The Institute of Paper Chemistry

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Doctor's Dissertation

The Mechanism of the Softening of Paper by Glycols

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THE MECHANISM OF THE SOFTENING OF PAPER BY GLYCERIN

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INTRODUCTION TO PAPERICAL

In the manufacture of paper, it is often necessary to render the paper soft and flexible to satisfy use requirements. Sometimes the desired softness can be obtained by proper selection of paper pulps, various pulp refining and papermaking techniques, and mechanical treatment of the finished sheet. Then these methods are not feasible, plasticizers or softening agents may be added to the paper to make it softer and more flexible, particularly at low relative humidities. For instance, glassine paper prepared from highly beaten pulp becomes brittle at low relative humidities and requires a softening agent to prevent cracking and breaking. Food wrapping papers which are exposed to low relative humidities in frozen food lockers must be softened to remain flexible and capable of conforming to the shape of the packaged article. Paper products, such as paper draperies, are given a characteristic clothlike softness with the aid of softening agents.

The words "softener, plasticizer, and humidant" have been used in the paper industry to describe materials added to paper to render the paper softer and more flexible, particularly at low relative humidities. The word "softener" is perhaps a better term than "plasticizer," in that it directly describes the function of the material. The term "plasticizer" suggests that plasticized paper may have properties of a plastic. Webster (2) defines a plastic material as one which is "capable of being deformed continuously and permanently in any direction without rupture under a stress exceeding the yield value." It is well known that plasticized papers do not fall into this category. "Humidant" is a hygroscopic substance which is added to a product for the purpose of increasing its
equilibrium moisture content, particularly at low relative humidities.

The use of the term is apparently rather new in the paper industry.

Many materials find use as softening agents for paper. Five (1) has classified them and differentiates between (1) lubricating, nonhygroscopic softeners, such as essential oils and water-miscible mineral oils; (2) nonlubricating hygroscopic salts; and (3) lubricating and hygroscopic softeners, such as glycerin, invert sugar, corn syrup, glycols, and sugar alcohols. Of the materials finding most common usage in the paper industry are in the third group. Of these the most desirable of this group is glycerin, because it does not crystallize at low relative humidities, has a low vapor pressure at ordinary temperatures, and is not poisonous.

Although softening agents have been used for some time, the mechanism of their action is not well understood. In the published work in this field, the various concepts advanced are either wholly speculative or not supported by sufficient evidence to warrant their acceptance. Of the many softeners for paper, the choice for this study was restricted to glycerin, for this compound finds use in all grades of softened paper. It is the hope that information concerning its action will aid in understanding the action of the many other softening agents.

The explanations for the mechanism of the softening action of the various agents for paper can be grouped under four headings:

1. The hygroscopic concept
2. The fiber lubrication concept
3. The flexibilizing of individual fibers concept
4. The weakening of fiber bonds concept
THE HYDROSCOPIC CONCEPT

It is well known in the paper industry that paper can be made softer by increasing its moisture content. However, the wide fluctuation in atmospheric humidity and the dependence of the moisture content of cellulosic materials on the humidity prohibit the use of moisture alone as a softening agent at low relative humidities. Therefore, hygroscopic materials have been added to paper with the idea that they would hold moisture in the sheet at low relative humidities and keep the paper soft and flexible.

In 1939, the Coniferous Raw Material Committee of the Technical Association of the Pulp and Paper Industry (2) in its annual report on the status of the commonly used softeners in the paper industry made mention of their softening mechanism. They attributed the softening action mainly to the hygroscopic nature of plasticizers and also reported that no successful agents of a nonhygroscopic nature had been found.

Leffingwell and Lessar (4), Katzenin (5), and Trorer (6) in their publications have stated that the softening action of softeners is dependent on their hygroscopic nature. In fact, the hygroscopic theory for softening has been tacitly assumed in the paper industry on the basis of the hygroscopic nature of the softeners. However, no actual data have been published to show that the moisture content of softened sheets at low relative humidities substantiates this theory.

The work of Pike (1) in 1936 on the moisture content of glycerintreated papers over a wide relative humidity range showed evidence contradictory to the hygroscopic theory. At relative humidities below 60 per cent
where the hygroscopic properties of a plasticizer are considered to be most important, he found that sheets containing 5 per cent glycerin had lower moisture contents than the untreated sheets. However, the treated sheets were softer at all relative humidities than the blank sheets. He concluded that plasticizers do not depend solely on an increased moisture content for their effect.

