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A Fundamental Study of the Softening Mechanism
of Paper Plasticizers

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A FUNDAMENTAL STUDY OF THE SOFTENING MECHANISM
OF PAPER PLASTICIZERS

A thesis submitted by

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INTRODUCTION

Although plasticizers have been employed in the paper industry for many years to produce softer and more flexible sheets, the exact nature of the softening mechanism is not well understood. Laboratory tests reported in the literature are of a practical, rather than fundamental, nature. Several theories have been proposed, but none has been totally acceptable and well-established experimentally. The unsatisfactory state of our knowledge of the softening action is to some extent indicated by the variety of definitions of "softness" and by the tendency toward the interchangeable use of the terms "plasticizer," "softener," and "humectant."

Webster (1) defines softness simply as "the property of yielding easily to physical pressure"; this would apparently relate paper softness most closely to stiffness and compressibility.

In the "Dictionary of Paper" (2), however, the softness of paper is defined as "...one of several properties of a sheet of paper. In the case of tissues and toweling, softness is often used to indicate a combination of surface smoothness with stiffness--e.g., the sheet may be crumpled in the hand to yield a sensory estimate of softness. Thus estimated, softness is related to surface smoothness and limpness or lack of stiffness and thickness of the sheet. In several restrictive uses of the term, softness is apparently related to stiffness alone. As opposed to hardness as evaluated by compressibility, softness is, in some senses of the term, directly related to the compressibility of the sheet."

The definition of softness, therefore, varies with the type of paper considered. In tissue, it is related to surface smoothness and the absence of sharp edges in the crumpled sheet; in glassines and wrapping papers, it involves ease of folding and creasing without elastic recovery; in paper draperies, it denotes sheet limpness and good draping characteristics.

The same confusion exists to some degree in the use of other terms. "Plasticizer" suggests that the treated paper may show the properties of a plastic--i.e., be "capable of being deformed continuously and permanently in any direction without rupture" (1). In general, plasticized papers do not behave in this manner. Reed (3) noted that, in tensile tests of paper strips, the elongation before failure was increased significantly in the cross-machine direction by the addition of plasticizers, but such deformation is not entirely permanent, and it is characteristic of only the cross-machine direction. The use of the term "plasticizer" in the restricted sense of softening, however, has been widely accepted by the paper industry and is wholly satisfactory, if this distinction is remembered.

"Softener" is probably a better term in this connection, for it more nearly describes the function of the agent. Here again, however, the question arises: what is softness? In those cases where only a loss in flexural rigidity is involved, the term "flexibilizer" might be less confusing, since it refers only to sheet pliability without regard to its surface characteristics.

Finally, the interchangeable use of "softener" and "humectant" implies that all such agents reduce the stiffness of a paper sheet only by increasing its equilibrium moisture content. Although in effect the two terms are synonymous for certain plasticizers, detailed experimental studies (4, 5) prove that, in many cases, the softening cannot be attributed entirely to the hygroscopic character of the softener.

LITERATURE REVIEW

Early attempts to explain the softening mechanism began with the simple observation that raising the moisture content of the sheet reduced its stiffness. Obviously then water itself was a plasticizer and, since the common softeners proved to be hygroscopic in character, it was logical to assume that softening was effected by raising the equilibrium moisture content of the sheet. In 1939 the Lenzitrous Raw Materials Committee of the Technical Association of the Pulp and Paper Industry (6), in describing the most common commercial plasticizers, attributed the softening entirely to their hygroscopic nature. Hansen (6) noted that no successful plasticizers of a nonhygroscopic character were employed in the industry. Later work on glycerin by Hoffingwell and Lesser (7), on glycols and sorbitol by Integris (8) and by Brorer (9), and on saccharinic acid derivatives by Reed (3) confirmed the close relationship between the softening effects and the hygroscopic properties of these agents.

However, such humectant effects cannot satisfactorily explain all types of softening. Pike (4), Jordanburg (10), and McPherson (5) demonstrated that sheets containing glycerin were softer than untreated sheets in the low relative humidity range, even though their moisture contents had been reduced by the addition of glycerin. Obviously such plasticizing at a low relative humidity could not be attributed to the hygroscopic character of the glycerin. Pike concluded that some other mechanism must be responsible and proposed the concept of fiber lubrication. If the fibers in a sheet of paper were lubricated, no reformed,

they could slip over one another more easily as the sheet was flexed, thereby reducing its resistance to bending.

Whether this softening is produced by some direct action of the plasticizer molecule itself or merely by the additional water which it holds in the sheet, the loss in stiffness might be explained by one or more of the following mechanisms: (1) lubrication of the fibers, (2) weakening or rupture of fiber bonds, and (3) flexibilizing the individual fibers.

LUBRICATION OF THE FIBERS

Genner and Heilmann (11) considered the theories of boundary and fluid lubrication and showed how these might be related to the surface-bound moisture and the capillary-condensed water, respectively, in the unplasticized sheet. They concluded that the softener, whether it is water or a commercial plasticizer, may be found, first, as surface-adsorbed softener and, secondly, as excess softener beyond the range of the adsorptive forces on fiber surfaces and deposited in the capillary interstices of the paper.

Thus, when the attractive force between molecules of the lubricant after plasticizing is less than that between the fibers before plasticizing, the surface-adsorbed softener should lower the resistance of the sheet to bending by boundary lubrication.

The excess softener might reduce the sheet stiffness further by fluid lubrication, in which case the fibers would be held apart

mechanically, and the frictional resistance would depend to some degree on the viscosity of the lubricant. Although such lubrication is possible in the plasticized sheet, it should be remembered that the distances between fibers must remain very small, if the paper is to hold together. A thick layer of lubricant could not be built up without dispersing the fibers and thereby destroying sheet strength entirely. Furthermore, fluid lubrication which does not involve swelling and penetration into the sheet has little effect on sheet rigidity. Sheets immersed in mineral oil show no significant drop in stiffness.

The work of LePherson (5) with glycerin in sheets of alpha pulp contributed to our understanding of the lubrication concept. As the glycerin content of the sheets was raised, a decrease in the hysteresis of their moisture sorption loops was observed. Evidently, the glycerin molecules had entered between the fibers, increased the distances between their surfaces, and prevented the collapse of the fiber structure at low relative humidities and the formation of irreversible bonds between fibers. His data showed that the internal friction of a sheet containing glycerin and water was increased and then reduced by increasing the plasticizer content. Apparently, the first increments of plasticizer opened the sheet by reducing bonds between fibers and thereby increased the internal slippage without actual lubrication. Later increments, however, produced fluid lubrication, as the glycerin and water formed more nearly continuous layers between the fibers, and the internal friction of the sheet dropped off accordingly.

STRENGTH OR IMPURE OF FIBER BODIES

The strength of any sheet of fibrous material depends largely upon the attractive forces between the fibers and, if these forces are weakened or destroyed in part, a softer, weaker sheet will be produced. Such reduction in bonding might be expected as a corollary to the lubrication concept of softening, for the strength of the unbalanced surface forces decreases rapidly with distance. Therefore, any substance which holds the fibers apart would reduce the degree of bonding between them.

Bielschafsky and his associates (12) in experiments with polyvinyl chloride plastics reported that van der Waals' forces between the plasticizer and polyvinyl molecules determine the rigidity of the sheet and, therefore, a plasticizer makes the sheet more plastic by separating the chain molecules of polyvinyl chloride.

This is similar to one of the basic mechanisms described by Ott (13) for plasticizing cellulose derivatives. Grapher, he claimed, softens celluloid by solvating the cellulose chain, increasing the average distance between chains, and thereby reducing the force which binds each chain to its neighbor.

According to another concept of sheet softening, however, the adsorbed softener molecules reduce bonding between fibers by partial satisfaction of the surface attractive forces. In this case, the moisture sorption capacity of the cellulose at any given relative humidity should be reduced as the plasticizer content is raised. This effect is usually masked at the high relative humidities because of the

by roseopic nature of the plasticizer, but at the lower extreme it is more apparent.

In a study of the absorption of glycerin on cotton lintors, Ketherson (5) compared the sum of the moisture contents of the glycerin alone and the cellulose alone with the moisture content of the two in combination at the same relative humidity. These data proved that, when glycerin is brought into contact with cellulose, each component satisfies at least a part of the other's sorption capacity.

When he raised the glycerin content of the sheets, Ketherson observed a linear decrease in their tensile strength. He was unable to make comparable tests on the individual pulwood fibers because of their short lengths and, therefore, he substituted cotton hairs. Their tensile strength was found to increase slightly with the addition of glycerin, and so it seemed apparent that the weakening of the glycerin-treated sheets could be ascribed only to a weakening of the bonds between fibers. Whether this reduction in bonding strength was caused simply by an increase in the distance between fibers or by a decrease in their bonding capacity could not be determined experimentally. Probably both factors were responsible.

WEAKENING OF INDIVIDUAL FIBERS

If plasticizers can weaken bonds between fibers, it is also conceivable that they might penetrate fibers and produce additional softening by a reduction of the bonding between intrafiber chains. If there is any relationship between the stiffness of the fibers and that

of the sheet, the reduction of fiber rigidity in plasticizing may contribute toward sheet softening.

Integrin (8) stated that the flexibility of the paper sheet depends in part on the structure of the cellulose molecules and micelles. These elements do not act as stiff rods but are flexible, he claimed, and this flexibility is determined by their moisture content. Thus, the addition of hygroscopic materials to the fibers should improve their flexibility by raising the water content. However, there are no direct experimental data available to test this hypothesis.

Connor and Hadelmann (11) believed that the softening action of plasticizers was the result of hygroscopic action, fiber lubrication, or fiber swelling, either singly or in combination with each other. Swelling of the fiber, they reported, should make it softer and more plastic. This had been suggested indirectly by Fress and Dinkowsky (14), who studied the swelling effects of a number of hydroxyl compounds on wood pulp. They observed that fibers beaten in methanol, ethylene glycol, or glycerin were swollen and consequently so plastic that they could be refined with a minimum of cutting action. Fibers beaten in media of lower swelling efficiency, however, remained relatively hard and brittle, and the beating action was primarily cutting.

No direct measurements of the softness of pulp fibers have been reported in the literature but, in the field of textile research, Pearce and his associates (15) have made extensive studies of the torsional rigidity of cotton hairs. For untreated cotton, this rigidity varied

inversely with the humidity, showing a linear relationship between β and 83 per cent relative humidities. Beyond these limits the change in torsional rigidity was even greater, so that its plot against humidity followed a sigmoid curve with a negative slope. The loss of rigidity, Peirce claimed, was caused by the swelling of the hairs with a resulting distension and partial release of the internal cohesive bonds. This swelling was not proportional to the total water content but only to the portion which is considered surface adsorbed. Additional tests were made with a modified Peirce's pendulum to measure the flexural rigidity of the cotton hairs. Although this test was less accurate, it did show that flexural rigidity varies in the same sense as the torsional rigidity for changes in relative humidity.

Similar studies were reported by Peirce (16) on the flexural rigidity of starch films, for which the Peirce's pendulum could be employed with greater accuracy. He observed a linear decrease in the film stiffness, as the concentration of the surface-adsorbed water was increased.

No analogous studies of the flexural rigidity of pulp fibers have been published in the technical literature, and no data are available to show the effect of water and other softening agents on this property.

MEASUREMENT OF SHEET STIFFNESS

Because the softness of a sheet apparently depends upon a combination of other physical factors, a variety of test instruments have been developed, all evaluating softness in terms of some other

more measurable physical property. Most of these actually determine the stiffness of the specimen, the property most closely related to softness in a wide range of papers.

The Carter stiffness tester, the Gurley stiffness tester, and the Smith-Zabor stiffness tester all apply a deflecting force at some fixed distance from the clamped end of the specimen and then measure strip deflection under a known load. These instruments have been studied and their limitations for research have been discussed (17).

The Clark softness tester (18) differs from these three instruments in that stiffness is measured for a uniformly loaded specimen, rather than for one to which a localized deflecting force is applied. The Clark rigidity values for a number of commercial papers correlated well with data obtained using a torsion pendulum, and the Clark softness factors checked closely with subjective tests for the softness of facial tissues, towels, waxed glassine, and bread wrappers. Accordingly, it has been accepted as a tentative method (P 451 e-45) for the measurement of paper softness by the Technical Association of the Pulp and Paper Industry.

One error inherent in all static measurements of sheet stiffness, however, is caused by plastic flow, which produces a change in sheet deflection with time. Thus, in most papers, the stress-strain curve is not a straight line but a loop; after the application and removal of the deflecting force, the paper does not generally return to its original shape. In order to determine the purely elastic con-

ponent of sheet stiffness, the bonding must be followed at once by relaxation in order to eliminate flow.

The method of the torsion pendulum is perhaps the most accurate of such dynamic measurements of sheet stiffness. This instrument (19) is a symmetrical mass suspended from a wire, and its vibration is rotational about the vertical axis of the wire. If a paper strip is clamped to the suspended mass in such fashion that the strip is bent when rotation occurs, the added restoring torque resulting from the bending of the strip causes a reduction in the period of rotational vibration. Then a comparison of the periods of the pendulum with and without the test strip makes it possible to compute the flexural rigidity of the strip.

Steenberg, in a recent paper (20), reported the determination of purely elastic stiffness by the measurement of the frequency of vibration producing resonance in a test specimen mounted as a cantilever beam. Such bending of the specimen, he claimed, was too rapid to allow flow and, since the deflections are small, Hooke's law may be applied. Steenberg compared this apparatus with the Clark softness tester in tests on commercial papers and reported that the two instruments correlated well.

An instrumentation study of the Gurley-Hill softness-porosity-smoothness tester (21) showed that this test is an indirect and poor measurement of compressibility; other properties, such as caliper and smoothness, are also involved.

In a study of paper napkins, tissue, and toweling, Brown (22) developed a "crumple" tester to determine paper softness. This device measured the force required to crumple and compress a paper sample of specified size into a definite volume.

MEASUREMENT OF FIBER STIFFNESS

In spite of the variety of instruments constructed to measure the flexural rigidity of sheets, similar tests for individual fibers have not been developed. Stress-strain studies have been made to determine the moduli of elasticity of fibers. These, however, are not at all satisfactory, since there may be a conversion of unaligned to aligned molecular and crystallite elements during loading of the fiber. Thus, when cellulose is submitted to stress, some chains in an unfavorable position may take the largest part of the tension and break or slip along one another early in the deformation. Other chains originally curled may disentangle and gradually become parallel. As such internal flow progresses, the cross-sectional area of the fiber decreases and stress rises accordingly, so that the resulting slope of the stress-strain curve is too variable for accurate interpretation.

Feyer and Lotmar (23) determined the modulus of elasticity of single filaments by measuring the velocity with which sound waves were propagated in the material. Standing waves of a given frequency were produced in 60-cm. lengths of the extended filaments, and the wavelengths were measured accurately. Knowing the wavelength and frequency, they calculated the velocity from which the modulus of elasticity could be determined with a probable error of about ten per cent.

Schiefer, Court, and Kropf (24) described an instrument designed to measure the flexural endurance of cotton hairs and other textile fibers of sufficient length. The ends of the test specimen were mounted in two rotating clamps placed at right angles to each other, so that the hair assumed the shape of a quarter circle in the axial plane of the clamps. The two clamps were synchronized to rotate at a speed of 1500 revolutions per minute. In each rotation an element of the fiber passed through a cycle of tension and compression resulting from flexural deformation, and the number of rotations required to cause failure was a measure of the flexural endurance of the specimen.

Poirco and his associates (15) measured the torsional rigidity of cotton hairs by the construction of small torsion pendulums. One end of each hair was clamped from above and the other was weighted by a short length of wire. In the test this wire was set into rotational vibration about the vertical axis of the hair. Measurements of the period of vibration made it possible to calculate the torsional rigidity of individual cotton hairs at given humidity levels.

In order to determine the flexural rigidity of these hairs, Poirco employed a Searle's pendulum. Two similar parallel pendulums were suspended by nonrigid threads and connected to each other by a number of test specimens. Forty cotton hairs were usually mounted together and tested simultaneously. The pendulums were set to swinging symmetrically and the resistance of the hairs to bending could be calculated from the period of swing. Although this instrument is quite

accurate when single wires and films are tested, its application to stiffness tests for fiber bundles introduced large errors; the results were, therefore, only approximate.

PREPARATION OF PAPER

Recent experimental studies of certain plasticizers have added considerably to our understanding of the concepts of lubrication and reduction in fiber bonding. However, the effect of these plasticizers on the fibers themselves has never been determined.

The influence of fiber properties on those of the resulting sheet has been the subject of much conjecture but only limited experimental study. Bray and Carran (25) investigated the effect of fiber morphology on many common strength properties of the sheets. They compared sheets rich in springwood fibers with those rich in summerwood fibers and observed significant differences in tensile, bursting, and tearing strengths. No measurements of sheet stiffness were reported.

When Clark (26) studied the effect of fiber length on sheet properties and prepared sheets which differed from each other only in the length, but not the fineness, of their fibers, he noted that the stiffness of the paper varied as the square root of the average fiber length.

In the field of textile research, Clark (27), Turner (28), and Herritt (29) attempted unsuccessfully to establish the nature of the correlation between the fiber strength and yarn strength of cotton hairs. That such a relationship should exist seemed likely, for increases in hair strength with increasing relative humidity or after mercerization were reflected in similar increases in yarn strength. As the result of numerous disturbing factors, however, the establish-

ment of such a correlation proved to be extremely difficult experimentally, and no significant relationship between fiber and yarn properties could be shown.

It is apparent that plasticizers reduce the strength of the bonds between pulp fibers. Whether or not the plasticizer molecules also penetrate the fibers, rupture internal cross-linkages, and thus reduce fiber stiffness has never been established experimentally. Even though it may not be possible to determine the influence of the single fibers on sheet stiffness, any study of fiber stiffness should be of considerable fundamental interest. No accurate experimental data on the effect of water or softening agents on the flexural rigidity of single fibers have been published. Such a study would require the development of a test instrument, since existing experimental methods do not give a satisfactory measure of fiber flexural rigidity.

Briefly, then, the problem for this dissertation involved three phases: (1) the establishment of an accurate procedure for the measurement of the flexural rigidity of fibers, (2) the investigation of the effect of plasticizers on the flexural rigidity of fibers, and (3) the study of the influence of fiber stiffness on sheet stiffness.

INVESTIGATION OF FIBER STIFFNESS AND ELASTICITY

Most commercial instruments which determine the flexural rigidity of a sheet measure either its deflection under a given load or the load required to produce a given deflection. The principal disadvantages to modifying such devices in order to handle single fibers are first, they could not be reduced easily to a scale where small differences in fiber stiffness would be measurable and, secondly, they are all fundamentally wrong in presupposing that cellulose fibers alone or in sheets are elastic without being plastic. If a true measure of flexural rigidity is desired, the plastic characteristics, which depend on time, must be eliminated.

It should be possible, however, to measure small changes in the stiffness of fibers when they are mounted as cantilever beams, by determining their frequencies of natural vibration. Thus, when a beam vibrates in resonance with an external vibration of known frequency, Timoshenko (30) has shown that the flexural rigidity of the beam is related to this resonance frequency by

$$\underline{EI} = (\underline{W} \omega^2 / \underline{g} \underline{I})^{1/4},$$

where \underline{W} is the weight per unit length of the beam,

ω is $2\pi \underline{f}$ (\underline{f} is the resonance frequency),

\underline{I} is a constant whose value depends upon the free length (\underline{l}) of the beam and the mode of vibration produced (for the first mode of vibration, $\underline{I} = 1.875$),

\underline{g} is the gravitational constant, and

\underline{EI} is the flexural rigidity of the beam.

Such a method should give a true measure of flexural rigidity, for rapid vibration of the test specimen during testing presumably eliminates all plastic flow. Although it has been used in other fields, this vibration technique is a recent innovation in the pulp and paper industry. Steenberg (20) employed it in a recent study of sheet stiffness but its application to single fibers has not been reported.

DESIGN AND CONSTRUCTION OF THE APPARATUS

Instead of vibrating the test specimens directly by a mechanical coupling to the source of vibration, it was sufficient to mount the fiber rigidly as a cantilever beam over a loudspeaker and induce the desired vibration by sound waves. In this way, it was possible to observe a number of test fibers simultaneously.

The source of vibration was an eight-inch permanent magnet Utah speaker, energized by a Hewlett-Packard Model 2003 variable oscillator and a Knight Model 143 amplifier. The cone of the speaker had a characteristic resonance frequency of its own at 140 cycles per second, which produced forced vibration of the test fibers, frequently masking the true resonance vibrations in that range. Attempts to reduce these forced vibrations by weighting the speaker cone or reducing its surface area were of little value. Therefore, the lengths of the test fibers were controlled so that resonance vibrations would be obtained at frequencies well above this range.

