanical properties resulting from drying under a load. Also, fibers which had been dried under a load, and rewet, and dried under no load, exhibited little difference in mechanical properties from those which were originally dried under no load.

He observed no significant difference in the crystallinity of fibers dried with and without loading:

However, the fibrillar or crystallite orientation of the fibers was increased by drying under load. No significant difference in crystallinity was noted between the never-dried and the once-dried and rewet fibers.

Loading and unloading cycles run on the dry fibers showed that those fibers dried under no load underwent an increase in the modulus of elasticity from cycle to cycle, while those dried under a load exhibited no such change.

Jentzen observed an extremely interesting phenomenon during drying of the fiber under an external load. The fibers underwent a sudden extension at the commencement of drying, which was almost independent of the drying load. After the sudden extension the fibers exhibited the expected axial shrinkage.

Based on his results, Jentzen came to the following conclusions. The sudden extension at the commencement of drying is caused partially by the shrinkage of the fiber diameter. The permanent set put into the fibers due to drying under load is caused by changes in crystallite orientation and molecular and fibril readjustment of position.

Jentzen further concluded that the two principal mechanisms by which his fibers underwent a change in mechanical properties due to drying under load were an increase in orientation and a more even distribution of stress among the fibrils of the fiber.

He stated that the fiber-to-fiber variation in mechanical properties was due to at least three factors: differences in the distribution of the stress among the fibrils, differences in the crystallite orientation, and differences in the cross-sectional area or mass per unit length. The fiber-to-fiber variation in mechanical properties decreased when the fibers were dried under load. This decrease undoubtedly was because of changes in the internal distribution of stress and increases in uniformity of crystallite orientation.

Jentzen felt that the mechanical properties of his fibers appeared to be governed by the $S_2$ layer, which comprises a large volume per cent of normal pulp fibers. The differences between the mechanical properties of springwood and summerwood fibers largely could be accounted for by the difference in the percentages of $S_2$ layer in the fiber cross section.

## APPROACH TO THE PROBLEM

Work by Jentzen and others indicated that an internal stress redistribution occurs in fibers when they are dried under an external load. The hypothesis of this investigation was that the wood pulp hemicelluloses, because of the reasons discussed in the preceding section, exert a strong influence on this internal stress redistribution.

It was decided to study the stress-strain mechanical properties of fibers with varying hemicellulose contents. The fibers were to be dried under several different loads using Jentzen's drying apparatus. The interaction of hemicellulose content and drying load revealed the changes in the internal stress distribution.

The selection of the loads under which the fibers were to be dried was based on the calculated force that the fiber is subjected to when a sheet of paper is dried under tensile load. These calculations, originally made by Jentzen (2) and verified by the writer, involved the use of Van den Akker's theory (1) and data by Schulz (46). The selected drying loads for both Jentzen's work and this work were 1, 3, and 5 grams.

A holocellulose longleaf pine pulp was selected as the base material. This pulp contained most of the original hemicelluloses because of the mild pulping conditions, yet contained only a small amount of lignin. The hemicelluloses were then to be selectively extracted from the pulp using varying concentrations of potassium hydroxide solution. An alternative approach would have been to use a hemicellulose-free fiber such as cotton for the base material, and to add hemicelluloses to the fiber structure. However, this method has a serious drawback in that one could never tell where in the fiber structure the added hemicellulose would locate themselves, and location of the hemicelluloses is judged to be a very important factor in fiber strength.

In order to prove that the changes in mechanical properties were due to removal of hemicelluloses, several possible side effects were planned for study: alkaline degradation, mercerization, and chemically-induced physical swelling.

X-ray diffractograms were to be obtained to show change in intrafiber bonding and electron micrographs were planned to show the effects of removal of the hemicelluloses on those fiber elements seen by the electron microscope. A limited number of loading and unloading cycles on fibers were planned to obtain additional information on internal stress distribution.

## EXPERIMENTAL APPARATUS AND PROCEDURES

### PREPARATION OF HOLOCELLULOSE PULP

Longleaf pine (Pinus palustris) was selected as the wood species to be used in this thesis for several reasons: (1) It has long fibers, simplifying handling procedures. (2) It has relatively wide growth rings, making separation of springwood and summerwood easy. (3) This species was used by Jentzen and additional information for the thesis could be obtained by comparing data from the two programs of work.

A 35-cm. diameter, 50-cm. long longleaf pine tree section weighing 102 lb. was obtained from the Union Bag-Camp Paper Corporation, Savannah, Georgia. The section was wrapped in wax paper and burlap immediately after cutting and arrived in good condition with no indication of drying. There was no evidence of biological deterioration. The log was debarked and split longitudinally into four sections. Two of these sections were further sawed into three-inch pieces (measured along the cylindrical axis). These pie-shaped quarter-circle sections were then cut parallel to the grain into smaller sections on a guillotine cutter to facilitate separation of summerwood and springwood.

The 27th and 28th growth rings of the 49-year old tree were selected for testing because these rings were well beyond the juvenile wood stage (45). Only the summerwood fibers were desired so the guillotine cutter was used to cut the summerwood chips out of the sections. This worked quite well provided that the pie-shaped sections were tangentially narrow, so that the arcs of the growth rings were nearly linear. Before the actual cutting operation, the sections of wood were impregnated with distilled water. This appeared to lubricate the fibers so that the separation of the summerwood chips did not appear to cause damage to the fibers. All sections not destined for immediate use were stored in 0.3% formaldehyde solution at 40°F.

After the chips were formed, they were examined and any unwanted wood (springwood or the summerwood) was cut off with a razor blade. This included the transition wood that occurs between the growth rings. The chips were then extracted in a Soxhlet extractor with a 1:1 mixture of chloroform—ethanol (47). Twice the number of passes theoretically needed for complete extraction of resins were run. The chips were then placed for 24 hours (under vacuum for about the first hour) in each of the following solvents: 100% methanol, 50% methanol, 25% methanol, and distilled water. After solvent exchanging, two previously weighed pieces were removed to determine the amount of water and extractives.

The pulping procedure utilized in converting the wood chips to holocellulose chips was basically that of Wise, et al. (48) as modified by Thompson and Kaustinen (47) and the writer. Wise's method specifies a mixture of sodium chlorite and acetic acid, this mixture producing the chlorine dioxide required for the delignification process. Thompson (47) suggested modification of this by eliminating the acetic acid and allowing the organic acids present in the wood to catalyze the reaction. This would allow penetration of the chemical to the innermost part of the chip before the reaction would begin, thus allowing more uniform pulping. A difficulty was encountered in applying this procedure in the present work. The pH of sodium chlorite solution at the concentration desired is about 10, and a solution of such alkalinity would cleave (saponify) the acetyl groups on the glucomannans, and thus make later extraction more difficult. To alleviate this problem, enough acetic acid was added to lower the pH to 6.8. Since the normal operating pH is several units less than this, this initial pH would still allow chip penetration of reacting chemical to occur while avoiding saponification of the glucomannan acetyl groups.

A 100 grams per liter sodium chlorite solution was made up in sufficient volume to achieve a liquor-to-wood ratio of 7.5:1 (volume:weight). The pH was lowered to 6.8 by addition of 2% acetic acid, and the resulting solution was added to an 8.5-inch vacuum desiccator containing the wood chips. A vacuum was drawn on the reaction mixture for one hour to remove entrapped air and to assist penetration of the cooking liquor, and then was released. The reaction, as indicated by evolution of chlorine dioxide, a yellow-green gas with a strong, suffocating odor, began about one-half hour after the vacuum was released.

Sodium chlorite was added during the three-week pulping period whenever gas ceased to evolve. An unusual observation was noted. While the pH of the cooking liquor of other investigators (14,49) appeared to be around 4, the pH of thi cooking solution appeared to be buffered around 2.6 to 2.8. The final pH was 4.0, however. The pH during the cook was not determined by the other investigators and, possibly, it dropped during cooking and, for some unknown reason, increased to 4 at the end of delignification. One other possible cause of the lower pH was that analytical-grade sodium chlorite was used in this work while the other workers used technical-grade chemical. The analytical grade contains less sodium hydroxide, and possibly this has an effect on the buffered pH value. During the course of this work, a cook was made with analytical-grade sodium chlorite solution on ammonia-impregnated chips. Here the pH of the solution buffered at 4. A ready explanation would be that the added ammonium salts provided the needed buffering action.

As delignification reached completion, the wood chips became spongy. When this point was reached, samples were removed and Klason lignins (50) were determined. When the proper delignification was indicated by this test, the chips were placed in distilled water for one week, the water being changed daily. Th allowed the soluble lignin and unreacted chemical to diffuse out of the chips.

The delignified chips were still relatively rigid. The nonextracted chips were defibered by peeling the chips into fine slivers and putting roughly one gram of the slivers in a one-liter plastic bottle filled with distilled water and containing 20 rubber balls, each weighing about 5 grams and having a diameter of about 16 mm. The plastic bottle was rotated for one hour at a rate of 10 r.p.m. The fiber slurry was decanted from the remaining slivers, fresh water added, and the cycle repeated until an adequate supply of single fibers had been collected. This method was selected to give a minimum amount of mechanical damage to the fibers.

The caustic-extracted chips were not defibered in the above manner but rather the chips were placed directly in the extraction solution. It was found that the initial extraction defibered the chips very nicely.

It should be mentioned that Jentzen pulped his wood for 8 months while these chips were pulped for 3 weeks. However, comparison of mechanical properties indicated no differences in the resulting fibers.

## EXTRACTION OF HOLOCELLULOSE PULP

The hemicelluloses were removed by aqueous alkaline extractions. The extractions were carried out in a three-step sequence, each step designed to remove a certain type of hemicellulose. Before placing the chips in each of the caustic solutions, nitrogen was bubbled through the solution for one-half hour to purge any oxygen. This nitrogen purge was continued throughout the extraction to prevent surface absorption of oxygen. The stream of nitrogen gas also produced a shear field in the liquid that both aided in extraction and also caused defibering of the chips to occur. A perforated parafilm covering was placed over the reaction beaker to prevent air from sweeping the surface of the liquid. This exclusion of air tended to minimize any degradative effects of the caustic on the cellulose.

After each extraction, the pulp was washed with distilled water in a Büchner funnel until the pH of the wash water was 7-7.5. Extreme care was taken to ensure that no air was drawn through the fiber mat. About 500 ml. of 1% acetic acid were then added to the slurry, and the suspension was washed again with distilled water until the wash water reached a neutral pH. Roughly 30% of the slurry suspension was removed, labeled, and stored at 40°F. after each extraction step. Enough phenyl mercuric acetate (PMA) was added to make up a 0.05% solution. PMA is an excellent bacteria and fungi inhibitor which does not react with the pulp fiber. The remaining pulp fibers were subjected to the next extraction step.

The details of the foregoing extractions were:

(1) 0.1N KOH for two hours at room temperature,

(2) 2% KOH for one hour at room temperature, and 9% KOH for one-half hour at 45°C. ± 2°C. (twice);

(3) 9% KOH-3% $H_3BO_3$ for one-half hour at 45°C. ± 2°C. (twice).

Limiting the length of extraction time minimized degradation of the cellulose; also, Nelson and Schuerch (44) found that the majority of the pentoses were removed in one-half hour. The purpose of heating the stronger caustic solutions was to decrease the chance of mercerization.

It was found that the chemicals in the third extraction were more difficult to remove by washing than the solutions used in the previous extractions. However, extensive washing appeared to remove all the chemicals. As a check, the pH of the slurry was checked weeks later to see if additional chemical had leached out of the fibers; none was detected, however, so it was assumed that all chemicals were removed.

# DRYING FIBERS UNDER LOAD

## DESCRIPTION OF JENTZEN'S DRYING APPARATUS

Although a thorough discussion of this piece of equipment has been given by Jentzen (2,8) a description will be given here to facilitate discussion of procedures and modifications of the equipment.

This apparatus has the capability of drying never-dried fibers under load. Its distinguishing features are: (1) a set of clamps which grip the fiber securely so that there is no slippage but at the same time do not damage the fiber excessively; (2) a device to measure the change in length of the fiber span during application of load, drying, and release of load; and (3) a means of applying a constant load which does not change appreciably with changes in the fiber span and is not affected by removal of water.

The apparatus is shown in Fig. 1 and a schematic diagram is shown in Fig. 2. The fiber was gripped between the movable clamp suspended from the chains and the fixed clamp attached to the water tank. The clamps, which were made of chromium-plated precision-ground steel, had been surface ground on all the surfaces which come in contact with other surfaces to ensure a good fit. A more detailed view of a clamp is shown in Fig. 3. The fiber was clamped between the ground faces of the base plate (A) and the clamping beam (B). The loading beam (C) is used to apply the load directly on the clamping surface in order to eliminate possible curvature in the clamping beam. The principle is the same as that employed in the zero-span jaws (51).

The clamping pressure is applied by means of the spring (D), which is compressed with the adjustable nut (E) attached to the loading rod (F). The loading rod fits through the slightly oversized holes in the base plate, clamping beam, and loading beam. A stainless steel pin (G) through the top of the loading rod

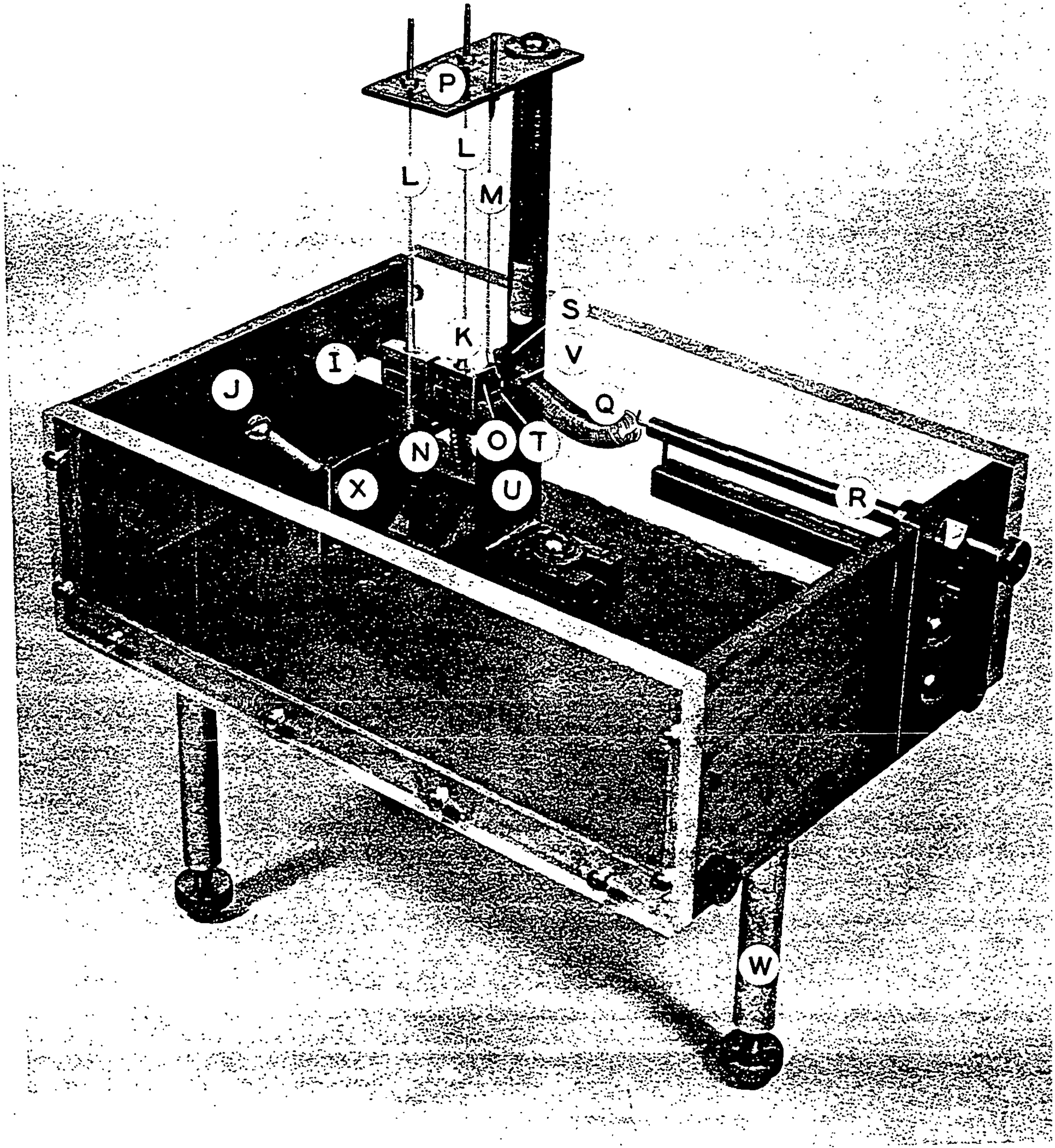


Figure 1. Apparatus to Dry Fibers under Load

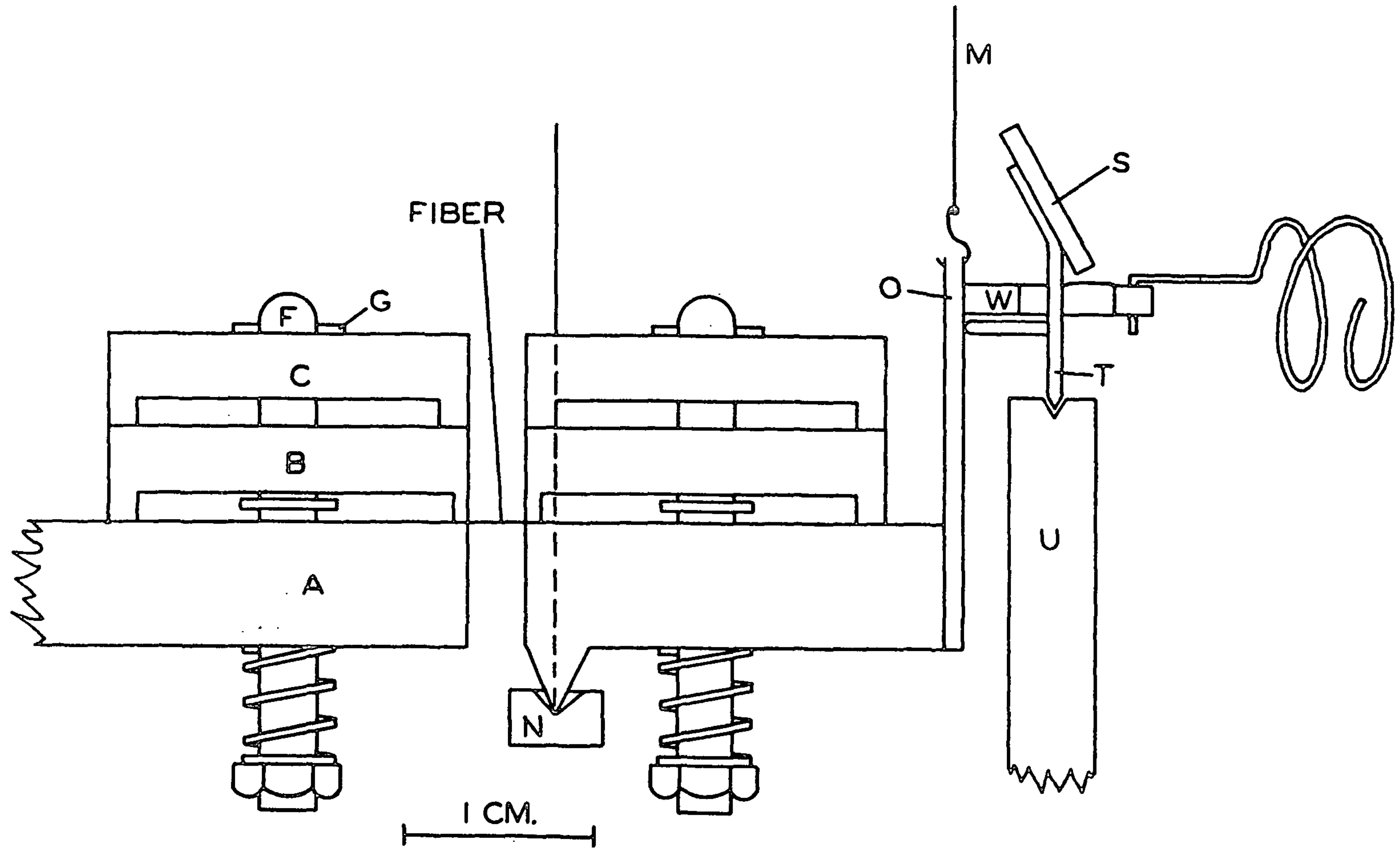


Figure 2. Schematic Diagram of Apparatus to Dry Fibers under Load

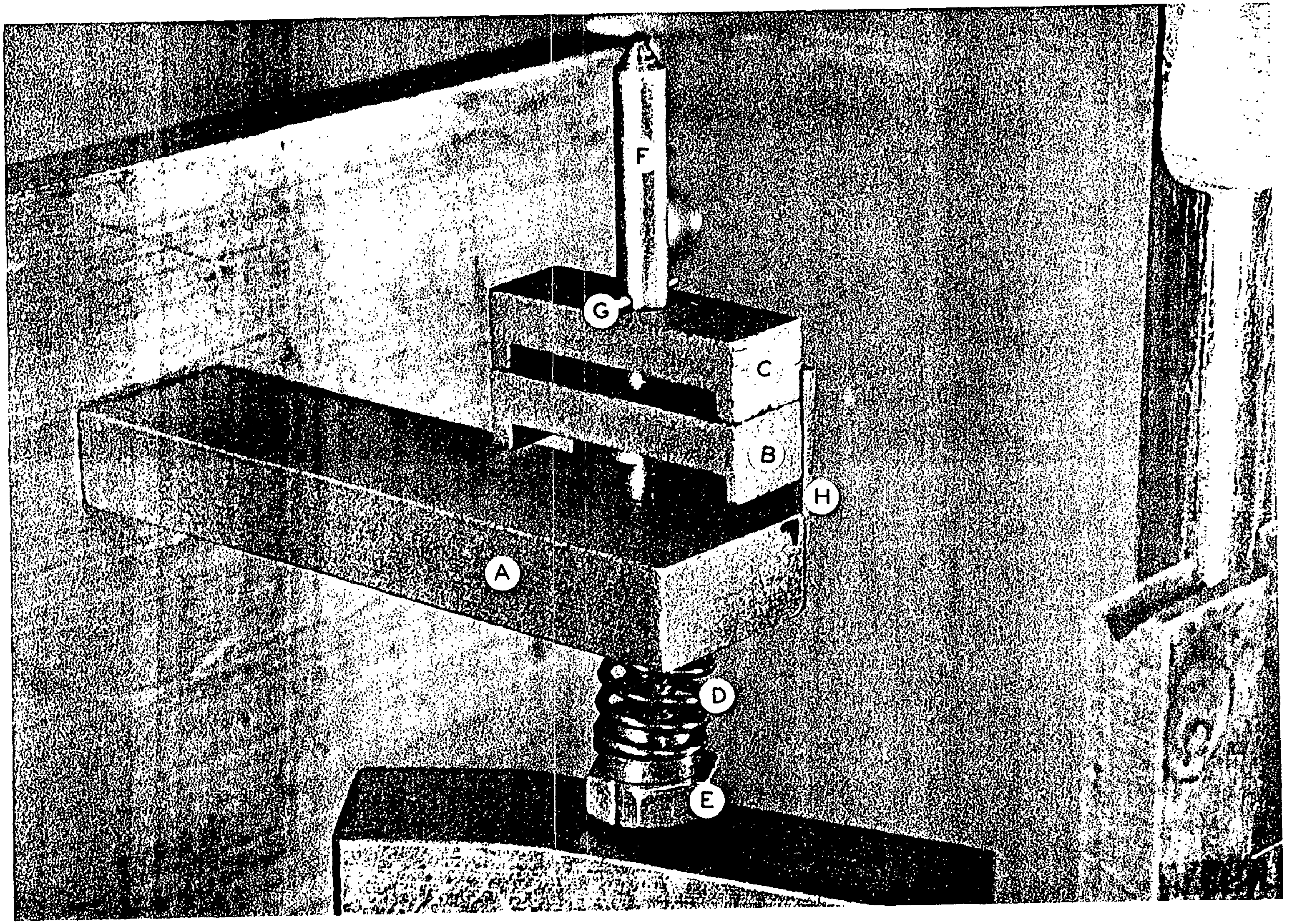


Figure 3. Detailed View of Clamp

applies the load to the loading beam. The guide plate (H) screwed to the side of the base plate keeps the clamping and loading beams aligned while the fiber is being gripped. There is only a partial guide plate on the movable clamp, allowing air to circulate around the clamp.