Hardenburg (7) made studies of the moisture content of glycerin-treated paper towels and tissues at several relative humidities. His data also indicate that, at low relative humidities, papers containing 5 per cent glycerin had lower moisture contents than untreated sheets. At the higher relative humidities, glycerin-treated sheets were found to retain greater quantities of moisture than untreated sheets. He also demonstrated that the loss of glycerin from paper with time is quite small.

Connor and Mehlemann (2) have set forth several concepts concerning the softening mechanism of glycerin. They concluded from the data of Hike (1) and Hardenburg (7) that hygroscopic action cannot be responsible for softening action at low relative humidities. To explain the deficiency in moisture content of glycerin-treated sheets at low relative humidities, they have postulated that glycerin takes moisture away from the fiber and gives it to the atmosphere until the glycerin reaches its equilibrium moisture content.

Apparently the humectant action of glycerin alone cannot explain the mechanism of softening, particularly at the low relative humidities where softening action is desired.
THE FIBER LUBRICATION CONCEPT

In light of his moisture data on glycerin-treated papers, Pike (7) concluded that some mechanism other than that of hygroscopic action must explain the function of glycerin as a softening agent for paper. He proposed the idea that the softness of glycerin-treated papers is a result of fiber lubrication. If the fibers in a sheet of paper were lubricated, they could slip over one another more easily in the process of flexing the sheet and would impart a softening effect to the sheet.

Connor and Hadelmann (8) considered the theory of boundary and fluid lubrication and showed how they might be related to surface-bound moisture and capillary-condensed moisture in an unbleached sheet. They concluded that the softener may be found as surface-bound softener and excess softener. They also stated that "an increase in softness may be imparted to paper either by use of softeners which possess fiber swelling efficiency higher than water or by having softener capillary condensed, or adsorbed in addition to surface bound water."

Although the lubrication concept may explain the softening action, no data are available to support it.

THE PLASTICIZING OF INDIVIDUAL FIBERS

In considering the way in which a sheet of paper might be softened, one might think that possibly the elements of the sheet structure, the individual fibers, could be made more flexible by a softening agent.

Kata-rik (5) stated that the structure of cellulose molecules and
sicles is important in regard to the flexibility of the paper sheet.
He did not think they act as stiff rods, but rather that they are flexible.
Their flexibility is determined by the moisture content which can be
affected by the addition of hygroscopic materials. He also pointed out
that the moisture content of a fiber at any relative humidity varies with
the fiber species and the chemical treatment given the fiber.

Brad (2) stated that glucose, which is used as a paper plastifi-
cizer, makes pulp fibers soft and flexible. Also, he reported that the
flexibility of paper can be greatly increased by the addition of glucose
solutions.

Connor and Nadelmann (3), in their discussion of the mechanism of
softening, stated that the swelling of a fiber may make it softer and more
plastic.

The work of Peirce and associates (10-12) on cotton hairs showed
that aqueous swelling coincides with a marked decrease in the torsional
rigidity of a fiber and an increase in plasticity.

It is evident that the flexibility of individual fibers in a
sheet of paper may be affected by softening agents and the softness of the
fibers may be related to the softness of the resulting sheet of paper.

THE STRUCTURE OF FIBER BUNDS

In most types of paper, the fibrous material is held together by
attractive forces between the fibers. If the attractive forces were weakened
or perhaps a portion of them removed in some fashion, a sheet of greater
softness and flexibility might be produced. One theory for the mechanism of the softening action visualizes the softener molecules entering the sheet between the fibers and weakening the fiber bonds either by forcing the fibers further apart or by destroying the bonds.

In their work on cellulose ethers and esters, Baker (14) and co-workers found that water acts as a plasticizer. It forces the cellulose chains apart by its swelling action. They state that moisture can easily provide the chain motion requisite for the dimensional changes so characteristic in cellulose plastics.

Nickerson (14), in his discussion of the structure, properties, and utilization of cotton, suggested that water may reduce the forces of association among cellulose molecules, first by combining with and de-activating hydroxyl groups and, secondly, by increasing intermolecular distances.

Ott (15) discussed two basic mechanisms for plasticizing cellulose derivatives along the following lines: In one mode of action, the plasticizer solvates the cellulose chain, increases the average distance between chains, and reduces the force which binds each chain to its neighbors. Celluloid is an excellent example of this type of action, a material in which the plasticizer, camphor, is firmly bound to the nitrocellulose molecule. Camphor owes its success as a plasticizer for nitrocellulose to the relatively stable complexes it forms with the nitrocellulose molecule. As a result of this reactivity with portions of the molecule, the camphor exerts a powerful solvating action on the chains, entering between them with an attractive force great enough to weaken the co-ordinate links and
held the cellulose chains apart except at rate intervals where the chains cross or touch and are still strongly bonded together.