Substitution of an oryphane unit as the source of vibration would have eliminated this problem of forced vibrations. The disadvan-

types of such a system, however, were (1) vibrations were limited to a small area, so that only one fiber could be tested at a time, and (2) the power output was too small to produce vibration of paper strips.

A variety of methods for mounting the test fibers was considered. Since measurements were to be made on a large number of specimens, mechanical clamps for the individual fibers were too cumbersome. Furthermore, the fibers were too fine to permit mounting in a molten wax or adhesive, for all attempts to introduce them endwise into the mounting media were unsuccessful. The most satisfactory method consisted of laying the fibers on a microscope slide, so that they were perpendicular to the length of the slide and projecting over its edge by six to eight mm. Then each fiber was anchored in position on the slide by a drop of molten paraffin wax. With such mounting several specimens could be tested without moving either the slide or the speaker. Other adhesives and waxes were considered, but paraffin wax was preferred because of its low melting point, its fast-setting properties, and the absence of solvents in it which might swell the fibers. Since paraffin-on-paraffin gave more satisfactory "wetting" than did paraffin-on-glass, further improvement in the mounting technique was obtained by laying down a thin film of the wax on the slide before the fibers were placed in position. To provide this base, the slides were dipped in molten wax and the excess was removed with a razor blade. Six fibers were spaced evenly along the length of each wax-covered slide and mounted in these positions by molten paraffin added from an eye-dropper. For the vibration tests the slide was placed on the metal shelf shown in

Figure 1, where it was held in place directly over the diaphragm of the loudspeaker by spring clips.

Provisions were also made to test paper strips with this instrument. Because of their greater width, such strips could not be mounted on a microscope slide in the same manner as the fibers, for accurate determination of the resonance frequency required close observation of the specimens along a plane perpendicular to their plane of vibration. Such close mounting would have interfered with the visibility of all strips. Because of this and also because fewer tests of strips would be required for an accurate evaluation of sheet stiffness, the method of multiple mounts used for fibers was not adopted for the strips.

The paper sheets to be tested were cut into strips of closely specified dimensions and placed singly between the parallel jaws of a metal screw clamp of the type employed in the Schopper tensile tester. A small template behind the jaws controlled the position of the strip, so that a constant free length of the specimen was obtained after the jaws were closed. This clamp in turn was mounted in a slot on the metal shelf over the loudspeaker and held in place rigidly by a metal yoke and bolts illustrated in Figure 1.

In order that the moisture content of the fibers and sheets could be controlled at any desired level, a cabinet was designed and constructed to provide a test chamber at a constant relative humidity. This is illustrated in Figure 2. The walls and floor of the cabinet



FIGURE 1

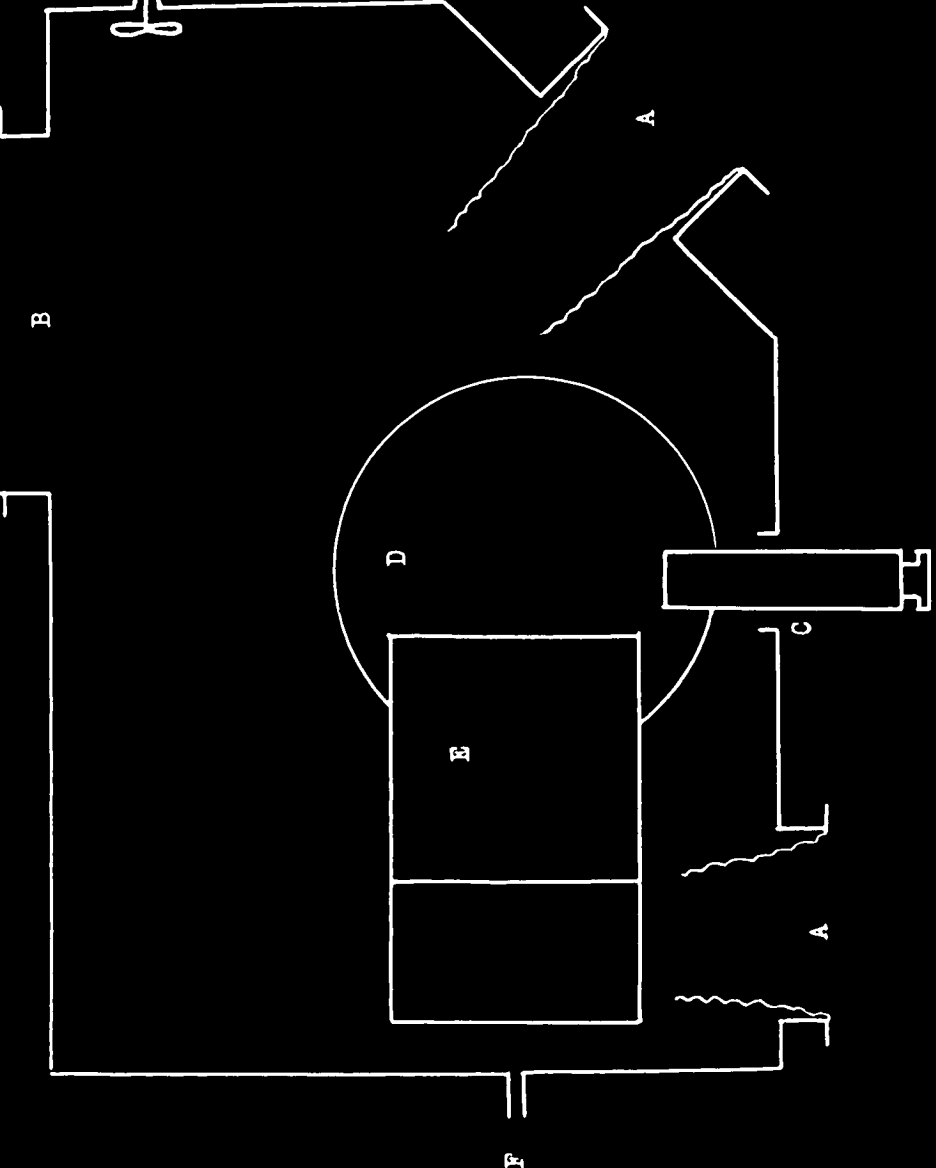


FIGURE 2

were made of galvanized iron, and the joints were soldered. A glass top covered the chamber, so that all testing operations could be seen from above, and modeling clay formed the seal between the glass and the metal walls.

Since the height of the cabinet was 12.5 inches, cavity resonance was obtained at 530 cycles per second and, to a lesser degree, at 265 cycles per second. This interfered in some cases by producing forced vibration of the test fibers and strips, but these false resonance points were easily identified as such and disregarded. To avoid cavity resonance in the upper frequency range and speaker resonance at the other extreme, the lengths of the test specimens were usually chosen so that resonance vibrations were obtained between 160 and 520 cycles per second.

Two ports for the arms of the operator were provided at A in Figure 2, although in practice only the right port was used. Thus, the left hand was free to control the oscillator and amplifier. A large window in the rear at B allowed for the entrance and removal of specimen and equipment. When not in use these three ports were sealed with glass plates clamped tightly against the rubber flanges. The circular port at C between the two arm holes permitted focusing the microscope, through which the mounted fibers could be observed, and the cap was closed by Pliofilm bellows.

The area directly in front of the microscope was occupied by the loudspeaker D resting on a cushion of sponge rubber to minimize

vibration of the chamber. Over this the horizontal shelf B was constructed, as shown in Figure 1, so that the test strips or fibers would be mounted directly over the cone of the speaker. The remaining space in the chamber was occupied by the electric hygrometer, by dishes containing the appropriate saturated salt solutions to assist in conditioning, and by racks holding the microscope slides or paper strips. During the vibration tests, the fibers themselves were not touched; when, however, paper strips were tested, some handling of the specimens was unavoidable. In such tests rubber-tipped forceps were used to insert and remove the strips, so that deformation of the specimens was kept at a minimum.

Conditioned air entered the chamber through a tube at F and escaped around the fan shaft at G. This fan was driven slowly by a small electric motor mounted outside the test chamber and promoted the rate of air circulation inside. Initially, rubber sleeves of dental gum were cemented on the arm holes at A to eliminate air leakage along the arm of the operator, but early tests showed that they were unsatisfactory as a moisture and alcohol vapor barrier. Therefore, they were replaced by Pliofilm sleeves formed by heat sealing; although these lacked the elasticity of the rubber, they did provide an effective barrier against vapor-pressure changes during testing. Air leakage between the arm of the operator and the sleeve was reduced by rubber tubing wrapped tightly around the outside of the sleeve.

It was necessary to wear a surgeon's rubber glove on the hand inside the test chamber to prevent the rapid transfer of moisture from

the hand into the cabinet at low relative humidities. In the early phase of the experimental work, such moisture leakage was further reduced by the application of a soft wax to the glove; later it became apparent that the same barrier could be produced more conveniently by dusting the hand first with talcum and then wearing two rubber gloves on the hand.

The test chamber was placed in a room in which the temperature was held at $73 \pm 2^\circ$ F., so that constant relative humidity conditions could be maintained. The air passing into the chamber was brought to the desired humidity by bubbling compressed air slowly through two gas washing towers containing appropriate saturated salt solutions. The normal rate of flow was ten cc. per second. For the low relative humidities, the air was passed first through two other towers of desiccant, since air from the compressor was normally quite humid. However, when air was to be conditioned at a high humidity, it was brought to saturation first by bubbling through a tower containing water. Otherwise the fritted-glass tips on the entrance tubes of the succeeding towers were plugged by crystallization of the salt from its saturated solution. Except for the initial study of the effect of water and alcohols on fiber rigidity, all other plasticized fibers and sheets were tested at relative humidities (R.H.) of 22.9, 50, and 11.1 per cent, respectively. To produce the high level, air was bubbled through saturated solutions of ammonium dihydrogen phosphate, and dishes containing this solution were placed in the chamber to accelerate the conditioning process. Since the test room was maintained at 50 per cent

R.H., vibration tests at this second level were performed with the chamber wide open and the conditioning towers cut off. Finally, tests at 11 per cent R.H. required bubbling air through a saturated solution of lithium chloride and here too, dishes containing the solution were inserted in the test chamber to assist in the conditioning.

The relative humidity in the cabinet was measured by electric hygrometers described by Van den Akker (31), and the microammeter was mounted alongside the test chamber, so that frequent readings could be made. Since, however, the reliability of the hygrometer in atmospheres below 11 per cent R.H. had never been checked, the moisture content of the filaments for tests near 0 per cent R.H. was determined by oven drying weighed samples of duplicate filaments conditioned in the test chamber. An electric hygrometer exposed to 0 per cent R.H. was spoiled, because later conditioning at 50 per cent R.H. caused flaking of the platinum film. A similar attempt to use an electric hygrometer near 0 per cent R.H. for the measurements of alcohol vapor pressures was also unsuccessful; changes in conductivity were obtained but the readings were not reproducible.

Experiments with volatile materials, such as the aliphatic alcohols, require proper control of the relative vapor pressure in order to keep the alcohol content of the fibers at equilibrium. For this purpose, a divided flow system was constructed and inserted in the compressed air line. After passing through the drying towers, one fraction of the air was bubbled slowly through two gas towers containing alcohol, so that it was saturated with alcohol vapor; next it was passed to a

mixing tower, and then to the test chamber. The other fraction of the drying air was passed directly to the mixing tower. By varying the proportions of the alcohol-saturated air and the air circulated around the alcohol towers, it was possible to obtain any desired relative vapor pressure in the test chamber.

In addition to determinations of resonance frequencies, this vibration procedure required accurate measurements of fiber length and weight. Since tests were to be made at several relative humidity levels, the corresponding values for length and weight under those conditions were needed.

The free lengths of the mounted fibers and strips were measured to 0.001 mm. with a Gaertner comparator, and the manner in which these lengths varied with the relative humidity was determined in a two-tower Heenan hygrometer described by Van den Vlier (32).

The average weight per unit length of the fibers was established by direct weighings on the microbalance, after the fibers had been brought to dryness over anhydrous. Then the weight of the plasticizer in each series of treated fibers or sheets was determined by well-established analytical methods; these will be considered in detail in a later section. Finally, the moisture content of the fibers at the test relative humidities was measured according to the section procedure developed by Wink (33). Thus, a Petri dish containing the sample was suspended in a closed chamber whose relative humidity was controlled by the saturated salt solution below. Weighings of the

samples were made at equilibrium with a series of such salt solutions to determine the moisture sorption curve.

SELECTION OF TEST FIBERS

Ideally, the vibration tests would have been made on pulpwood fibers, since then the plasticizer data would have had the most practical significance. Since the counting and testing techniques required fibers with a minimum length of seven mm., studies based on wood fibers were out of the question.

Some preliminary work was done with cotton hairs, which possess satisfactory length. Cotton, however, has the disadvantages of (1) great variation in the diameter and shape of different hairs, requiring large numbers of tests to yield acceptable average values, and (2) a natural tendency to twist and kink, making length measurements with the comparator somewhat unreliable. Nevertheless, the flexural rigidity of 35 cotton hairs at 50 per cent R.H. was determined by the vibration method and calculated to be 1.64×10^{-2} dyne-cm. This is in the same range as the value of 3.4×10^{-2} obtained by Poirce (15) using a modified Scourle's pendulum to evaluate another species of cotton. When vibration tests were attempted at the other relative humidity levels, however, the spiral fibril orientation of the cotton produced pronounced twisting of the mounted specimens. Therefore, all plans to employ cotton in later studies were rejected. Flax behaved in a similar manner.

The only two types of fibers studied which possessed sufficient length but remained straight under changing relative humidity

conditions were ramie and viscose rayon. Rayon filaments were ideal from an experimental viewpoint in their uniformity, their high content of amorphous cellulose, and their availability in straight and unlimited lengths. Since rayon contained a higher proportion of amorphous cellulose than wood, greater plasticizer sorption and, therefore, more pronounced softening were expected. Thus, it seemed likely that the effect of plasticizers on wood fibers might be magnified by the use of viscose filaments. The viscose filament selected was Cordura, a highly oriented tire-cord rayon manufactured by Du Pont from purified cotton. The yarn was obtained without twist, pigment, or finishing treatment and came as a continuous filament rather than as staple fiber. Photomicrographs in the technical literature revealed a nearly circular cross section.

Ramie fibers, on the other hand, lacked the uniformity of synthetic filaments but possessed the inherent advantage of being natural fibers, were available in satisfactory lengths for vibration tests, and could be formed into sheets for comparative studies of sheet and fiber stiffnesses. A supply of the degummed, bleached ramie fibers was obtained from Newport Industries, Inc.

Hermans (34) investigated the ratio of crystalline and amorphous cellulose in many natural and synthetic fibers by moisture adsorption and heat of swelling methods, by density measurements, and by x-ray diffraction data. He reported that the amount of crystalline cellulose in ramie was about 60 per cent, in wood pulp about 50 per cent, and in rayon about 25 per cent. Thus, it is apparent that the two test

Fibers chosen, ramie and Cordura, ranked on both sides of wood fibers in regard to crystallinity. Although no comparative data were available on the orientation in Cordura, it was probable that a similar situation existed for ramie, wood, and Cordura in their degrees of orientation. If plasticizers did have an effect on fiber stiffness, these characteristics of crystallinity and orientation should have a definite influence on the softening produced. Therefore, it was hoped that the behavior of plasticized Cordura and ramie might indicate the expected effects of softeners on wood fibers.

The weights per unit length of Cordura and ramie were obtained directly on the microbalance. The lengths of six Cordura filaments roughly 150 cm. long were measured accurately; these filaments were then brought to dryness over anhydrous and weighed separately on a microbalance. The average weight per unit length was calculated to be 2.372 micrograms per cm. with a standard deviation of 0.063 microgram per cm. Similarly, 50 ramie fibers with an average length of 11 cm. were chosen, carefully straightened, and measured for length to the nearest millimeter. These were cut into smaller lengths for storage in the microweighing bottles, brought to dryness over anhydrous, and weighed as four separate samples. The average weight per length was 6.12 micrograms per cm. with a standard deviation of 2.19 micrograms per cm.

DEVELOPMENT OF TESTING TECHNIQUE

Since it was apparent that large numbers of strips and fibers would have to be tested in order to obtain reliable average values,

every effort was made to standardize the test procedure. All specimens for vibration tests were mounted at 50 per cent R.H. and brought to equilibrium with the highest humidity test level. After the first series of vibration tests had been made at this point, the humidity was dropped to the next test level, the mounted specimens were again brought to equilibrium, and the next series of vibration data were taken. This procedure was repeated as often as necessary to complete the stiffness evaluation, so that all test levels except the first were approached by desorption. Except for the initial studies of water and alcohol, all plasticized specimens were tested at 93, 50, and 11 per cent R.H., since this cycle was considered sufficient for evaluation of the softening agents. Moisture sorption and hygroexpansivity were determined at the same humidities and in the same order, so that errors caused by hysteresis would not interfere.

Early attempts to measure the hygroexpansivity of single Corduro filaments were largely unsuccessful because of the rupture of the specimen under tension. This was remedied by substituting loops of 20 to 30 filaments, so that the load was distributed. Even though the loops were allowed to hang freely without any external tension between readings, a small but significant elongation of the Corduro was obtained in the expander. When length readings were made around the entire test cycle, it was apparent that the principal creep had occurred in the first conditioning period--i.e., at 93 per cent R.H. Since the mounted filaments in the vibration tests were not under any comparable tension, this initial elongation produced in the expansi-

meter was ignored, and hygroexpansivity values were recalculated on the basis of the loop lengths at 50 per cent R.H. approached by desorption.

Because of their high degree of crystallinity, ramie fibers did not show any significant extensibility during the hygroexpansivity tests. Since, however, specimen lengths of over six inches were required, these determinations could not be made on single ramie fibers. Therefore, fine strands of ramie carefully combed to eliminate the loose fibers were substituted. The complete test cycle was repeated with no changes observed in the length readings, indicating that no irreversible slip had occurred between the fibers.

In the normal testing procedure for Cordura and ramie, the lengths of the mounted fibers were determined at 50 per cent R.H. before the test cycle began. Then the specimens were conditioned in the test chamber at 93 per cent R.H. for 48 hours (24 hours were sufficient for the unplasticized mounts) before the vibration measurements were made. After this, conditioning periods of 24 hours were satisfactory for all specimens at the 50 and 11 per cent R.H. test levels. This procedure was unchanged for the early water and alcohol studies, except that the frequency measurements were made at four to six levels of plasticizer content; the conditioning periods, however, were the same.

For experiments on ramie sheets, however, the preparation of the strips was somewhat different, and the sequence of testing was

reversed. The resin sheets at 50 per cent R.H. were cut into test strips of carefully specified dimensions on the angle cutter designed for the Taber stiffness tester. This produced strips 3.815 x 10.80 cm., which were then cut crosswise on a trimming board with a properly designed template to yield test specimens with average dimensions of 0.341 x 3.815 cm. The strips were tested first at 11 per cent R.H., then preconditioned at 93 per cent R.H., conditioned and tested at 50 per cent R.H., and finally conditioned and tested at 93 per cent R.H. It should be noted, however, that the 11 and 50 per cent test levels were still approached by desorption, so that moisture sorption and hygroexpansivity data obtained in the usual manner would not be invalidated by hysteresis effects. This rather awkward sequence was necessary because the stiffness of plasticized strips varied so sharply with the relative humidity that the original strips did not show resonance vibrations in the acceptable frequency range of 160 to 520 cycles per second at all three test levels. Therefore, after the frequency measurements had been made at relative humidities of 11 and 50 per cent, the strips were shortened by trimming, the new lengths were measured, and the vibration tests were concluded at the 93 per cent level.

VARIATION OF THE TEST METHOD

After the experimental techniques had been developed, it seemed desirable to check the accuracy of the flexural vibration by comparing it with the torsion pendulum described by Van den Esker (19). Tests were made on strips cut from aluminum foil, polystyrene film,

and nine commercial paper sheets of exceptionally good formation, and the rigidity values were calculated on the basis of unit width. The data are presented in Table I and Figure 3.