As shown in Fig. 1, the fixed clamp (I) is fastened securely to the brass end plate of the water tank (J) and the movable clamp (K) is suspended by three fine jeweler's chains (L,M). The two chains (L) closest to the fixed clamp are attached to the agate plate holder (N) on which the knife edge of the clamp rests. The single chain (M) is attached by a fine hook to the optical lever plate (O). Adjustment of the movable clamp in all directions is provided by the chain holder (P), facilitating alignment of the two clamps and allowing adjustment of drying span length of the fiber. The fixed clamp is opened by sliding the tapered brass bar (X) under the loading rod of the fixed clamp.

The load is applied to the fiber by the spring (Q) attached to the spring support (V). The spring support is attached to the upper part of the optical lever plate so that the spring is out of the water at all times. The extension of the spring which determines the load is controlled by the micrometer screw arrangement (R) attached to the spring. The spring characteristics were chosen so that the elongation of the fiber at a given load was less than 1% of the extension of the spring necessary to produce the load. This insured that the load will remain essentially constant while the fiber elongates or contracts.

An optical lever is used to measure the change in length of the fiber. A mirror (S) is glued to the T-shaped mirror support (T). The bottom of the support had been ground to a knife edge, and this fits in the V-shaped groove of the mirror support holder (U). A stainless steel pin attached to the mirror support rests against the optical lever plate of the movable clamp. The image of a hairline, following reflection of the beam by the mirror, was focused on a distan scale. When the fiber span changed, the movable clamp moved the corresponding amount, which caused the mirror support to rotate on its knife edge. Thus, the position of the hairline image changed on the scale. The scale is a 50-cm. translucent scale divided into 1-mm. units. The hairline was clearly visible on the far side of the translucent scale even in bright room light. The scale was positioned so that (a) the reflected beam struck the scale perpendicularly at the center of the scale, and (b) so that the average fiber extension covered the central portion of the scale.

The ends and bottom of the water tank are made of brass plate, while the sides are constructed of Plexiglas as an aid to viewing the clamps. A drain is located in the bottom of the tank so that the water can be removed when the fiber is to be dried. The water tank is supported on three adjustable legs (W) for leveling the tank.

The whole apparatus rests on a heavy stone table weighing approximately 500 pounds. The adjustable legs of this table stand on 1/4-inch steel plates which bear on 1-inch thick Unisorb pads. The net result of this is that external room vibrations are not noticeably transferred to the drying apparatus. The table wa carefully leveled, as was the drying tank.

Before this apparatus could be used, it was necessary to calibrate both the spring used for applying the load and the optical lever. The apparatus shown in Fig. 4 was used to determine the spring constant. A piece of graph paper on whi 45° lines were drawn was taped to the board. A rod was mounted along the top of the board in such manner that a washer could be slid freely along it. One end the spring was securely fastened to the board and the other was attached by a nylon thread to the washer.

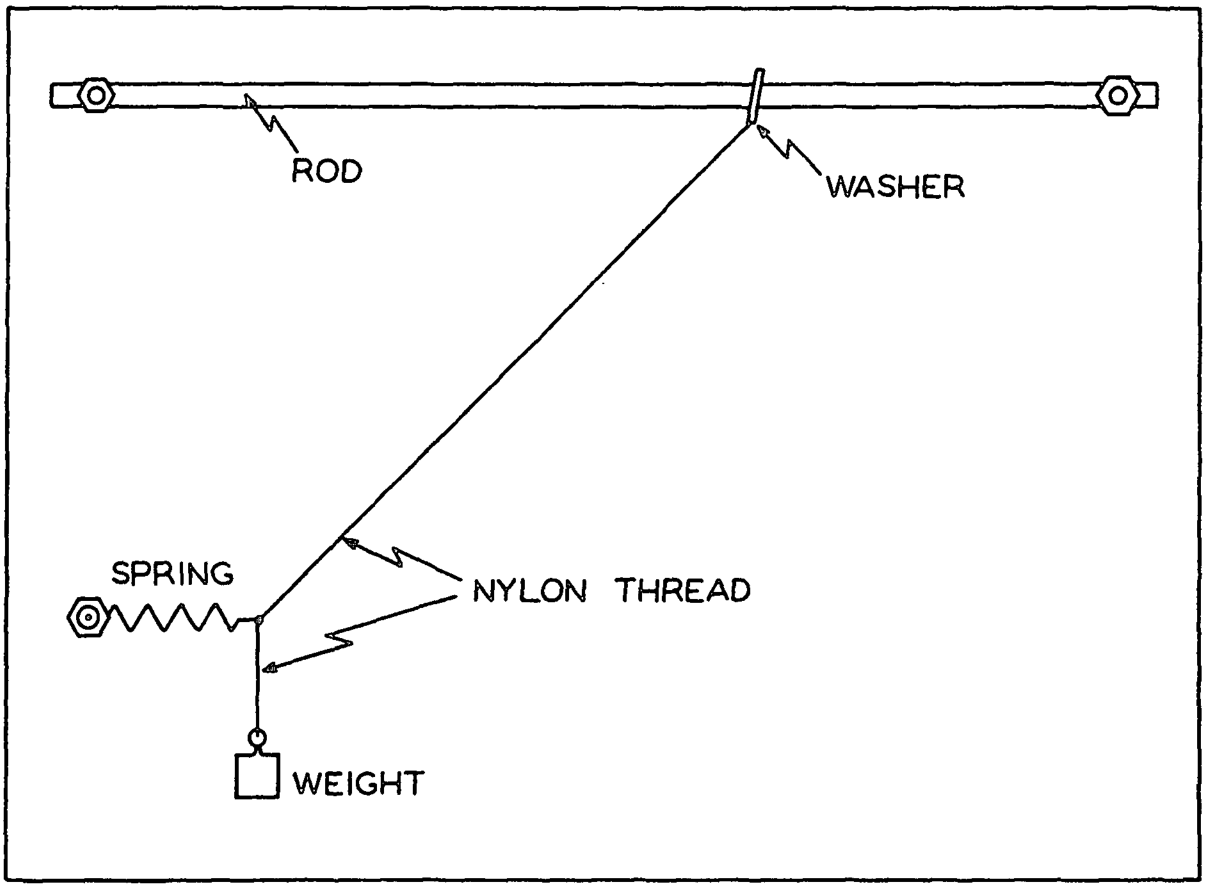


Figure 4. Spring Calibration Apparatus

The spring was calibrated by placing the nylon filament at a 45° angle (referred to the vertical) and measuring the length of the spring. The effective load at this point was half the weight of the spring. Various weights were then hung, in turn, from the free end of the spring, the nylon thread was adjusted to a 45° angle for each weight, and the extension was measured. A force analysis shows that the force extending the spring is equal to the weight suspended from the end of the spring and line plus half the weight of the spring. The spring constant was calculated to be 1.001 grams per centimeter.

The calibration of the optical lever was done with a micrometer screw arrangement, using 0.0005-inch increments. The optical lever multiplication facto was calculated to be 910; Jentzen (2) noted that the relationship between the movement of the movable clamp and the scale reading was not linear. He derived a theoretical relationship based on the geometry of the system. In the followin equation, $S$ is the scale reading (in centimeters) and $h$ is the displacement of the clamp (in centimeters):

$$h = 0.652 \cos\left\{47.26^\circ - (1/2) \arctan[(S + 43.1)/629]\right\} - 466$$

## MODIFICATION OF JENTZEN'S DRYING APPARATUS

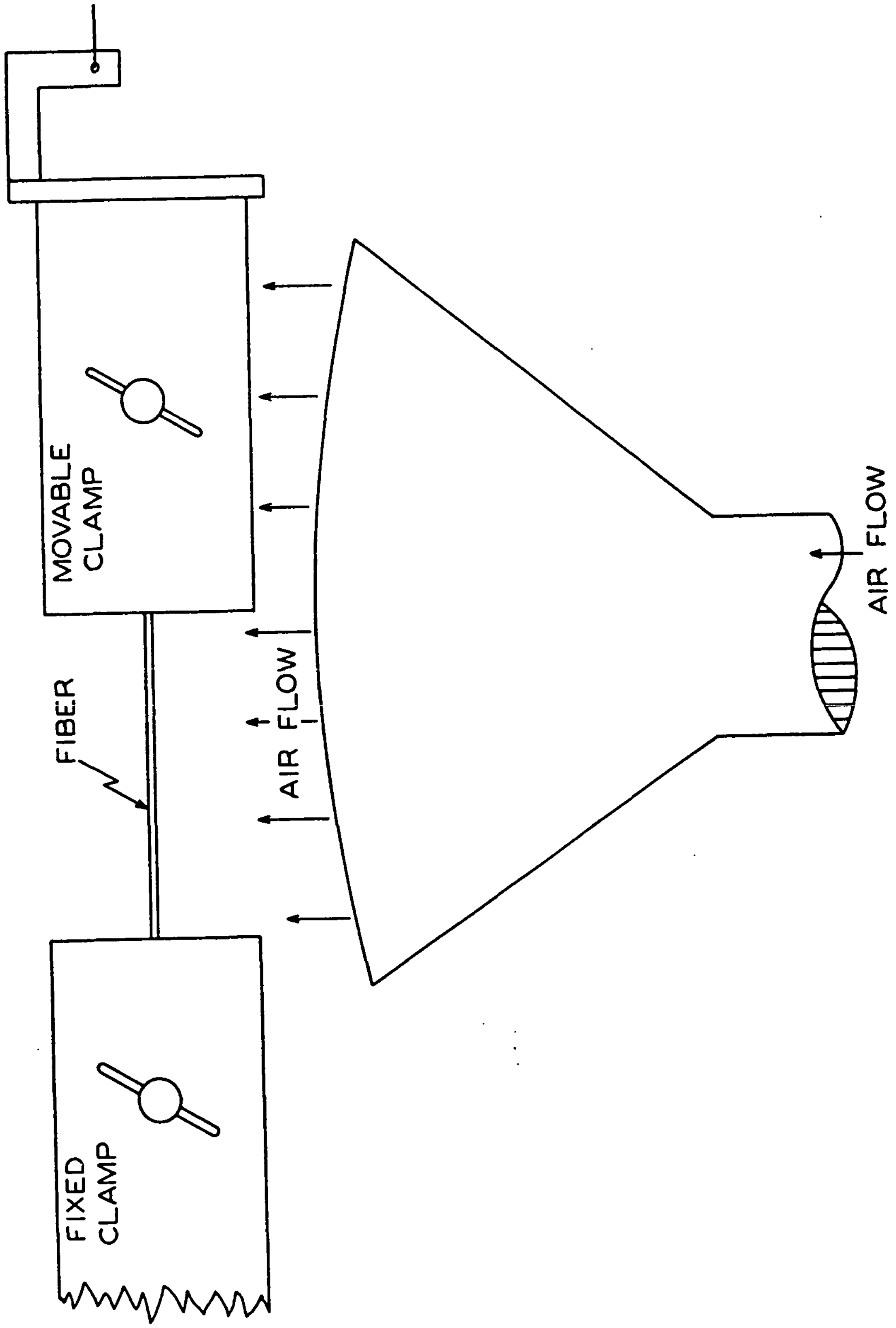
Several modifications were made to Jentzen's original equipment. Some have already been described, such as the translucent meter scale, and the vibration-free apparatus table. The most important modification was a device that directe a low-velocity current of air across the fiber and the clamps. Jentzen had fil the crevices in the movable clamp with paraffin wax to prevent adherence of wat However, this appeared to leave a thin layer of water trapped under the wax and clamp in the vicinity of the gripped fiber end. The portion of the fiber which was in the movable clamp remained wet until removal of the fiber from the clamp

The wet portion then dried quickly, this process being characterized by a rapid twisting of the wet portion (usually less than 1/2 mm. in length). No change in the dried portion was noted.

Removal of water in the movable clamp by vacuum was attempted but it was impossible to do this without jostling the clamp occasionally. This, of course, would put an unknown stress on the fiber. It was found that a low-velocity current of air would remove the water from the movable clamp in the proper time.

The device to accomplish this, pictured in Fig. 5, consists of a 1/125-h.p., 2950-r.p.m. blower with a piece of 16-mm. glass tubing inserted into the blower outlet through a rubber stopper. This glass tube is connected by a piece of flexible rubber tubing to a longer piece of 16-mm. glass tubing that is bent through 90° at its far end. A Bunsen burner wing tip is glued on the far end of the glass tube. An adjustable pinch clamp on the rubber hose acts as an air flow throttling valve. The wing tip was positioned to allow a smooth, slow current of air to move across the fiber and clamps. This air, of course, was conditioned room air that entered the blower inlet. Tests were made with an electric hygrometer to determine the relative humidity (R.H.) in the region of the fiber. After draining the tank, the fan was turned on and the R.H. was read in the vicinity of the clamps. The hygrometer R.H. reading in the fan stream was 52.5% *versus* 51.5% in the room.

The velocity of air that passed across the fiber was low enough to minimize side effects while still accomplishing drying. The air appeared to move the clamp a barely discernible amount perpendicular to the fiber in the direction of the air stream. Thus, the force exerted by the air stream on the movable clamp was negligible (estimated to be about 0.05 gram).


MOVABLE CLAMP
FIBER
AIR FLOW
AIR FLOW
FIXED CLAMP

## PROCEDURE

Jentzen's procedure for mounting the wet fibers was also used in this work. The movable clamp was placed in a special jig filled with distilled water and the jaws were opened. The fiber to be dried, which had to be longer than 3.5 mm., was removed from a dilute slurry by gripping one end with precision ground tweezers, and then transferred to the jig holding the movable clamp. Care was taken to ensure that the fiber was wet at all times. The fiber was centered in the clamp and gripped. The jig containing the movable clamp was placed next to the tank, which had been filled with water. The movable clamp was positioned for a 2-mm. span. The jaws of the fixed clamp were opened and the movable clamp was quickly placed in the tank and maneuvered under water to the supports, and thus suspended from the three chains. The free end of the fiber was guided between the fixed jaws, and with the aid of a mirror under the clamps, the fiber was aligned and gripped. The spring for applying the load was positioned and a 1-gram load was applied. A load of 1 gram was needed to straighten the fiber and to steady the movable clamp and the optical lever mirror support resting against the clamp. The mirror was positioned carefully with the pin of the support aligned on the center line of the fiber and spring. The fiber was then in position for initiation of the test. The 1-gram load was applied approximately 1 min. before the first reading.

The following procedure was used in drying a fiber under load. A reference reading was first taken at the 1-gram load, and the desired load was then applied within 30 seconds, and a reading at 1 minute was taken. Another reading at 5 minutes was taken and the water was removed. The water clinging to the fixed clamp was quickly and carefully removed by vacuum and blotting paper. A reading was taken at 6 minutes; the fan was turned on at 6:02 and a reading was taken at

6:17. Readings at 7 and 15 minutes were taken, the load was reduced to 1 gram in 30 seconds and a reading at 16 minutes was taken. The fiber was removed and stored in a marked test tube.

Each fiber received an identification code containing four numbers indicat ing the chemical treatment, drying load in grams, month during which the fiber was tested, and an individual number. This fiber identification number was lis in the research notebook and on each load-elongation record card.

The fibers dried under no load were dried on a black glass plate thinly coated with teflon (52). The teflon had been rubbed somewhat to yield a very thin, polished layer. This resulted in a surface that prevented the fibers fr curling excessively while drying, yet allowed the dried fibers to be removed f the plate without significantly stressing them.

## LOAD-ELONGATION MEASUREMENTS

All load-elongation measurements on the individual fibers were made on th I.P.C. Fiber Load-Elongation Recorder (FLER) (53). The dried fibers were glue to the pins by first tacking them to the pins with ethylhydroxyethyl cellulose Care was taken to be sure that the ethylhydroxyethyl cellulose was not near th ends of the pins where the epoxy resin would later go. Epon 907, a two-part resin manufactured by Shell Chemical Company, was used to glue the fiber. Th glue was prepared by weighing 10 parts of component "A" and eight parts of co ponent "B" and then mixing thoroughly. Before application, the glue was allo to age for about 5 minutes to achieve enough set to prevent flow of the glue the fiber. Generally, about 25 to 30 fibers could be glued from one mix befo the resin became too viscous. A negligible number of fibers pulled out from glue (less than 0.1%), indicating a good bond.

The nominal span length for all fibers was 1.03 mm. This was set by inserting a feeler gage between the pins before mounting the fiber. After the fiber was mounted, the span was further checked with a calibrated eyepiece in a bifocal microscope. Any end effects which were caused by mechanically gripping the fibers in the drying apparatus were eliminated through the use of a test span (1.03 mm.) that was appreciably smaller than the 2-mm. span used to dry fibers under load.

A 10-r.p.m. motor and a 9.17-g./cm. chain were used in the FLER for all testing, resulting in a loading rate of 2.0 g./sec. Room conditions were kept at 73°F. and 50% relative humidity.

## CROSS-SECTIONAL AREA MEASUREMENTS

The fiber cross-sectional area was determined with the I.P.C. Compacted Fiber Dimension Apparatus (CFDA) (54). Here the fiber was compressed between two optical glass plates. The compressive force collapsed the pores and lumen of the fiber and the area measured was that of the solid fiber (54). The thickness was measured by a linear-variable transducer, which measured the separation of the plates by the differences between two null point readings. The width was determined by a Cooke-A.E.I. image-splitting eyepiece* inserted in a 10-power microscope (total magnification was 100X),.

The area was calculated by a formula that took into account the rounded edges of the compressed fiber:

$$A = 0.001482TW - 0.000007802T^2,$$

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*Vickers Instrument Ltd., York and Croydon, England.

where T = the thickness in transducer values, W = the difference in the image-splitting eyepiece micrometer readings, and A = the cross-sectional area in square microns.

## MERCERIZATION ANALYSIS AND CRYSTALLINITY DETERMINATIONS

To check for mercerization effects and to measure changes in internal bonding upon extraction of hemicelluloses, x-ray diffractograms were obtained for each pulp sample. All x-ray diffractograms were taken with a Norelco x-ray unit. The operational data are listed in Table IV.

### TABLE IV

### X-RAY DIFFRACTION OPERATIONAL DATA

X-ray; tube CuK, 35 kv., 20 ma.
Slits; 1/2° dev., 0.0006" rec., 1/2° scat.
Scan; Goniometer 1/2°/min., Plot 2°/inch.
Scale Fact. 8, Mult. 0.6, Time Const. 8.

One-half gram of air-dried pulp was compressed in a disk mold (diameter 2.5 cm.) at 1400 kg./cm.$^2$ for 15 seconds. The disk was placed in the x-ray unit and scanning began at $2\theta = 10°$ and ended at $2\theta = 45°$.

## DETERMINATION OF EXTENT OF ALKALINE DEGRADATION

The extent of degradation of the cellulose caused by the alkali extraction of the holocellulose fibers (holofibers) was determined through measurement of the intrinsic viscosities for the different pulp samples.

The fibers were air dried, Wiley milled to pass a 20-mesh screen, and then dissolved in cupriethylenediamine according to TAPPI method no. 230 as used by the I.P.C. Analytical Department. Four concentrations were made from each sample. A No. 150 Cannon-Fenske viscometer was used in a 30°C. constant-temperature bath. The reduced viscosity was plotted *versus* concentration on a semilogarithmic plot utilizing a linear regression formula, and the calculated intercept at zero concentration was determined as the intrinsic viscosity.

## EFFECT OF SWELLING ON MECHANICAL PROPERTIES

It was desired to learn what effect the structural swelling of the holofibers caused by the extraction solutions had on the mechanical properties of the fibers. After some deliberation it was decided to test cotton fibers, which have a structure very similar to that of wood pulp fibers except that they lack hemicelluloses. Any change in properties upon treatment with the extraction solutions would be purely a result of structural swelling.

A quantity of raw Deltapine cotton fiber was obtained which had never been carded, hence had never been subjected to appreciable mechanical stresses (55). The cotton fibers were extracted with a solution of 1:1 chloroform-ethanol using a procedure already described for wood fibers.

After removal of waxes and resins, it was necessary to remove the pectinaceous material, which is present in the cotton to the extent of 3-4% by weight. The normal procedure for accomplishing this is to kier-boil the cotton in 1% sodium hydroxide solution. However, since the effect of alkali on cotton was desired, this procedure would not be applicable. After some investigation it was decided that 0.5% ammonium oxalate solution would be the most satisfactory extractant, being a good solvent for pectinaceous materials and having a relatively neutral pH of 6.5.

Fifteen grams of dry cotton fibers were placed in 1600 ml. of the solution. The temperature was increased from ambient conditions to 75°C. and maintained there for 23 hours. The extraction vessel was a three-necked round-bottom flas with a thermometer inserted in one neck, a reflux condenser in another, and a nitrogen gas tube in the third neck. The condenser maintained the same concentration of the extraction solution and the bubbling nitrogen gas produced conti uous mixing. The cotton was removed after 23 hours and washed thoroughly in a Büchner funnel with four liters of distilled water. An analysis revealed some pectin remaining so the procedure was repeated. The second extraction reduced the pectin content to 0.4%, which was considered an acceptable level.

The analysis for pectin was conducted according to the I.P.C. Analytical Chemistry Group's analysis for galacturonic acid (56), with the following modification. Instead of eluting the sugars off the chromatograph, several known concentrations and quantities of galacturonic acid were spotted on the chromat graph sheet along with the unknown. Comparison of the size and intensity of t known and unknown spots gave the per cent pectin in the sample.

After removal of pectins, the cotton fibers were treated with the alkali extraction solutions under the same conditions already described for wood pulp fibers. In removing fractions of the cotton following each treatment, care wa taken to obtain a random sampling of the treated cotton to avoid any accidenta sampling bias. The cotton slurries were stored in the cold room in 0.05% PMA solution and were removed as needed.

A total of 45 fibers from each extraction sample were dried under no loa on the teflon-coated glass plate and then were mechanically tested on the Fib Load-Elongation Recorder with the wood pulp fiber procedure already described. Due to the extreme length of the fibers (one-half inch to one inch), it was necessary to cut the fibers into shorter lengths to facilitate removal of single fibers from the group and to mount these single fibers on a 1.03-mm. span. This was accomplished by cutting the cotton clumps with shears into approximately 3/8-inch strips. This allowed single fibers to be removed from the clumps without undue stress on the fibers.