There is another type of plasticizing action: the formation of a network of membranes and filaments of solvated cellulose derivatives, filled with a more complete solution of derivative in the plasticizer. A simple picture is that of two phases, only partially miscible—the more fluid phase (plasticizer-rich) is held by surface tension in the areas of the other more solid phase, thereby preventing collapse of the structure. This type of plasticization yields a cell-type of structure, and is indicated if a very soft, pliable composition is desired.

Another portion of the same article may aid in the understanding of the plasticizing mechanism. It explains that it is also possible to prepare derivatives which have the plasticizing molecules attached temporarily. One example of how this phase of the problem can be approached, the mixed ester, cellulose acetate butyrate, may be considered. Here the relatively large butyrate groups tend to hold the chains far apart at intervals, thus preventing a great amount of contact and developing rather weak attractive forces. In such a case, we should expect just what we find—an effect on physical properties similar to that developed by plasticization. This mixed ester exhibits greater solubility, a lower softening point, and greater flexibility than the straight acetate—such greater than could be expected from the simple rules of mixing acetate and butyrate derivatives.

Liebnersky and co-workers (16) have explained the mechanism of plasticizing by the sorption of polyvinyl chloride chain molecules.
They state: "The surface forces between liquidizer and vinyl chloride
could easily explained with the vinyl chloride by an raising from one another
the chain molecules of which the liquidizer is composed. As liquidizer is
removed, the vinyl chloride forms new molecules and brings them closer to-
gether; thus it becomes more difficult for the remaining liquidizer
molecules to cut out, and the volume additive property characteristic
of these plastics is conserved."

In an instance similar to that of softening paper with
glycerin, Platt and Jeff [17] concluded that glycerin is absorbed by the
cellulose. They based their conclusions on three different experiments.

In the first, glycerin-treated sheets of cellulose and cellulose were hung
in an oven at 960° C., with a constant stream of fresh air passing through
the oven. The sheets lost weight rapidly at first and then reached constant
weight. Even after reconditioning the sheets with water or other
solvents were to swell them, and recondition for 14 days, the sheets retained
the same glycerin content. Although different sheet weights were used and
various percentages of glycerin were added to the sheets, they had the same
final glycerin content after heating.

In the second experiment, sheets of cellulose were hung in a
vacuum box. A glycerin solution was also in the box which was sealed and
heated to 98° C. The sheets were removed and weighed from time to time;
the increase in weight indicated a glycerin evaporation losses. In the
third experiment, cellulose sheets were dipped into glycerin solutions of
various concentrations. After equilibration was attained, the sheets were
removed, squeezed out, and analyzed for glycerin. The solutions were also
analyzed for glycerin. Curves indicating glycerin adsorption were obtained.

The authors suggested that the adsorbed glycerin is held at the
end of the micelles and that the adsorbed glycerin, especially the free or
capillary-bound glycerin, should soften a sheet and make it more pliable.

Mayer (15) stated that "the force acting between the hydroxyl
groups (of cellulose) can be diminished by intermicellar swelling agents,
such as water, and still more so by intramicellar swelling agents."

A good review on the present concepts of the structure of cellulose and its surface properties, which are so important in considering the
role of fiber bonding in softening a sheet of paper, is found in "Incisive
Wood Chemistry" in the chapters by Park (12) and Stem (20).

Another more recent work concerning the physical properties of
cellulose and synthetic fibers is that of Hermans (21), in which the
presence of amorphous and crystalline regions in all types of cellulose and
the implications thereof are discussed.

In view of the explanations advanced for plasticizing mechanisms
in cellulose derivatives, it would seem very likely that the same theories
might be of value in explaining the softening mechanism of paper softeners.

At the present time, that property of paper known as softness is
not readily evaluated because no definition of this property is generally
accepted and because the methods for evaluating softness are usually of a
subjective nature.
In the "dictionary of paper" (22), softness of paper is defined as follows: "Softness may be one of several properties of a sheet of paper. In the case of tissues and towelin, 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 sensorily attractive 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."

Clark (23) also defined softness. "The softness of paper is the feeling of softness when a sheet is crumpled in the hand. This depends upon the ease of crumpling together with the absence of sharp edges in the crumpled sheet." In this article, Clark discussed the property of softness and its measurement, and described an instrument for measuring softness.