TABLE I

COMPARISON OF THE TORSIONAL VIBRATION AND FLEXURAL VIBRATION METHODS FOR THE MEASUREMENT OF SHEAR STIFFNESS

Sample	I Torsion Pendulum \underline{G} , dyne-cg. cm.	II Flexural Vibration \underline{G} , dyne-cg. cm.	$\frac{II}{I}$
Aluminum foil	2210	1130	0.51
Polystyrene film	50	27	0.54
Paper A	2790	1430	0.51
Paper B	5260	3510	0.67
Paper C	3050	2035	0.67
Paper D	580	320	0.55
Paper E	420	360	0.86
Paper F	885	460	0.52
Paper G	1460	670	0.46
Paper H	3270	1870	0.57
Paper I	2500	1120	0.47

Although the absolute values obtained by the two methods were not in good agreement, Figure 3 indicates that there was a fairly constant ratio of proportionality between the two. An independent determination of the flexural rigidity of the aluminum foil was made by measuring the deflection of the foil caused by its own weight, when it was mounted as a cantilever beam. This value checked reasonably well with the torsion pendulum figure. However, such a discrepancy between the absolute stiffness values did not detract from the feasibility of the flexural vibration method in this investigation, for relative effects

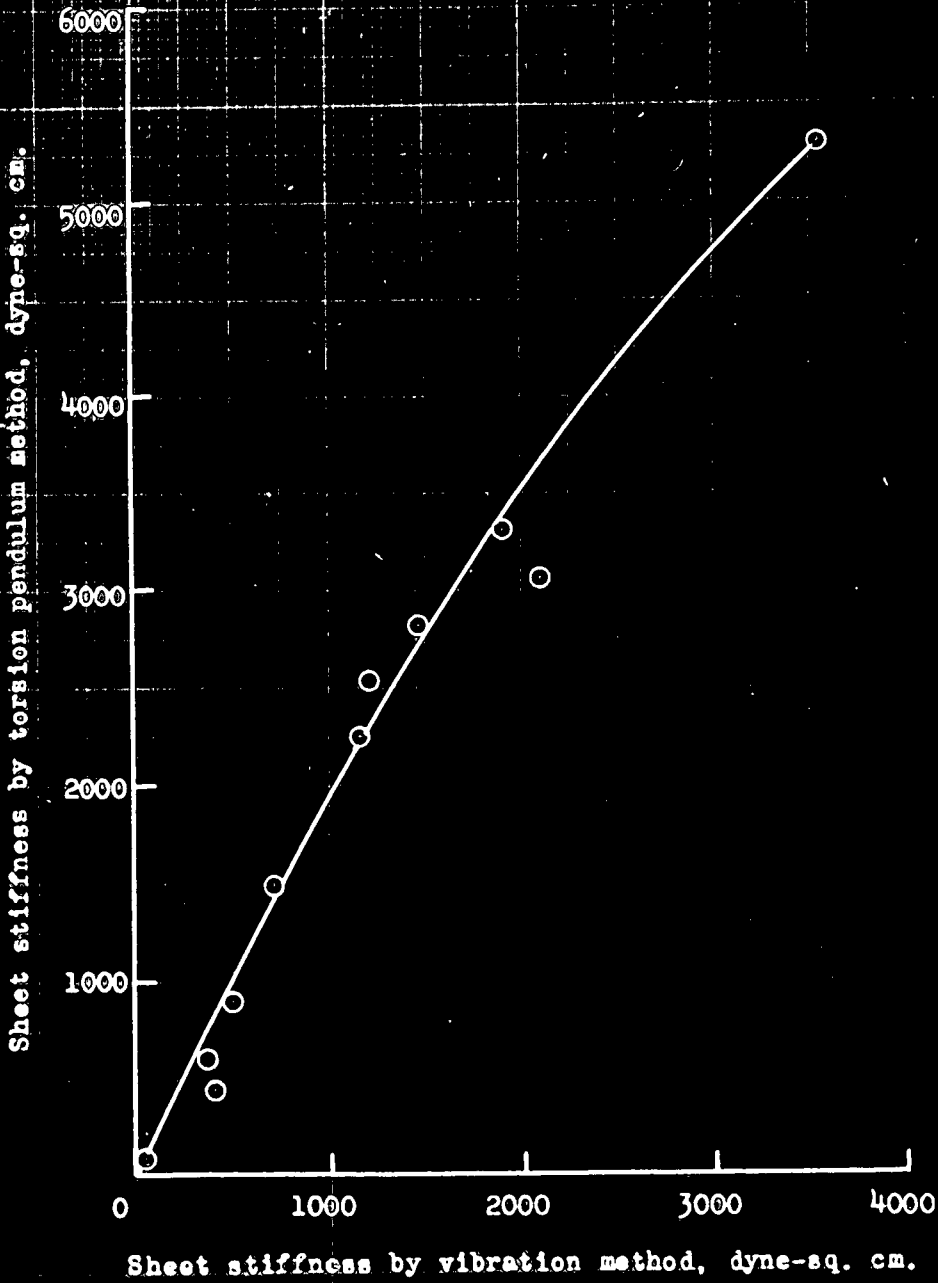


FIGURE 3

Comparison of Torsion Pendulum and Vibration Stiffness

were fully as significant as the absolute values in revealing the action of plasticizers on fibers.

Before vibration tests were begun on the plasticized fibers, a study was made of the principal sources of variation in the test procedure. Errors from fluctuations in testing conditions were reduced to a minimum by preparing, conditioning, and measuring the fibers and sheets in a room held at $73 \pm 2^{\circ}$ F. and 50 ± 2 per cent R.H. The electric hygrometers were standardized over saturated salt solutions of known relative vapor pressure, and the variable oscillator was calibrated against a 60-cycle line frequency over the range of acceptable vibration frequencies, through the use of Lissajous' figures on the screen of a cathode ray oscilloscope. Changes in the specimen length and weight at the various test levels were determined by hygroscopicity and sorption studies. There still remained probable errors as a result of unavoidable variations in specimen size, in counting, and in the experimental techniques. These were calculated from statistical studies wherever possible; otherwise they were estimated.

In the plasticizer studies which followed, 36 Cordura filaments were mounted for each test series; of these about 25 gave measurable frequency readings at the three test levels and, accordingly, the stiffness calculations were based only on them. Similarly, 72 rayon fibers were mounted for each plasticizer test and roughly 50 were satisfactory. Finally, in the sheet experiments, 30 strips were prepared for each interval and, with only isolated exceptions, all were acceptable for the calculations. It is true that probable errors

in the vibration method might have been reduced even farther by increasing the number of specimens tested. However, this would have prolonged the time required for testing proportionately, and errors from air leakage in the test chamber would have become increasingly significant.

It is important to distinguish between errors which affect only absolute values and those which also alter the relative values-- i.e., the percentage change in stiffness produced by a given change in relative humidity for any particular plasticizer content. Since the same mounts were used for the tests at all three relative humidities, differences in the shapes, density, or diameters of the fibers or in the caliper of the sheets had no effect on the relative changes in average stiffness. Furthermore, since accurate absolute values were unnecessary, the lengthy stiffness calculations were shortened immeasurably by determinations of average fiber length and average resonance frequency. Then instead of calculating the stiffness of each fiber separately and averaging these, a single average stiffness based on average fiber length and average resonance frequency was calculated in one operation. Early calculations made by both methods showed that the shorter procedure gave absolute values which were 6 to 8 per cent low. However, this shorter method made no significant difference in the relative stiffness values and, therefore, it was adopted for all subsequent calculations.

However, even the relative values were subject to certain unavoidable variations, and these were considered in detail. Thus, for fiber studies, there were four probable errors:

1. Reading errors in length measurements caused principally by parallax and free play in the moving stage of the comparator. The standard deviation here was 0.03 mm. For 25 Cordura filaments, this produced a standard error of 0.64 per cent in the mean flexural rigidity; similarly for 50 ramie fibers the standard error was 0.48 per cent.

2. Reading errors in length measurements caused by fiber curl. This was never observed in the Cordura filaments but did interfere to a limited degree in the ramie studies. An error of 1 per cent in the average length was estimated, and this corresponded to a standard error in the mean flexural rigidity of 4 per cent for the ramie.

3. Reading error in frequency measurements on the variable oscillator. A standard error of 1.6 per cent was calculated for single readings. For 25 Cordura filaments, this produced a standard error of the mean stiffness of 0.7 per cent; for the 50 ramie fibers, it was 0.5 per cent.

4. Errors caused by changes in the relative humidity during testing operations. If the chamber relative humidity ever drifted more than 5 per cent, the tests were discontinued until the original level had been regained. Assuming a maximum change in the average relative humidity of 3 to 4 per cent, the standard error of the mean stiffness was roughly 4 per cent for both ramie and Cordura.

In a similar manner, the probable errors in studies of ramie sheet stiffness were:

1. Errors as a result of variations in the free lengths of the test strips after clamping. To evaluate this, 30 strips were clamped

in position for testing and their free lengths were then measured with the Gortner comparator. A standard error of 0.1 per cent in the mean length was obtained, corresponding to a standard error of 0.4 per cent in sheet stiffness for 30 tests.

2. Errors in frequency readings caused by variations in the clamping pressure. Repeated clamping at the same relative humidity produced no significant change in the resonance frequency of a test strip, but some variation was expected between different humidity test levels. Assuming that this produced a standard deviation of 10 cycles per second for single readings, a standard error of 2.4 per cent in the mean stiffness would have resulted.

3. Reading errors in frequency measurements with the oscilloscope. An error of 1.6 per cent had been calculated for single readings. For 30 radio strips, this produced a standard error of 0.6 per cent in the mean stiffness.

4. Errors from changes in the relative humidity during testing. A maximum change of the average relative humidity of 3 to 4 per cent was assumed. Since sheets are much less responsive than fibers to transient fluctuations in the relative humidity, the error in mean stiffness for the sheets was estimated to be 2 per cent.

Then the combined effects of these expected variations in the relative stiffness values were determined. The results are presented in Table II, where the total variations are expressed as the over-all standard errors of the average stiffness values.

TABLE II

STANDARD ERROR IN THE DETERMINATION OF STIFFNESS

Test Material	Number of Test Specimens	Standard Error of Mean Stiffness, s
Corduroy filaments	25	4.1
Ramie fibers	50	5.7
Ramie sheets	30	3.2

EFFECTS OF PLASTICIZERS ON THE FLEXURAL RIGIDITY OF COTTON FIBERS

With the development of a satisfactory test method for the evaluation of sheet and fiber stiffness, it was possible to proceed to a study of the various softening agents. Specifically, data were desired to show how the flexural rigidity of a fiber varied with its moisture content, with its plasticizer content, and with the character of the plasticizer molecule. If, for example, the degree of paper softening was related in any way to the number of certain functional groups in the plasticizer molecule or to its dimensions, this effect might be apparent in the fiber stiffness as well.

Speel (35) reported that increasing the chain length of the polyalcohols decreased their hygroscopicity and, hence, their plasticizing effect on paper. Thus, ethylene glycol imparted greater initial flexibility to the sheet than did glycerin, although the effect was only temporary, because of the former's volatile character. Glycerin, in turn, was more effective than sorbitol.

On the other hand, Reed (3) compared the degree of softening produced in plasticine by a series of aliphatic esters of gluconic acid. He stated that the plasticizing action apparently increased with the size of the esterifying alcohol molecule. His conclusions, however, were based on folding endurance, tensile strength, stretch, and tearing strength data.

Briefly, then, the second phase of the experimental program, a comparative study of selected softening agents, was designed to

produce data in answer to such questions as the following:

How does fiber stiffness vary with water content?

Does fiber softening depend on the size of the plasticizer molecule?

Does fiber softening depend on the number of functional groups in the plasticizer molecule?

How is the fiber softening produced by purely humectant agents related to the water content of the fibers?

How is fiber softening related to fiber swelling?

How is fiber stiffness affected by such common commercial plasticizers as glycerin and urea?

The experimental work was restricted to Cordura, whose low crystallinity made it more sensitive than rayon to softeners. In the studies of all plasticizers except water and the aliphatic alcohols, the tests were carried out in the presence of water vapor at three relative humidity levels: 93, 50, and 11 per cent. Softening agents were introduced into the filaments by overnight immersion of the Cordura in aqueous solutions of the required plasticizer concentration. The filaments were pressed twice between dry blotters for two minutes apiece under pressures of 50 pounds per square inch to remove the excess softener solution and allowed to come to equilibrium at 50 per cent R.H. They were mounted, trimmed, and measured for length at this humidity before the test cycle was begun.

TABLE II

The effect of water on the stiffness of Cordura filaments was determined by vibration measurements at seven humidity levels. Before the conditioning cycle was begun, vibration tests were made at 50 per cent R.H.; then the normal cycle of tests was made at relative humidities of 93.9, 75.5, 53.5, 32.9, 11.1, and approximately 0 per cent. Calculations were based on the 26 filaments that had shown resonance vibrations in the acceptable frequency range at all test levels.

The hygroexpansivity was determined in a similar manner by conditioning duplicate Cordura loops at the various humidity levels in their order of vibration testing. Moisture content values were obtained by weighing duplicate samples at equilibrium with these same humidities in accordance with the procedure described by Vink (33). The stiffness data are summarized in Table III and Figure 4.

TABLE III

EFFECT OF WATER CONTENT ON STIFFNESS OF CORDURA FILAMENTS
 BEFORE VIBRATION TESTS

Relative Humidity, %	Water Content (Overdry Basis), %	Change in Length, %	Flexural Rigidity, (Dyne-cm. $\times 10^2$)
50	10.7	0	4.45
67	20.3	1.2	2.85
74	18.1	1.0	3.10
93	13.5	0.8	3.55
37	10.2	0.1	3.05
14	5.8	-0.4	4.35
0 (approx.)	2.1	-1.9	4.50

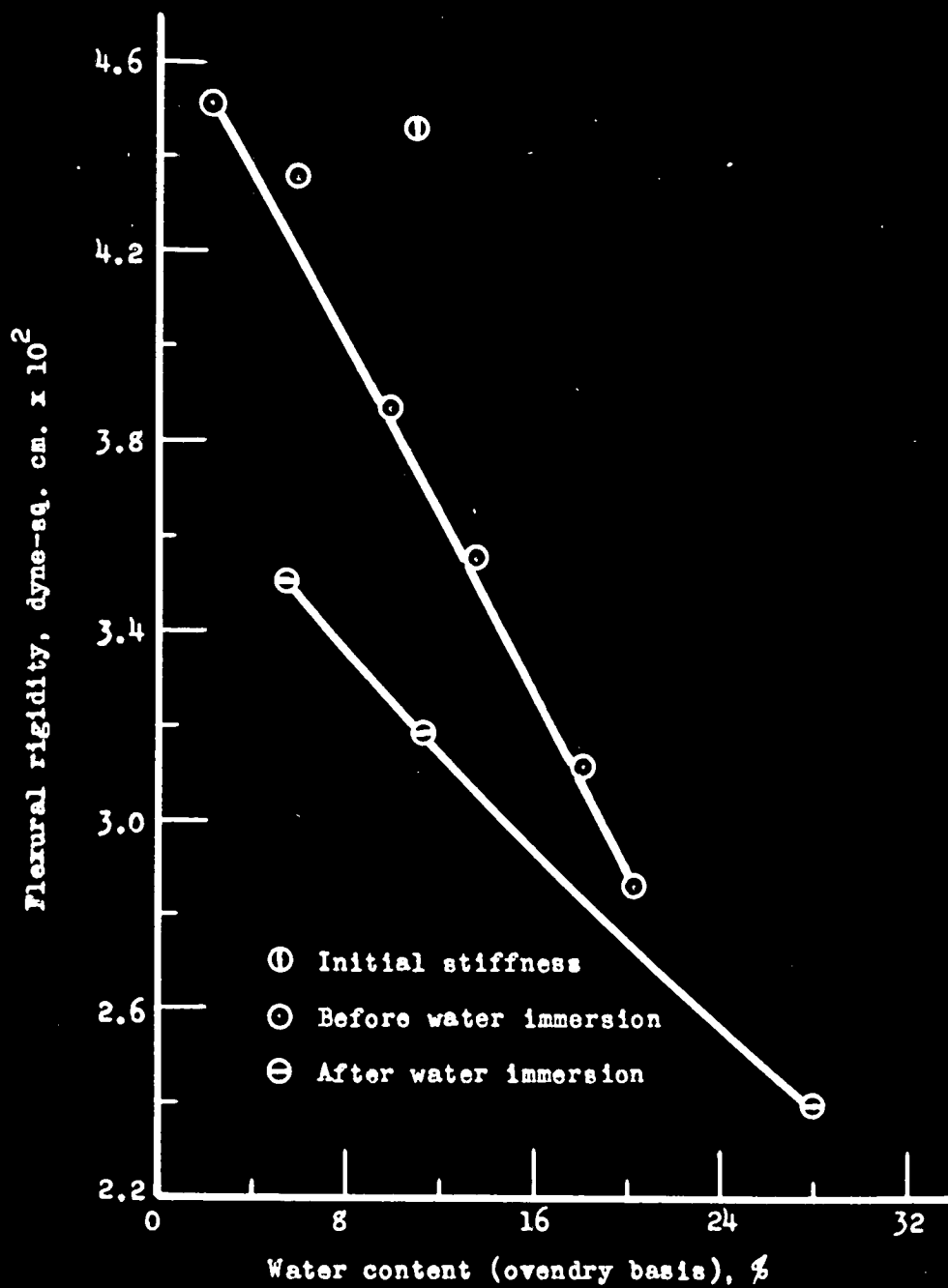


FIGURE 4

Effect of Water Content on Stiffness of Cordura Filaments

Figure 4 indicates that, between 93 and 11 per cent R.H., the flexural rigidity varied inversely as the water content of the filaments. It is also evident that exposure of the filaments to a high relative humidity produced an irreversible loss in initial stiffness, for the original rigidity at 50 per cent was regained only after drying at roughly 0 per cent R.H. Probably internal strains produced in the manufacturing operation were relaxed at the high humidity levels by the penetration of water and subsequent swelling of the filaments. Such abnormal strains would not reform in natural drying at the lower test levels.

It must be remembered that these data are for dry Cordura filaments, which had not been exposed to liquid water. In subsequent studies of softening agents, however, the filaments were immersed in aqueous solutions of the plasticizers. Therefore, to provide a true base for comparisons, the untreated Cordura filaments should have been tested only after a similar immersion in water. Such data for water-soaked Cordura were obtained in the blank determinations of four independent studies of other plasticizers. Although these results will be considered individually later, they are summarized in Table IV and Figure 4 to illustrate the effectiveness of water itself as a plasticizer.

Because variations in average filament diameters affect the absolute stiffness values, comparisons of different sets of filaments should be made only on a relative basis. For that reason, changes in stiffness with relative humidity are presented as a percentage of the stiffness at 50 per cent R.H.

TABLE IV

EFFECT OF WATER CONTENT ON STIFFNESS OF COTTON FILAMENTS AFTER IMMERSSION IN WATER

Relative Humidity, %	Water Content (Ovendry basis), %		Change in length, %		
	93%	50%	11%	$\frac{EI_{93}}{EI_{50}}$	$\frac{EI_{11}}{EI_{50}}$
93	27.8		0.8		
50	11.2		0.2		
11	5.3		-0.5		
Source of Data	Flexural Rigidity, dyne-sq. cm. x 10 ²				
	93% R.H.	50%	11%	$\frac{EI_{93}}{EI_{50}}$	$\frac{EI_{11}}{EI_{50}}$
Glycerin study	2.40	3.30	3.55	72.8	107.7
Glycol and sorbitol	2.30	3.10	3.50	74.3	113.0
Urea and calcium chloride	2.40	3.15	3.45	76.2	109.4
Formamide	2.40	3.15	3.50	76.2	111.3
Average	2.37	3.17	3.50	74.9	110.3
Standard deviation	0.04	0.07	0.03		

The standard deviation of the stiffness at each level was calculated to show the expected variation in absolute values. These data were employed later to determine if the apparent softening of any plasticizer was real or simply the result of expected variation in filament properties.

Figure 4 shows that the plot of average filament stiffness against water content is roughly linear in the range studied. The slope levels off somewhat at the high humidity, indicating that the last increments of water may have been held by capillary condensation, so that they had little effect on the fiber stiffness.

A comparison of Tables III and IV demonstrates that the immersion in water raised the moisture contents of the filaments at the test humidity levels. However, this increase in sorption capacity alone cannot explain the decrease in stiffness shown in Figure 4, for at equal moisture contents the water-soaked filaments were consistently less stiff than the dry filaments. This difference in rigidity was especially noticeable at the lower humidities. It seems probable that the immersion in water caused pronounced filament swelling, and this was not entirely lost as the filaments were dried. Thus, at low humidities, these swollen filaments were significantly softer than the others. However, as the humidity was raised, it produced some swelling of the unsoaked filaments and, accordingly, the difference in stiffness between the two series was reduced.