More difficulties were experienced with determining the cross-sectional area of the cotton fibers than with the wood fibers due to the smaller cross-sectional area of the cotton fibers (90 square microns versus 400 square microns). This made the image in the Dyson image-splitting eyepiece harder to align and also resulted in very low readings of thickness for certain cotton fibers. There is a certain random error involved in all measurements of this sort. When the random error for the cotton fiber measurements became greater than 10% of the instrument values for individual fibers, these fiber values were not averaged in the final result. Their properties were calculated, however, and generally the values of these fibers tended to be 100 to 300% higher than the mean value of the population. The percentage of fibers removed for this reason were roughly 5-10% of each extraction sample.

## ELECTRON MICROGRAPHS OF FIBER SURFACES

Electron micrographs were taken of the surfaces of fibers randomly selected from each of the groups. Some of the micrographs were taken of the fibers' main body and others were taken of broken ends of sections of the fibers.

The fibers were stored in slurry form (in 0.05% PMA) until used. They were dried on a glass plate before micrographing them. Those that were to be broken were pulled apart by grasping each end with precision ground tweezers. About 15 fibers from each group were selected for micrographing.

The procedure used for obtaining the micrographs was that of Swerdlow and Seeman (57), as modified by Smith (58). The developed plates were enlarged three times and printed for better clarity.

# EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

## INTRODUCTION

The hypothesis of this work is that the hemicelluloses increase the strength of wood pulp fibers by allowing an internal redistribution of stress to occur in the fibers. In particular, it is hypothesized that the highly branched polymers that exist between the cellulose fibrils exert the greatest influence on the fiber's mechanical properties. As the hemicelluloses are removed, the flexible hemicellulose-cellulose-hemicellulose bond is replaced by a more rigid cellulose-cellulose bond, resulting in stress concentration at the individual bonds, and lowered fiber strength. (The bonds referred to are not simply hydrogen bonds, Van der Waal's forces, etc., but rather the summation of all such bonds between two fibrils or other similar internal element of fiber structure.)

This hypothesis will be developed throughout the section on Discussion of Results.

## CHEMICAL CONTENT OF PULP SAMPLES

Samples of each pulp fiber group were analyzed by means of the I.P.C. microtechnique for sugar analysis. This method is a modification of the standard method of Saeman, _et_ _al_. (_59_). Triplicate determinations were made on each sample. The results of this sugar analysis are shown in Table V.

Table VI gives the comparative values corrected for yield. The first extraction partially removed the araban and galactan, and affected only small amounts of the mannan and moderate amounts of the xylan. The araban polymer remaining is probably that associated with the xylan. The 9% KOH extraction removed the xylan successfully, and also removed some of the mannan polymer.

## TABLE V

## SUGAR ANALYSIS OF UNEXTRACTED AND EXTRACTED HOLOPULPS

| Sample | Glucan, % | Xylan, % | Mannan, % | Araban, % | Galactan, % |
|---|---|---|---|---|---|
| Unextracted[a,b] | 56.0[c] | 6.86 | 15.8 | 1.28 | 1.88 |
| holopulp | 55.8 | 6.50 | 16.4 | 1.38 | 1.79 |
| | 54.7 | 6.68 | 14.6 | 1.22 | 1.78 |
| Holopulp | | | | | |
| extract with | 64.9 | 6.51 | 17.9 | 0.96 | 1.12 |
| 0.1N KOH | 67.6 | 6.48 | 17.7 | 1.06 | 1.46 |
| | 62.1 | 6.20 | 17.3 | 0.98 | 1.34 |
| Holopulp | | | | | |
| extract with | 70.4 | 1.64 | 15.9 | – | 1.15 |
| 0.1N KOH + | 68.8 | 1.72 | – | – | 1.07 |
| 2% + 9% KOH | 71.4 | 2.02 | 15.7 | – | 1.22 |
| Holopulp | | | | | |
| extract with | | | | | |
| 0.1N KOH + | 73.6 | 1.84 | 10.9 | – | 0.74 |
| 2% + 9% KOH + | – | 1.86 | 11.3 | – | 1.16 |
| 9% KOH-3% $H_3BO_3$ | 73.9 | 1.79 | 11.2 | – | 1.44 |

[a] Klason lignin, 0.45%, I.P.C. Method No. 428.
[b] Resins and moisture = 42.1% based on original wood.
[c] All percentages are based on dry sample as analyzed.

Based on the glucose removed, it is probable that this is not the normal glucomannan polymer that is usually reported for softwoods which has a glucose-mannose (G-M) ratio of 1:2.7 (35). This ratio is about 1:1.1. Ward and Morak (60) have reported a 1:2 G-M polymer based on early alkali extraction, and Linnell (49) has extracted polymers with an over-all ratio of about 1:1. However, when Linnell isolated the extracted sugars, he found G-M polymers with 1:3.8 ratios. Evidentl in his case, at least, glucans comprised a large portion of the extract. Glucan polymers might possibly be present in the writer's extracts, also.

TABLE VI

SUGAR ANALYSIS OF HOLOPULPS CORRECTED FOR YIELD[a,b]

| Sample | Yield, %[c] | Glucan, % | Xylan, % | Mannan, % | Araban, % | Galactan, % |
|---|---|---|---|---|---|---|
| Unextracted holopulp | 72.1 | 55.5 | 6.68 | 15.6 | 1.29 | 1.82 |
| Holopulp extract with 0.1N KOH | 62.1 | 56.0 | 5.52 | 15.2 | 0.86 | 1.13 |
| Holopulp extract with 0.1N KOH + 2% + 9% KOH | 54.2 | 53.0 | 1.35 | 11.9 | - | 0.86 |
| Holopulp extract with 0.1N KOH + 2% + 9% + 9% KOH-3% $H_3BO_3$ | 50.1 | 51.1 | 1.28 | 7.76 | - | 0.78 |

[a] Data taken from Table V.
[b] All percentages referred to unextracted holopulp.
[c] Based on extractive- and moisture-free wood.

The glucomannan removed by the last extraction step has a calculated ratio of 1:2.74, closely approximating reported values.

A contradiction appears to exist in the 0.1N extraction. Although the total amount of sugars removed was small, about 2%, the loss of material was about 10%. It is possible that what was removed in addition to sugars at this stage was what is termed soluble lignin (14). In each extraction after the initial one, the loss in weight corresponds to the loss in sugars.

## CRYSTALLINITY OF PULP SAMPLES

X-ray diffractograms were obtained on each pulp sample in order to measure the degree of cellulose-cellulose bonding (higher crystallinity indicating more cellulose-cellulose bonding). The diffractograms were analyzed according to the crystallinity index method of Segal, Creelay, Martin, and Conrad (61), and the width at half height method of Klug and Alexander (62) (no correction was made for instrument line broadening). The crystallinity values are listed in Table VII.

## TABLE VII

## CRYSTALLINITY VALUES OF PULP SAMPLES

| | Unextracted Holofibers | 0.1N KOH Extracted | 9% KOH[a] Extracted | 9% KOH-3% $H_3BO_3$[a] Extracted |
|---|---|---|---|---|
| Width at half height, degrees | 2.87 | 2.82 | 2.73 | 2.57 |
| Crystallinity index, % | 54.4 | 56.7 | 58.3 | 60.9 |

[a] These extractions were in series as indicated in Table V. However, to conserv space, this nomenclature will be used in this and all following tables.

Removal of the hemicellulose fraction of the fiber increases the crystalli ity of the fiber. The change in the CrI is difficult to interpret because two phenomena are occurring simultaneously, a decrease in amorphous scatter and an increase in cellulose-cellulose bonding. CrI is defined as: CrI = $(I_{002max} - I_{min})\ 100/I_{002max}$, where $I_{002}$ = the maximum intensity of the 002 diffraction pe and $I_{min}$ is the diffracted x-ray beam's intensity at $2\theta = 18°$ and is a functior the amorphous background scatter of the fiber. Removal of the amorphous hemicellulose also removes some of this scatter, hence this removal will change the $I_{min}$ value and consequently the CrI could change in a manner other than by inc in cellulose-cellulose bonding.

The width at half height measurement of crystallinity is not influenced by the removal of the amorphous background scatter, hence these data are an indication of increased cellulose-cellulose bonding. The width at half height is related to the size of the average cellulose crystallite: $\underline{D} = \underline{K}\lambda/\beta \cos\theta$ , where $\beta$ = the angular width at half maximum intensity and $\underline{D}$ = the mean dimension of the crystallite. $\underline{K}$ and $\cos\theta$ are constants, $2\theta$ being the angle at which the diffracted beam is measured. $\lambda$ is the wavelength of the incident x-ray beam and is dependent upon the voltage. $\underline{D}$ calculated from this equation reflects the lowest value in a range of dimensions that contains the true crystallite size. All imperfections in the crystallites tend to increase $\beta$ and thus decrease the value of $\underline{D}$.

## ALKALINE DEGRADATION AND MERCERIZATION OF PULP SAMPLES

In order to obtain information on the extent of degradation of the cellulose caused by the alkali extraction of the holofibers, intrinsic viscosities were determined for the different pulp samples. The data are listed in Table VIII.

### TABLE VIII

### CUPRIETHYLENEDIAMINE INTRINSIC VISCOSITIES OF EXTRACTED HOLOFIBERS

| Pulp Sample | Intrinsic Viscosity |
|---|---|
| Unextracted holofiber | 8.18 |
| 0.1$\underline{N}$ KOH extracted holofiber | 9.69 |
| 9% KOH extracted holofiber | 9.87 |
| 9% KOH-3% $H_3BO_3$ extracted holofiber | 10.0 |

The increase in intrinsic viscosity of the holofibers when extracted with 0.1*N* KOH probably is due to the removal of the short-chain hemicelluloses in this extractive step. The increase for all subsequent extractions is very small, due to the increased chain length of the hemicelluloses removed in the three fractions. While viscosity-average degree of polymerization (D.P.) is neither number-average nor weight-average D.P., it is related most closely to weight-average D.P. and consequently would not be expected to change appreciably upon removal of lower D.P. materials. No formula existed for converting intrinsic viscosity to D.P. but a rough check using a formula for cotton cellulose (63) placed the D.P. in the range of 1900 to 2100. These data indicate that little, if any, degradation occurs in the cellulose fiber upon extraction with the alkaline solutions used in this work.

According to Ott, *et al.* (64), a 9% solution of KOH at 45°C. should not mercerize the cellulose fiber. However, the data in Ott's book were for sodium hydroxide and cotton and, while the two systems are comparable, a check for mercerization was necessary. Diffractograms were obtained from two pulp samples The data obtained from these diffractograms along with known data for Cellulose and II (cotton linters) are listed in Table IX.

TABLE IX

COMPARISON OF EXPERIMENTALLY DETERMINED X-RAY MAXIMA OF 9% KOH EXTRACTED PULP WITH LITERATURE DATA

| Miller Indices | Cell. I (65) | Trial 1 | Trial 2 | Cell. II (66) |
|---|---|---|---|---|
| 101,° | 14.6 | 14.9 | $15.4^a$ | - |
| $10\bar{1}$,° | 16.2 | 16.2 | $16.5^a$ | 20.0 |
| 002,° | 22.6 | 22.5 | 22.5 | 21.5 |

[a] Estimated values.

These data confirm that no detectable Cellulose II was present and that no mercerization occurred during extraction. The pulp obtained from the 9% KOH-3% $H_3BO_3$ extraction step was analyzed and this also indicated that no Cellulose II was present, as would be expected since this solution is of much lower alkalinity.

## THE EFFECT OF ALKALINE SWELLING ON THE MECHANICAL PROPERTIES OF CELLULOSE FIBERS

As mentioned earlier, treatment of the holopulp fibers with alkaline solutions could result in three changes to the mechanical properties of the fibers other than those caused by removal of the hemicelluloses: cellulose degradation, mercerization, and structural swelling. Since these changes could mask any changes caused by the hemicellulose removal, it was desirable to learn the magnitude of these effects. Investigating degradation and mercerization was relatively simple, and has been described. Investigation of swelling was more nebulous, for it was necessary to swell the fiber structure while avoiding subsequent removal of hemicelluloses.

Several solutions were found that would swell the fiber without appreciably extracting the hemicelluloses such as dimethylsulfoxide, but all of these compounds would remove some hemicellulose and in addition the swelling caused by these compounds might be different from that type and degree of swelling caused by the alkaline extraction solutions.

It was decided that the best answer was to treat cotton fibers with the alkaline extraction solutions. Specially purified cotton fibers contain no hemicellulose, yet have an internal structure similar to wood pulp fibers. Hence, any change in the mechanical properties of the cotton upon treatment with alkaline solution would have to be due to swelling.

The results of the load-elongation tests performed on the cotton fibers are listed in Table X. In addition, x-ray data are listed in this table.

TABLE X

STRESS-STRAIN AND X-RAY DATA OF ALKALI-TREATED COTTON FIBERS

| Property | Fiber Treatment | | | | |
|---|---|---|---|---|---|
| | Unextracted | 0.1N KOH | 9% KOH-<br>3% $H_3BO_3$ | 2% KOH | 9% KOH |
| Breaking stress, dynes/$\mu^2$ | 76.8 | 75.5 | 77.7 | 87.3 | 96.4 |
| Breaking strain, $\mu/\mu$, % | 9.30 | 8.76 | 8.42 | 8.92 | 8.70 |
| Modulus of elasticity, dynes/$\mu^2$ | 1321 | 1290 | 1430 | 1378 | 1852 |
| Width at half height, degrees | 1.52 | 1.60 | 1.58 | 1.63 | 1.58 |
| Crystallinity index, % | 82.5 | 76.5 | 75.0 | 74.7 | 75.0 |

These data are also plotted in Fig. 6, 7, and 8 versus equivalents of potassium hydroxide. The normality of the alkali-borate solution was calculated assuming that all the boric acid was neutralized by the caustic present in the solution. This calculation yielded an active alkali concentration of 0.2 equivalent.

Treatment of the cotton fibers with increasing concentration of aqueous potassium hydroxide solution increased the modulus of elasticity and breaking stress and decreased the breaking strain and the crystallinity of the fibers.

The trend in the breaking stress and modulus of elasticity was significant at the 98% level, using the t-test for two unknown means. This was obtained by comparing the zero and 9% KOH levels of extraction and is statistically highly

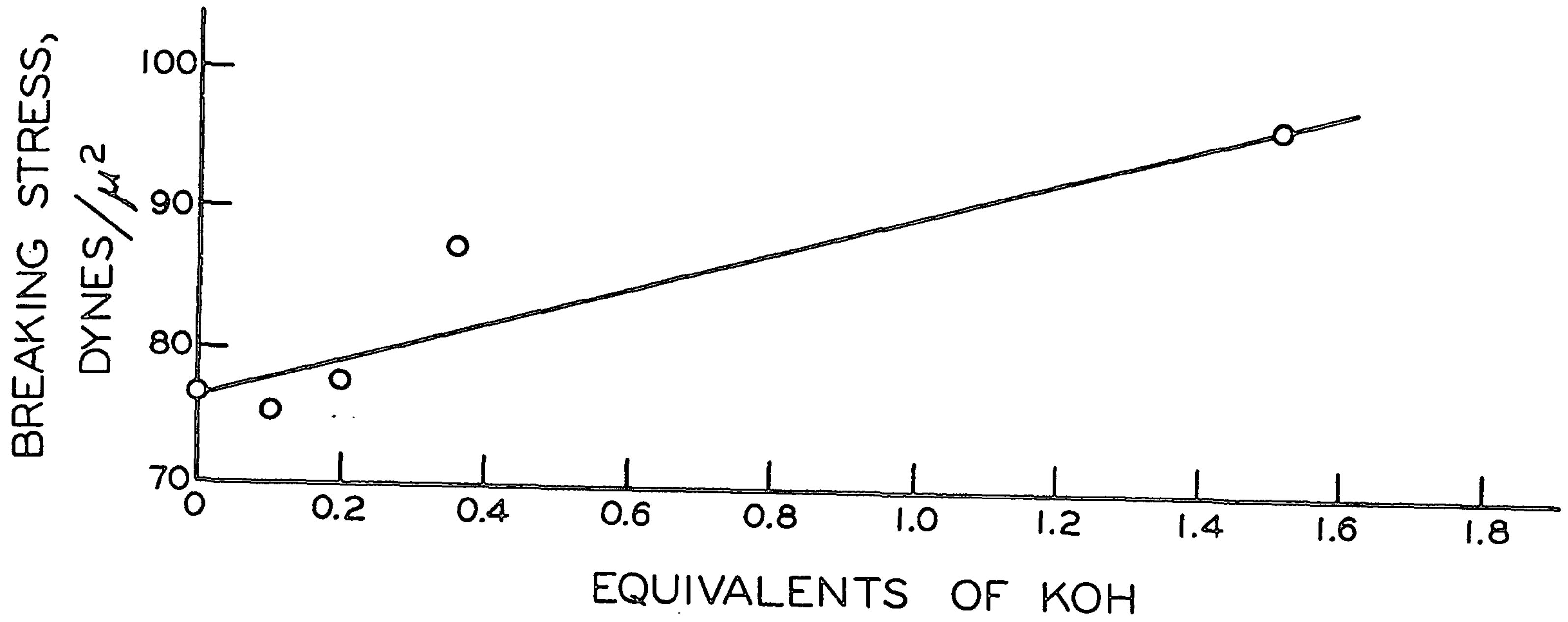

Figure 6. Effect of Swelling on Breaking Stress of Cotton Fibers

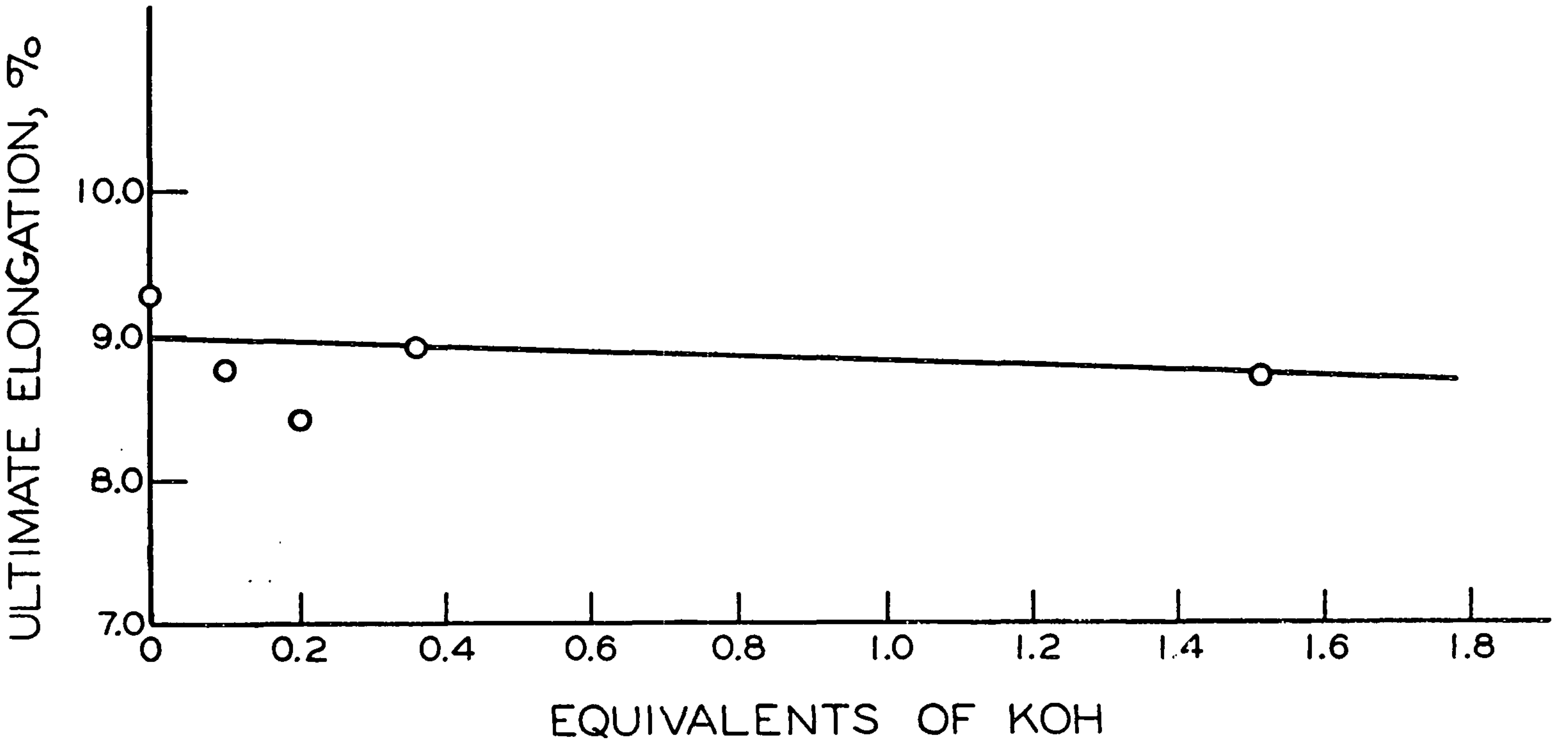

Figure 7. Effect of Swelling on Ultimate Elongation of Cotton Fibers

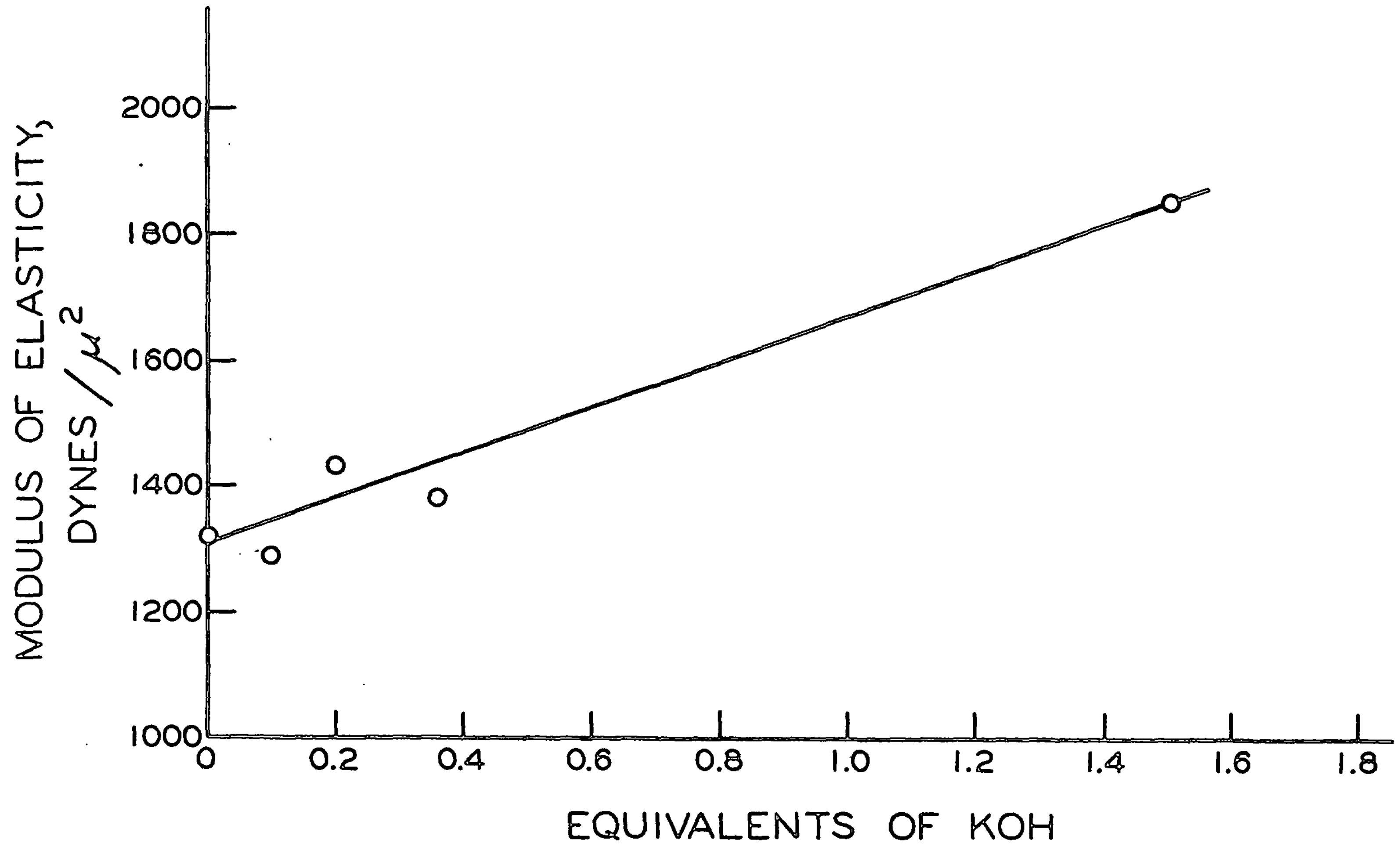

Figure 8. Effect of Swelling on Modulus of Elasticity of Cotton Fibers

significant. The trend for breaking strain, although in agreement with the other data, is not statistically significant.