The Clark softness tester has been evaluated at the Institute of Paper Chemistry (24). It was found that Clark rigidity was well correlated with flexural rigidity as determined by a research method involving a torsion pendulum. Subjective tests for softness of facial tissues, towel tissue, waxing glassine, and bread wrappers were found to correlate well with the mean of the machine-direction and the cross-direction Clark softness values. The Clark method for the measurement of softness has been accepted as a tentative method (T 451 m-45) by the Technical Association of the Pulp and Paper Industry. The Surley stiffness tester was also investigated and found to be seriously in error for lightweight sheets. The same group (25) investigated the Surley-Mill E-1-S tester.
They found that the softness test was an indirect but poor measurement of compressibility.

Brown (25) measured softness of papers in a crumple tester. He measured the force necessary to crumple a specimen into a definite volume. This was done with paper making, tissue, and paper toweling. He also noted an increase in softness with increasing relative humidity.
The problem undertaken in this thesis is that of investigating and attempting to explain the action of softeners in making paper softer and more flexible than it would be without their addition. It is evident from the published literature in this field that no concept has been sufficiently investigated to explain satisfactorily the mechanism of softening. Therefore, the method of attack used in this problem is to investigate the various concepts already proposed to see if their examination would permit elucidation of the softening mechanism. In this study of the mechanism of softening paper with glycerin, the hydroscopic concept, the fiber lubrication concept, and the weakening of fiber bonds concept for the mechanism of softening paper are investigated. The matter of individual fiber softness is the subject of another dissertation.

One of the most widely used paper softeners, glycerin, was chosen for this work. The other common plasticizers for paper (such as the glycols, sugar syrups, and sugar alcohols) are less hydrophilic than glycerin in nature. It might be expected that they would exhibit softening mechanisms similar to that of glycerin.

A purified cellulose was chosen to make the sheets of paper used in this thesis because the alpha-cellulose content is high and substances which might interfere in interpreting the basic mechanism of the plasticizer are avoided.
THE HYDROSCOPIC CONSUMPTION OF GROUND-PEARL SODA

The work of Pike (1) and Hardenburg (2) gave evidence that sheets containing 5 per cent glycerin had a lower moisture content than untreated sheets at low relative humidities but the treated sheets were softer at all relative humidities. In order to examine more closely the possible hygroscopic action of glycerin in softening paper, it was decided to determine the moisture content of glycerin-treated pulp and papers at several relative humidities. Such an investigation might give further evidence for an understanding of the apparently anomalous behavior of glycerin in paper at low relative humidities.

EXPERIMENTAL

PREPARATION OF GLYCERIN-TREATED CELLULOSIC MATERIAL

A relatively pure source of cellulose, cotton linters, was chosen for the initial study of the moisture content of glycerin-treated cellulosic materials at various relative humidities. The sorption characteristics of cellulose are well known and require no new investigation. Sturm (30) gives a good review of the work done in this field. The use of a relatively pure cellulosic material enables a study of the hygroscopic action of glycerin without concern for the effects of glycerin on such a variety of components as are commonly found in wood pulps.

The cotton linters used in this work were obtained from the Hercules Powder Company. Their method of purifying is to direct the raw linters with 2.5 to 3.5 per cent of caustic soda and detergent. Then the linters are heated in a closed vessel with steam at a pressure of 30-100
p.s.i. for 2-6 hours. To prevent oxidation and degradation, air is removed from the disaster during the cooking process. The linters are thoroughly washed after the cooking process and given a mild bleach with chlorine. The linters used in this thesis were taken from a batch which had the analysis shown in Table I.

TABLE I

CHEMICAL ANALYSIS OF COTTON LINTERS

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<tr>
<th>Component</th>
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<tr>
<td>Alpha-cellulose</td>
<td>98.3%</td>
</tr>
<tr>
<td>Ash</td>
<td>0.13%</td>
</tr>
<tr>
<td>Copper number</td>
<td>0.06</td>
</tr>
<tr>
<td>Cuprammonium viscosity</td>
<td>124 centipoises</td>
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The analytical results are expressed on an oven-dry basis.

To further purify the linters of fats, oils, or waxes, they were extracted with benzene in a Soxhlet extractor for 4 hours. The linters were then given two one-hour extractions with boiling water to remove all the benzene and also water-soluble carbohydrate material. The purified linters were sucked dry on a Büchner funnel and allowed to air dry in a room conditioned at 50 per cent R. H. (relative humidity) and 73° F.

The purified linters were soaked in glycerin solutions to give them various glycerin contents. The glycerin used in these experiments was the c.p. product of the Baker Chemical Company. By trial, it was found that pulps would retain about 80 per cent of the glycerin that would theoretically be taken up as calculated from the glycerin concentration in the bath and the gain in weight of the wet linters. It was also found that
Some of soaked linters could be squeezed to about 25 per cent dryness on a Buchner funnel.