ALIPHATIC ALCOHOLS

Since the plasticizing effect of water has frequently been attributed to its hydroxyl group, a similar degree of softening might be expected with alcohols. Therefore, studies of stiffness were made on Cordura filaments containing the lower aliphatic alcohols. Frey-Hessling and Reich (36) showed by a study of the indices of refraction that such alcohols will penetrate cellulose fibers, and Hermann (34) actually observed the penetration of methanol and ethanol into his model viscose filaments.

In order to secure maximum retention of the alcohols on Cordura, the filaments were first swollen by exposure to a high relative humidity or by immersion in liquid water. However, subsequent

analyses indicated that subsequent immersion of these moist filaments in the alcohols did not effect a quantitative displacement of the water, except in the case of methanol. Therefore, to avoid the complexities of an alcohol-water-cellulose system, the fibers were immersed in water, pressed, conditioned at 50 per cent R.H., mounted, and measured for length. Then they were brought to dryness in the test chamber at approximately 0 per cent R.H. and their resonance frequencies were determined. The work of Russell, Measa, and Campbell (37) had shown that such immersion in water raised the alcohol sorption capacity of cellulose fibers, even when this was followed by drying at 0 per cent relative humidity. After the first series of vibration tests had been completed, the chamber was brought to equilibrium with a water-free, alcohol-saturated atmosphere. The vibration tests were repeated at this maximum level of alcohol retention.

Previous studies by weight measurements of alcohol adsorption on Cordura had established the relationship between alcohol adsorption and the vapor pressures for each of the aliphatic alcohols. Thus, by proper control of the relative vapor pressure, it was possible to vary the alcohol content of the test mounts, and vibration tests were made at three to five retention levels along the desorption curve. With increasing chain length, however, the sorption of the alcohols fell off rapidly and, therefore, no alcohols above propanol could be studied.

The data are summarized in Table V, where the values obtained in the study of the effect of water on dry Cordura are included for comparison. In this table, the relative effect of each softener

TABLE V
EFFECT OF ALIPHATIC ALCOHOLS ON STIFFNESS OF CORNURA FILAMENTS

Softener	Filaments Tested	Wendry %	Softener Content Koles x 10 ⁴ per gram of fiber	Length Change, %	EI, dyne-sq. cm. x 10 ²	EI/EI ₀
Water	25	2.1	0.0	-1.9	4.50	100
		20.3	103.3	1.2	2.85	63
		18.1	88.8	1.0	3.10	69
		13.5	63.3	0.8	3.55	79
		10.5	46.7	0.1	3.85	86
		5.8	20.5	-0.4	4.35	97
Methanol	19	0.0	0.0	-1.9	5.05	100
		15.2	47.5	-1.6	4.40	87
		12.0	37.5	-1.7	4.55	90
		8.2	26.1	-1.7	4.80	95
		3.9	12.2	-1.8	4.90	97
		0.0	0.0	-1.9	4.85	100
Ethanol	26	4.2	9.0	-1.5	4.75	98
		3.1	6.8	-1.6	4.85	100
		1.0	2.1	-1.7	4.80	99
		0.0	0.0	-1.9	4.85	100
Propanol	36	0.0	0.0	-1.9	4.25	100
		4.0	6.7	-1.7	4.25	100
		2.3	3.9	-1.8	4.30	101

is calculated on the basis of its original stiffness at roughly 0 per cent R.H. The dimensional changes are based on the filament length at 50 per cent R.H., after immersion in the water but before drying at 0 per cent R.H.

Since filaments dried at roughly 0 per cent R.H. in the test chamber still retained an average of 2.1 per cent water, this moisture content was employed as the baseline in Table V. Thus, the "moles of water" represent the difference between the true water content and this residual 2.1 per cent value.

In the range studied, methanol appeared to be as effective, molecule-for-molecule, as water in reducing the stiffness of Cordura. This is illustrated in Figure 5. The changes produced by ethanol and propanol were too small to be significant. Conceivably their molecules were too large to swell and penetrate the filaments. Hermans (34) had observed that ethanol penetrated his dry viscose rayon filaments only after several days' exposure. Consequently, the alcohol molecules may have been retained on the external surfaces, where they would have no effect on fiber stiffness.

These data emphasize the close relationship between softening and swelling and confirm the findings of Aress and Bialkowsky (14). They reported that increasing the chain length of aliphatic alcohols reduces their swelling efficiency in cellulose fibers. It is not, however, correct to conclude that the softening effect itself is less for ethanol than for methanol. If water-swollen filaments had been immersed

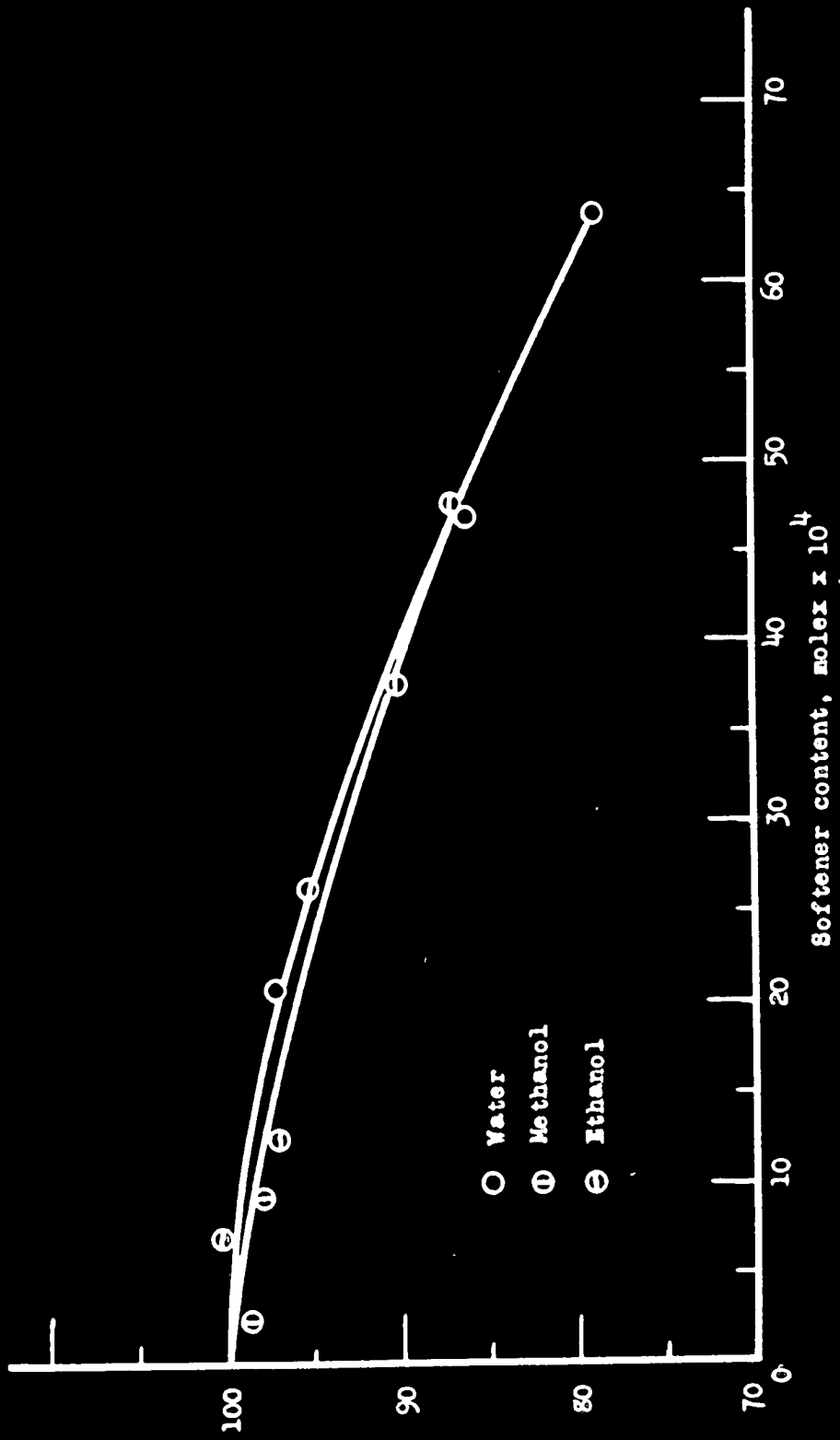


FIGURE 5
Effect of Water and Aliphatic Alcohols on Stiffness of Cordura Filaments

in these alcohols, so that thorough penetration of each was obtained, quite different trends might have been observed.

POLYHYDRIC ALCOHOLS

This class of compounds includes many of the common commercial plasticizers employed in the paper industry. They were selected for the present investigation not only because of their practical significance, but because it was hoped that such test data might indicate the influence of the number of hydroxyl groups in the plasticizer molecule.

Ethylene glycol, glycerin, and sorbitol were added to the filaments from aqueous solutions according to the standard procedure, and the retention values were determined by a periodic oxidation analysis developed by Malaprade (38) and modified by Allen, Charbonnier, and Coleman (39). Hydroexpansivity and moisture sorption values were determined in the usual manner.

Ethylene Glycol

The results of this study were only approximate, because the glycol was gradually lost from the filaments by evaporation. Since the mounted filaments were conditioned at 93 per cent R.H. for 48 hours, it was probable that most of the softener had been lost before the vibration tests began, leaving the filaments somewhat swollen, perhaps, but essentially glycol-free. Moisture sorption data indicate that the glycol increased the water content of the filaments at a high relative

humidity but reduced it at the lower levels. In the calculations of flexural rigidity, the original glycol content was employed in the weight factor, since the exact retention at the time of testing was indeterminate. Thus, the stiffness values are erroneously high, and the actual loss in stiffness produced by the glycol is certainly greater than indicated.

TABLE VI

EFFECT OF ETHYLENE GLYCOL ON STIFFNESS OF CORDURA FILAMENTS

Glycol, %	Filaments Tested	Relative Humidity, %	Length Change, %	Water Content, %	$\frac{EI}{\text{dyne-sq. cm.} \times 10^2}$
0	24	93	0.8	27.8	2.30
		50	0.0	11.2	3.10
		11	-0.5	5.3	3.50
5.4	21	93	1.0	31.0	2.25
		50	0.0	11.5	2.85
		11	-0.5	3.5	3.35

According to the data in Table IV, the standard deviation of the flexural rigidity of untreated filaments at 50 per cent R.H. is 0.07. In Table VI, the observed deviation between the stiffness values of treated and untreated filaments is 0.25. It is probable, therefore, that ethylene glycol had a significant flexibilizing effect on the Cordura filaments at 50 per cent R.H. but no more definite conclusions may be drawn from these data.

Glycerin

Glycerin is one of the most effective commercial plasticizers employed in the paper industry, and Leffingwell and Lesser (7) have

described its properties in some detail. More recently, its effect on sheets produced from cotton linters has been investigated by McPherson (5), who studied the concepts of plasticizing by lubrication and by reduction in fiber bonding.

No data are available, however, to indicate the influence of glycerin on the stiffness of individual fibers. Some softening might well be expected, for Hermans (34) had observed that aqueous solutions of glycerin penetrated viscose filaments for all concentrations of glycerin under 70 per cent by weight. Above that value, the glycerin was retained on the surface of the filaments, for there was insufficient water present to produce the necessary swelling.

In the present study, bath concentrations ranged from 0 to 50 per cent glycerin. Three levels of glycerin-treated filaments were prepared; the test data are summarized in Table VII.

TABLE VII
EFFECT OF GLYCERIN ON STIFFNESS OF CORIURA FILAMENTS

Glycerin, %	Filaments Tested	Relative Humidity, %	Length Change, %	Water, %	$\frac{EI}{l}$, dyne-sq. cm. x 10^2
0.0	16	93	0.8	27.8	2.40
		50	0.0	11.2	3.35
		11	-0.5	5.3	3.55
5.9	14	93	1.0	35.3	2.00
		50	0.0	10.8	3.05
		11	-0.4	3.8	3.75
14.1	11	93	0.8	49.6	2.20
		50	0.0	11.9	3.30
		11	-0.4	4.7	3.85
27.3	16	93	0.5	86.0	2.00
		50	0.0	11.8	2.90
		11	-0.2	3.8	3.70

It should be noted that the number of filaments tested at each glycerin level was less than usual and, accordingly, the absolute values for average stiffnesses were subject to greater probable error. The initial conditioning period of 24 hours proved to be insufficient for equilibrium and, therefore, it was necessary to repeat these high humidity vibration tests after the entire testing cycle had been completed. Consequently, the number of acceptable mounts was reduced.

The moisture sorption data showed that, at high humidities, glycerin raised the water content of the filament markedly. Below 50 per cent, however, the total moisture contents of the treated filaments varied only slightly with their glycerin contents. Differences in the stiffness at these lower levels cannot be attributed, though, to the softening action of the glycerin molecules per se, for the water contents actually available for flexibilizing the filaments were not necessarily equal.

A graph of filament stiffness against the molar content of the water per gram of fiber showed that the flexibilizing of treated filaments in the low moisture range could not be explained simply by their increase in water content. This is illustrated in Figure 6. Apparently, the glycerin molecule had some softening effect beyond that resulting from its humectant properties. In order to compare the effectiveness of these molecules of glycerin and water in plasticizing, flexural rigidities were plotted against the moisture content plus the effective glycerin content. Various ratios of glycerin and water were examined to determine which assumed equivalence of glycerin showed the

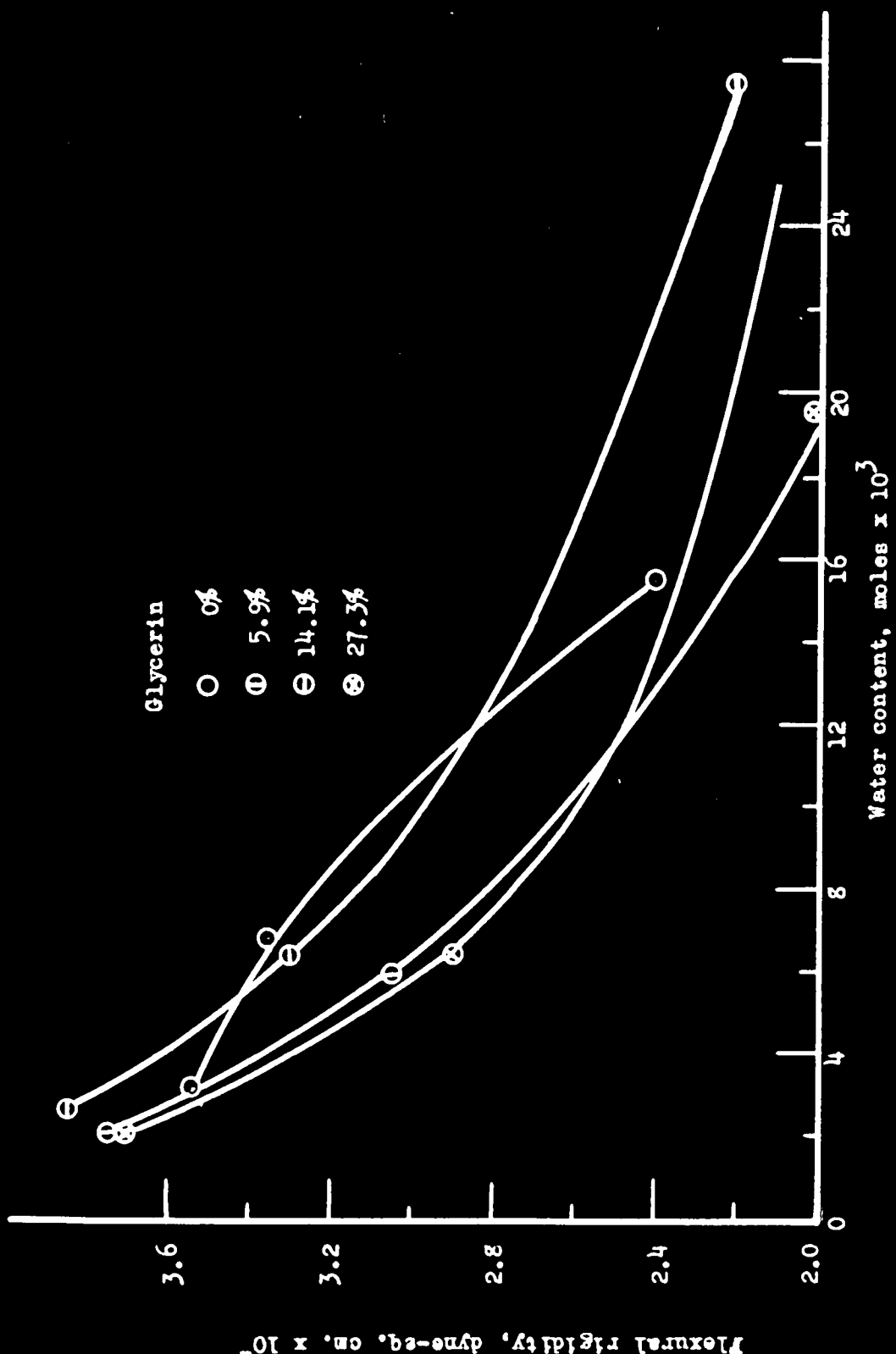


FIGURE 6

Effect of Water Content on Stiffness of Gels Containing Glycerin

best correlation with decrease in stiffness. Such comparative plasticizing effects are admittedly crude and should not be interpreted too closely.

The most satisfactory correlations were obtained when one molecule of glycerin was assumed equivalent to one or two molecules of water, but there was little choice between these two (see Table 1 and 5). In his study of sheet stiffness, McPherson (1930) found the best correlation when one molecule of glycerin was assumed equivalent to two molecules of water. It should be remembered that such assumed equivalences are probably statistical in nature and therefore, only indicative of trends. For all practical purposes, glycerin was considered less effective molecule-for-molecule than water. The spread in plotted values was excessive.

When filament stiffness was plotted against the combined glycerin and water molar content, the curves obtained for those filaments containing 5.9% glycerin and 11.8% water for the untreated filaments, the graph was similar to that shown in Figure 4. Figure 4 shows that the stiffness varied as the square of the molar content. The semilogarithmic plot for 27.1% glycerin and 54.2% water curved upward, indicating that the later additions of glycerin were less effective than the first in softening the filament.