A check of the literature revealed that there was precedence for an increase in strength and a decrease in extensibility upon treatment of cotton fibers with alkali. Schubert (22) in 1932 placed parallel bundles of cotton fibers in sodium hydroxide solutions of different concentrations for one hour each, then washed, dried, and tested them. The range in caustic soda concentration was from 0 to 40%. No tables of data were given in the book but a graph taken from Schubert's work was shown.

Schubert showed a constant increase in breaking load up to 10-11% sodium hydroxide and a decrease in extensibility up to this point. This is the beginning point for mercerization. The magnitudes of his slopes were different, being less than the writer's for breaking load and greater than the writer's for the extensibility. The device that Schubert used to measure his ultimate load and elongation was not described.

Wakeham and Spicer (20) found that treatment with 18% NaOH increased the strength of cotton fibers. They attributed this to the relieving of internal stresses at fibril spiral reversal locations in the cotton wall. They suggested that these reversal areas were regions of high crystallinity and high stress and that swelling tended to reduce these conditions somewhat. Ott and co-workers (67) also have observed increases in cotton fiber strength upon reduction in crystallinity.

Comparing the cotton data with the strength properties of wood pulp fibers dried under no load illustrated in Fig. 9 and 10 shows that the wood pulp fibers exhibit a decrease in modulus of elasticity and breaking strength upon treatment with these same solutions, an effect opposite to that for the cotton fibers.

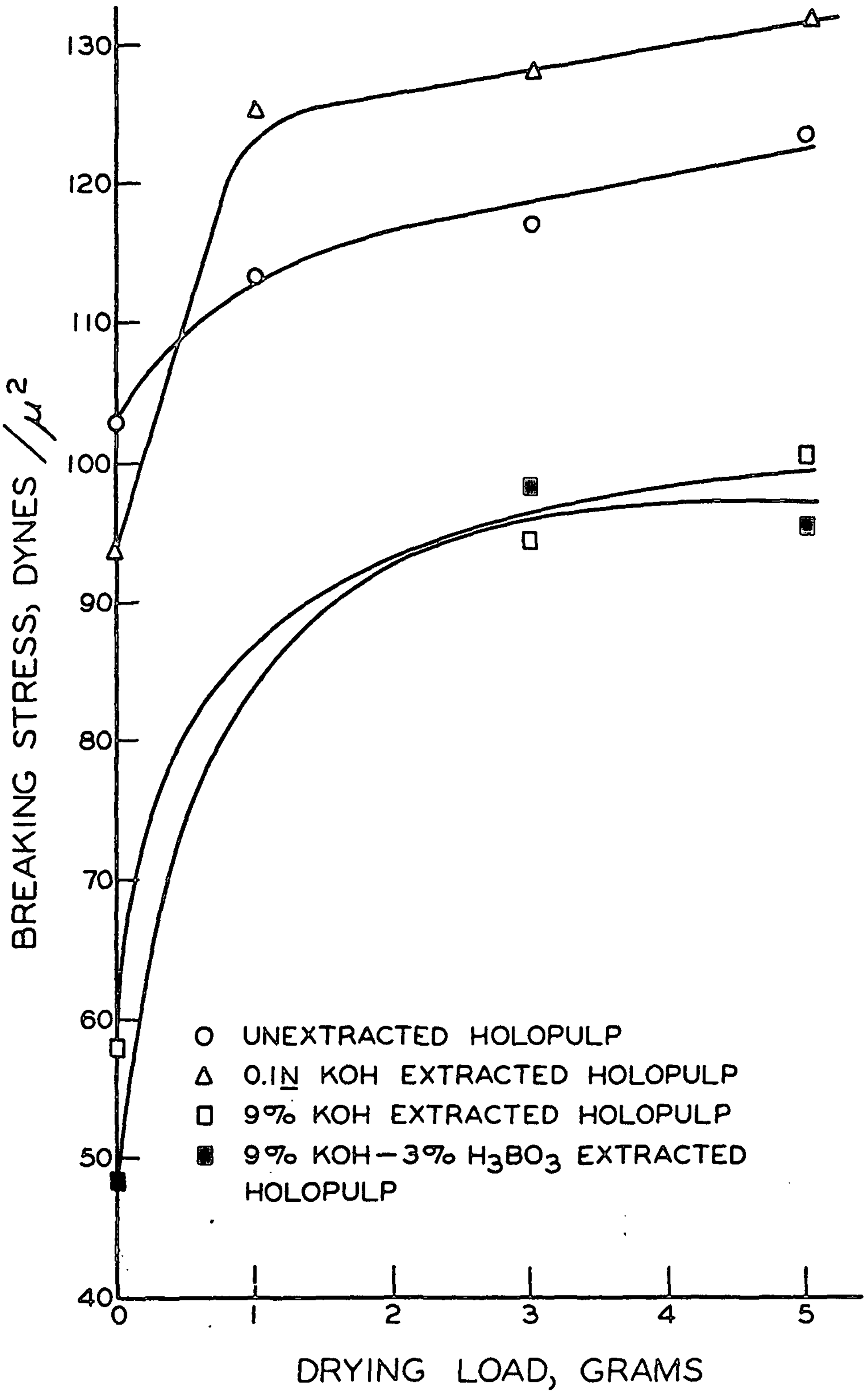

Figure 9. Effect of Drying Load on Breaking Stress Based on Measured Fiber Area

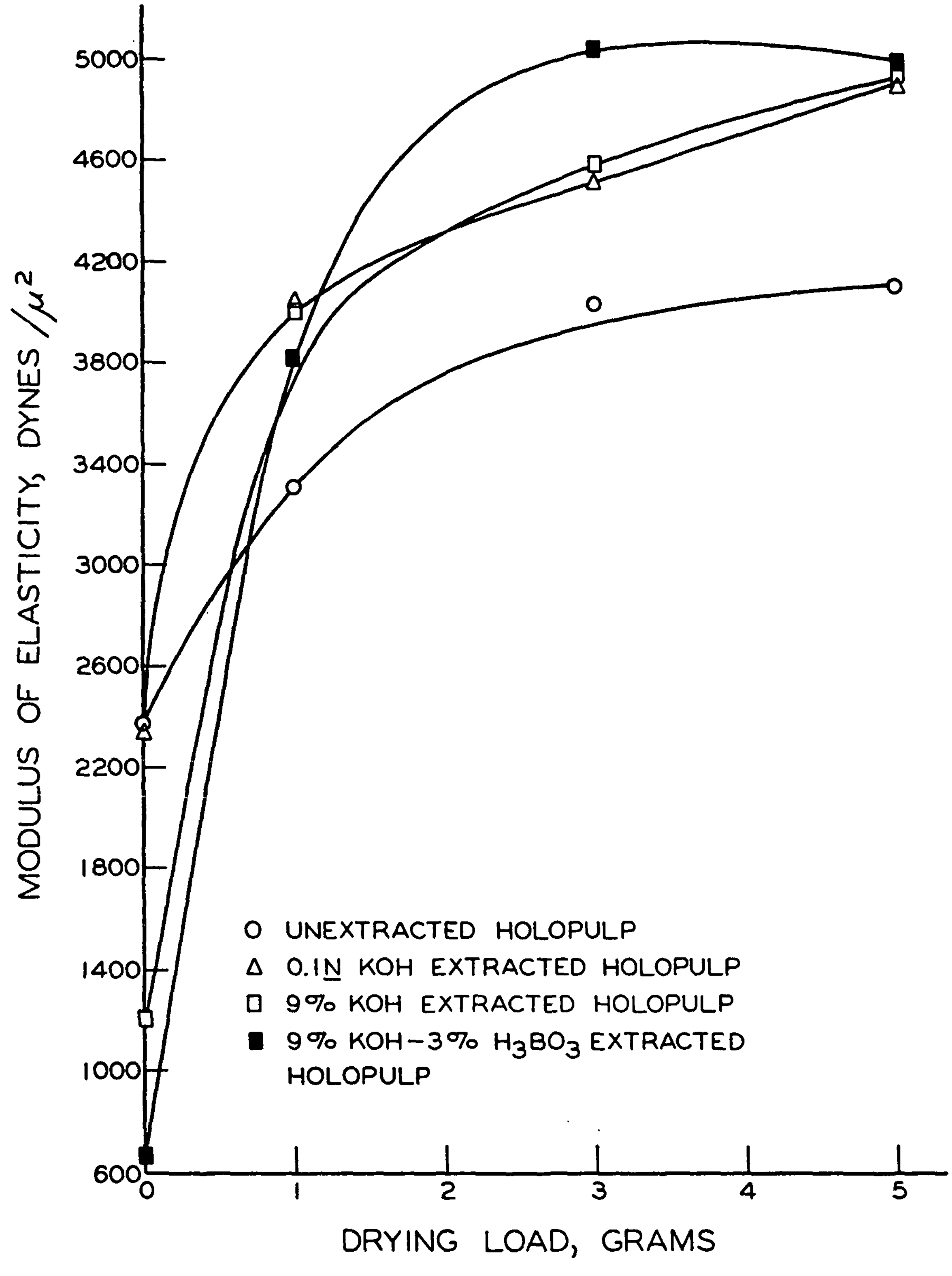

Figure 10. Effect of Drying Load on Modulus of Elasticity Based on Measured Fiber Area

As will be shown later, the effect of removal of the hemicelluloses is to appreciably lower the tensile properties of the fiber, while any effect of alkali-induced swelling slightly increases those properties. Hence, the effect of removal of the hemicelluloses is real and may be substantially greater than the data indicate due to swelling effects.

## ELECTRON MICROGRAPHS OF REPRESENTATIVE HOLOPULP AND EXTRACTED HOLOPULP FIBERS

In order to investigate the effects of alkaline extraction of hemicelluloses on the external and internal structure of the holofiber, electron micrographs of various magnifications were obtained on selected fiber surfaces and of broken ends of fiber sections. The broken ends of these fiber sections should show the internal fibrillar structure. The fibers were broken by gripping each end with tweezers and pulling them apart.

Examples of micrographs are shown in Fig. 20-24 in Appendix VII. There was no fibrillar structure as such in evidence for the unextracted fibers. The surface appeared to be covered with a smooth plasterlike substance. Some exposed fibrils began to appear in the fibers after the first mild extraction. The "coating" on the surface of the fiber was observed also by Jurbergs (68) who extracted fibers with alkali and took electron micrographs after each step.

The micrographs taken of the broken ends of the fiber were surprising. Instead of seeing many fibrils extending out of the fiber, only broad "fingers" were in evidence and each finger was covered with this smooth plasterlike substance. After the fibers were subjected to the second and third extraction steps, the fibrillar structure was exposed in greater amounts. The fibrils were seen to be crossing these fingers at a large angle. The fingers appeared oriented along the fiber's longitudinal axis, while the fibrils were oriented about 50°

to the fiber axis. These fibrils were probably in the primary wall. The finger-like structure appeared to exist under at least the primary wall layer of the fiber. Table XI lists a series of measurements taken from the electron micrographs indicating the size of the fingers and of the fibrils. The fingers appeared to be similar in size to Frey-Wyssling's macrofibrils (13) while the fibril appeared to be of two sizes, one approximating Frey-Wyssling's microfibrils and another his elementary fibrils.

TABLE XI

MEASURED SIZE OF ELEMENTS OF FIBER STRUCTURE

| Treatment | No. of Micrographs[a] | No. of Observations | Average Size, μ | Suggested Structural Feature |
|---|---|---|---|---|
| Unextracted holofibers | 4 | 5 | 1 | macrofibril |
| 0.1N KOH-extracted holofibers | 6 | 8 | 1.1 | macrofibril |
| 9% KOH-extracted holofibers | 10 | 10 | 1 | macrofibril |
| | 3 | 14 | 0.2 | macrofibril |
| | 1 | 10 | 0.07 | microfibril |
| | 1 | 10 | 0.01 | microfibril or elementary fibril |
| 9% KOH-3% $H_3BO_3$-extracted holofibers | 1 | 5 | 0.1 | macrofibril |
| | 3 | 10 | 0.03 | microfibril |
| | 1 | 10 | 0.003 | elementary fibril |

[a] Magnification range from 9,000 to 45,000.

It is interesting to hypothesize the significance of these elements and their relationship to the hemicelluloses' effect on fiber strength. If one assumes that one particular structural element is the smallest element that contains no hemicellulose in its internal structure, the amount of cellulose surface of this element that can be covered by the existing hemicellulose can be calculated. These calculations are listed in Appendix I. By assuming different structural elements and knowing the effect of removal of certain hemicellulose on fiber strength, one can surmise the location of the hemicellulose and verify the correctness of the assumption of the structural element's size.

From the calculations in Appendix I, it would seem possible that the size of the pertinent structural elements could range down to 100 A. Probably there exists a range in size of these elements, perhaps even from 100 A. to 10,000 A. (one micron).

## MECHANICAL PROPERTIES OF UNEXTRACTED AND EXTRACTED HOLOFIBERS

The data derived from the individual load-elongation curves for fibers broken in the FLER were converted to breaking stress, breaking strain, modulus of elasticity, yield point stress, yield point strain, and work-to-rupture (area under curve up to breaking point). The averaged data are listed in Tables XII and XIII along with the statistical variance of each population as expressed by per cent standard deviation (% S.D.) (see Appendix IV on elimination of data for pullouts). In addition, the average cross-sectional area of each fiber population and the number of fibers tested for each group are listed. The strength and modulus of elasticity values listed in Table XII are also plotted in Fig. 9 and 10. The curves for the 0.1N KOH extraction were surprising. Although this extraction removed some of the hemicellulose material, the breaking stress and modulus for these fibers when dried under a load were greater than for the unextracted fibers, which is in contradiction with the rest of the data. Considering the quantity and type of hemicelluloses removed, one would expect little change, and that change a lowering of the fiber's strength. Figure 11, which shows the per cent elongation to the breaking point, exemplifies this point.

## TABLE XII

## AVERAGE MEASURED STRESS-STRAIN VALUES OF HOLOFIBERS

| | | Pulp Sample | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Unextracted Holofibers | | | | 0.1N KOH-Extracted Holofibers | | | | 9% KOH-Extracted Holofibers | | | | 9% KOH-3% $H_3BO_3$-Extracted Holofibers | | | |
| | | Drying Load, g. | | | | Drying Load, g. | | | | Drying Load, g. | | | | Drying Load, g. | | | |
| | | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 |
| Breaking load, g. | Av. | 50.1 | 64.6 | 57.2 | 63.8 | 45.3 | 54.1 | 60.5 | 60.5 | 23.4 | 35.7 | 36.8 | 41.5 | 17.4 | 32.0 | 35.1 | 38.9 |
| | S.D., % | 32.6 | 21.3 | 23.0 | 25.9 | 29.8 | 23.8 | 23.3 | 27.1 | 28.1 | 19.5 | 16.7 | 20.4 | 32.1 | 24.4 | 18.3 | 18.0 |
| Breaking stress, dynes/$\mu^2$ | Av. | 103 | 113 | 115 | 124 | 93.8 | 126 | 128 | 132 | 58.0 | 87.6 | 94.3 | 101 | 48.3 | 86.0 | 98.1 | 95.4 |
| | S.D., % | 26.7 | 20.0 | 15.7 | 18.8 | 25.8 | 28.3 | 13.1 | 22.0 | 24.0 | 12.1 | 17.5 | 18.2 | 22.4 | 21.3 | 15.1 | 14.6 |
| Modulus of elasticity, dynes/$\mu^2$ | Av. | 2380 | 3350 | 4030 | 4080 | 2340 | 4050 | 4510 | 4900 | 1210 | 3820 | 4580 | 4940 | 673 | 4050 | 4970 | 4960 |
| | S.D., % | 32.3 | 15.8 | 11.0 | 13.0 | 31.6 | 23.5 | 13.4 | 16.0 | 32.7 | 27.9 | 17.3 | 12.4 | 38.5 | 20.9 | 10.6 | 12.1 |
| Yield point stress, dynes/$\mu^2$ | Av. | 49.3 | 45.1 | 47.6 | 52.2 | 42.2 | 44.8 | 49.8 | 51.9 | 19.0 | 31.5 | 45.3 | 50.1 | 13.2 | 23.4 | 46.6 | 47.1 |
| | S.D., % | 56.6 | 28.0 | 19.4 | 20.9 | 57.8 | 47.6 | 19.8 | 18.2 | 72.8 | 43.9 | 24.2 | 22.8 | 67.3 | 24.8 | 32.4 | 22.2 |
| Work-to-rupture, dynes-$\mu/\mu^3$ | Av. | 2.89 | 3.18 | 2.75 | 2.79 | 2.65 | 3.56 | 3.03 | 2.90 | 1.44 | 1.78 | 1.44 | 1.45 | 1.24 | 1.68 | 1.52 | 1.32 |
| | S.D., % | 30.1 | 17.7 | 29.5 | 34.0 | 43.3 | 33.9 | 28.8 | 40.8 | 34.0 | 17.4 | 25.3 | 29.4 | 44.2 | 31.8 | 27.6 | 26.1 |
| Cross-sectional area, measured, $\mu^2$ | Av. | 479 | 570 | 489 | 505 | 476 | 429 | 464 | 456 | 397 | 403 | 388 | 410 | 348 | 374 | 353 | 403 |
| | S.D., % | 16.0 | 12.1 | 12.0 | 17.0 | 15.0 | 17.6 | 19.3 | 22.0 | 16.8 | 15.1 | 17.1 | 16.7 | 18.7 | 24.6 | 15.3 | 15.5 |

# TABLE XIII

## AVERAGE MEASURED STRAIN VALUES OF HOLOFIBERS

| | | Pulp Sample | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Unextracted Holofibers | | | | 0.1$\underline{N}$ KOH-Extracted Holofibers | | | |
| | | Drying Load, g. | | | | Drying Load, g. | | | |
| | | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 |
| Ultimate elongation, % | Av. | 5.44 | 4.78 | 3.96 | 3.99 | 5.45 | 4.84 | 4.11 | 3.74 |
| | S.D., % | 27.0 | 18.4 | 17.5 | 16.8 | 34.1 | 21.0 | 19.2 | 23.2 |
| Yield point elongation, % | Av. | 2.09 | 1.20 | 1.24 | 1.30 | 1.89 | 1.12 | 1.13 | 1.10 |
| | S.D., % | 49.0 | 19.6 | 19.3 | 18.2 | 54.3 | 32.4 | 18.3 | 16.0 |
| No. of fibers tested | | 33 | 21 | 23 | 29 | 31 | 21 | 24 | 26 |

| | | 9% KOH-Extracted Holofibers | | | | 9% KOH-3% $H_3BO_3$-Extracted Holofibers | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Drying Load, g. | | | | Drying Load, g. | | | |
| | | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 |
| Ultimate elongation, % | Av. | 5.30 | 3.53 | 2.73 | 2.56 | 6.15 | 3.53 | 2.66 | 2.47 |
| | S.D., % | 26.9 | 40.6 | 15.4 | 15.7 | 39.1 | 25.4 | 14.5 | 14.8 |
| Yield point elongation, % | Av. | 1.69 | 0.88 | 1.03 | 1.03 | 2.00 | 0.63 | 0.96 | 0.98 |
| | S.D., % | 75.9 | 34.1 | 26.0 | 21.7 | 67.2 | 24.1 | 27.3 | 21.9 |
| No. of fibers tested | | 32 | 21 | 26 | 26 | 27 | 20 | 24 | 25 |

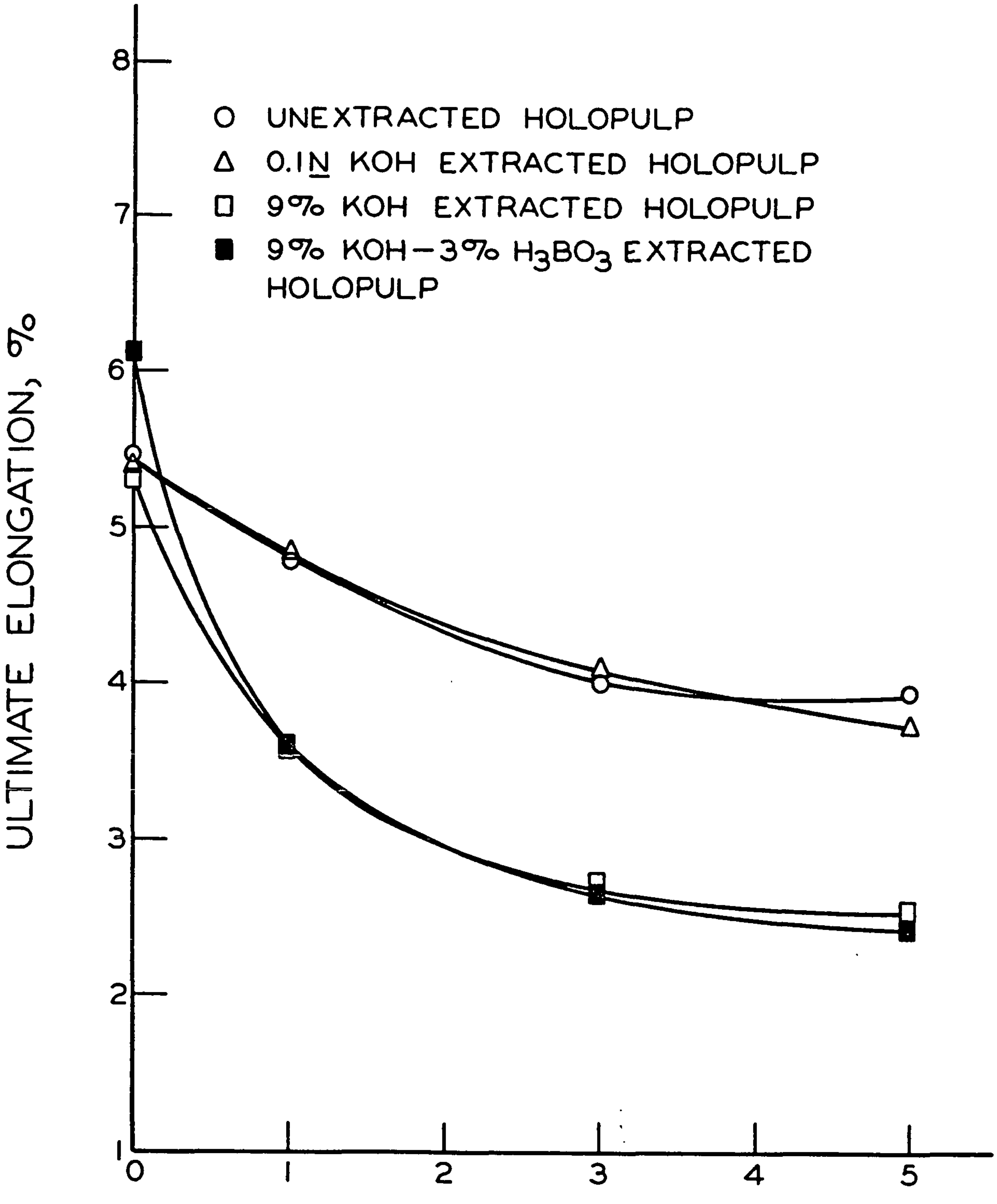

Figure 11. Effect of Drying Load on Ultimate Elongation

Looking at the cross-sectional area data in Table XIV gives the answer to this seeming anomaly.