Cotton linter samples of 0, 0.5, 1.0, 2.5, 5, 10, 15, and 20 per cent glycerin content were desired for the moisture content experiments. Accordingly, samples of nearly dry cotton linters weighing about 13.5 grams each were soaked in 500 cc. volumes of glycerin solutions for about 4 hours. Glycerin solutions of 0.2, 0.5, 1.0, 1.7, 5.0, 11.7, and 15 per cent glycerin by weight were made up with distilled water for the soaking bath. The soaked linter samples were filtered on a Buchner funnel and thoroughly air-dried at 50 per cent R.H. at 73°F.

Glycérin in cotton linters and also in wood pulp sheets can be determined by its oxidation with nitrites. The method is applicable to the determination of polyhydric alcohols containing hydroxyl groups on adjacent carbon atoms as shown by Polayeschild (27). The reaction proceeds as follows:

\[
\text{HOCH}_2\text{CH}(_2\text{OH})\text{CH}_2\text{OH} + 2\text{KIO}_3 \rightarrow 2\text{HIO}_4 + 2\text{H}_2\text{O} + \text{H}_2\text{O}_2 + 2\text{K}_2\text{O}.
\]

The amount of KIO4 and KIO3 present at the end of the reaction is estimated by adding an excess of potash iodide and titrating the iodine liberated with standard thiosulphate solution. The reactions involved are:

\[
\text{KIO}_4 + 7\text{KI} + 4\text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + 4\text{K}_2\text{SO}_4 + 4\text{H}_2\text{O}
\]

\[
\text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}
\]

\[
\text{I}_2 + 2\text{Na}_2\text{C}_2\text{O}_4 \rightarrow \text{Na}_2\text{CO}_3 + 2\text{I}^-\text{I}
\]
Reagents and Solutions

Sodium thiosulfate  0.1 N (standardized)
Potassium permanganate  approximately 0.1 N
(Blank is run on this solution when it is used.)
Sulfuric acid  10% by weight
Potassium iodide  10% by weight
Starch solution.

Procedure

To a sample of glycerin in water (the proper size is 20 to 30 mg. of glycerin) is added exactly 30 ml. of potassium permanganate solution and 50 ml. of sulfuric acid solution. The reaction mixture is then heated in a boiling water bath for ten minutes, cooled to room temperature, treated with 10 ml. of potassium iodide solution, and titrated with thiosulfate, using starch solution in the usual way. Blanks are run on the potassium permanganate solution following an identical procedure, except that distilled water is substituted for the sample solution. Because iodine is liberated by the reaction of potassium iodide with either potassium dichromate or potassium iodate (in a ratio of 4 to 3), it is essential that the volume of thiosulfate required for the samples be at least 0.75 of the value of the blanks. One ml. of 0.1 N thiosulfate solution is equivalent to 0.302 mg. of glycerin.

Extraction of Cotton Linters and Alpha pulp Sheets

In order to apply the above method of analysis to cotton linters or alpha pulp sheets, it is necessary to extract the glycerin from the pulp or sheets. This may be accomplished by refluxing the sample with water.

The pulp or paper sample containing 20-30 mg. of glycerin is put into a 100-ml. round-bottomed flask with 50 ml. of water and partly refluxed.
for 45 minutes. The solution is cooled and decanted through a filter into an Erlenmeyer flask. The sample is washed with several small portions of water.

Because it is possible for some of the degradation products of cellulose to react with periodate, it is necessary to make a blank analysis on paper or cellophane known to be free of glycerin in order to establish what correction, if any, is to be applied to the determinations.

PREPARATION OF GLYCERIN-TREATED SHEETS

Sheets of glycerin-treated paper were required for making certain physical tests in the investigation of the softening of paper described later in this thesis. The moisture content data for these sheets at various relative humidities were also required in those investigations. These data were of additional use in investigating the hydrorheology concept of plasticizing and, therefore, are included in this section.