To summarize, it is evident that glycerin has a definite softening action of its own, which is more effective as water on a molar basis. From

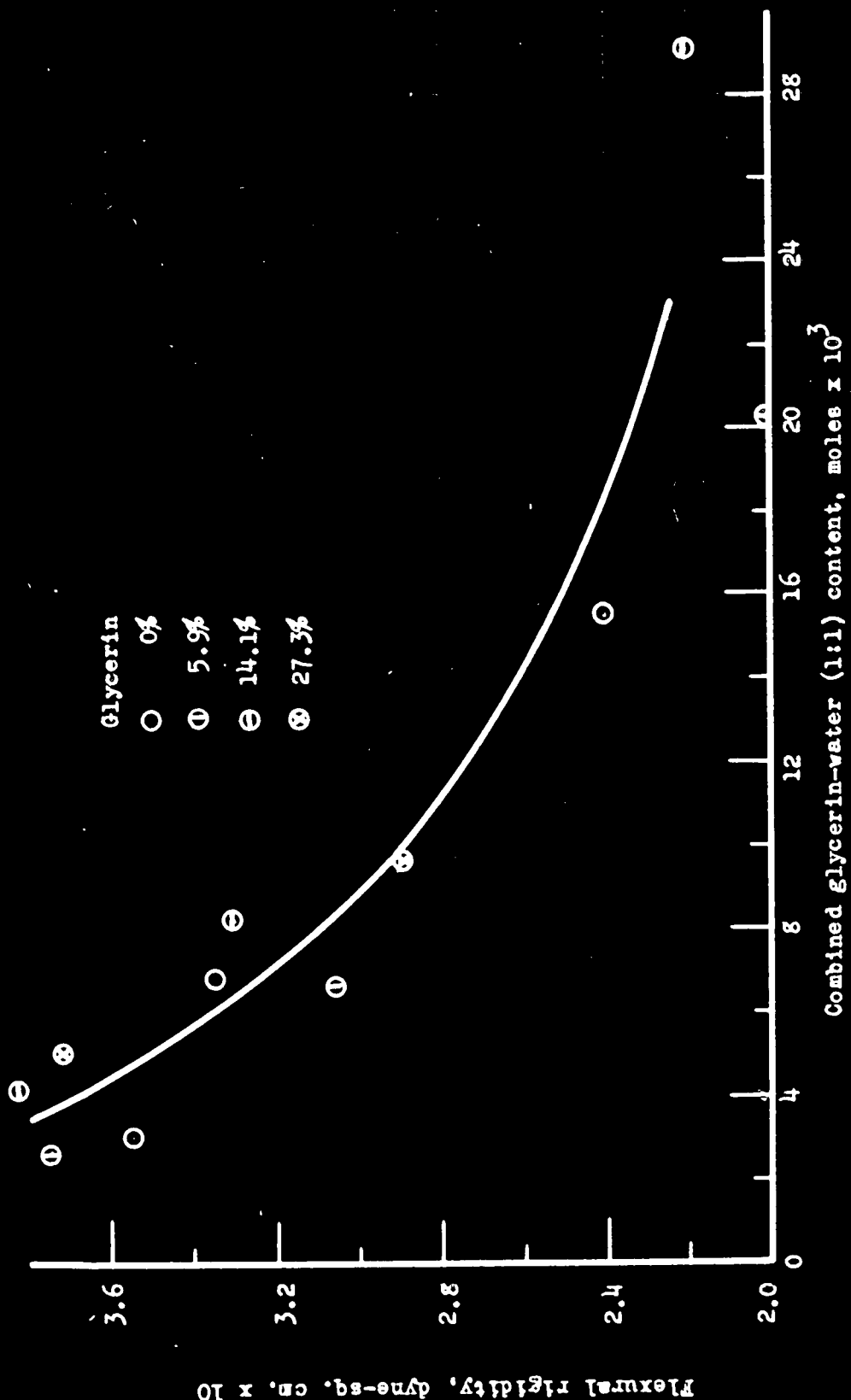


FIGURE 7

Effect of Glycerin and Water on Stiffness of Cordura

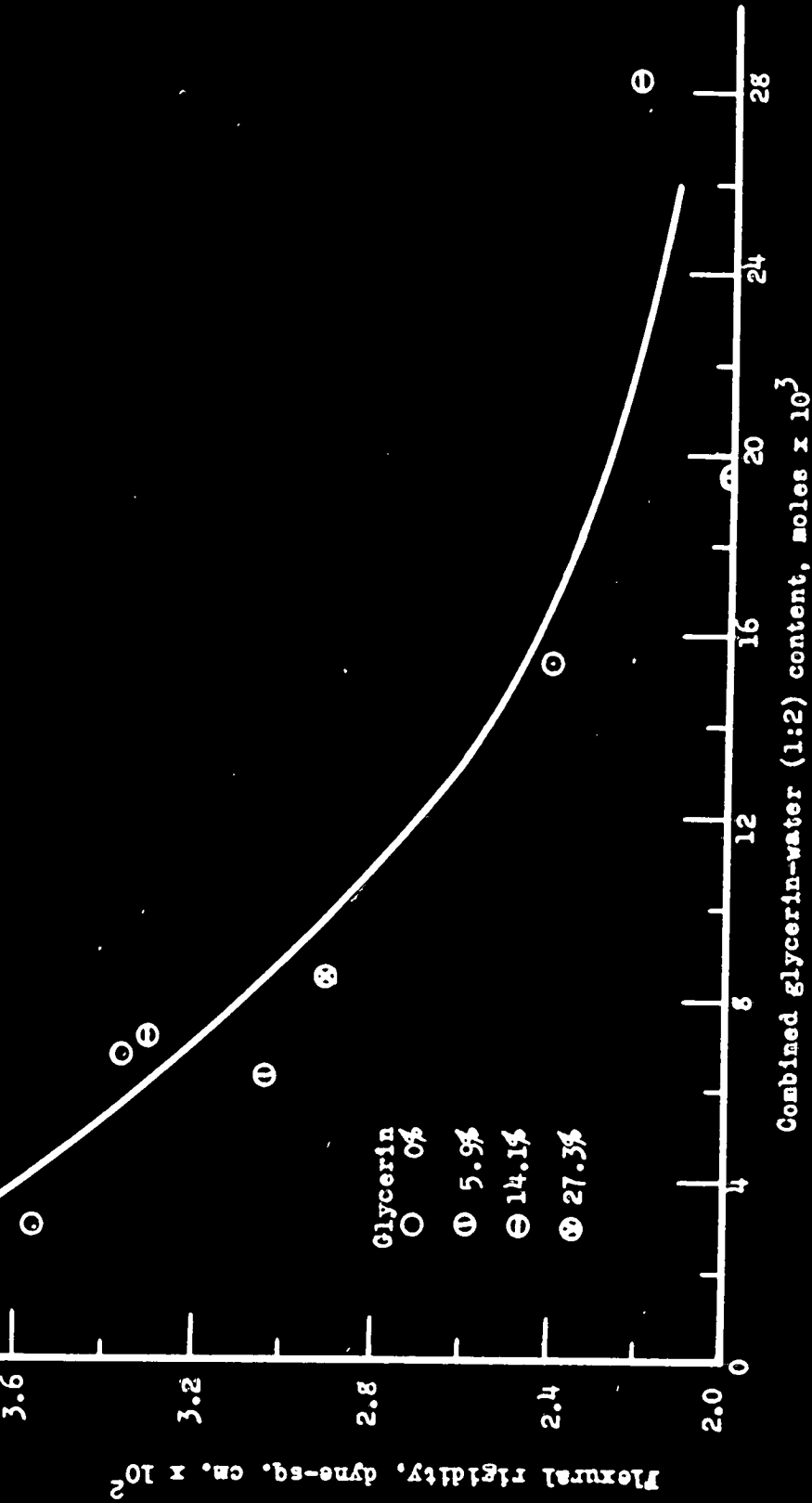


FIGURE 8

Effect of Glycerin and Water on Stiffness of Cordura

however, a molecule of glycerin is not equivalent to three molecules of water. Because of the spatial configuration of the hexose units in the cellulose chains, it is hardly likely that all three hydroxyl groups of glycerin would be attracted to corresponding hydroxyl groups.

Sorbitol

This plasticizer finds limited use in the paper industry and was chosen here to complete the study of the homologous series containing methanol, glycol, and glycerin. Moisture sorption measurements at the three relative humidity test levels showed that sorbitol was only moderately hygroscopic at a high humidity, and it reduced the water content of the filaments at low humidities. In this respect, it was similar to glycerin and glycol. The test data are presented in Table VIII.

TABLE VIII

EFFECT OF SORBITOL ON STIFFNESS OF CORDURA FILAMENTS

Sorbitol, %	Filaments Tested	Relative Humidity, %	Length Change, %	Water, %	EI, dyne-sq. cm. x 10 ²		
0	24	93	0.8	27.8	2.30		
		50	0.0	11.2	3.10		
		11	-0.5	5.3	3.50		
6.3	26	93	0.8	32.6	2.05		
		50	0.0	12.8	2.90		
		11	-0.3	5.2	3.55		
17.1	26	93	0.8	38.1	2.00	--	--
		50	0.0	9.9	3.30	3.95	3.75
		11	-0.3	2.3	1.75	6.20	5.10

In order to check the apparent stiffening observed with filaments containing 17.1 per cent sorbitol at the low and medium relative humidities, two independent series of similar filaments were tested; their data are included in Table VIII. Stiffness values for these mounts could not be determined at 93 per cent R.H., for the filaments were too long to give resonance vibrations in the acceptable frequency range. When rigidity values for the three runs were averaged, it was apparent that the high sorbitol content flexibilized the filaments only in the high humidity range, and this was probably because of the softener's humectant character. At lower humidities, however, the high sorbitol content actually stiffened the filaments. Such stiffening was too great to be attributed simply to the slight reduction in the filament's moisture content at 11 per cent R.H. caused by the sorbitol. Conceivably, the sorbitol had crystallized inside the filament or on its outer surface, forming a continuous sheath which increased the resistance of the filament to bending.

The effect of the lower sorbitol content, however, was different. At 11 per cent R.H. it produced no significant softening or stiffening. At 50 per cent R.H., though, the difference in stiffness between the treated and untreated filaments was 0.20×10^{-2} dyne-sq. cm.; since the standard deviation of the average stiffness for the untreated filaments was 0.07, it seems probable that the 6.3 per cent sorbitol had a slight flexibilizing effect. Further softening was observed at the 93 per cent R.H. level, and this can probably be explained entirely by the hygroscopic properties of sorbitol.

Graphs were made of filament stiffness against various proportions of sorbitol and water to determine the relative effectiveness of sorbitol molecules as such in the softening mechanism. These graphs were not especially enlightening, however, because the molar content of sorbitol present was very small compared with that of the water. An assumed equivalence of one sorbitol to one water molecule gave a slightly smoother curve than one of stiffness against the molar content of water alone, but the difference was within the range of probable experimental errors.

On the basis of the total hydroxyl contents, it was apparent that the sorbitol molecule was not six times as effective as water in reducing filament rigidity. In light of the spatial configuration of the hydroxyl groups in the cellulose chains, this is not at all surprising. It does suggest, however, that the degree of softening depends more upon the ability of the plasticizer molecule to swell and penetrate the fibers than simply upon its hydroxyl content.

When plotted against the logarithm of the water content alone (Figure 9), the stiffness values of filaments containing sorbitol fall along straight lines.

CALCIUM CHLORIDE

In order to determine how the softening produced by purely humectant agents was related to the total water content of the treated filaments, the effect of calcium chloride on fiber rigidity was investigated. Calcium chloride is an example of a hygroscopic material

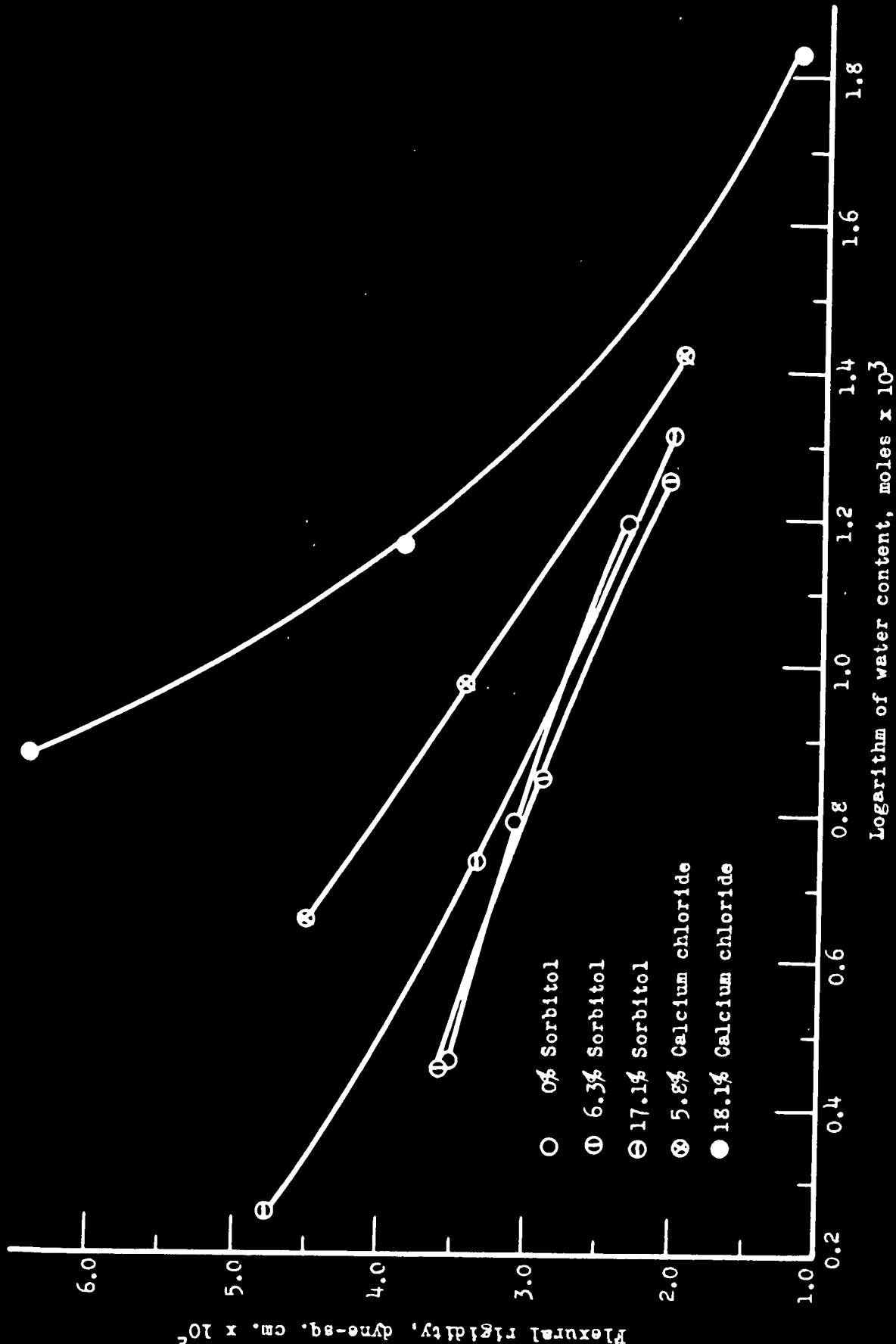


FIGURE 9

Effect of Water on Stiffness of Cordura Containing Sorbitol and Calcium Chloride

employed occasionally in the industry to produce softening at high relative humidities. In drier atmospheres, however, abnormal stiffening of the sheet is commonly reported.

Unlike the polyhydroxy plasticizers described previously, all of which reduced the moisture sorption of the treated filaments at low relative humidities, calcium chloride actually increased it, as shown in Table IX. In more humid atmospheres, of course, the equilibrium water content was unusually high.

TABLE IX

EFFECT OF CALCIUM CHLORIDE ON STIFFNESS OF CORDURA FILAMENTS

Calcium Chloride, %	Filaments Tested	Relative Humidity, %	Length Change, %	Water, %	EI, dyne-sq. cm. x 10 ²
0	25	93	0.8	27.8	2.40
		50	0.0	11.2	3.15
		11	-0.5	5.3	3.45
5.80	27	93	0.5	47.9	1.90
		50	0.0	16.3	3.40
		11	-0.5	8.2	4.50
18.07	27	93	0.5	120.0	1.20
		50	0.0	27.3	3.85
		11	-0.5	13.5	6.40

A study of the moisture sorption capacities of calcium chloride alone, of untreated Cordura alone, and of the two in combination with each other, showed that the last was definitely less than the sum of the first two. This loss in sorption capacity may have been caused by mechanical blocking of the available adsorbing surfaces or

by partial satisfaction of the attractive forces on the filament surfaces by the calcium chloride molecules.

Vibration tests were made for calcium chloride contents of 0, 5.8, and 18.1 per cent on the oven-dry basis. The concentration of the humectant on the filaments was measured by ashing weighed samples, sulfating the ash, igniting, and weighing as calcium sulfate.

Because of the wide difference in stiffness values at relative humidities of 93 and 11 per cent and, hence, in the spread between their average resonance frequencies, it was impossible to obtain acceptable frequency readings between 160 and 520 cycles per second at all test levels. Therefore, it was necessary to trim the filaments after the normal cycle of tests had been completed, remeasure their lengths, and repeat the vibration tests at 93 per cent R.H.

A plot of filament stiffness against the relative humidity showed that the flexural rigidities for the three calcium chloride levels were equal at about 65 per cent R.H. At higher humidities, raising the humectant content decreased the stiffness moderately; at the other extreme, it produced a sharp rise in the stiffness. Since a desiccant could essentially strip the filaments of their moisture at very low humidities, the stiffening may be partly the result of the loss in moisture held by the filament itself, even though the total moisture content has been raised. Conceivably, crystallization of the salt in or on the filaments might have increased their resistance to bending even further.

In Figure 9 the filament stiffness values were plotted against the logarithms of the moisture contents. Extension of the curve for the untreated filaments into the region of higher water contents shows that the softening produced by the calcium chloride at the higher relative humidities was never greater than could be explained by the additional water. Apparently, there was no plasticizing action by the calcium chloride molecules themselves, and softening observed at the high humidities was caused by the salt's humectant character.

FORMAMIDE

If, as Connor and Nadelsen suggested (11), fiber swelling and softening are closely related to each other, swelling agents should reduce filament stiffness considerably. Kress and Bialkowsky (14) had shown that formamide was more effective than water in swelling cellulose fibers and, therefore, its effect on the stiffness of Cordura was investigated. Vibration tests were made in the usual manner on filaments with an initial formamide content of 12.0 per cent. This retention value was determined by a modified Kjeldahl analysis employing selenium (40). However, the test results were only approximate, for the formamide was slightly volatile, and its exact concentration on the filaments at the time of testing could only be estimated. Stiffness calculations were based on an approximate formamide content of 2 per cent--a value obtained by a second Kjeldahl analysis of a similar sample after conditioning in the test chamber for four days. This was the normal period required for a complete test cycle at the three relative humidity levels. If the calculations had been based on the

original formamide content, the degree of softening would still have been pronounced.

Even though the data in Table X are only approximate, it is apparent that the formamide had caused a considerable decrease in filament stiffness.

TABLE X
EFFECT OF FORMAMIDE ON STIFFNESS OF CORDURA FILAMENTS

Formamide, %	Filaments Tested	Relative Humidity, %	Water, %	$\frac{EI}{\text{dynes-sq. cm.} \times 10^2}$
0	25	93	27.8	2.40
		50	11.2	3.15
		11	5.3	3.50
2	31	93	33.2	1.70
		50	11.1	2.30
		11	4.5	2.55

UREA

Urea has been used widely commercially, especially in recently patented plasticizing processes. In mill work, it is applied either alone or in chemical combination with other additives, usually inorganic salts. From the standpoint of a fundamental study, however, it seemed better to investigate the effect of urea alone, rather than that of a mixture of compounds.

Hermans (34) observed that saturated urea solutions penetrated viscose filaments, although the rate of penetration was much less than that of pure water. Like glycerin and sorbitol, the urea

reduced the moisture sorption of the Cordura at low relative humidities but raised it considerably at the higher levels. This is evident in Table XI. After the usual test cycle had been completed, it was necessary, as in the calcium chloride study, to repeat the vibration measurements at 93 per cent R.H. on trimmed fibers. Tests were made on filaments containing 0, 11.5, 15.7, and 34.8 per cent urea, after the Kjeldahl analysis described by Poe and Halder (40) had established the plasticizer contents.

TABLE XI
EFFECT OF UREA ON STIFFNESS OF CORDURA FILAMENTS

Urea, %	Filaments Tested	Relative Humidity, %	Length Change, %	Water, %	EI, dyne-sq. cm. x 10 ²
0	25	93	0.8	27.8	2.40
		50	0.0	11.2	3.15
		11	-0.5	5.3	3.45
11.5	19	93	1.0	36.3	1.75
		50	0.0	9.3	2.50
		11	-0.5	2.2	3.25
15.7	27	93	1.0	47.7	1.05
		50	0.0	9.3	2.55
		11	-0.5	2.2	3.40
34.8	21	93	1.0	94.0	1.10
		50	0.0	11.3	2.90
		11	-0.5	2.4	4.30

These data indicate that urea reduced filament stiffness at all test levels and plasticizer contents, except for the highest urea concentrations at 11 per cent R.H. In that single case, some stiffening did occur either as a result of crystallization of the urea or of

partial immobilization of the filament's water content by the urea molecules. At 50 per cent R.H., the difference in stiffness between the treated and untreated filaments was at least 0.26×10^{-2} dyne-cm. This is almost four times the standard deviation of the stiffness of the untreated filaments in Table IV, and so the loss in rigidity cannot be explained by normal variations in the untreated filaments.

Finally, the test data obtained at 93 per cent R.H. show that the rigidity dropped off rapidly as the urea content was raised to 15 per cent on the oven-dry basis. Beyond this, however, further additions of urea did not produce more softening. Perhaps the internal adsorbing surfaces of the swollen filaments were saturated with urea at this level; then additional plasticizer molecules would be retained on the outer surfaces or in gross capillaries, where they would not reduce filament stiffness at 93 per cent R.H. Even in such external positions, however, this excess urea could affect filament stiffness at the low relative humidities by crystallization.