TABLE XIV

AVERAGE CROSS-SECTIONAL AREA OF FIBER POPULATIONS

| Sample | Number of Fibers Tested | Cross-Sectional Area, $\mu^2$ |
|---|---|---|
| Unextracted holopulp | 124 | 499 |
| 0.1N KOH-extracted holopulp | 113 | 456 |
| 9% KOH-extracted holopulp | 114 | 392 |
| 9% KOH-3% $H_3BO_3$-extracted holopulp | 111 | 369 |

Each extraction resulted in a decrease in cross-sectional area. Since the 0.1N extraction had reduced the cross-sectional area, the calculated stress was correspondingly increased, although there was no essential change in breaking load.

When each population was put on a reference area basis, correcting for the decrease in area, the strength of the 0.1N extracted fibers closely followed that of the unextracted fibers (Fig. 12). This agreed with the sugar analysis. Only the 0.1N fibers dried under no load exhibited a drop in breaking stress. This can be explained by the fact that the loss of hemicellulose was beginning to affect the strength, but that when dried under a load, the redistribution of internal stresses in the fiber accomplished by drying was great enough to overcome the small loss of hemicelluloses.

The stress values shown in Fig. 12 are substantially higher than in Fig. 9. It was quite obvious that properly comparing the strength properties of the fibers

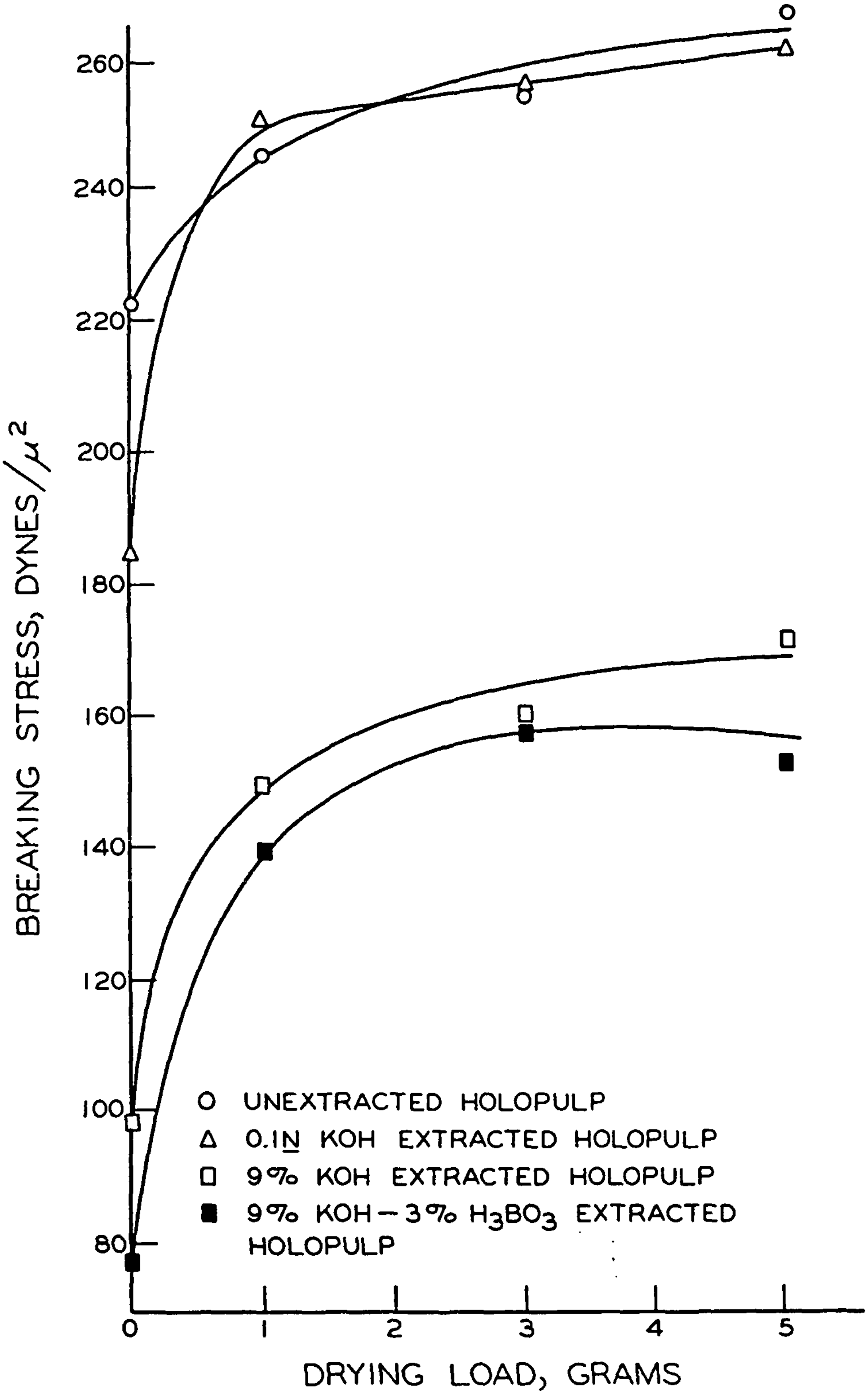

Figure 12. Effect of Drying Load on Breaking Stress Based on Area of Cellulose

required all to be on a suitable reference area basis. The question was, what basis? A quite reasonable assumption considering fiber structure is that the hemicellulose polymers make no direct contribution to the strength of the fiber and only the cellulose fibrils directly support the externally applied load. The external loads supported by the single fiber seem too large to allow much internal contribution of the short-chain hemicelluloses directly to the fiber strength. If this assumption is correct, then a logical cross-sectional area with which to calculate the actual breaking stress, modulus of elasticity, etc., of the fiber would be the cross-sectional area of the cellulosic portion of the pulp fiber. This cellulosic cross-sectional area would be difficult to determine positively, but a reasonable approximation can be made by plotting per cent glucose (of each fiber group) versus average cross-sectional area of each group and extrapolating to 100% glucose (Fig. 16).

The per cent glucose in each fiber sample was converted to a 100% sugar basis (one may note that the sugars in Table V do not add up to a 100% total) and this per cent was plotted versus the average cross-sectional area listed in Table XIV. The extrapolated value obtained at 100% glucose (231 $\mu^2$) was exchanged for the measured average fiber area in the calculation of stress, etc., and these corrected values were listed in Table XV and Fig. 12, 13, 14, and 15. All values referred to henceforth that were calculated using cross-sectional area will be these adjusted values.

As already mentioned, removal of the hemicelluloses in the first extraction step did not reduce the strength, except for those fibers dried under no load. Removal of the hemicelluloses in the second extraction sharply reduced the strength of the no-load dried fibers. The third extraction also lowered the fiber strength but the magnitude of the change was not nearly as great as that caused by the second extraction.

## TABLE XV

## AVERAGE STRESS-STRAIN VALUES OF HOLOFIBERS BASED ON CELLULOSE AREA

| | | Pulp Sample | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Unextracted Holofibers | | | | 0.1$\underline{N}$ KOH-Extracted Holofibers | | | | 9% KOH-Extracted Holofibers | | | | 9% KOH-3% $H_3BO_3$-Extracted Holofibers | | | |
| | | Drying Load, g. | | | | Drying Load, g. | | | | Drying Load, g. | | | | Drying Load, g. | | | |
| | | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 | 0 | 1 | 3 | 5 |
| Breaking stress, dynes/$\mu^2$ | Av. | 222 | 245 | 249 | 267 | 186 | 250 | 254 | 261 | 98.8 | 149 | 161 | 171 | 77.5 | 138 | 157 | 153 |
| | S.D., % | 26.7 | 20.0 | 15.7 | 18.8 | 25.8 | 28.3 | 13.1 | 22.0 | 24.0 | 12.1 | 17.5 | 18.2 | 22.4 | 21.3 | 15.1 | 14.6 |
| Modulus of elasticity, dynes/$\mu^2$ | Av. | 5150 | 7240 | 8720 | 8830 | 4640 | 8020 | 8910 | 9700 | 2060 | 6500 | 7800 | 8400 | 1080 | 6490 | 7990 | 7980 |
| | S.D., % | 32.3 | 15.8 | 11.0 | 13.0 | 31.6 | 23.5 | 13.4 | 16.0 | 32.7 | 27.9 | 17.3 | 12.4 | 38.5 | 20.9 | 10.6 | 12.1 |
| Yield point stress, dynes/$\mu^2$ | Av. | 107 | 97.3 | 103 | 113 | 83.8 | 89.0 | 99.0 | 103 | 32.5 | 53.8 | 77.4 | 85.7 | 21.2 | 37.5 | 74.1 | 75.5 |
| | S.D., % | 56.6 | 28.0 | 19.4 | 20.9 | 57.8 | 47.6 | 19.8 | 18.2 | 72.8 | 43.9 | 24.2 | 22.8 | 67.3 | 24.8 | 32.4 | 22.2 |
| Work-to-rupture, dynes-$\mu/\mu^3$ | Av. | 6.26 | 6.89 | 5.95 | 6.05 | 5.25 | 7.05 | 6.00 | 5.75 | 2.46 | 3.04 | 2.45 | 2.46 | 2.00 | 2.70 | 2.44 | 2.12 |
| | S.D., % | 30.1 | 17.7 | 29.5 | 34.0 | 43.3 | 33.9 | 28.8 | 40.8 | 34.0 | 17.4 | 25.3 | 29.4 | 44.2 | 31.8 | 27.6 | 26.1 |
| Cross-sectional area, calculated, $\mu^2$ | Av. | 221 | 264 | 227 | 233 | 240 | 217 | 234 | 230 | 234 | 237 | 228 | 240 | 217 | 234 | 220 | 252 |
| | S.D., % | 16.0 | 12.1 | 12.0 | 17.0 | 15.0 | 17.6 | 19.3 | 22.0 | 16.8 | 15.1 | 17.1 | 16.7 | 18.7 | 24.6 | 15.3 | 15.5 |

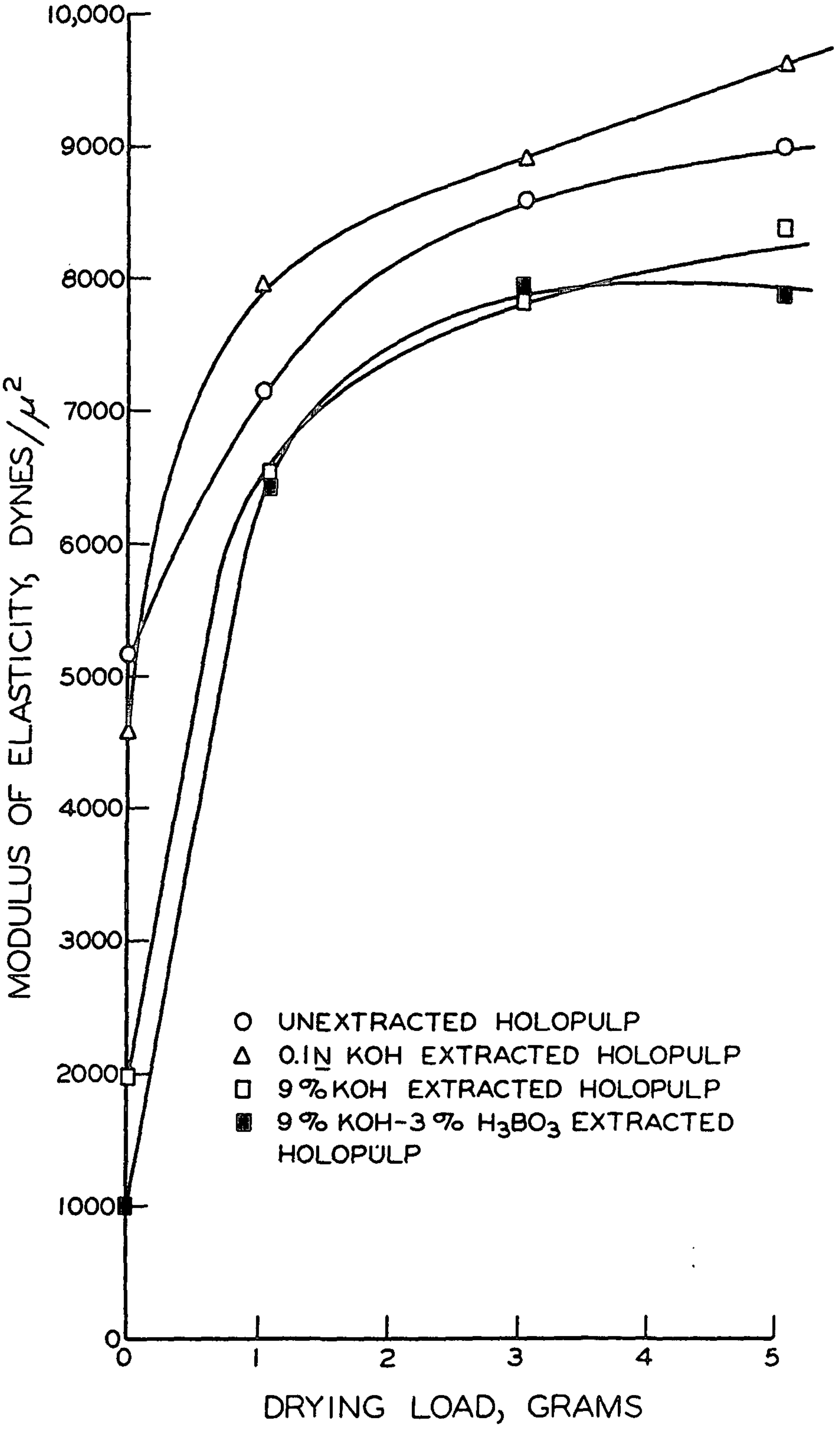

Figure 13. Effect of Drying Load on Modulus of Elasticity Based on Cellulose Area