Commercial softwood al be pulp, a product of the Brown Company, was used in the preparation of the pulp sheets\(^1\). The pulp was disintegrated and beaten in the laboratory beater according to TAPPI Standard T 200 m-45. A beating time of 36 minutes, with 6500 grams on the bedplate, was required to give a pulp having a freeness of 670 cc, as measured with the Schoeniger-Stepler freeness tester. The beaten pulp was diluted with water to give about a 1% suspension. Twenty sheets of an average weight of 2.5 grams and about 8.5 inches square were made on the table and good sheet mold. The sheets were coughed off the wire on blotters, placed between dry blotters,

\(^1\) The term "al be sheets" is used hereafter to denote the sheets of paper made from al be pulp.
and removed after 1 minute at 20 °C. in the Williams press. The sheets were then removed and dried on a cold and hood revolving dryer, in which the steam pressure was 25 °C. A retention time of two minutes was required to get in dry, cockle-free sheets. The sheets were hung in the humidity-controlled room to condition at 50 per cent R. H. and 73° F.

Four sheets with five levels of glycerin content—0, 4%, 10, 15, and 20 per cent—were desired for the experiment. The experience of the Iwai in the laboratory at the Institute of Paper Chemistry showed that glycerin soaking baths containing approximately 3%, 10, 15, and 20 per cent glycerin by volume were necessary to give sheets of the desired glycerin content. Four sheets for each level of glycerin concentration were dipped into the respective glycerin baths. At the same time, five blotters were dipped into the bath solution. A photographic developing tray, 12 by 15 inches, was used for the bath. The sheets were allowed to soak in the bath for 15 minutes and then were removed and placed between the glycerin-soaked blotters. The sheets and blotters were allowed to stand for 10 days in this saturated condition. Then, each blotted sheet adhering to it was lightly pressed at 30 °C. for one minute in the Williams press. This was done to remove and remove any and all of five sheets of uniform glycerin content. After pressing, the sheets were removed from the blotters and dried for 2 minutes on the table and cut into the desired size. Five sheets were used at each level of 0, 4%, 10, 15, and 20° F. The glycerin-treated sheets were selected for glycerin content described in the next section. A total of 14 per cent of glycerin was found on the untreated 15° F. sheets. To hold one of the lower chain cellulose material in the sheets was worked out and consumed residue in the determination.
The method of measuring the moisture content of cotton linters and alpha sheets at various relative humidities was that described by Link (26). Essentially, the method involves weighing the sample of linters at several relative humidities to determine its moisture content at those humidities. A Petri dish containing the sample is suspended in a chamber in which the relative humidity has been fixed by the presence of a saturated salt solution. The suspending device for the Petri dish is given entrance to the conditioned chamber through a hole which is closed with a plug at all times except during the weighing. The sample is brought to constant weight at each relative humidity.

To determine the moisture content of the glycerin-treated sheets at the various relative humidities, it was first necessary to obtain the weight of the empty Petri dish in the relative humidity chamber. Then samples of approximately 1 gram each were weighed in the dishes at 50 per cent R. H. in the humidity- and temperature-controlled room. Duplicate samples were prepared for each of the different glycerin content levels of the cotton linters and duplicate samples were prepared for the alpha sheets.

Link (26) included a table of the relative humidities of various saturated salt solutions at three temperatures. The solutions used to establish various relative humidities in order to determine the moisture content of glycerin-treated sheets are listed in Table II with their equilibrium relative humidities at 75 ± 10° F.
TABLE II

EQUILIBRIUM RELATIVE HUMIDITIES FOR DISTILLED WATER SOLUTIONS

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>R. H. (at 75° F.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium chloride</td>
<td>LiCl</td>
<td>11.1</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>32.8</td>
</tr>
<tr>
<td>Barium nitrate</td>
<td>Ba(NO₃)₂</td>
<td>53.2</td>
</tr>
<tr>
<td>Sodium nitrite</td>
<td>NaNO₂</td>
<td>64.6</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>75.4</td>
</tr>
<tr>
<td>Ammonium phosphate</td>
<td>NH₄H₂PO₄</td>
<td>92.8</td>
</tr>
</tbody>
</table>

It is well known that cellulose shows hysteresis in its moisture content when water is sorbed or desorbed. Therefore, definite cycles of moisture desorption and adsorption were made in this study. The use of cotton linter samples was given a desorption-adsorption cycle by first desorbing from 50 per cent R. H. down to the dry condition over phosphorus pentoxide, with measurements of the moisture content being made at 32.8 and 11.1 per cent R. H. The samples were allowed to adsorb moisture and weighings were made at 32.8, 53.2, 64.6, 75.4, and 92.8 per cent R. H. The cycle was completed by obtaining points at 53.2 and 53.2 per cent R. H. The reverse of this cycle (an adsorption-desorption cycle) was applied to other samples of glycerin-treated lintors. The cycle consisted of adsorbing from 50 to 92.8 per cent R. H., desorbing to the dry condition over phosphorus pentoxide, and adsorbing back up to 53.2 per cent R. H., with several intermediate points below taken. The moisture content of these sheets was also determined at several points in the desorption-adsorption cycle. The sheets were first desorbed from 50 per cent R. H. down to the
dry state over phosphorus pentoxide with points being determined at 32.8 and 11.1 per cent R.H. Next, the sheets were subjected to increasing relative humidities with points being taken at 11.1, 32.8, 53.2, 64.6, and 75.4 per cent R.H. The cycle was completed by obtaining points at 64.6 and 32.8 per cent R.H.