When filament stiffness was plotted against the water content as in Figure 10, it was evident that urea produced a greater degree of softening than could be explained by its humectant properties. As before, a series of graphs was prepared of filament rigidity against various ratios of the plasticizer and water, in order to determine the relative effectiveness of the urea molecules. If the stiffening produced at the 34.8 per cent urea level is ignored, the best correlation exists when two molecules of urea are considered equivalent to one molecule of water, as illustrated in Figure 11. Even this

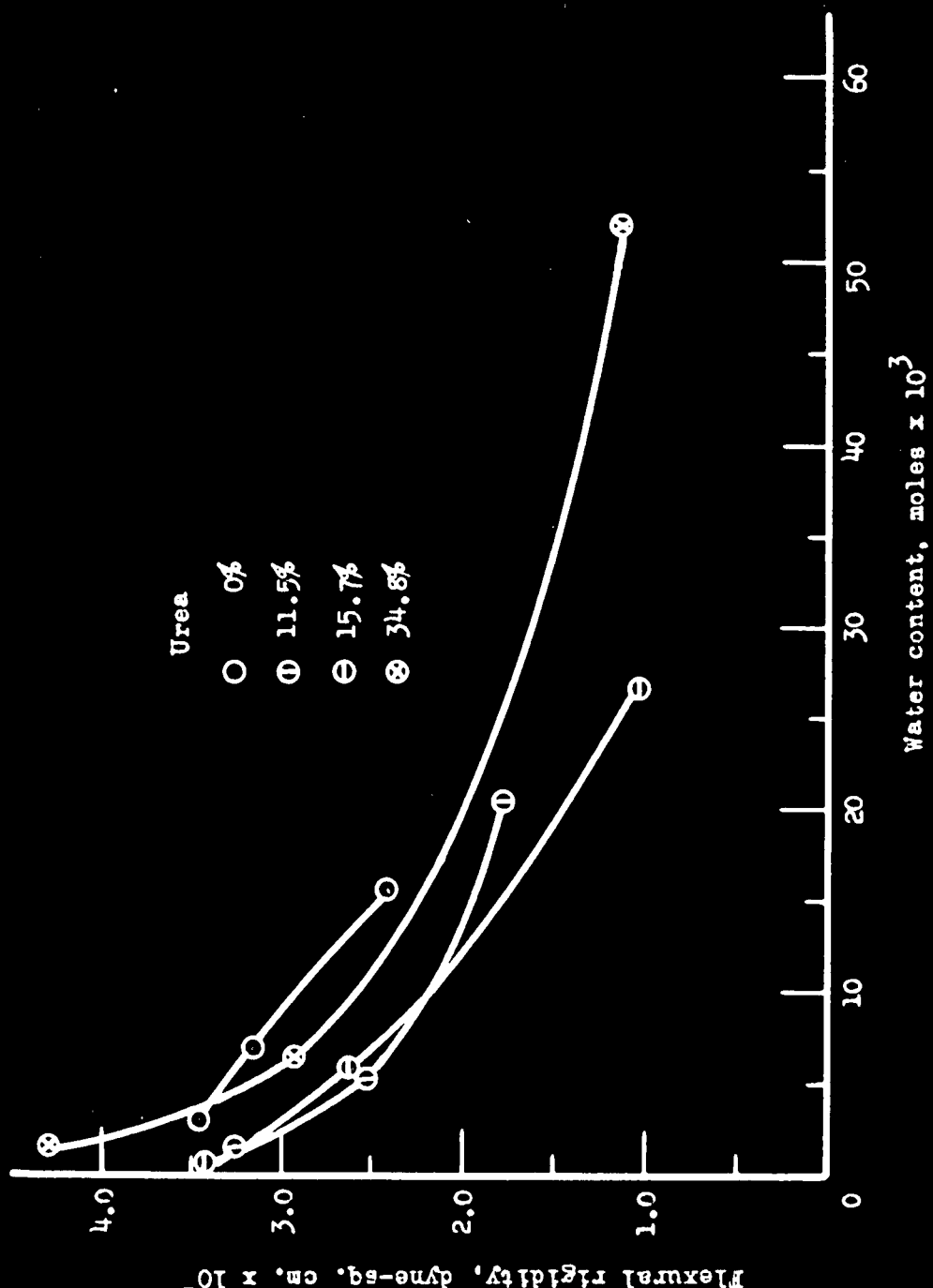


FIGURE 10

Effect of Water Content on Stiffness of Cordura Containing Urea

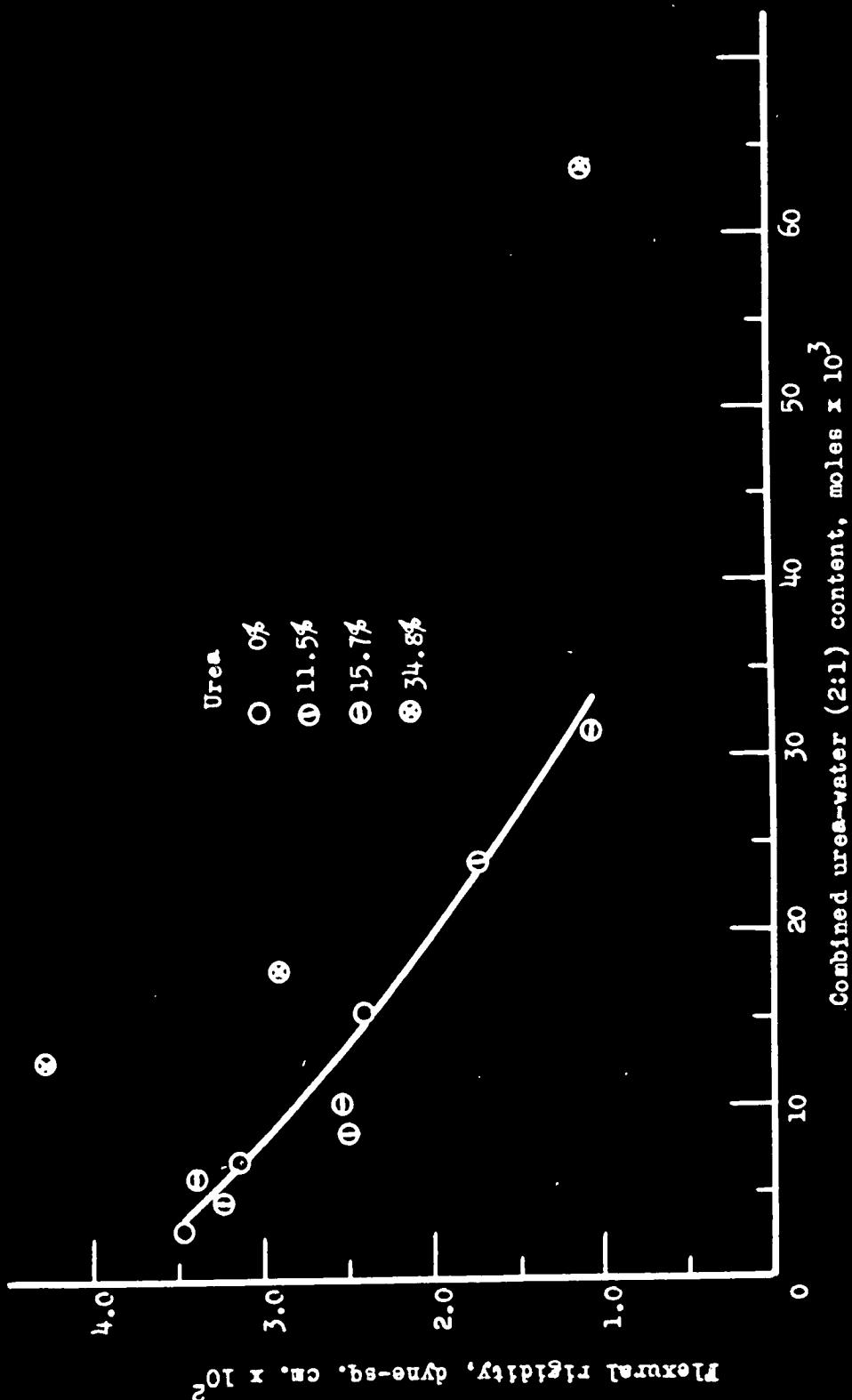


FIGURE 11

Effect of Urea and Water on Stiffness of Cordura

correlation is not especially satisfactory, but it indicates that the effectiveness of the urea molecule per se in the softening mechanism is less than that of a water molecule. Since urea and water are so dissimilar in structure, it is not at all surprising that attempts to correlate their effectivenesses as plasticizers are less acceptable than those of glycerin and water.

CORRELATION OF FIBER STIFFNESS AND SHEET STIFFNESS

The final phase of the experimental program was an attempt to determine the influence of fiber stiffness on that of the sheet. Simple reasoning would seem to indicate that, if such a correlation does exist, it would vary greatly with the degree of bonding in the sheet. Thus, in a dense, well-bonded sheet, fiber stiffness would probably be considerably less critical than the bonding aspects in determining sheet behavior. On the other hand, in an open, slightly beaten sheet, the properties of the individual fibers may be highly significant.

Since Cordura filaments could not be formed into satisfactory sheets, ramie fibers were employed instead. Ramie was expected to be less sensitive than Cordura to the flexibilizing action of plasticizers, because of its lower amorphous cellulose content and, therefore, ramie fiber studies were limited to three of the most effective softening agents--water, glycerin, and urea. Immersion baths of the appropriate concentrations were prepared to produce ramie fibers and sheets with approximately equal plasticizer contents.

Then with fibers and sheets at the same plasticizer levels, stiffness tests were made to show how the softeners affected both. It should be noted, however, that refining the ramie stock prior to sheet formation so reduced the fiber length that stiffness measurements could not be made on individual fibers of beaten ramie. Therefore, it was necessary to employ unbeaten stock for the single fiber tests and beaten stock for the sheet tests. This unavoidable difference may not

interfere with the interpretation of the data, however, for beating does not increase the hygroscopicity or sorption capacity of fibers markedly.

FIBER STIFFNESS

The plasticizing treatment and mounting procedure were similar to those developed for the Cordura tests. The order of testing, however, was reversed, since it seemed probable that fiber trimming would be necessary to yield measurable resonance frequencies at the 93 per cent R.H. level. Therefore, the mounted fibers were tested first at 11 per cent R.H., preconditioned at 93 per cent, conditioned and tested at 50 per cent, trimmed and remeasured for length at 50 per cent and, finally, conditioned and tested at 93 per cent. In this way, the three test levels were approached from the same direction as in the Cordura studies, even though the order of testing was different. Hygroexpansivity determinations showed that changes in the length of the untreated and treated fibers never exceeded 0.1 per cent and, therefore, this factor was ignored in the fiber stiffness calculations.

Water

The effect of moisture content on the flexural rigidity of untreated ramie fibers before immersion in water was investigated early in the experimental program, before refinements in the chamber design and testing procedure had rendered the method less sensitive to fluctuations in the relative humidity. Vibration measurements were made first at 50 per cent R.H. and then at 90, 70, 55, 34, and 15 per cent, in that order. Of the 72 fibers mounted, 57 showed resonance fre-

quencies in the acceptable range at all six test levels and were, therefore, included in the calculations. The test data are presented in Table XII and Figure 12.

TABLE XII

EFFECT OF WATER CONTENT ON STIFFNESS OF UNTREATED RAMIE FIBERS BEFORE IMMERSION IN WATER

Relative Humidity, %	Water Content (Ovendry Basis), %	$\frac{EI}{\text{dyne-sq. cm.} \times 10^2}$
50	5.5	61.0
90	13.0	50.0
70	8.9	55.0
55	6.5	59.5
34	4.2	62.5
15	2.1	67.0

Figure 12 indicates that the initial stiffness value at 50 per cent R.H. fell directly in line with those which followed on the desorption curve after exposure at 93 per cent R.H. It will be recalled that, for Cordura, the initial rigidity had been considerably higher than the corresponding value at 50 per cent after conditioning at 93 per cent. Evidently, swelling of the Cordura filaments at the high humidity had ruptured some internal cross-linkages which did not reform completely on desorption. Ramie's high degree of crystallinity and orientation may have been sufficient to prevent fiber swelling and the resulting rupture of internal bonds.

Since plasticizers were to be applied to ramie fibers from aqueous solutions, however, it was necessary to redetermine the effect of moisture on fiber stiffness only after a comparable immersion of

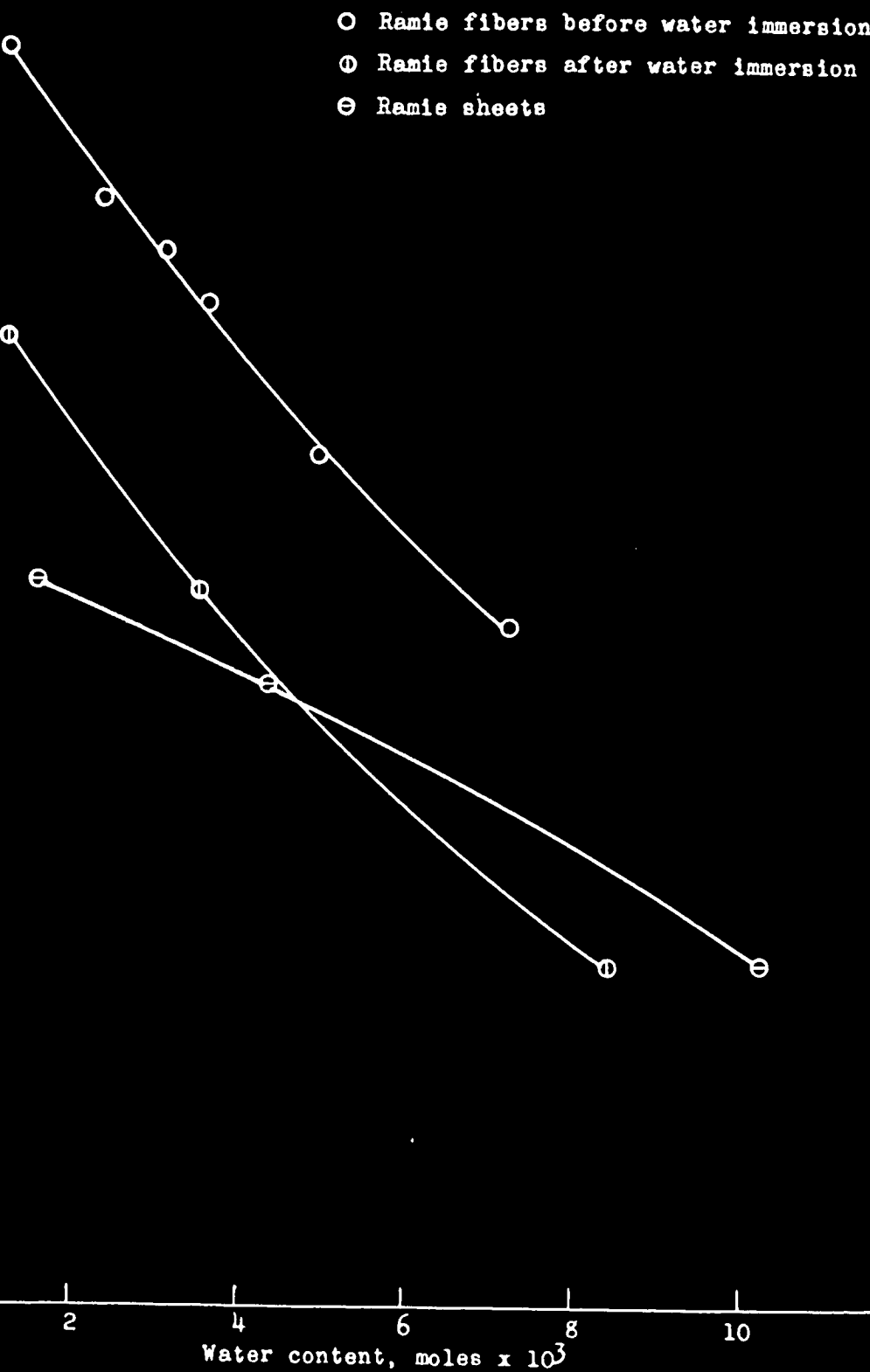


FIGURE 12

Effect of Water on Stiffness of Untreated Ramie Fibers and Sheets

the untreated fibers in water. This was accomplished in three independent series of tests, whose data are summarized in Table XIII and Figure 12. Exposure to liquid water increased the moisture sorption capacity of the ramie only slightly, but its effect on fiber stiffness was pronounced.

TABLE XIII

EFFECT OF WATER CONTENT ON STIFFNESS OF UNTREATED RAMIE FIBERS
AFTER IMMERSION IN WATER

Filaments Tested	Relative Humidity, %	Water, %	$\frac{EI}{L^3}$, dyne-sq. cm. x 10^2	$(\frac{EI}{EI_{50}})_{50}$
I 51	11	2.1	58.5	115
	50	6.4	51.0	100
	93	15.0	40.0	78
II 28	11	2.1	40.0	113
	50	6.4	35.5	100
	93	15.0	27.5	77
III 58	50	6.4	49.5	100

The second series of fibers tested demonstrated the effect of a limited sample size on the absolute stiffness values. Of the 72 fibers mounted, only 28 gave resonance vibrations in the acceptable range at all three test levels. The fibers had been trimmed so short initially that only 28 of the least stiff vibrated at resonance below 520 cycles per second. The resulting absolute values for fiber stiffness illustrate the lack of uniformity among natural fibers. On the basis of relative stiffness values, however, this second series checks well with the first in showing the effect of changes in moisture content. To substantiate the absolute data in the first determination, a

third independent series of fibers was tested at 50 per cent R.H.; the average stiffnesses for the two were in close agreement, as is evident in Table XIII.

Glycerin

Ramie fibers at two levels of glycerin concentration were tested to determine the effect of this plasticizer on flexural rigidity. The particular glycerin contents were chosen to correspond closely with the retention by ramie sheets, so that the degrees of softening could be compared. Fiber tests were made in the usual manner; the data are given in Table XIV and Figure 13.

TABLE XIV
EFFECT OF GLYCERIN ON STIFFNESS OF RAMIE FIBERS

Glycerin, %	Filaments Tested	Relative Humidity, %	Water Content, %	RI, dyne-sq. cm. x 10 ²
0	51	11	2.1	58.5
		50	6.4	51.0
		93	15.0	40.0
12.3	52	11	1.4	60.0
		50	7.1	48.0
		93	34.8	42.0
21.1	53	11	1.5	57.0
		50	7.5	45.0
		93	52.3	38.0

It is apparent that the effect of the glycerin on the ramie fibers was only slight. In spite of the glycerin and the increased water content at high humidities, fiber stiffness values were substantially the same as those of the untreated fibers. On Cordura, glycerin had a

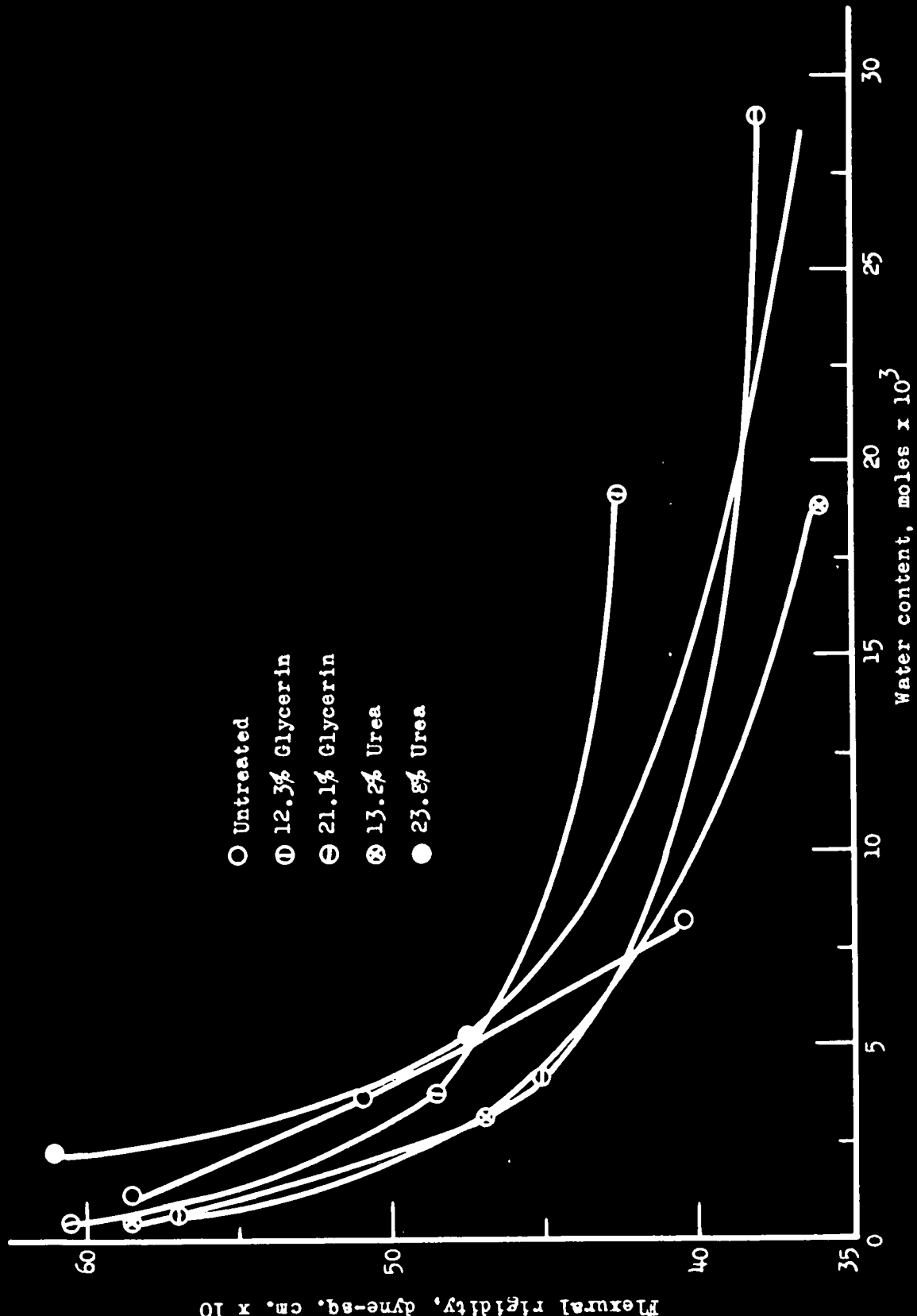


FIGURE 13

Effect of Water Content on Stiffness of Matted Paper Fibers

definite softening effect of its own beyond that attributed to its humectant character. On ramie, however, neither glycerin nor its associated water produced any significant softening over the entire humidity range. Probably ramie's high degree of crystallinity and orientation prevented sufficient fiber swelling to allow penetration of the glycerin molecules into the fiber. Thus, if they were retained on the external surfaces, glycerin molecules would have no effect on fiber stiffness, even though their influence on sheet properties might be considerable.