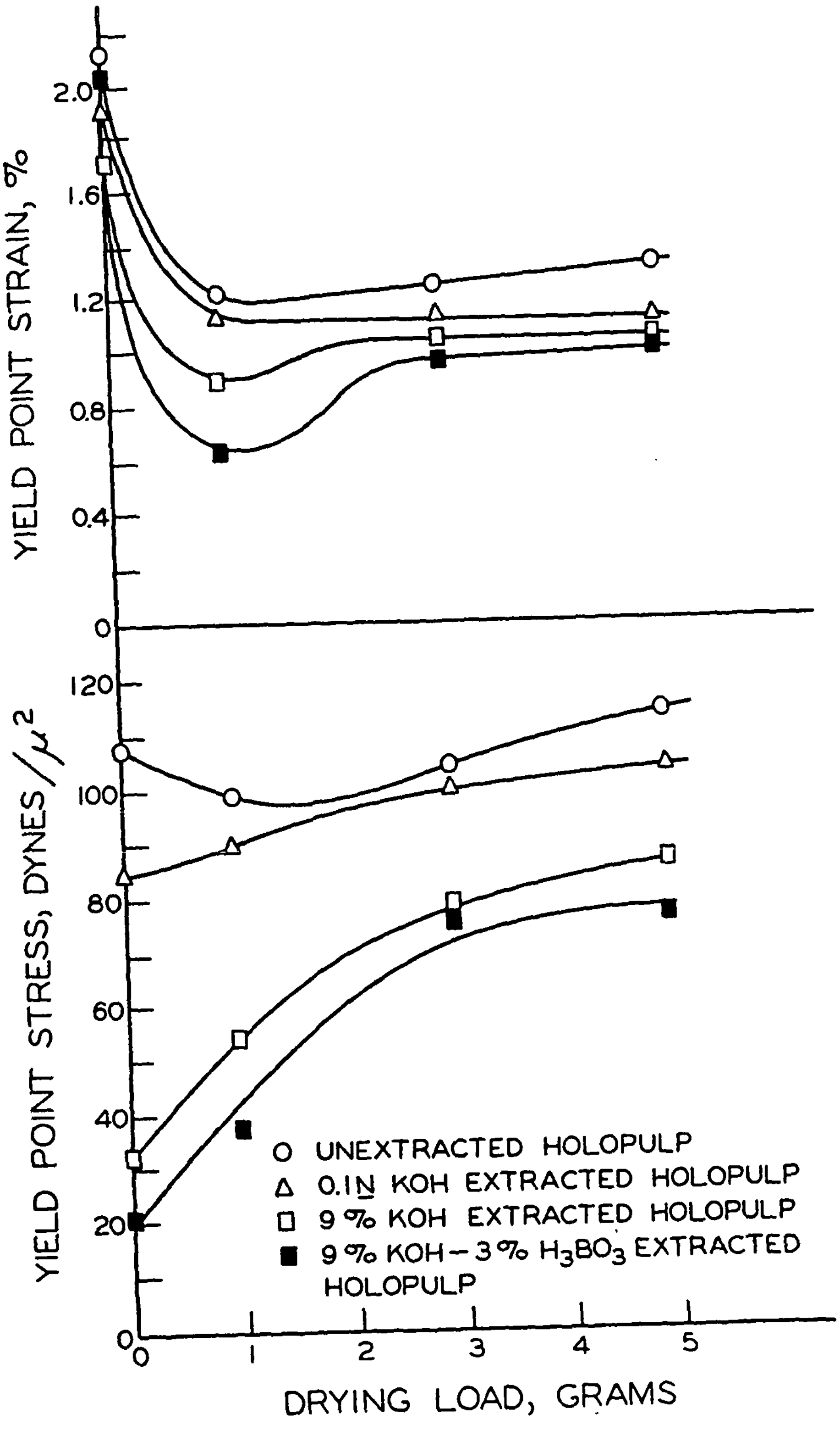

Figure 14. Effect of Drying Load on Yield Point Stress and Yield Point Strain

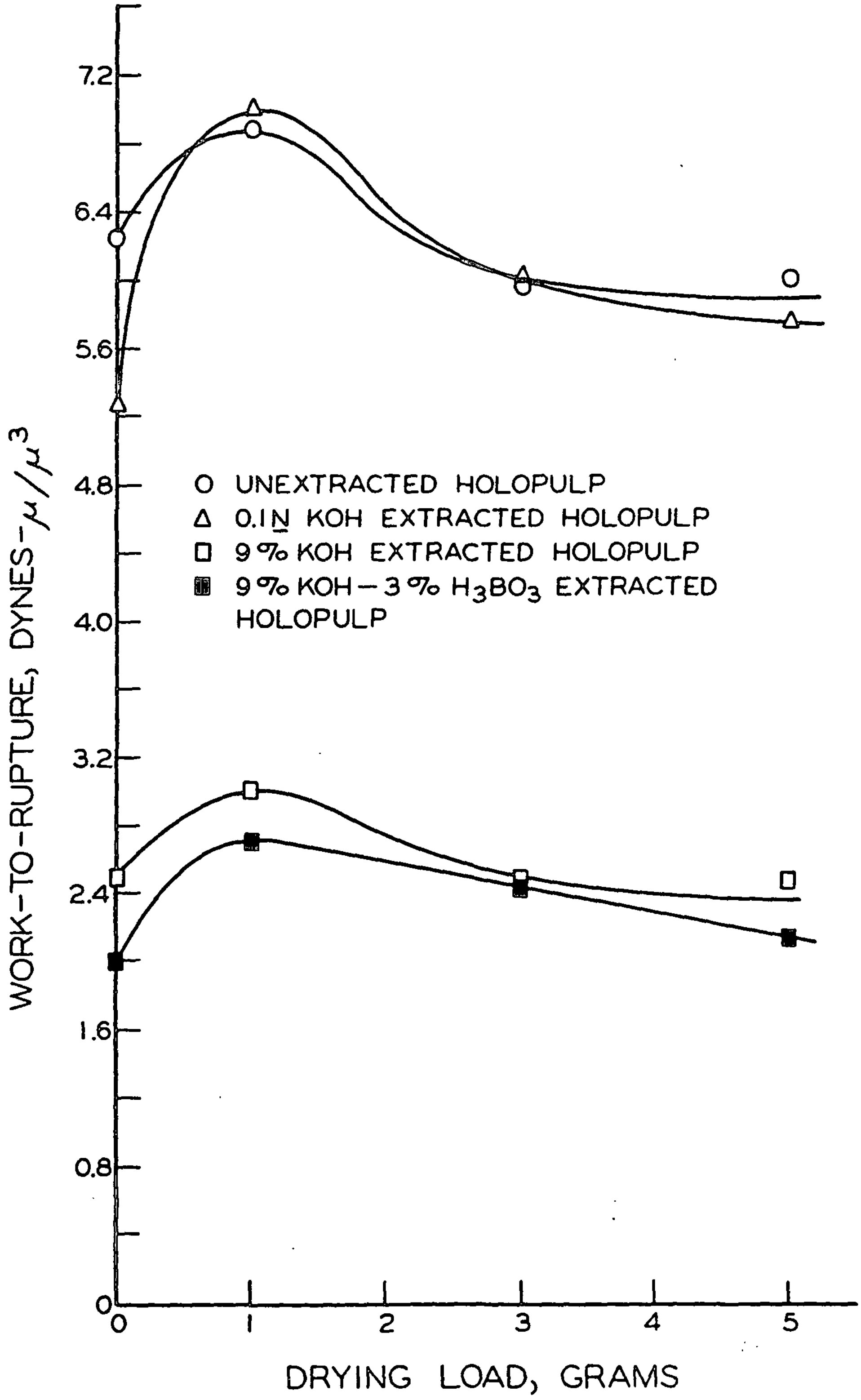

Figure 15. Effect of Drying Load on Work-to-Rupture

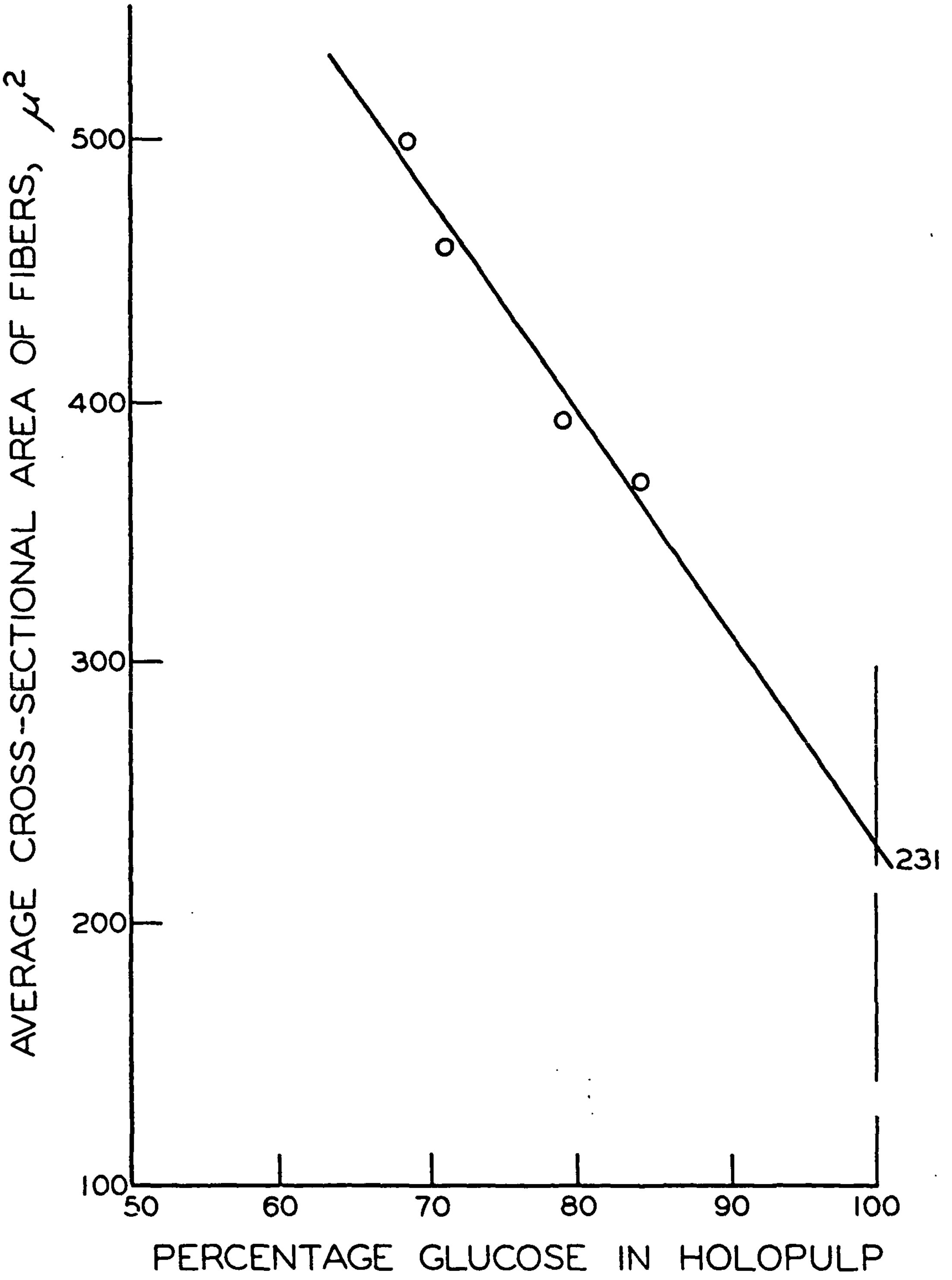

Figure 16. Determination of Cross-Sectional Area of Cellulose Portion of Fibers

When these fibers were dried under a load, the magnitude of the increase in strength was slightly greater than for the unextracted fibers and the percentage increase was much greater, but the breaking stress of the highly extracted fibers never reached that of the unextracted and mildly extracted fibers.

The differences between all breaking stress levels for fibers dried under no load were significant. Generally speaking, the differences between the unextracted and 0.1N KOH-extracted fibers and the 9% KOH- and 9% KOH-3% $H_3BO_3$-extracted fibers dried under a load were not significant but the drop in strength upon extraction with 9% KOH was highly significant.

Examination of the adjusted modulus of elasticity curves (Fig. 13) reveals several interesting results. For the fibers dried under no load, the removal of the hemicellulose caused a sharp reduction in the modulus. However, when the fibers were dried under increasing loads, their moduli appeared to approach a common plateau. With the exception of the 0.1N fibers dried at 5 grams, there was no significant difference between the values of modulus of elasticity of all fibers dried under a load. Here, and in all other cases, unless specified otherwise, the test for significance is at the 95% confidence level as defined in Davies (69).

Consider the physical meaning of the modulus of elasticity of a fiber or of any material. It is calculated from the initial slope of the linear portion of the stress-strain curve. With steel specimens, the slope is linear up to the proportional limit. This is supposedly the portion of the curve in which an increase in load does not break internal bonds but only elastically stretches the structure. With "homogeneous" steel specimens, the load can be released and the specimen strain will be recovered. Since fibers are such a heterogeneous mixture of components, it is unlikely that this completely elastic behavior occurs, even at low loads. This is borne out by the work of Jentzen and also the work of this thesis, in which fibers dried under no load were recycled to increasing strains and significant nonrecoverable deformation was observed.

Since the fiber is such a heterogeneous structure, it is probable that only a fraction of the bonds can be stressed in the initial slope region without being broken. This fraction should be greater for those fibers that contain hemicelluloses than for those that lack hemicelluloses. The presence of hemicelluloses should allow many bonds to be brought into play, allowing a high stress to be supported for a given strain; hence, increasing the hemicellulose content should result in a greater modulus of elasticity (Fig. 13).

As the hemicellulose content is reduced, the mobility of the cellulose fibrils relative to each other is correspondingly reduced due to increased cellulose-cellulose bonding, and internal stress concentrations will develop as the fiber is externally stressed. A particular highly stressed cellulose-cellulose bond may exhibit great individual strength, undoubtedly greater than if hemicellulose polymers separated the cellulose fibrils, but if it acts alone, it contributes little to the externally supported stress. When it ruptures, the stress it supports will be shifted to the next bond. The rupture will be accompanied by a sudden extension. The net result of these microruptures and extensions will be a lower slope than for the fibers containing hemicelluloses.

When the extracted fibers are dried under a load, however, the more uniform stress distribution caused by the drying conditions should allow the bonds to strain together, increasing the modulus. This was what occurred as the extracted fiber values approached the unextracted fiber values when dried under increasing load.

The breaking stress of the extracted fibers dried under a load did not attain that of unextracted fibers (Fig. 12). This at first seems inconsistent with the modulus of elasticity data. However, if one compares the phenomena occurring in the internal fiber structure when stressed in the "elastic" region, and when stressed to the breaking point, the difference in the breaking stress values can be understood. Beyond the elastic region, extreme bond breakage occurs, and the momentary redistribution of stress caused by drying under a load only partially helps, once appreciable bond breakage has occurred.

In light of the previous discussions, though, one would expect a greater per cent increase in breaking stress for the extracted fibers than for the unextracted fibers upon drying under a load since the extracted fibers, lacking hemicelluloses, would have a greater need for "additional help" in stress redistribution. This occurred and is listed in Table XVI. It shows the increase in breaking stress from fibers dried under no-load conditions to fibers dried under one-gram load.

TABLE XVI

CHANGE IN BREAKING STRESS FROM DRYING AT NO-LOAD CONDITIONS TO DRYING AT ONE-GRAM LOAD

| Drying Load, g. | Breaking Stress, dynes/$\mu^2$<br>Unextracted Holofiber | 0.1N KOH-Extracted | 9% KOH-Extracted | 9% KOH-3% $H_3BO_3$-Extracted |
|---|---|---|---|---|
| 0 | 222 | 185 | 98.7 | 77.2 |
| 1 | 245 | 246 | 146 | 136.4 |
| Per cent change | 10.3 | 33.0 | 48.0 | 76.8 |

Yield point stress was defined as the stress at which the stress-strain curve was no longer approximately linear; i.e., where the "elastic" deformation region ends and the plastic deformation region begins. The data, tabulated in Table XV and plotted in Fig. 14, show that the yield point stress of the holofiber was lowered as the hemicelluloses were removed. When the fibers were dried under a load, however, the extracted fiber yield point stress approached that of the unextracted fibers. This behavior is similar to that of other fiber mechanical properties.

The values for the unextracted fibers were relatively unchanged when the fiber was dried under increasing loads. The slope of this line was nearly horizontal. However, as the hemicelluloses were removed, the slope of the yield point stress *versus* drying load curve became steeper.

When discussing modulus of elasticity earlier in this report, it was stated that the elastic region of the fibers' stress-strain curve was defined as that region in which the slope is essentially linear, and, in theory, relatively little bond breakage occurs. Due to the lower stresses in this region, probably little creep occurs, but such creep as does occur is compensated for by the experimentally proved increase in modulus upon straining a fiber (2,8). As the hemicelluloses are removed, the minute movements of the cellulose fibrils apparently are hampered, and appreciable bond breakage occurs at a lower stress, resulting in a lower yield point stress. However, the redistribution of stress caused by drying under a load increased the yield point stress of the extracted fibers to nearly the level of the unextracted fibers. It would appear that drying under load resulted in a more uniform distribution of stress in bonds, thus allowing a greater stress to be supported without appreciable bond breakage. Apparently, for yield point stress, the redistribution of stress is not as important for the unextracted fibers.

Predictably, the yield point strain decreased when the fiber was dried under a load. However, the strain appeared to approach a common value at higher drying loads. Although the yield point strain average values were scattered a little more than the yield point stress, removal of the hemicelluloses generally lowered the strain value of the fiber.

The work-to-rupture is given in Table XV and plotted in Fig. 15. The effect of removal of the hemicelluloses on the work-to-rupture of the fibers dried at no load closely parallels the effect on the breaking stress. However, the effect of drying both the unextracted and extracted fibers on the work-to-rupture was appreciably different from the effect of drying on breaking stress. The work-to-rupture for all fibers increased when the drying load was increased from zero to one gram, and then decreased as the drying load was increased to three and five grams. The first increase was probably due to the fact that the ultimate stress increased more rapidly than the breaking strain decreased, resulting in an increased absorption of energy. The apparent decrease at three and five-grams load may be a false impression. The drying procedure itself imparted energy into the system. The fibers were subjected to constant loads while straining, which resulted in a work input. The work thus done per unit volume can be calculated by multiplying the load by the strain and dividing by the cross-sectional area. On the assumption that the dry fiber has stored energy from the wet state, the two energies can be mathematically added. This assumption has little substantiation as an exact principle, but it is of interest to attempt the addition. The results, which are shown in Fig. 17 and listed in Table XVII, indicate a leveling off of energy input with increasing drying tension. The fluctuations in energy with increasing drying tension are not significant.

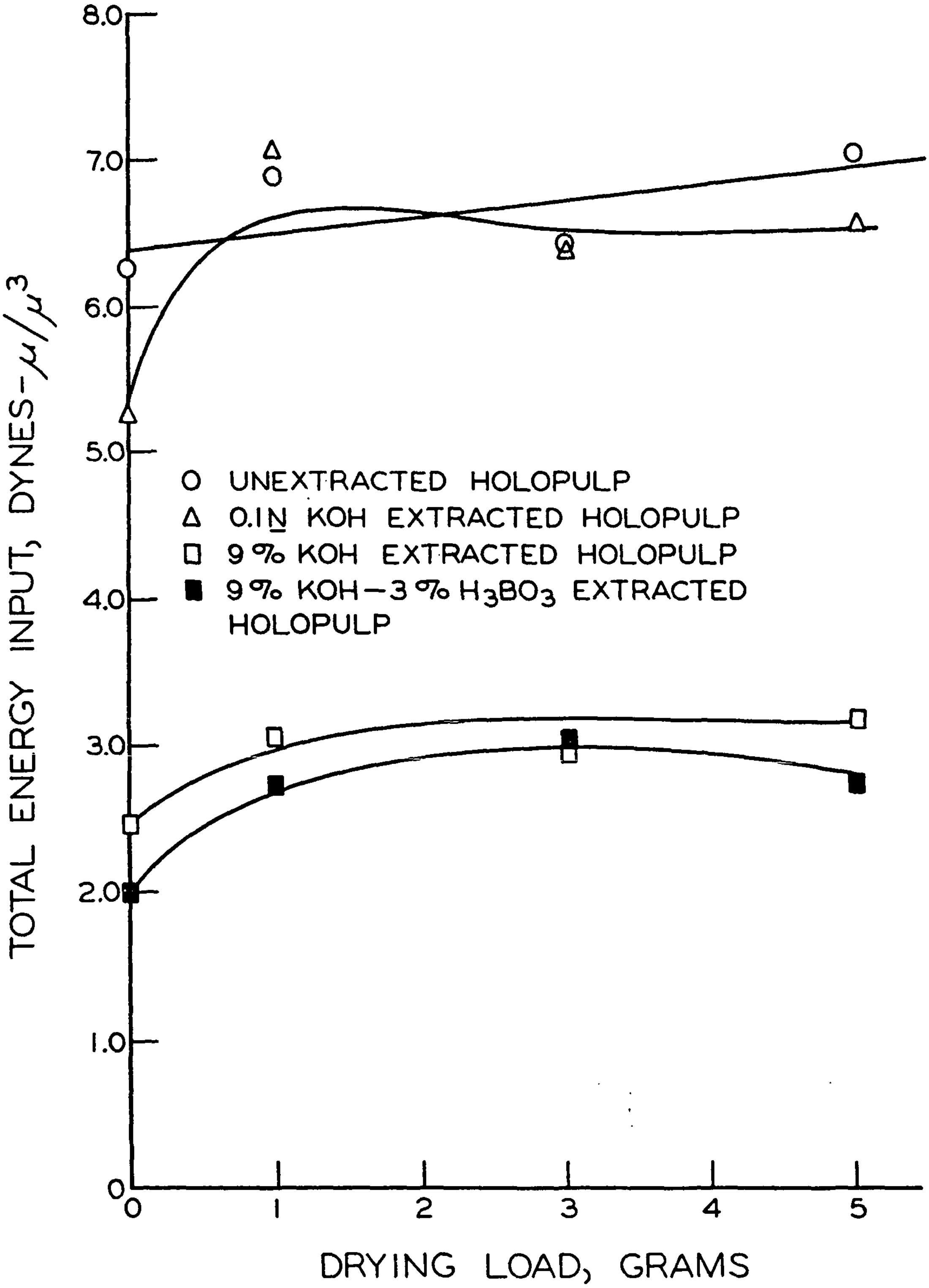

Figure 17. Effect of Drying Load on Total Energy Input for Holofibers

## TABLE XVII

## TOTAL ENERGY INPUT FOR HOLOFIBERS

| Treatment | Load, g. | Drying Strain Energy, dynes-$\mu/\mu^3$ | Stress-Strain Energy, dynes-$\mu/\mu^3$ | Total Energy, dynes-$\mu/\mu^3$ |
|---|---|---|---|---|
| Unextracted holofibers | 5 | 0.97 | 6.05 | 7.02 |
| | 3 | 0.45 | 5.95 | 6.40 |
| | 1 | | 6.89 | 6.89 |
| 0.1$\underline{N}$ KOH-extracted holofibers | 5 | 0.78 | 5.75 | 6.53 |
| | 3 | 0.37 | 6.00 | 6.37 |
| | 1 | | 7.05 | 7.05 |
| 9% KOH-extracted holofibers | 5 | 0.72 | 2.46 | 3.18 |
| | 3 | 0.50 | 2.45 | 2.95 |
| | 1 | | 3.04 | 3.04 |
| 9% KOH-3% $H_3BO_3$-extracted holofibers | 5 | 0.60 | 2.12 | 2.72 |
| | 3 | 0.57 | 2.44 | 3.01 |
| | 1 | | 2.70 | 2.70 |

Jentzen obtained valuable information by recycling the loading on dry fibers with ever-increasing loads until rupture occurred. He found that the modulus of elasticity increases as the fiber is stressed, indicating that an internal redistribution of stress occurs.

On the basis of the hypothesis that hemicelluloses aid this redistribution, it was felt that removal of the hemicelluloses would lessen this redistribution effect and thus hinder the increase in modulus that Jentzen noted. To test this, the loading of a dry fiber was increased until a certain elongation was reached and then the load was released. The fiber was reloaded immediately. Three elongation intervals were chosen: 0.00935, 0.01870, and 0.02805. The first interval is roughly 20% of the average breaking strain.

Four slopes were obtained (the initial plus the three corresponding to the three levels of straining). The moduli of elasticity calculated from these slopes are given in Table XVIII. In addition, the moduli for fibers dried under five-grams load are included in the table. All recycling was done on fibers dried at no load.

## TABLE XVIII

### MODULI CHANGE THROUGH STRAINING AS COMPARED WITH THAT THROUGH DRYING UNDER LOAD

| | Modulus of Elasticity, dynes/$\mu^2$ | | | |
|---|---|---|---|---|
| | Unextracted Holofibers | 0.1$\underline{N}$ KOH-Extracted Holofibers | 9% KOH-Extracted Holofibers | 9% KOH-3% $H_3BO_3$-Extracted Holofibers |
| Initial slope of recycled fibers | 5520 | 3580 | 2200 | 1140 |
| Recycle 1 | 6700 | 4420 | 2760 | 1500 |
| Recycle 2 | 7210 | 5500 | 3620 | 2390 |
| Recycle 3 | 7750 | 6600 | 4670 | 3260 |
| Dried at 5-grams load | 8830 | 9700 | 8400 | 7980 |
| $\Delta\underline{E}$[a] | 1080 | 3100 | 3730 | 4720 |

[a] $\Delta\underline{E}$ = modulus of fibers dried at five-grams load minus 3rd cycle modulus of fibers dried at no load.

Recycling the unextracted fibers increased the modulus until the third recycle modulus value approached the value obtained for fibers dried at five-grams load. However, as the hemicelluloses were removed, the difference between the third recycle modulus value and the "five-gram" modulus became greater. This was an independent test of the effect of hemicelluloses on a mechanical property of fibers and clearly shows the inhibition of internal stress redistribution caused by removal of the hemicelluloses. Inhibition of the internal redistribution of stress prevented the high modulus which would have resulted from dry straining.

In addition to changes in modulus of elasticity, the tensile elastic recovery of the recycled fibers was measured. Tensile elastic recovery, according to Meredith (70) is the amount of elongation recovered in the fiber upon release of load divided by the total elongation at that load. The elastic recovery data are listed in Table XIX.

## TABLE XIX

## TENSILE ELASTIC RECOVERY BEHAVIOR OF UNEXTRACTED AND EXTRACTED HOLOFIBERS

| Pulp Sample | Cycle[a] | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Unextracted holofibers, % | 71.4 | 62.7 | 59.1 |
| 0.1N KOH-extracted holofibers, % | 69.2 | 56.1 | 48.8 |
| 9% KOH-extracted holofibers, % | 50.9 | 41.1 | 35.1 |
| 9% KOH-3% $H_3BO_3$-extracted holofibers, % | 40.1 | 30.7 | 28.5 |

[a] See earlier definition of cycle.

The elastic recovery decreased as the strain increased. This was noted by Wakeham (71) and is typical. As the internal structure is rearranged upon straining, the ability to return to the original internal configuration decreases.

Of particular interest is the decrease in elastic recovery upon removal of the hemicelluloses. This clearly shows that the hemicellulose-cellulose-hemicellulose bond is more flexible (see introduction to this section for description of bonds) than the cellulose-cellulose bond, allowing a greater strain to occur without irreversible deformation of the bond. The removal of the hemicelluloses in the second extraction changed the elastic recovery the greatest amount, which is in agreement with the tensile strength data.

An interesting comparison can be made between the strength properties of the highly extracted wood pulp fibers and the cotton fibers tested in this study. The cotton fibers are essentially pure cellulose and the pulp fibers at this stage of extraction are about 85% cellulose, with the remaining portion mostly glucomannan. The values are compared in Table XX. All fibers have been dried under no load.

TABLE XX

COMPARISON OF STRENGTH PROPERTIES OF COTTON AND WOOD PULP FIBERS

| Sample | Breaking Stress, dynes/$\mu^2$ | Modulus of Elasticity, dynes/$\mu^2$ |
|---|---|---|
| Unextracted holofibers | 222 | 5140 |
| Heavily-extracted holofibers (9% KOH-3% $H_3BO_3$) | 77 | 1080 |
| Cotton fibers | 75 | 1300 |

The strength properties of the cotton fibers approximate those wood pulp fibers that contain almost no hemicellulose. One could assume from this that purified cellulosic fibers have essentially a common strength and that addition of hemicelluloses in strategic locations in the cellulose structure increases the strength. Thus, if one could suitably insert hemicelluloses in the cotton fiber structure, the strength should increase.

The data allow no more than just speculation on this point, since other factors enter into fiber strength, such as orientation of the fibrillar structure. However, the magnitude of the differences illustrated in Table XX are greater than can be attributed to these factors.

## FIBER DRYING ELONGATION CHARACTERISTICS

The data showing the elongation behavior of the fibers can be divided into two groups, those fibers that were dried with Jentzen's procedure (2) and those that were dried with the procedure described in this report. The latter fibers will be referred to as fan-dried fibers. The two procedures were quite dissimilar in the procedure for drying the fiber and in the time involved, but the results obtained were quite comparable (see Appendix III). The data are listed in Tables XXI and XXII.

The sudden extension noted by Jentzen to occur when water left the surface of the fiber (2) was also noted for the unextracted and extracted fibers dried under load in this work. The magnitude of the sudden extension appeared to be less for the extracted fibers than for the unextracted fibers (Table XXI). The data were quite scattered but the trend was significant.

No sudden extension value is listed for the fan-dried fibers. The action of the air against the clamp moved the clamp laterally a slight amount, and caused a change in the elongation reading, obscuring the true change in the fiber span. This occurred for all readings taken while the fan was operating.

The per cent elongation upon initial application of the load did not vary significantly among the extracted and unextracted fiber populations. However, the wet strain measured after the application of the load decreased significantly upon removal of the hemicelluloses.

## TABLE XXI

## ELONGATION BEHAVIOR OF FIBERS DRIED USING JENTZEN'S PROCEDURE

| Pulp Sample[a] | | Initial Wet Strain, % | Wet Creep Strain, % | Sudden Extension, % | Dry Creep Strain,[b] % | Contraction Load Released, % | Total Elongation, % |
|---|---|---|---|---|---|---|---|
| Unextracted holofibers | Av. | 3.13 | 0.18 | 0.53 | 0.02 | 1.96 | 3.86 |
| | S.D., % | 43.6 | 28.5 | 38.5 | 410 | 53.2 | 35.1 |
| 0.1N KOH-extracted holofibers | Av. | 3.12 | 0.13 | 0.38 | 0.10 | 1.66 | 3.73 |
| | S.D., % | 34.0 | 47.6 | 46.2 | 142 | 31.0 | 32.6 |
| 9% KOH-extracted holofibers | Av. | 2.65 | 0.12 | 0.20 | 0.00 | 1.09 | 3.97 |
| | S.D., % | 39.8 | 63.9 | 105 | 762 | 44.7 | 36.3 |
| 9% KOH-3% $H_3BO_3$-extracted holofibers | Av. | 2.72 | 0.10 | 0.34 | 0.01 | 1.34 | 3.17 |
| | S.D., % | 30.4 | 40.0 | 68.4 | 264 | 54.2 | 30.5 |

[a] All fibers dried under a five-gram load.