The sheets were weighed to a constant weight at each of the relative humidities. At relative humidities of 53.2 per cent and below, it was possible to weigh the sheets to about 0.2 mg. However, at the higher relative humidities and with sheets containing large quantities of glycerin, in many cases it was not possible to weigh the sheets more accurately than to a constant weight of 1 to 2 mg. Small fluctuations in temperature cause a fluctuation in relative humidity and a large fluctuation in the moisture content of any free glycerin in the sheets or linters.

At the low relative humidities, periods of about 100 hours were found necessary to establish constant weight. However, at the high relative humidities and for samples containing large amounts of glycerin, constant weight often was obtained only after 180 hours.

Although no method is considered to be accurate for the determination of water in cellulose, because it is not possible to determine the point at which water of constitution is driven off, constant weight of cellulose over phosphorus pentoxide is considered to give a fairly satisfactory end point for dry cellulose. The samples, therefore, were dried over phosphorus pentoxide and this dry weight served as a base line from which the moisture content at each relative humidity point in the cycle could be calculated. This method also possessed advantage in that the sample was not destroyed in determining the dry weight.
The method described above for determining moisture at various relative humidities is applicable only when the sole variable in the weighing is the water content of the cell-loss. The glycerin content of the sheet cannot be considered to be strictly constant because glycerin does have a measurable vapor pressure at 50° C. and 0.9925 mm. of mercury. This vapor pressure might account for some loss of glycerin when it is considered that periods of one to two months were required to take the samples through the relative humidity cycle. The relative humidity chamber in which each sample is confined is small and the atmosphere therein is not changed except at each change in relative humidity condition. However, the saturated salt solution is not saturated with respect to glycerin and, therefore, it would be possible to lose glycerin from the sheet to the solution by evaporation.

Actually, the cotton linters were weighed over phosphorus pentoxide at the end of the relative humidity cycles and a very small loss of glycerin was found. The loss increased with glycerin content and the largest losses were in the order of 1 to 2 mg. from the linters containing the most glycerin. Fortunately, this loss is not large enough to interfere with the moisture determination of the glycerin-treated sheets.

Presentation of Moisture Content Data of Glycerin-Treated Cotton Linters

The moisture content data for the glycerin-treated cotton linters are found in Table III and IV. In Table III, the relative humidity cycle followed was one of moisture desorption followed by adsorption. The reverse is true for the moisture content data found in Table IV—i.e., the
TABLE III

MOISTURE CONTENT OF GLYCERIN-TESTED COTTON LINTERS AT VARIOUS RELATIVE HUMIDITIES
Desorption-Adsorption Cycle

<table>
<thead>
<tr>
<th>Glycerin Content (at 50% R.H.), mg./g.</th>
<th>32.8</th>
<th>64.6</th>
<th>92.8</th>
<th>32.8</th>
<th>64.6</th>
<th>92.8</th>
<th>53.2</th>
<th>64.6</th>
<th>92.8</th>
<th>53.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity, %</td>
<td>11.1</td>
<td>32.8</td>
<td>53.2</td>
<td>64.6</td>
<td>75.4</td>
<td>92.8</td>
<td>92.8</td>
<td>64.6</td>
<td>53.2</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Moisture content calculated on the basis of dry glycerin-free linters, mg./g.

0 | 0 | 47.8 | 24.3 | 41.6 | 59.8 | 72.1 | 87.6 | 154 | 84.1 | 69.5 |
0.62 | 6.6 | 47.4 | 23.1 | 40.9 | 58.7 | 73.6 | 90.8 | 165 | 86.1 | 70.2 |
1.06 | 11.3 | 46.5 | 22.4 | 40.3 | 60.7 | 73.4 | 91.6 | 171 | 85.8 | 69.0 |
2.53 | 27.5 | 43.8 | 19.4 | 38.0 | 57.1 | 74.6 | 96.6 | 198 | 85.4 | 67.4 |
5.75 | 72.0 | 42.7 | 17.2 | 37.9 | 63.6 | 84.6 | 115 | 297 | 81.0 | 68.3 |
11.72 | 142.9 | 45.6 | 16.0 | 41.6 | 76.1 | 111.2 | 164 | 491 | 114 | 79.1 |
1.9 | 177.1 | 54.8 | 16.2 | 51.4 | 108.2 | 160.6 | 252 | 967 | 164 | 107.3 |
3.2 | 323 | 69.2 | 19.6 | 68.5 | 149.7 | 213.3 | 336 | 1340 | 218 | 141.1 |