Urea

The test procedures for urea were identical with those employing glycerin. Two series of fibers were prepared at different urea levels, which corresponded with those of plasticized ramie sheets. The results of these vibration measurements are presented in Table XV. Figure 13 compares the softening action of water, glycerin, and urea.

TABLE XV
EFFECT OF UREA ON STIFFNESS OF RAMIE FIBERS

Urea, %	Filaments Tested	Relative Humidity, %	Water Content, %	$\frac{EI}{\text{dyne-sq. cm.} \times 10^2}$
0	51	11	2.1	58.5
		50	6.4	51.0
		93	15.0	40.0
13.2	55	11	1.0	58.5
		50	5.8	46.5
		93	34.1	36.0
23.8	65	11	4.5	60.5
		50	9.6	47.0
		93	75.4	37.5

The test data in Table XV show that urea probably has a very limited flexibilizing effect on ramie fibers at relative humidities of 50 and 93 per cent. When the total water contents of treated and untreated fibers are considered at those two test levels, however, it is apparent that urea molecules and their associated water molecules are relatively ineffective as softening agents, especially when compared with unbound water. As in the case of glycerin, the urea molecules were probably unable to penetrate the fibers completely and, therefore, their effect on fiber stiffness was only limited.

SHEET STIFFNESS

To compare the degrees of softening produced by plasticizers in fibers and in sheets, ramie fibers were converted into handsheets. Since the influence of fiber stiffness on that of the sheet probably decreases as beating progresses, it was desirable to produce sheets of good formation with a minimum of beating. Sheet uniformity was essential, because vibration tests were to be performed on narrow strips of less than 4 mm. width, and a scattered formation would have produced undesirable variations in stiffness among these test specimens.

Stock prepared in a Dilts beater was not acceptable, because the Schopper-Riegler freeness dropped to 290 ml. before the fibers were short enough to yield uniform handsheets. Similar attempts to refine the stock in a 1.5-pound Valley beater at normal consistencies were unsuccessful because of plugging at the backfall.

A limited supply of satisfactory sheets was finally prepared by first cutting the fibers to 0.25-inch lengths and then beating at

0.3 per cent consistency in the Valley beater for 15 minutes with 6500 grams on the bedplate. This operation produced a relatively free stock with a Schopper-Riegler freeness of 430 ml. The stock was then passed through a 12-gage vibrating screen, fractionated further by a mechanical stirrer which combed out the remaining long fibers, and then formed into sheets in the British mold. The sheets were pressed twice between blotters at 50 pounds per square inch to correspond to the treatment for the ramie fibers described previously.

However, air drying samples of the pressed sheets produced an undesirable cockle, which would have interfered seriously with the vibration tests. Therefore, the handsheets were dried between blotters on a steam cylinder at 230° F. for five minutes, and conditioned at 50 per cent R.H. This difference in the drying procedures for fibers and sheets was unavoidable and should not affect the interpretation of the test data.

The sheets were prepared at two levels of plasticizer retention, which corresponded to the urea and glycerin contents studied in the ramie fiber experiments. After conditioning at 50 per cent R.H., the sheets were immersed in plasticizer baths of the appropriate strengths, allowed to steep overnight, pressed between blotters at 50 pounds per square inch, dried on the steam cylinder between blotters, and again conditioned at 50 per cent R.H. Then thirty test strips of standard dimensions were cut for each plasticizer level and tested at 11, 50, and, after trimming, at 93 per cent R.H. Unlike the individual fibers, however, ramie sheets showed significant changes in length at various

relative humidities, and hygroexpansivity data were necessary for the stiffness calculations. The principal experimental data are presented in Table XVI. Repeat determinations were made on the untreated sheets and those containing 9.7 per cent glycerin to check questionable values; both series are included in Table XVI. Graphs of sheet stiffness, however, are based on the average values for the two.

For the untreated sheets, stiffness decreased uniformly with increasing moisture content, showing a roughly linear relationship in the range studied. The effects of moisture on the fiber and sheet stiffnesses of untreated ramie are compared in Figure 12, where it is evident that the fibers are slightly more sensitive to changes in the water content than are the sheets.

In the treated sheets, the addition of the plasticizers produced marked reductions in sheet stiffnesses at the medium and high relative humidity levels. In the lower range of water contents, the only significant softening was observed in sheets containing 21 per cent glycerin.

It will be recalled that the increase in moisture content caused by the plasticizer had little effect on the stiffness of the individual ramie fibers. When these fibers are converted to sheet form, however, the additional water becomes highly significant. This is hardly unexpected if the water associated with the plasticizer molecules is held on the fiber surfaces because, in such a position, it could reduce bonds between fibers and, hence, sheet stiffness without altering fiber stiffness.

TABLE XVI

EFFECT OF SOFTENERS ON STIFFNESS OF RAINY SHEETS

Softener	Softener Content (Ovendry), %	Relative Humidity, %	Water Content, %	Length Change, %	EI, dynes-sq. cm.	
					I	II Average
Water		93	18.4	0.8	405	385
		50	7.9	-0.1	495	470
		11	3.0	-0.4	520	505
Glycerin	9.7	93	30.4	0.9	285	270
		50	7.5	-0.1	450	470
		11	1.8	-0.5	520	515
Urea	21.4	93	61.3	0.6	205	
		50	10.4	-0.5	375	
		11	3.0	-0.7	445	
Urea	11.8	93	35.1	1.0	210	
		50	6.8	0.1	420	
		11	1.2	-0.5	515	
Urea	24.8	93	83.4	1.1	130	
		50	9.0	-0.2	375	
		11	3.2	-0.8	520	

Reed (3) observed an excellent correlation between the Clark stiffness values and the water contents of sheets plasticized with sodium saccharinates, saccharinic acids, glycerin, and water. In a more detailed study of glycerin, McPherson (5) evaluated sheet stiffness with a torsion pendulum and reported that the best correlation between the stiffness of the cotton sheets and their total plasticizer content was obtained when one molecule of glycerin was considered equivalent to two molecules of water.

To determine if the softening of ramie sheets in the present study was entirely the result of the hygroscopic properties of the glycerin and urea molecules, flexural rigidities were plotted against the water contents in Figure 14. These plots indicate that softening observed in the treated sheets at 50 per cent R.H. could not be explained completely by the humectant concept of plasticizing. Evidently the glycerin and urea had an additional softening effect of their own, which was distinct from that produced by their associated water.

The relative effectiveness of urea, glycerin, and water is demonstrated roughly by plots of sheet stiffness against various ratios of the molar contents of plasticizer and water. These are illustrated in Figures 15, 16, 17, and 18.

For glycerin, the best correlation was observed when two molecules were assumed equivalent to one of water. Thus, glycerin appeared to be less effective than water in reducing ramie sheet and fiber stiffnesses, whereas earlier it had been shown to be more effective than water in reducing the filament stiffness of Cordura.

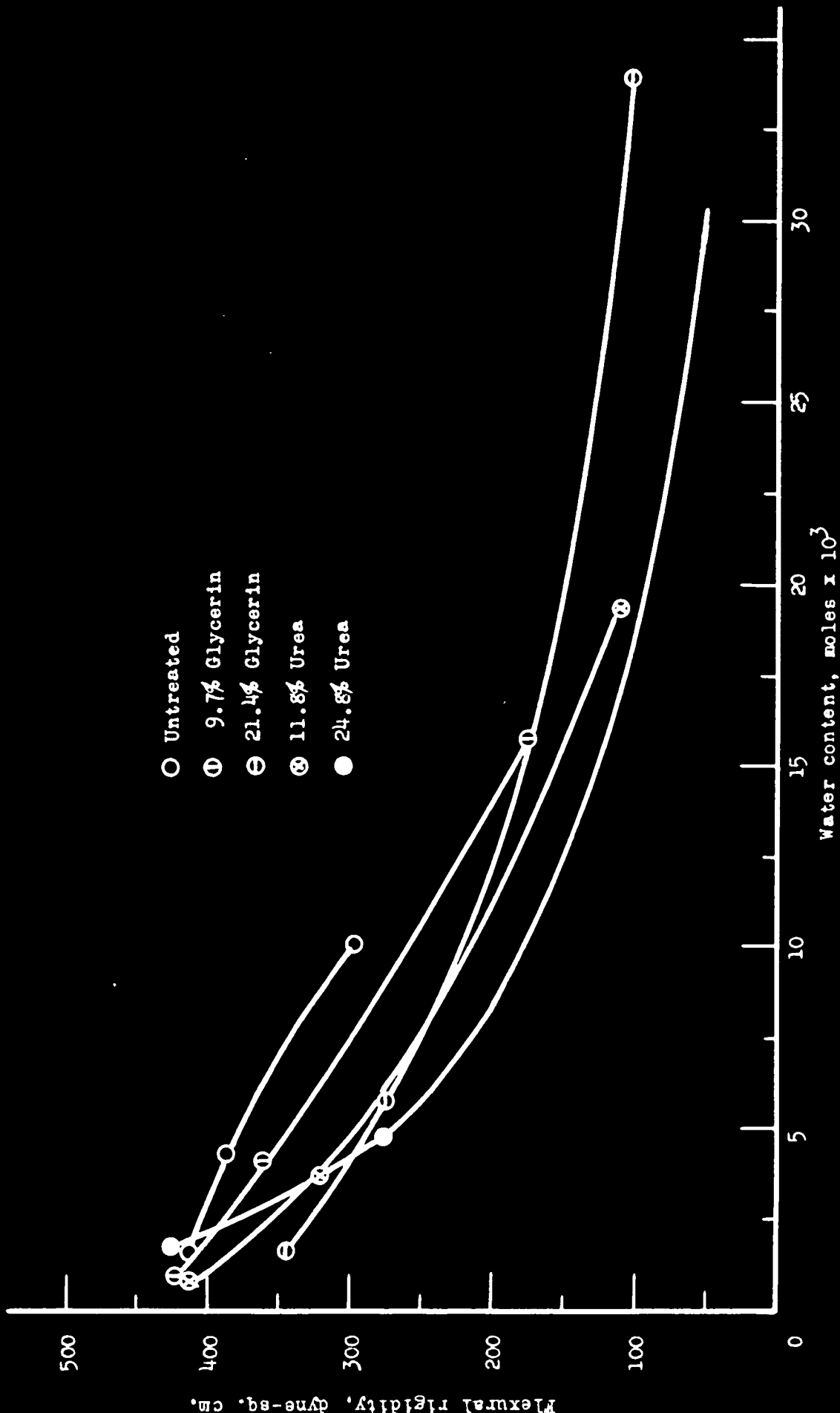


FIGURE 14
Effect of Water Content on Stiffness of Treated Ramie Sheets

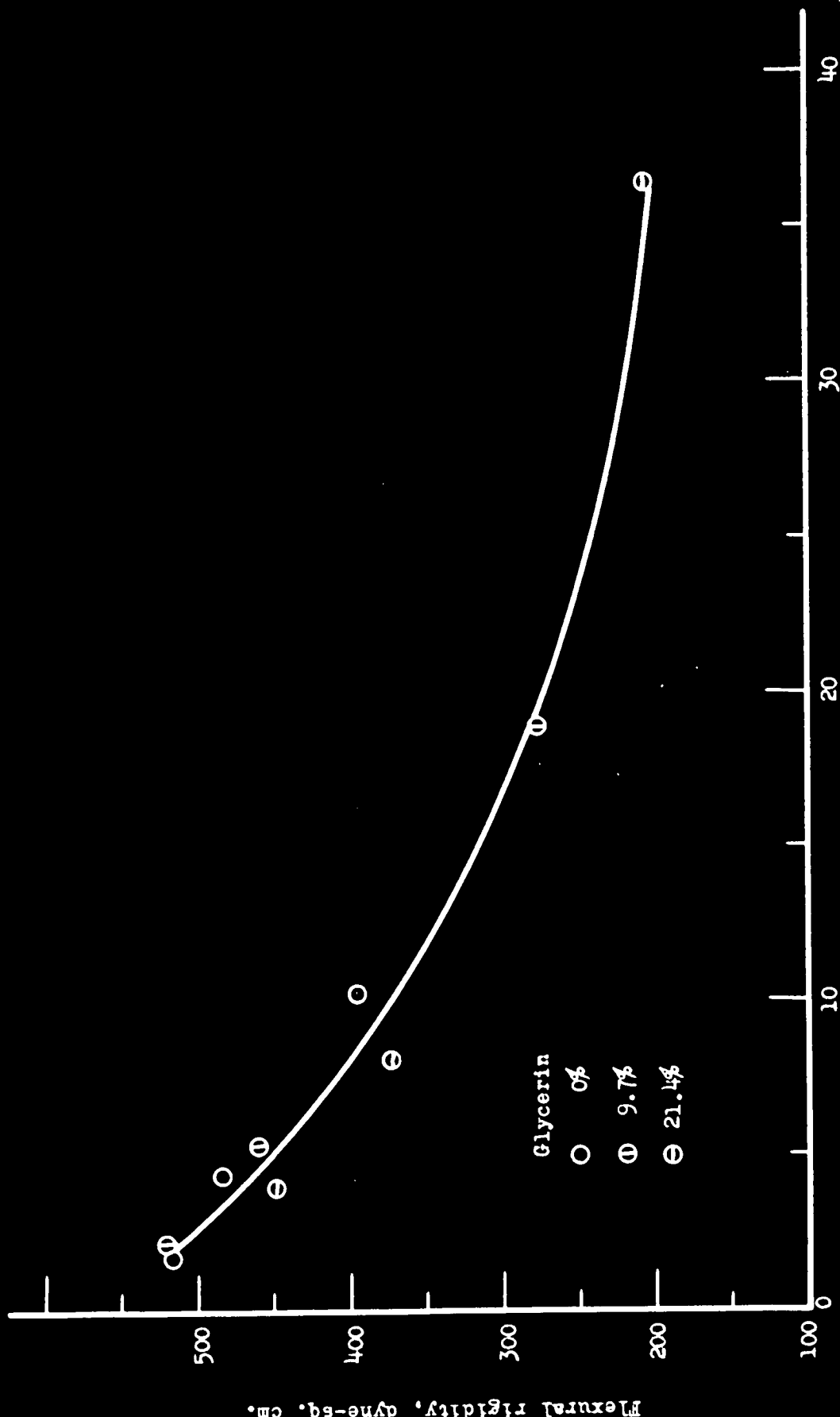
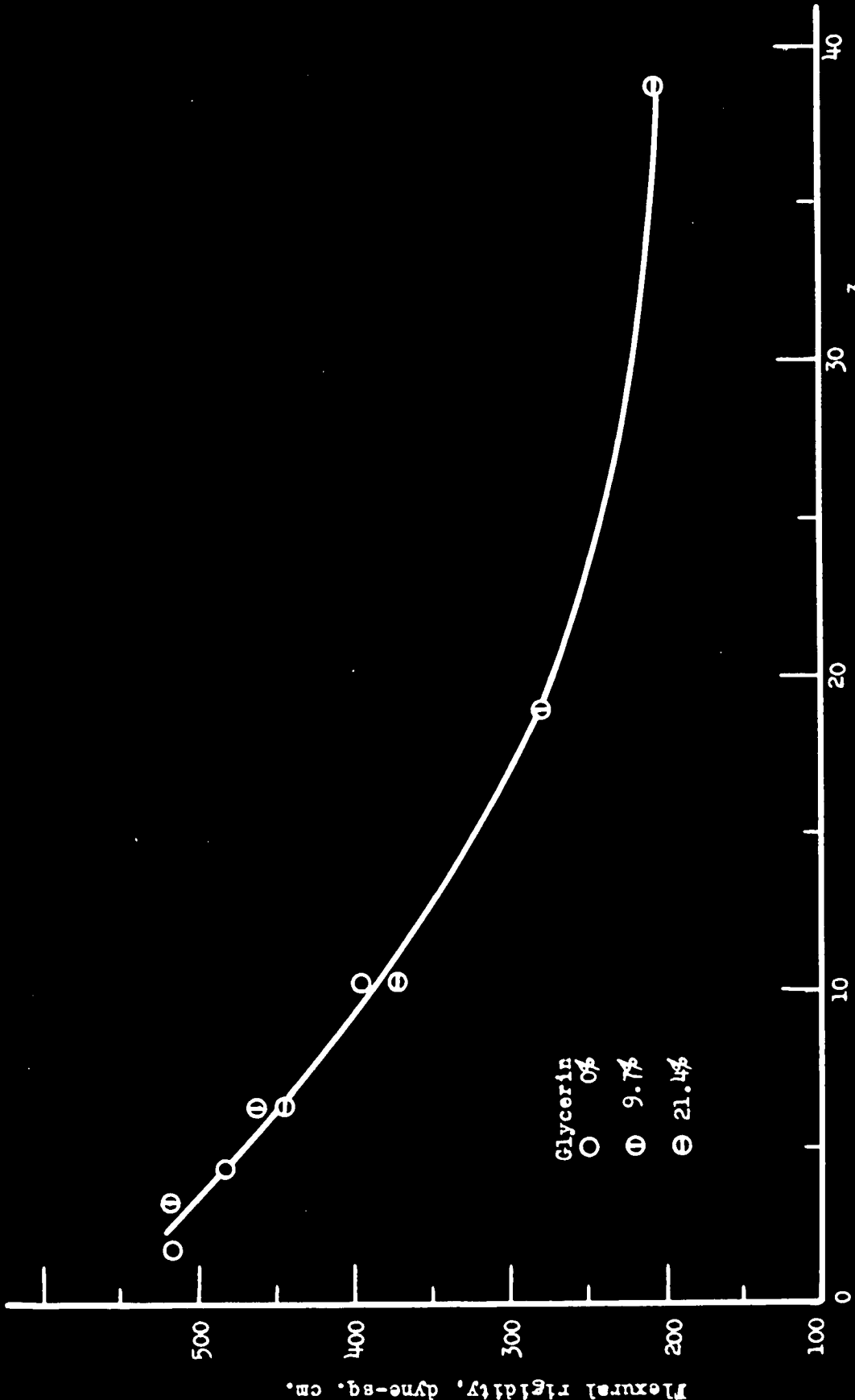