[b] Dry strain average is summation of positive and negative values.

TABLE XXII

ELONGATION BEHAVIOR OF FAN-DRIED FIBERS

| Sample | | Initial Wet Strain, % | Wet Creep Strain, % |
|---|---|---|---|
| Unextracted holofibers | Av. | 2.64 | 0.14 |
| | S.D., % | 54.8 | 48.5 |
| 0.1N KOH-extracted holofibers | Av. | 2.50 | 0.13 |
| | S.D., % | 54.7 | 51.4 |
| 9% KOH-extracted holofibers | Av. | 2.44 | 0.11 |
| | S.D., % | 50.2 | 37.1 |
| 9% KOH-3% $H_3BO_3$-extracted holofibers | Av. | 2.56 | 0.10 |
| | S.D., % | 56.6 | 46.7 |

The elastic recovery or per cent contraction when the load was released decreased significantly as the hemicelluloses were removed. The difference between the 9% KOH and the 9% KOH-3% $H_3BO_3$ value is not significant, however. The total per cent elongation also significantly decreased as the hemicelluloses were removed.

The following significance can be attached to the difference in elastic recovery. The bonds between the structural elements in the fibers containing hemicelluloses apparently are more elastic, and are able to deform more without breaking. Hence, the elastic recovery would be greater. The strain imparted by drying under a load is "locked in" to a greater extent in the fibers with the hemicellulose removed as compared to the fibers with the hemicelluloses present. This correlates with the stress-strain data obtained for the dry fibers.

The reason for the drop in wet strain is a little hard to understand, in light of all the other data. While in the wet state, it would seem that all fibers would strain the same amount. Apparently, the initial load elongation is due to reorienting of the fibrils, etc., since there is no significant difference in the samples. However, the fact that the creep experienced in the wet strain period decreases as the hemicelluloses are removed indicates a retardation of movement in the microstructure even in the wet state.

## RELATIONSHIP OF MECHANICAL PROPERTIES TO HEMICELLULOSE CONTENT

The discussion concerning hemicelluloses up to this point has treated them as a group, or as a fraction removed in one extraction step. An attempt will be made to correlate the effect of each individual hemicellulose polymer on the fibers' mechanical properties. Following Leopold's method of correlating per cent sugar retained versus tensile breaking strength of the fibers, these factors are plotted in Fig. 18 and 19. The shape of the curves resembles Leopold and McIntosh's work (3), and indicates that the strength of the fibers is more dependent on xylan content than on glucomannan content. The strength of the fibers correlates linearly with the xylan content of the fiber, with the exception of the last extraction point. Here a slight drop in strength occurs with essentially no change in xylan content. Analyzing the glucomannan-strength curve, removal of the sugars in the first two extractions lowers the strength of the fiber. However, the third extraction, which removes only glucomannan, does not appreciably reduce the strength. Since the data show that removal of the mannans and xylans in the first and second steps reduces the strength but removal of the glucomannan alone in the third extraction step does not appreciably reduce the fiber strength one can surmise that either the xylan principally affects the strength, or the mannans removed in the first and second extraction are different from the mannans

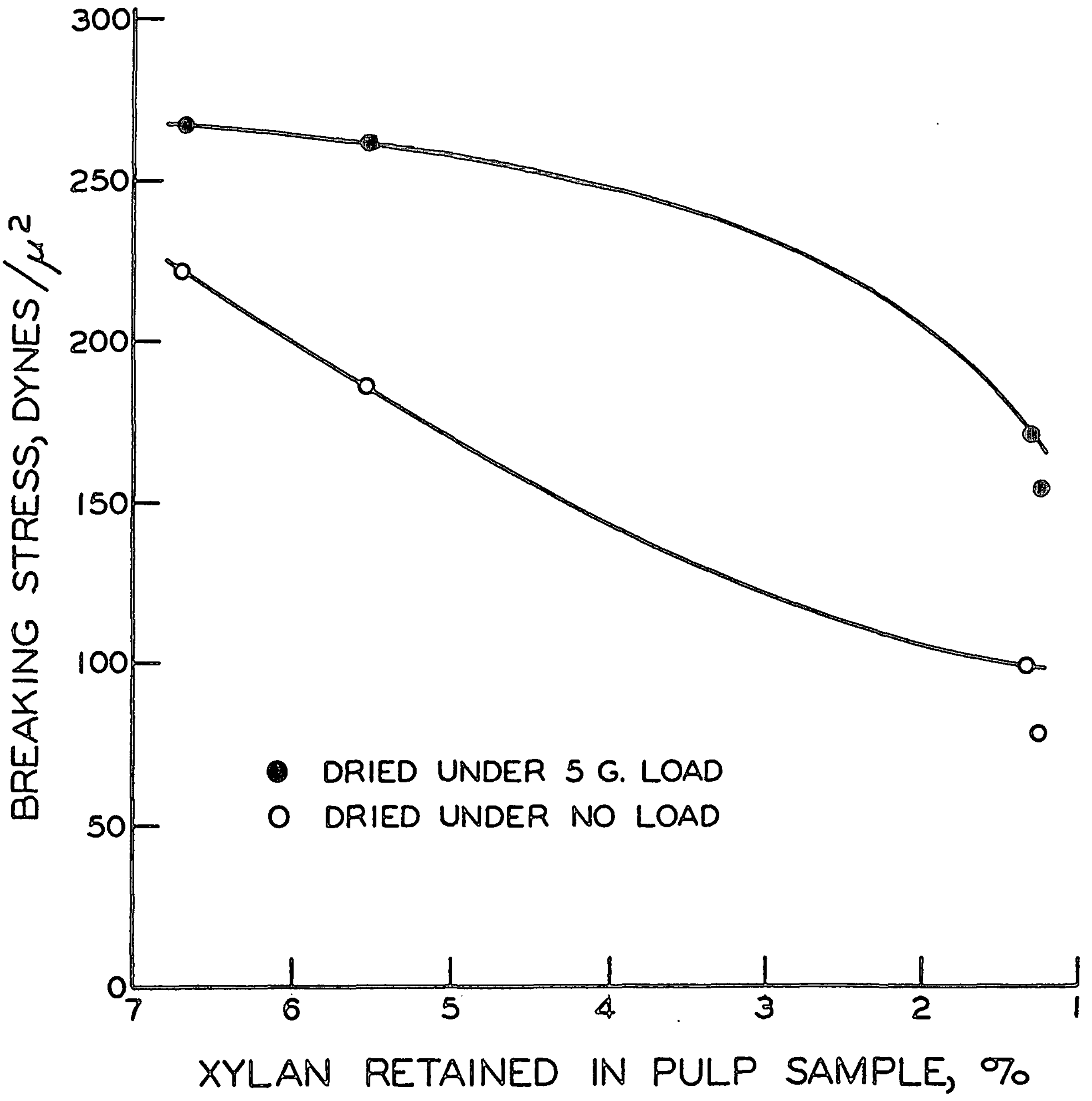

Figure 18. Effect of Xylan on Fiber Strength

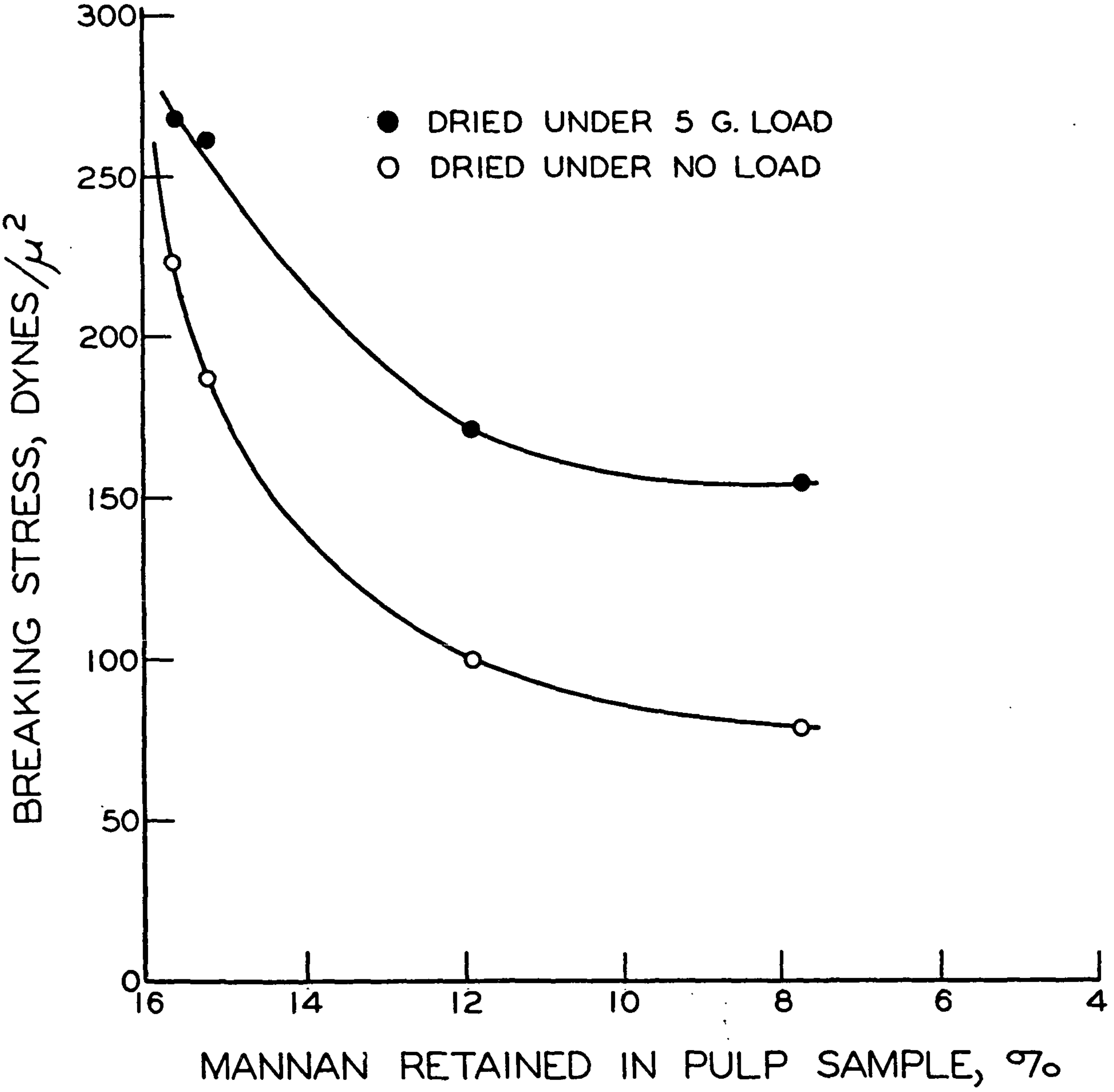

Figure 19. Effect of Mannan Content on Fiber Strength

removed in the third extraction as regards location in the internal fiber structure, and relationship to the cellulose fibrils. This is possible, of course. The most positive statement that can be made about the polysaccharides removed is that the easily extractable polysaccharides (exclusive of the pectic materials and the galactans and arabinans) appear to affect the strength of the fibers much more than those extracted with great difficulty. This suggests that the polysaccharides located outside the crystalline cellulose network, be they xylans alone or xylans in combination with some form of glucomannan or galactoglucomannan, are the ones that affect fiber strength. This lends support to the other evidence already presented that the contribution of the hemicelluloses to fiber strength is in the manner with which they allow the cellulose fibrils to adjust internally to an externally applied stress. In order to accomplish this, the hemicelluloses would have to surround these cellulose fibrillar elements.

## BOND BREAKAGE IN THE STRESSED FIBER

The stresses supported by the single fiber are high, especially for the unextracted holofiber. It is interesting to speculate on what kind of bond breakage occurs when the fibers are stressed to the rupture point.

When the fiber is stressed, some secondary bonds undoubtedly break first. This allows the molecules and fibrils to move relatively to one another, leading to a straightening of the molecules and fibrils, and a more uniform redistribution of stress among these structural elements. Additional stressing may lead to chain scission or additional secondary bond breakage, depending upon how uniformly the load is distributed across the secondary bonds. Wakeham (71) has presented theoretical strengths for various breaking mechanisms, shown in Table XXIII.

## TABLE XXIII

## CALCULATED THEORETICAL FIBER STRENGTH BASED ON VARIOUS BREAKING MECHANISMS (71)

| Breaking Mechanism | Estimated Tensile Strength, dynes/$\mu^2$ |
|---|---|
| Cellulose chain scission | |
| Based on -C-O- bond energy | 720 |
| Based on potential energy function | 1500 |
| Cellulose chain separation | |
| No overlapping (Van der Waal's forces) | 27 |
| Slippage with breaking of secondary (hydrogen) bonds | 117 |

The maximum average tensile strength observed for fibers tested in this study was 267 dynes/$\mu^2$. Comparison of this figure with Wakeham's estimated values suggests that cellulose chain scission is one of the mechanisms by which internal failure is occurring. It should be understood, however, that these theoretical estimations are at best crude approximations and that any conclusions derived from this comparison are purely speculative.

Meyer and Lotmar (72) calculated a theoretical modulus of elasticity of 12,000 dynes/$\mu^2$. Experimentally they found that ramie and hemp averaged 9200 and 8200 dynes/$\mu^2$, respectively. The maximum value of Young's modulus obtained in the writer's work was 9700 dynes/$\mu^2$, indicating that when the stress values are based on the cross-sectional area of the cellulosic portion of the fiber, this theoretical value of Young's modulus can be closely approached in the case of fibers dried under tension.

In his thesis, Jentzen (2) incorrectly attributed a figure of 9000 dynes/$\mu^2$ to Meyer and Lotmar. This is discussed in more detail in Appendix II.

## SUMMARY OF RESULTS AND CONCLUSIONS

The objectives of this thesis were to determine the effect of the hemicelluloses in the wood pulp fiber on the mechanical properties of the individual pulp fibers, to determine the effect on these mechanical properties of drying individual pulp fibers of varying hemicellulose content under an axial tensile load, and to determine the structural changes which occur in the fiber upon removal of the hemicelluloses. To fulfill these objectives, a holocellulose pulp was prepared from summerwood fibers taken from two growth rings of a longleaf pine tree. Several fiber groups containing varying amounts of hemicelluloses were obtained by selectively extracting the fibers with aqueous solutions of potassium hydroxide. The load-elongation properties of the randomly selected fibers from the fiber groups were measured at several drying loads. Alkaline degradation, mercerization, and chemically-induced physical swelling were investigated as possible side effects. To determine changes in the fibers' internal structure, x-ray diffractograms were obtained. Electron micrographs were taken of the fiber surfaces and of broken ends visually to note the effect of extraction of the hemicelluloses. The results show that:

1. Partial removal of the hemicelluloses resulted in a 66% decrease in breaking strength, a 79% decrease in modulus of elasticity, a 68% decrease in work-to-rupture, and an 80% decrease in yield point stress for fibers dried under no load (calculations based on cellulose area).

2. Drying the fibers under a load increased the tensile strength and modulus of elasticity of all fibers. The modulus of elasticity of all fibers dried under a load tended to approach the same value, while the increase in tensile strength of the extracted fibers, although of a greater percentage than for holofibers, never reached the level of the latter.

3. The ultimate elongation and the yield point elongation of all fibers decreased when the fibers were dried under load.

4. Removal of the hemicelluloses resulted in an increase in crystallinity, indicating an increase in cellulose-cellulose bonding.

5. Electron micrographs showed a plasterlike substance covering the fiber surfaces. This substance was gradually removed upon extraction of the hemicelluloses, suggesting that the substance was some form of hemicellulose.

6. Investigation of side effects showed that little, if any, alkaline degradation occurred and that no mercerization took place. Cotton fiber data indicated that alkaline swelling tended to increase the strength and modulus of elasticity values of the cellulosic fiber, producing an effect opposite to that of the removal of hemicelluloses. The investigation of side effects thus showed that the effect of hemicelluloses on fiber mechanical properties was real.

7. Loading and unloading cycles run on fiber groups dried under no load showed that all fibers exhibited an increase in modulus of elasticity from cycle to cycle. The modulus value obtained by dry straining of unextracted fibers approached the value obtained by drying under load. As the hemicelluloses were removed, however, the ability of the fiber to approach this value by dry straining decreased.

8. The tensile elastic recovery of the fibers decreased as the hemicelluloses were removed.

9. The percentage standard deviation of the mechanical properties decreased because of drying under a load. The percentage standard deviation of the fiber's breaking load generally decreased when converted to breaking stress.

10. All fibers underwent the sudden extension at the commencement of drying that had been noted by Jentzen. There was a significant difference between fiber groups in this sudden extension, however, the effect decreasing as the hemicelluloses were removed.

11. Extraction of hemicelluloses produced a significant decrease in the contraction experienced when the drying load was released.

12. Although fibers dried using Jentzen's procedure were not dry on the end clasped in the movable clamp, the water droplets evidently did not migrate along the fiber, since the changes observed by Jentzen upon drying under a load were also observed in this work, with the exception that the mechanical properties of the fibers did not peak at 3 grams drying load, as did Jentzen's (see Appendix III).

13. Heavily-extracted holofibers and cotton fibers exhibited essentially the same breaking stress and modulus of elasticity, suggesting that these cellulosic fibers behave in a similar manner after the hemicelluloses have been removed from the holofibers.

14. The work-to-rupture increased when the drying load was increased from zero to one gram, and then decreased as the load was increased to three and five grams. Correction for total energy input including drying strain energy indicated an increase in energy input upon drying under one-gram load with a subsequent leveling off of energy input as the drying load was further increased.

15. The yield point stress decreased upon removal of hemicelluloses, but drying under load increased the extracted fiber values to those of the unextracted fiber. Drying under load did not appreciably change the yield point stress of the unextracted fibers. The yield point strain for all fibers decreased initially

upon drying under a load, and was relatively constant for larger drying loads. Removal of hemicelluloses appeared to decrease the yield point strain, but the results were scattered.

16. The highly branched hemicelluloses, the xylans and possibly galactoglucomannans, appear to have the greatest effect on the mechanical properties of wood fibers.

These results strongly support the theory of partially accounting for changes in fiber strength on the basis of internal stress redistribution. The idea of internal stress redistribution is not particularly new and reference is made to this phenomenon many times throughout the literature, but relating the hemicellulose portion of the wood pulp fiber to this stress redistribution is new.

Most of the evidence presented in this paper is indirect, of course. Among other things, it would be extremely helpful in interpreting the data to know the minute distribution of the various hemicelluloses in the fiber structure (between fibrils, microfibrils, etc.). Nevertheless, the model of the internal fiber structure and the role of the hemicelluloses in the structure as presented fits the data closely in all cases.

The hemicellulose polymer that appeared to have the greatest effect on the strength of the holofibers is the xylan polymer. This agrees with work by Leopold (3) and also with data obtained on commercial-type pulps from work done by Thompson, Peckham, and Thode (42) and Peckham and Van Drunen (43). The agreement with the latter works is perhaps surprising considering the side effects that must occur in commercial pulping. It is suggested that the highly branched configuration of the xylan polymer makes it very suitable for aiding internal stress redistribution because the branched structure prevents close packing of the cellulose fibrils. The load that can be supported by a single fiber is very large, particularly when it is a wood pulp fiber rich in hemicelluloses. The data indicate that when the secondary bonds are allowed to take up the stress uniformly, failure probably occurs at least in part by cellulose chain scission.

Drying fibers under an external load increases the strength of the fibers. Furthermore, the percentage increase for fibers lacking hemicelluloses is greater than for fibers containing hemicelluloses. Jentzen (2), considering Van den Akker's theory of varying drying forces depending on angular orientation (1) and his own data, suggested that the differences in mechanical properties between the two principal directions of a machine-made sheet of paper may be in part attributable to the changes in fiber properties caused by drying of fibers under tension. Considering the removal of hemicelluloses in commercial pulping operations, the role of tension drying should be more important for commercial pulps than for Jentzen's holopulp; hence, the directional differences in paper sheet properties attributable to fiber properties may be even larger than Jentzen suggested.

# ACKNOWLEDGMENTS

Almost every endeavor that man carries out is the summation of contributions, both large and small, of a number of individuals. This thesis was no exception. It would be impossible to list all people who have made a contribution and a simple expression of appreciation will have to suffice.

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## LITERATURE CITED

1. Van den Akker, J. A. Some theoretical considerations on the mechanical properties of fibrous structures. In Bolam's The formation and structure of paper. Vol. 1, p. 204-41. London, Technical Association of the British and Board Maker's Association, Inc., 1962.

2. Jentzen, C. A. The effect of stress applied during drying on the mechanical properties of individual pulp fibers. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1964. 130 p.

3. Leopold, B., and McIntosh, D., Tappi 44, no. 3:235-40(1961).

4. McIntosh, D., Tappi 46, no. 5:273-7(1963).

5. Howsman, J. A., and Sisson, W. A. Submicroscopic structure of cellulose fibers. In Ott's Cellulose and cellulose derivatives. 2nd ed. Part I. p. 231-346. New York, Interscience, 1954.

6. Hearle, J. W. S., J. Polymer Sci. 28, no. 117:432-5(1958).

7. Hearle, J. W. S., J. Textile Inst. Proc. 53, no. 8:449-64(Aug., 1962).

8. Jentzen, C. A., Tappi 47, no. 7:412-18(1964).

9. Lindenmeyer, P. H., J. Polymer Sci. 10, no. 1:5-40(1963).

10. Tønnesen, B. A., and Ellefsen, Ø., Norsk Skogind. 14, no. 7:266-9(1960).

11. Manley, R. St. J. Summary, I.P.C. Pioneering Research Program. p. 88-101. Appleton, Wis., The Institute of Paper Chemistry, 1964.

12. Dolmetsch, H., Papier 17, no. 12:710-21(1963).

13. Frey-Wyssling, A. The general structure of fibers. In Bolam's Fundamentals of papermaking fibers. p. 1-6. Kenley, Surrey, England, Technical Section of the British Paper and Board Maker's Association, Inc., 1958.

14. Thompson, N. S. Personal communication, 1964.

15. Ohad, I., and Mejzler, D., J. Polymer Sci. 3A, no. 1:399-406(Jan., 1965).

16. Mejzler, O., J. Polymer Sci. 3A, no. 1:389-98(Jan., 1965).

17. Hock, C. W. Microscopic structure of native cellulose. In Ott's Cellulose and cellulose derivatives. 2nd ed. Part I. p. 347-78. New York, Interscience, 1954.

18. Rollins, M., and Tripp, V., Forest Prod. J. 493-7(1961).

19. Meier, H., Pure Appl. Chem. 5:37-52(1962).

20. Wakeham, H., and Spicer, N., Textile Res. J. 21:187-92(1951).

21. Wakeham, H., Radhakrishnan, T., and Viswanathan, G., Textile Res. J. 29, no. 5:450(1959).

22. Schubert, C. Doctor's Dissertation. Dresden, 1932. In Ward's Chemistry and Chemical Technology of Cotton. p. 391. New York, Interscience, 1955.

23. Meier, H., J. Polymer Sci. 51:11(1961).

24. Sultze, R. F., Jr., Tappi 40:985-93(1957).

25. Hamilton, J., and Quimby, G., Tappi 40, no. 9:781-6(1957).

26. Leopold, B., Tappi 44, no. 3:232-5(1961).

27. Jones, J., Wise, L., and Merler, E., Can. J. Chem. 35:634(1957).

28. Meier, H., Acta Chem. Scand. 12:1911(1958).

29. Ward, K., Jr., and Murray, M., Tappi 42, no. 1:17(1959).

30. Ward, K., Jr., and Morak, A. Proceedings of the Wood Chemistry Symposium. p. 77. Montreal, Canada, 1961.

31. Nelson, R., Tappi 43:313-19(1960).

32. Leopold, B., Tappi 44, no. 3:230-2(1961).

33. Hamilton, J., and Kircher, H., J. Am. Chem. Soc. 80:4703(1958).

34. Jones, J. K. N., Wise, L. E., and Jappe, J., Tappi 39:134(1956).

35. Timell, T. Wood hemicelluloses. Syracuse, New York, The College of Forestry at Syracuse University, 1963. 209 p.

36. Lindberg, B., and Meier, H., Svensk Papperstid. 60:785(1957).

37. Thompson, N. S., and Kaustinen, O., Paper and Timber 46, no. 11:637-50 (Nov., 1964).

38. Heuser, E., and Bartunek, R., Cellulosechemie 6:19(1925).

39. Nelson, R., J. Polymer Sci. 51:27-58(1961).

40. Rånby, B. G. The fine structure of cellulose fibrils. In Bolam's Fundamentals of papermaking fibers. p. 55-92. Kenley, Surrey, England, Technical Section of the British Paper and Board Maker's Association, Inc., 1958.

41. Annergren, G., and Rydholm, S., Svensk Papperstid. 62:737(1959).

42. Thompson, N. S., Peckham, J. R., and Thode, E. F., Tappi 45, no. 6:433-42 (1962).

43. Peckham, J. R., and Van Drunen, V. J., Tappi 48, no. 4:193-203(1965).

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44. Nelson, R., and Schuerch, C., J. Polymer Sci. 22:435(1956).

45. Wardrop, A., Austral. J. Sci. Research (B4) 4, no. 4:391-414(1951).

46. Schulz, J. H. The effect of strain applied during drying on the mechanical behavior of paper. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1961. 161 p.

47. Thompson, N. S., and Kaustinen, O., Tappi 47, no. 3:157-62(March, 1964).

48. Wise, L. E., Murphy, M., and D'Addieco, A. A., Paper Trade J. 122, no. 2:35 (1946).

49. Linnell, W. Personal communication, 1963.

50. Institute Method no. 428. Appleton, Wis., The Institute of Paper Chemistry.

51. Wink, W. A., and Van Eperen, R. H., Tappi 45, no. 1:10-24(1962).

52. Physics staff procedure. Appleton, Wis., The Institute of Paper Chemistry.

53. Hardacker, K. W., Tappi 45, no. 3:237-46(1962).

54. Hardacker, K. W. To be published.

55. Ward, K., Jr. Personal communication, 1964.

56. I.P.C. Method no. 424. Appleton, Wis., The Institute of Paper Chemistry.

57. Swerdlow, R., and Seeman, H., Textile Res. J. 18:536-50(1948).

58. Smith, O. Personal communication, 1964.

59. Saeman, J. F., Moore, W. E., Mitchell, R. L., and Millett, M.A., Tappi 37: 336(1954).

60. Ward, K., Jr., and Morak, A., Pure Appl. Chem. 5, no. 1-2:77-89(1962).

61. Segal, L., Creelay, J., Martin, A., and Conrad, C., Textile Res. J. 29, no. 10:786-94(1959).

62. Klug, H., and Alexander, L. X-ray diffraction procedures. p. 491. New York, John Wiley and Sons, Inc., 1954.

63. Immergut, E., Rånby, B., and Mark, H., Ind. Eng. Chem. 45:2482(Nov., 1963).

64. Ott, E., Spurlin, H. M., and Grafflin, M. W. Cellulose and cellulose derivatives. 2nd ed. Vol. 5. Part I. p. 283. New York, Interscience, 1955.

65. Immergut, E. H. In Browning's The chemistry of wood. New York, Interscience, 1963. 530 p.

66. Gillespie, R., Mueller, M., Swenson, H., and Ward, K., Jr., Tappi 44, no. 9: 662(1961).

67. Orr, R. S., Burgis, A. W., Andrew, F. R., and Grant, J. N., Textile Res. J. 29:349-55(1959).

68. Jurbergs, K. A., Tappi 43, no. 6:561-8(June, 1960).

69. Davies, O. L. Statistical method in research and production. New York, Hafner Publishing Company, 1958. 396 p.

70. Meredith, R., J. Textile Inst. 36:T107, T147(1945); 37:P469(1946).

71. Wakeham, H. Mechanical properties of cellulose and its derivatives. In Ott's Cellulose and cellulose derivatives. 2nd ed. Vol. 5. Part III. p. 1270. New York, Interscience, 1955.

72. Meyer, K., and Lotmar, W., Helv. Chim. Acta 19, no. 1:68-86(1936).

## APPENDIX I

## ESTIMATION OF SIZE OF PERTINENT FIBER STRUCTURAL ELEMENTS

Assume that the smallest dimension of fibril that has hemicelluloses surrounding it is the macrofibril of one-micron width that has been measured. The cross section, assuming a roughly square configuration, would be $10^8$ A.$^2$ and would contain $4 \times 10^6$ cellulose chains, assuming a unit cell of 5 by 5 A., of which $8 \times 10^3$ would be on the surface or perimeter. The percentage of chains on the surface is then 0.2%. The available sugars in the fibers are calculated as follows:

Glucose content of unextracted fiber = 55.5%
(-) glucose in glucomannan = 5.2%
(-) uronic acid in xylan (estd.) = 1.0%
Pure glucose = 49.3%

Xylan content = 6.7%
Portion of arabinose, galactose and uronic acid assocd. with xylan = 1.5%
Total xylan = 8.2%

Per cent cellulose on the surface of the fibril = 0.002 x 49.3 = 0.099. Assuming that the same weight of xylan can cover a given weight of cellulose (glucose), one can see that the xylan can cover this cellulose fibril easily. In fact, it could be removed to the extent that it is in the extractions carried out in this study (down to 1%) and still completely cover the cellulose.

Using the same calculations, one can calculate the xylan-cellulose relationship assuming different size fibrils. The summation of these calculations follow:

| Assumed Size of Fibril | Xylan/Cellulose Ratio |
|---|---|
| 1 micron | 8.2/0.1 = 82 |
| 0.1 micron | 8.2/1 = 8.2 |
| 0.01 micron = 100 A. | 8.2/10 = 0.82 |

One could also assume that the surface of the fibril is not smooth and represents more cellulose chains on the surface for a given size fibril. Also if Jentzen's assumption that the $S_2$ layer plays the primary role in affecting the fiber strength is correct, then the xylan and cellulose content must be corrected for the known distributions in the layers of the fiber wall.

These calculations indicate, however, that the size of the cellulose fibril with which the xylan can associate and cause the variance in strength must be quite small, possibly of the order of 100 A. to 500 A., since any dimension of fibril larger than these values could be covered with xylan even after extensive extraction of the xylans.

# APPENDIX II

## THEORETICAL MODULUS OF ELASTICITY

A partial translation of the article of Meyer and Lotmar (72) revealed that the figure of 9000 dynes/$\mu^2$ for a calculated theoretical Young's modulus of perfectly oriented cellulose quoted by Jentzen (2) and attributed to Meyer and Lotmar was in error. Meyer and Lotmar, using the Meyer and Mark cellulose model and estimating forces deducted from Raman spectra, arrived at two values of a theoretical Young's modulus. If they assumed that the magnitude of the angular (valence bond distorting) forces was 10% of the bond energy, they arrived at a Young's modulus value of 8000 dynes/$\mu^2$. Assuming a value of 20% for the angular forces yielded a modulus value of 12,000 dynes/$\mu^2$. They experimentally tested native fibers of high orientation such as ramie, hemp, and flax and found the Young's modulus values of these fibers tended toward a limit value of 11,000 dynes/$\mu^2$. Ramie averaged 9200 and hemp averaged 8200 dynes/$\mu^2$. Meyer and Lotmar then concluded that the assumption of 20% for the angular forces was a more valid one.

The bond energy they refer to is the carbon-carbon and carbon-oxygen bond energy and the angular forces they refer to is that energy required to change the angle of the carbon-carbon and carbon-oxygen bond.

The maximum value of Young's modulus for cellulose obtained in this writer's work was 9700 dynes/$\mu^2$ (Table XV), indicating an agreement with Meyer and Lotmar's conclusion that 12,000 dynes/$\mu^2$ was the more valid value.

# APPENDIX III

## INVESTIGATION OF JENTZEN'S DRYING PROCEDURE

As mentioned previously in this report, fibers dried using Jentzen's procedure appeared to be wet in that part of the fiber that was fixed in the movable clamp. It was important to determine whether the water that obviously existed on the end of the fiber could migrate along the fiber. If this was possible, then fibers dried using Jentzen's procedure may not always be completely dry. This procedure, then, would result in fibers only partially dried under a load.

An experiment was conducted with Uranine B dye solution to determine if water could migrate from the clamp in Jentzen's apparatus onto the dry fiber. A 0.25% aqueous solution of Uranine dye was made up. This concentration had the optimum fluorescing intensity.

A drop of dye solution was placed in the fixed clamp cavity (the clamp and fiber were previously dry) and the area was bathed with ultraviolet light. Surface tension forces gradually pulled the liquid into the crevices of the clamp and under the jaw part of the clamp. The jaw, of course, was raised slightly due to the fiber being under the jaw.

A drop of liquid was also placed on the movable clamp. This liquid immediately moved along the jaw line as this jaw was still wet from the preceding water film. The dye very slowly moved onto the fiber and proceeded a total of 0.2 mm. out of a total span of 3 mm. The total elapsed time was about five minutes. Although the fiber was watched for another 10 minutes, no more dye migrated into the fiber.

Additional trials revealed that more migration occurs from both the fixed clamp and the movable clamp, with the more extensive travel coming from the movable clamp. The dye traveled half the length of the fiber from the movable clamp and about one-fourth the length of the fiber from the fixed clamp.

There is no proof that the water remains on the fiber for say 15 minutes (Jentzen's drying time) after drying commences. The Uranine B dye has a "memory" concerning cellulose, and will continue to fluoresce after the water recedes. What this experiment did establish is that it is possible for water to migrate from the clamp into a dry fiber if there is a reservoir of water on the clamp.

There is no such reservoir of water on the fixed clamp during drying, of course, but the amount on the movable clamp usually remaining after the water is drained corresponded to the amount of dye solution added.

The stress-strain data obtained by Jentzen corresponded closely to the stress-strain data obtained from the fan-dried fibers tested in this study, indicating that the migration of water along the fiber had little, if any, effect on the fiber properties of the fibers dried under load. However, the use of the fan to dry the fibers eliminated any last vestige of doubt.

## UNUSUAL BEHAVIOR OF DRYING FIBERS

By observing with a 30-power microscope (using Jentzen's procedure) fibers drying under load, it was noticed that some of the fibers dried in a most unusual manner. While the water in the great majority of the fibers receded uniformly in the fiber along the whole length of the fiber, some fibers appeared to dry in one longitudinal section of the fiber while the rest of the fiber remained wet. This phenomenon was observed in about 5% of the fibers tested. In each case, there appeared to be a constriction in the fiber that prevented water from moving from the wet end of the fiber to the dry end.

This phenomenon was usually started by an uneven distribution of water droplets left on the fiber after removal of the water from the drying apparatus. Usually the water remained on the fiber in small droplets dispersed along the length of the fiber. However, occasionally, the water would collect in one large droplet, and this tended to cause the drying behavior just described.

# APPENDIX IV

## ELIMINATION OF DATA

At the time of testing on the Fiber Load-Elongation Recorder, the failure point was noted as being one of three possible locations: in the fiber span, at the glue line, and a pullout of the fiber from the glue. All data from pullouts were discarded and were not used. However, the data from breaks at the glue line were used because a statistical analysis revealed that there was no significant difference between those breaks in the fiber span and those breaks occurring at the glue line. Leopold and McIntosh (3) made the same observation.

Following is an example of the statistical variance of the two groups of data:

TABLE XXV

COMPARISON OF FIBERS BROKEN AT GLUE LINE TO FIBERS BROKEN IN THE SPAN[a]

| | | Breaking Stress, dynes/$\mu^2$ | Ultimate Elongation, % | Modulus of Elasticity, dynes/$\mu^2$ | No. of Fibers |
|---|---|---|---|---|---|
| Broken at glue line[b] | Av. | 126 | 4.34 | 3920 | |
| | S.D., % | 20.3 | 18.3 | 10.2 | 10 |
| Broken in fiber span[b] | Av. | 120 | 3.81 | 4110 | |
| | S.D., % | 18.1 | 14.0 | 13.8 | 19 |

[a] Stress calculated on measured area.

[b] All fibers unextracted and dried at 5-grams load.

# APPENDIX V

## TITRATION OF KOH SOLUTIONS TO DETERMINE ACTUAL NORMALITY

Analytical-grade KOH was used in preparing all extraction solutions. The solutions were titrated against aqueous solutions of potassium acid phthalate, a standard for titration of bases. Phenolphthalein was used as an indicator. The results are listed in Table XXVI.

TABLE XXVI

TITRATED NORMALITIES OF EXTRACTION SOLUTIONS

| Solution | Normality | Normality if were 100% KOH |
|---|---|---|
| 0.1N KOH | 0.0882 | 0.1 |
| 2% KOH | 0.316 | 0.363 |
| 9% KOH | 1.51 | 1.74 |

The normality for the 9% KOH-3% boric acid solution is not reported because it is not known. As mentioned in the cotton work, 0.2N or the number of equivalents left after complete neutralization of the boric acid was used for plotting of data. Titration of the solution yielded a normality of 1.458. Neither result is probably correct due to the equilibrium of the various constituents, and thus the true normality lies somewhere in between these extreme values, probably much closer to the 0.2N value.

# APPENDIX VI

## NOMENCLATURE

I.P.C. – Institute of Paper Chemistry

Holocellulose – delignified wood chips that are still in chip form

Holofibers – defibered holocellulose

Holopulp – large amount of holofibers

Fibrils – structural elements in the fiber composed principally of cellulose. May be any of three types of fibrils defined by Frey-Wyssling (13), depending on context.

D.P. – degree of polymerization

Hemicellulose – cellulose bonds – as used in this thesis, these bonds are the summation of all the hydrogen bonds, Van der Waal's forces, etc., in a given area (say, between two adjoining fibrils). The hydrogen bonds and other forces are the same for both cellulose and hemicellulose polymers, but the manner in which the movement of one fibril is transmitted through these bonds to another fibril varies with the structure of the connecting element (i.e., hemicellulose chains *versus* cellulose chains; or more important, nonuniform branched structures *versus* uniform linear structures).

# APPENDIX VII. ELECTRON MICROGRAPHS OF HOLOCELLULOSE FIBERS

Figure 20. Nonextracted Holocellulose Fiber 43,000 X

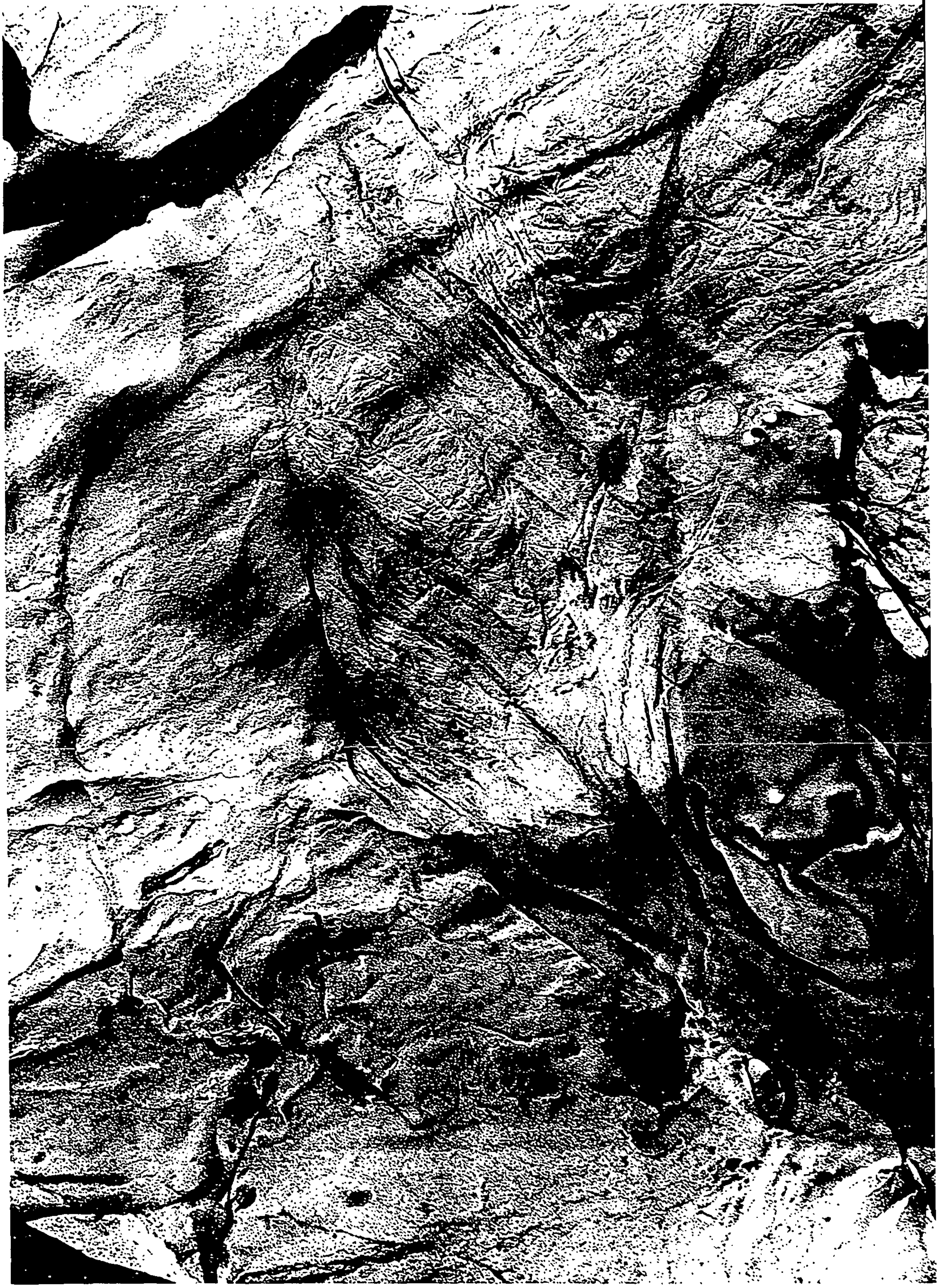

Figure 21. 0.1$\underline{N}$ KOH-Extracted Holocellulose Fiber
30,000 X

Figure 22. 9% KOH-Extracted Holocellulose Fiber
43,000 X

Figure 23. 9% KOH-3% $H_3BO_3$-Extracted Holocellulose Fiber
30,000 X

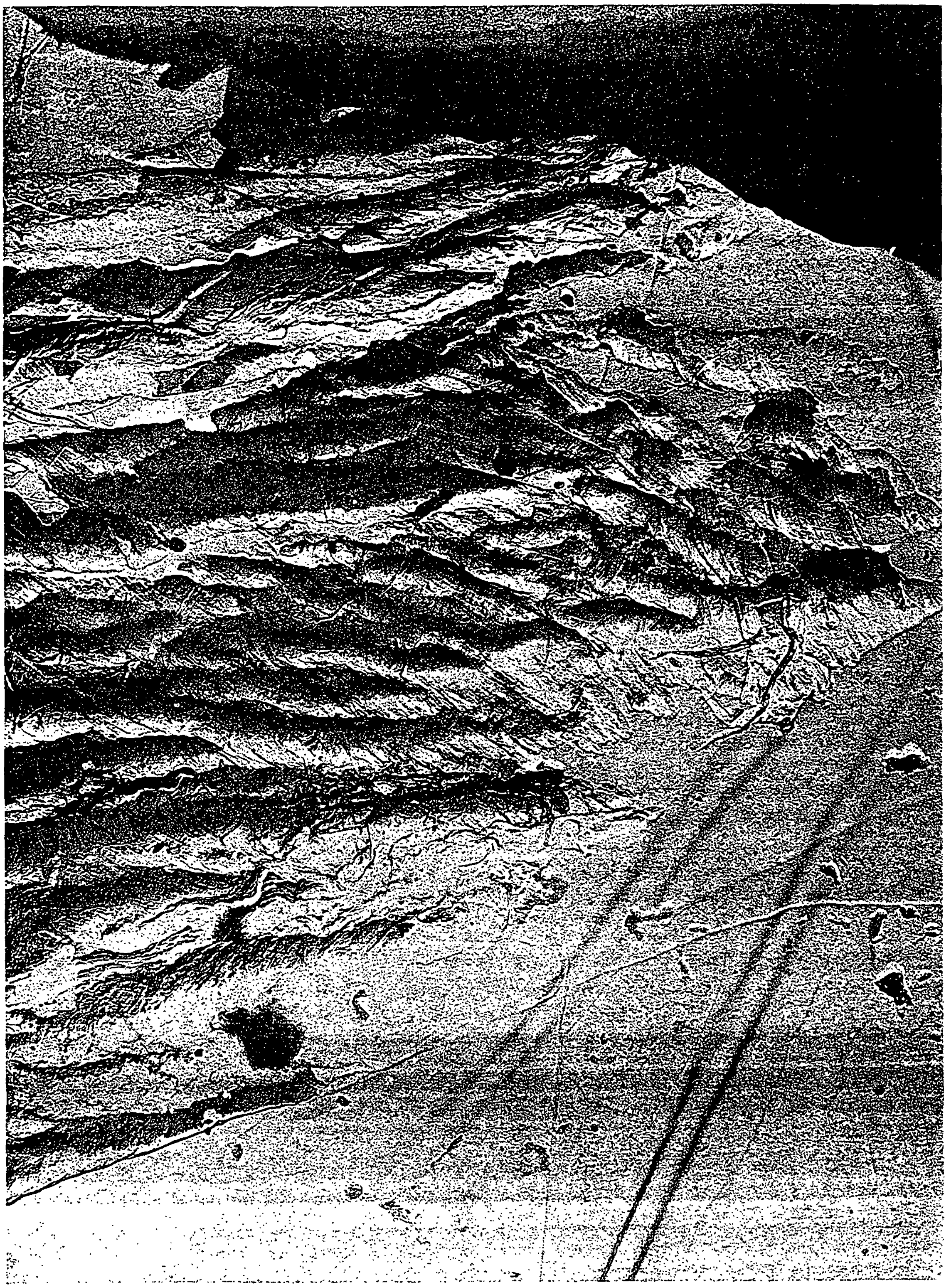

Figure 24. 9% KOH-3% $H_3BO_3$-Extracted Holocellulose Fiber 10,000 X