FIGURE 15
Effect of Glycerin and Water on Stiffness of Plastic Sheets



Combined glycerin-water (2:1) content, moles x 10³

FIGURE 16

Effect of Glycerin and Water on Stiffness of Dental Sheets

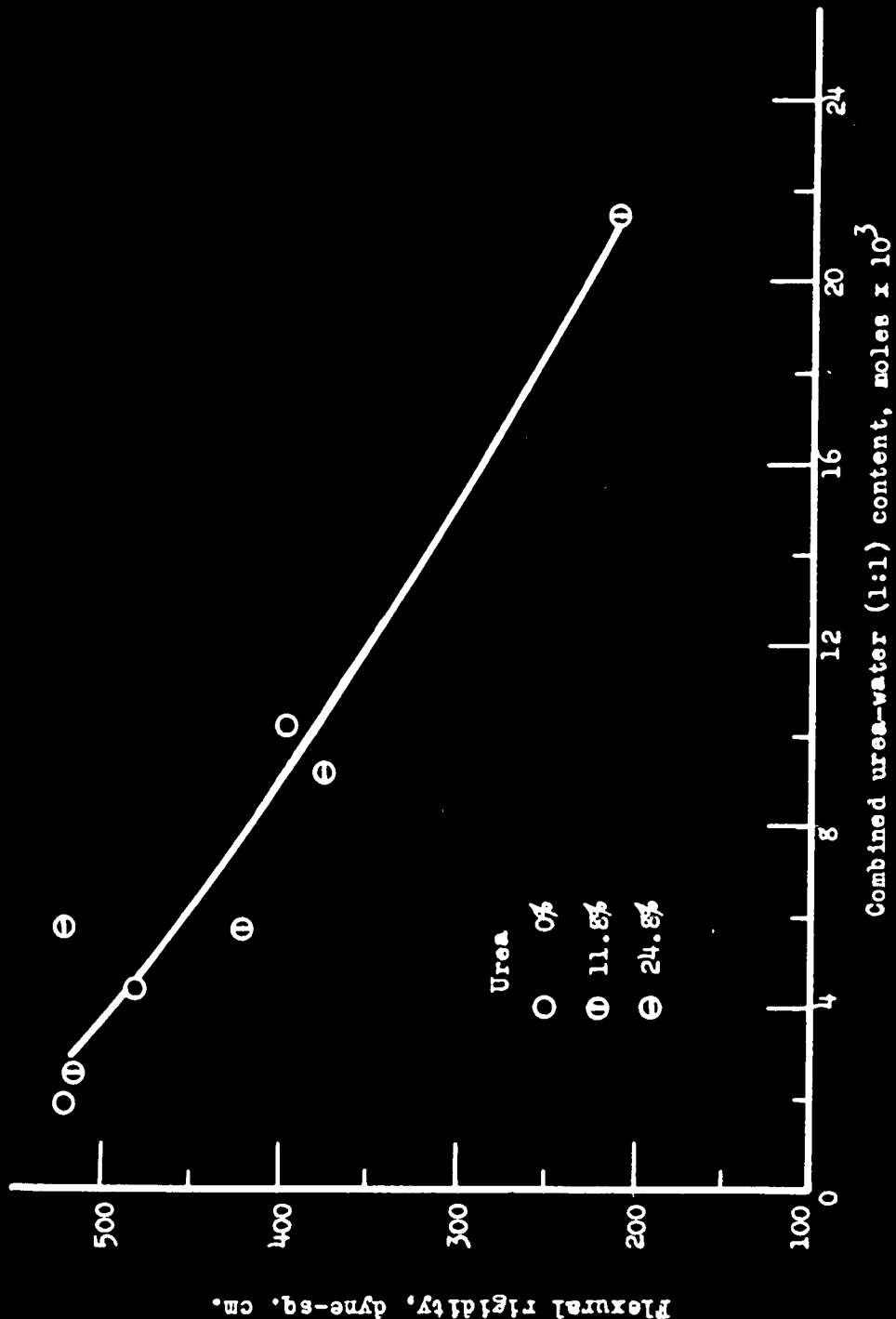


FIGURE 17

Effect of Urea and Water on Stiffness of Resin Sheets

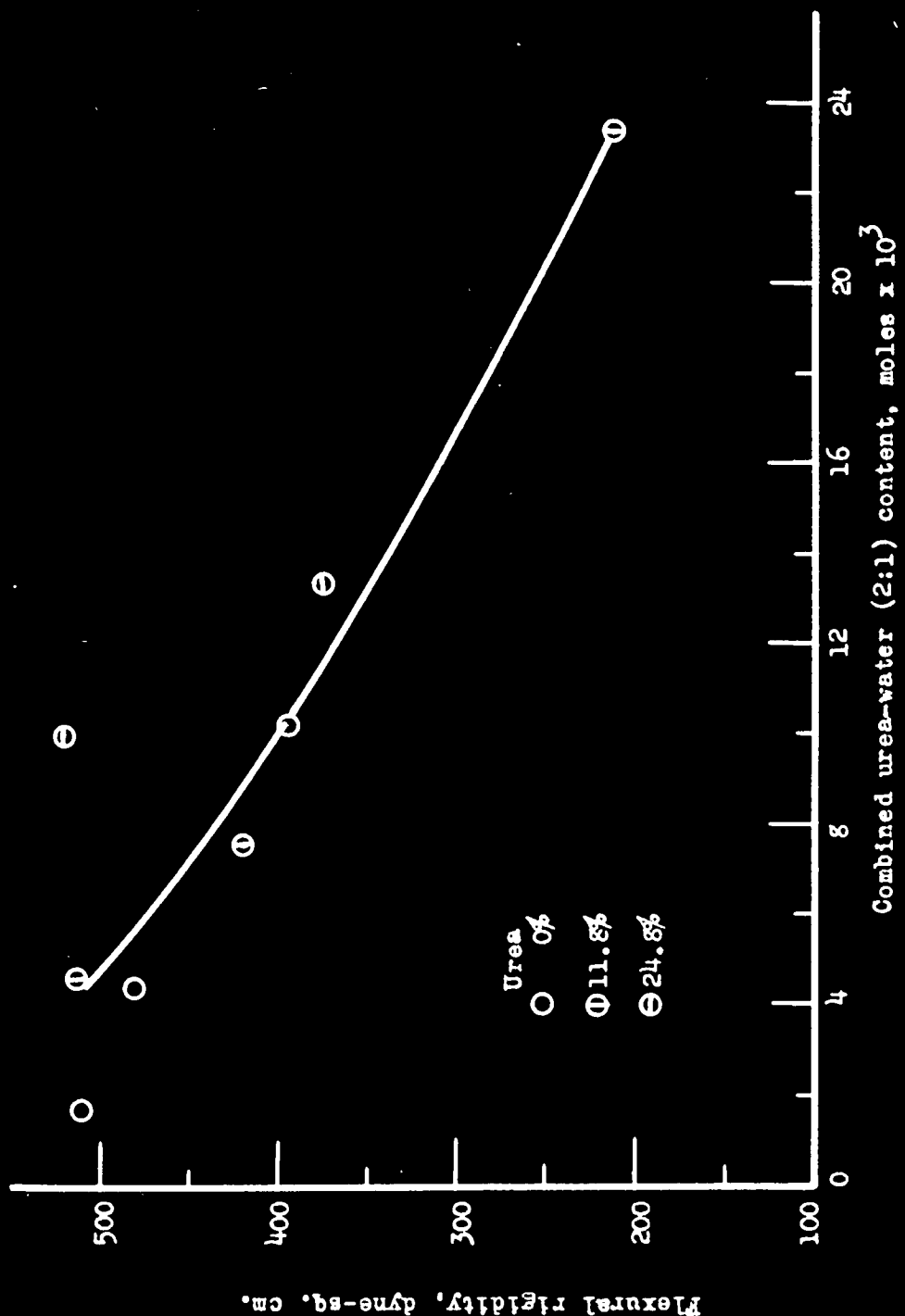


FIGURE 18

Effect of Urea and Water on Stiffness of Ramie Sheets

However, such conclusions are based on rough comparisons and should be regarded as approximations only.

For urea, no simple whole-number ratio of urea:water produced an especially satisfactory correlation of sheet stiffness and plasticizer content. Figure 14 indicates that urea had a definite plasticizing action of its own, but this was not at all comparable with that of water. As explained before, this is not unexpected, because urea and water are so unlike in structure. Water alone produced a uniform decrease in stiffness over the entire range of moisture contents studied, as is apparent in Figure 12. Urea, however, reduced sheet rigidity sharply only in the region of low water contents; at higher moisture levels its effect was much less pronounced. Figures 17 and 18 show the spread of values obtained when one and two molecules of urea were assumed equivalent to one molecule of water. In an approximate way urea and water appear to be equally effective molecule-for-molecule in reducing sheet rigidity.

GENERAL SUMMARY

This fundamental study of softening was concerned chiefly with the effect of plasticizers on the individual fibers. The concepts of softening by lubrication and by a reduction of the bonding between fibers had been investigated previously by other workers. No experimental data were available, however, to indicate the action of softening agents on the fibers themselves.

Since there were no satisfactory methods for the measurement of fiber rigidity, the first phase of the experimental work was the development of an acceptable test instrument and procedure. In the method finally adopted, the fibers were mounted as cantilever beams in a field of strong sonic vibrations, and the frequencies which produced resonance vibration in the fibers were determined. With these frequencies and accurate data on fiber lengths and weights, the flexural rigidities of the fibers could be calculated.

A test chamber was constructed so that measurements of stiffness could be made under controlled humidity conditions, and a divided flow system was introduced into the conditioning system to produce the desired vapor pressures. By such control and by other refinements in the testing techniques, the experimental variations were reduced to a minimum, so that the standard errors of the mean stiffness were under six per cent.

This vibration method was also adopted for measurements of sheet stiffness by proper modification of the mounting procedure. In

this way it was possible to determine the purely elastic component of sheet stiffness, for rapid vibration of the specimens during testing eliminated plastic flow.

The accuracy of this method was checked by a torsion pendulum. Flexural rigidities of a number of commercial foils and papers were determined by both instruments, and the data were compared. Although there was poor agreement between the absolute values, on a relative basis, the two instruments correlated well. Therefore, the flexural vibration method was accepted as a valid measure of stiffness.

Since wood fibers were too short for this procedure, however, the stiffness measurements were made on viscose rayon and ramie. The rayon filaments were employed in the second phase of the experimental work, a comparative study of various softening agents, because of rayon's high sorption capacity. In the final phase, the study of the correlation between fiber and sheet stiffnesses, ramie fibers were used.

The second phase began with an investigation of the effect of the water content on the stiffness of untreated filaments. The test data revealed that the flexural rigidity varied inversely with the water content in the range studied. Immersion of the filaments in water reduced all subsequent stiffness values, presumably by internal swelling and a decrease in the bonding within the filaments.

A study of the softening effect of aliphatic alcohols was limited in scope, because of insufficient adsorption of alcohol vapors on the dry filaments. The vibration tests were made at 0 per cent R.H.,

so that variations in the water content would not interfere. During the test cycle, the alcohol content of the filaments was varied by proper control of the chamber's atmosphere. These tests, however, were preceded by adsorption studies which related the alcohol retention on the filaments with the relative vapor pressure of the surrounding air. It was apparent that increasing the chain length of the alcohol molecules reduced their sorption on the filaments markedly. Thus, the adsorption of ethanol and propanol were too limited to show significant softening effects; however, on a molar basis, methanol appeared to be as effective as water in decreasing filament stiffness.

Polyhydroxy alcohols were investigated to determine the effect of the molecule size and the number of hydroxyl groups on the softening mechanism. Ethylene glycol, glycerin, and sorbitol were selected for this study as representative members of a homologous series.

The glycol tests, however, were not conclusive, because of the plasticizer's volatile character. It was apparent that some flexibilizing had resulted, but the data were too approximate for comparative purposes.

Glycerin had a pronounced softening effect on the rayon filaments, and graphs of the data indicated that this action could not be explained entirely by glycerin's hygroscopic character. Plots of stiffness against various ratios of glycerin and water showed the best correlation when one molecule of glycerin was assumed equivalent to one or two molecules of water. Thus, on a molar basis, glycerin per se was

at least as effective as water in reducing fiber stiffness. However, in terms of its total hydroxyl content glycerin was not equivalent to three molecules of water, and the softening, therefore, was not directly proportional to the hydroxyl content of the plasticizer. Other factors, such as molecular size and the ability to produce swelling, were probably more critical. The further addition of glycerin beyond an oven-dry content of 15 per cent had little effect on fiber stiffness, indicating that the filaments were probably saturated with glycerin at this level. Apparently, later increments were retained on the fibers' external surfaces, where they could not affect fiber stiffness.

Sorbitol at high humidities had a less pronounced flexibilizing action than glycerin, and the softening observed may have been due entirely to sorbitol's hygroscopic properties. In the extremely low humidity range a high sorbitol content produced stiffening; this may have been caused by crystallization on or in the filaments. Plots of stiffness against various ratios of water and sorbitol were rather inconclusive, but they did indicate that the degree of softening produced was not directly proportional to sorbitol's hydroxyl content.

Calcium chloride was investigated as an example of a purely humectant plasticizer. At low humidities, even a limited calcium chloride content had a remarkable stiffening effect. This may have been partly because of the crystallization of the salt on the filaments or the desiccation of the filaments by the salt. At high humidities, however, significant softening was obtained, but this was never greater than could be explained by the additional water held by the plasticizer.

Thus, there was no evidence to indicate softening by the calcium chloride molecules beyond that attributed to their humectant character.

Formamide was included in the plasticizer study because of its remarkable ability to swell cellulose fibers. In this respect formamide is more effective than water. Because of its volatile character, however, the results of the vibration tests were only approximate. Even so, it was apparent that formamide had an appreciable flexibilizing effect on the rayon filaments on a molar basis probably surpassing water as a softening agent. This provides additional proof of the close relationship between fiber softening and swelling.

The last plasticizer to be considered was urea, which reduced fiber stiffness at all plasticizer contents at the 50 and 93 per cent R.H. test levels. In the low humidity range, however, a high plasticizer content produced some stiffening, probably because of crystallization of urea on the filaments. Urea had a greater softening action than could be explained simply by its humectant character. Attempts to determine the relative effectiveness of water and urea as softening agents were not especially successful, probably because of the difference in the structures of the two but, on a molar basis, urea and water were just about equally effective.

In the third and final phase of the experimental program, the effects of plasticizers on fibers and on sheets were compared. Water, glycerin, and urea were selected as the softening agents. Since rayon filaments could not be formed into satisfactory sheets, ramie fibers

were employed. The ramie stock was beaten moderately and converted into sheets which were then pressed and dried according to a standard procedure. The sheets and samples of individual fibers were immersed in appropriate plasticizing baths to absorb equal contents of the softening agents.

The individual ramie fibers were tested first, and the effect of water on the untreated fibers proved to be similar to that observed with the rayon filaments. In the range studied, fiber stiffness decreased linearly as the water content was raised. There was no flattening of the curve in the high humidity range to indicate that the last increments of water were held in gross capillaries or on the external surface, where they would not affect fiber stiffness.

Immersion of the dry filaments in water before the vibration testing apparently caused some fiber swelling, for the stiffness was reduced significantly without any marked change in the moisture sorption. For these water-soaked fibers, the average stiffness still varied inversely as the fiber's water content in the range studied.

Glycerin, however, showed no pronounced softening action on the ramie fibers. It did reduce fiber stiffness slightly at 50 per cent R.H., but this effect was not evident at the 11 per cent level. At 93 per cent R.H., where the glycerin more than doubled the fiber's equilibrium moisture content, there was no significant decrease in stiffness. Thus, neither the glycerin molecules nor their associated water molecules seemed to affect the rigidity of ramie fibers seriously.

Urea was only slightly more effective than glycerin in its action on the individual ramie fibers. Both levels of urea content produced a limited degree of softening at relative humidities of 50 and 93 per cent, but these were not at all proportional to the attendant increases in moisture content.

It seemed evident from these results that the glycerin and urea molecules were unable to penetrate into the highly crystalline, well-oriented ramie fibers. Apparently, molecules of unbound water succeeded in diffusing into the intermicellar capillaries, where they weakened internal bonds and thereby reduced the fiber stiffness. Glycerin and urea, on the other hand, were probably retained on the fiber surfaces or in gross capillaries, so that neither they nor their associated water could affect the fiber rigidity. The slight degree of flexibilizing produced by these plasticizers may have been the result of limited penetration into the amorphous regions of the ramie.

Thus, softening agents proved to be capable of plasticizing highly amorphous rayon filaments but had no comparable effect on the more crystalline ramie fibers. Consequently, their action on wood fibers cannot be deduced from these data with any degree of certainty. It seemed likely, however, that some softening by urea and glycerin might be expected, because Cady and Williams (41) observed that these molecules diffused freely into wood samples of cedar, fir, hemlock, and pine. Since, however, stiffness measurements could not be made on the wood fibers directly, this hypothesis cannot be checked experimentally.

The effect of these plasticizers on ramie sheets was quite pronounced. For the untreated sheets, as for the untreated fibers, stiffness varied inversely with the moisture content, revealing a linear relationship in the range of retentions tested.

It is of interest to note that the average stiffness of the individual fibers was more sensitive than that of the sheet to changes in the moisture content. This may serve indirectly to indicate that fiber stiffness does not play a major role in determining sheet stiffness. An increase in the moisture content would be expected to increase lubrication between fibers or decrease their degree of bonding. Therefore, if sheet rigidity depended to a significant degree upon fiber rigidity, it should have decreased at least as rapidly as fiber stiffness, when its water content was raised. Since this was not the case, it would seem that fiber rigidity in this case did not have a critical effect on the stiffness of sheets made from moderately beaten ramie stock.

In the plasticized ramie sheets, urea and glycerin molecules were highly effective as softening agents. The studies of fiber stiffness demonstrated that molecules of these plasticizers were probably retained on the fiber surfaces, where they apparently reduced sheet stiffness by weakening bonds between fibers.

Graphs of sheet stiffness against the total water content of the treated sheets revealed that the softening produced by urea and glycerin was not entirely the result of their hygroscopic character. As a crude approximation, glycerin molecules appeared to be only half

as effective as water molecules in softening the ramie sheets. On the other hand, urea was roughly equivalent to water in this respect, but comparisons based on such graphs are likely to be misleading.

No direct data could be obtained to indicate the influence of fiber stiffness on sheet stiffness after plasticizing. If it is true, however, that the rigidity of the individual fibers does not have a critical effect on that of the unplasticized sheet, its importance in the plasticized sheet would probably be even less, for the softening agent would cause lubrication and a reduction in fiber bonding, so that bending of the sheet would produce internal slippage between fibers rather than flexure of the fibers.

In the dense well-beaten sheets for which plasticizers are usually employed commercially, fiber stiffness has probably been essentially destroyed by the heavy beating, and the stiffness of those sheets before plasticizing must depend almost entirely upon the strength of the bonds between the fibers.

CONCLUSIONS

1. An instrument has been developed to measure the flexural rigidity of fibers and filaments rapidly and without interference from plastic flow. In the testing procedure, the sample sizes were sufficient to give standard errors of stiffness not exceeding six per cent.

2. By suitable modification of the mounting procedure, this instrument could measure the flexural rigidity of paper sheets with a standard error of the stiffness of only three per cent for samples of 30 strips.

3. The flexural rigidities of untreated rayon filaments and ramie fibers varied inversely as a linear function of their water contents. Such softening was probably caused by a weakening of the fiber's internal bonds by water molecules, which penetrated the fibers and separated their cellulose chains.

4. The addition of methanol to rayon filaments produced a roughly linear decrease in their stiffness; water and methanol appeared to be equally effective in softening filaments.

5. The studies of polyhydroxy alcohols showed that filament softening was not proportional to the total hydroxyl content of the plasticizer. On a molar basis, glycerin was at least as effective as water, but the relative effectivenesses of ethylene glycol and sorbitol could not be established.

6. Crystalline softening agents such as calcium chloride, sorbitol, and urea produced fiber softening in the high humidity

range but, in sufficient concentration, they caused stiffening at the low humidities.

7. Urea was roughly as effective as water in softening filaments at high and medium relative humidities.

8. Glycerin and urea had only limited effects as softening agents on ramie fibers. Probably they were unable to swell and penetrate the highly crystalline fibers. Thus, it seemed evident that plasticizers softened fibers only when the plasticizer molecules either were small enough to penetrate the water-swollen fibers or were able to produce the additional fiber swelling necessary for penetration. Apparently, fiber softening and swelling were closely related.

9. The relationship between the water content and the flexural rigidity of untreated ramie sheets was substantially linear. The addition of urea and glycerin, however, produced greater softening than could be explained by their hygroscopic properties; as a rough approximation, two molecules of glycerin or one molecule of urea was equivalent to one molecule of water in sheet softening.

10. The stiffness of the individual fibers was probably not highly significant in determining sheet stiffness, especially in the plasticized sheet, but this could not be definitely demonstrated experimentally.

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