TABLE IV

MOISTURE CONTENT OF GLYCERIN-TESTED COTTON LINTERS AT VARIOUS RELATIVE HUMIDITIES
Adsorption-Desorption Cycle

<table>
<thead>
<tr>
<th>Glycerin Content (at 50% R.H.), mg./g.</th>
<th>53.2</th>
<th>64.6</th>
<th>92.8</th>
<th>32.8</th>
<th>53.2</th>
<th>64.6</th>
<th>92.8</th>
<th>64.6</th>
<th>92.8</th>
<th>53.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity, %</td>
<td>11.1</td>
<td>32.8</td>
<td>53.2</td>
<td>64.6</td>
<td>75.4</td>
<td>92.8</td>
<td>92.8</td>
<td>64.6</td>
<td>53.2</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Moisture content calculated on the basis of dry glycerin-free linters, mg./g.

2.53 | 62.4 | 77.1 | 97.9 | 154 | 85.7 | 68.2 | 45.9 | 13.5 | 17.7 | 38.0 | 57.8 |
11.72 | 74.5 | 108.3 | 155 | 433 | 108.5 | 78.9 | 41.9 | 15.4 | 13.7 | 37.6 | 70.7 |

1 All sheets were conditioned at 50% R.H., before the cycle was started.
2 on total weight of sheet.
3 Calculated on the basis of dry glycerin-free linters, mg./g.
4 Average of three determinations.
linters were first given a moisture absorption treatment followed by a
description. In the tables the sequence of relative humidities is the one
followed experimentally. Each moisture content value is the average for
three specimens of the same glycerin content.

The work of Hille (1) and Kriemunberg (2), which indicated that
glycerin does not soften paper by its lysozyme action at low relative
humidities, has been substantiated by the moisture content data obtained
for glycerin-treated cotton linters. Linters containing less than 6.3
per cent of glycerin had lower moisture contents at relative humidities up
to 93 per cent than the untreated linters. At 12 per cent relative
humidity, samples containing as much as 9.3 per cent glycerin had lower
moisture contents than the blank. Apparently, at the low relative
humidities, glycerin does not soften paper by virtue of its lysosyme in
properties.

The moisture content data obtained for the absorption-desorption cycle of Table VII were not widely different from the data for the adsorption-desorption cycle found in Table VII at comparable points. The results of this comparison served to demonstrate that glycerin is not irreversibly
bundled in some way to the cellulose at low relative humidities nor has it
any pronounced effect on the sorption characteristics of the cellulose when
taken through the drying cycle. If the glycerin were absorbed irreversibly
by the cellulose, the cellulose cycle would not be free to absorb moisture
as well as before the glycerin was added.

Another effect noted was the decrease in hysteresis of the moist-
ure content in the cotton linters with the increase in their glycerin
content. For instance, at 53.2% relative humidity, linters containing no glycerin had 10.4% more water than when exposed to the lower relative humidity by adsorption. However, linters containing 11.79% of glycerin had 1.9% more water on desorption. The hysteresis in moisture content of cellulose is explained by Urquhart and Millers (29) to be a result of swelling and collapse of cellulose fibers in the adsorption and desorption cycles. In the original water-soaked condition, the free hydroxyl groups of cellulose are practically all satisfied by water. When the cellulose is dried, these hydroxyl groups are freed and, as a result of the shrinking, the fibers are drawn together so that the individual groups of adjacent molecules mutually satisfy each other. Upon desorption, part of the hydroxyl groups that have not been satisfied are not freed by water adsorption, thus causing a decreased adsorption. The action of glycerin in affecting a decrease in hysteresis of the moisture content of cotton linters might be that of satisfying a portion of the hydroxyl groups so that they could not become irreversibly bonded together on drying. The polyhydric nature of glycerol might permit an attraction between glycerol and cellulose by hydrogen bonding. The physical size of the glycerol molecules, if they were adsorbed in the minute capillaries of cellulose, might also prevent collapse on drying. It seems very likely that glycerin penetrates well into the fiber structure to prevent hysteresis changes. The penetration of glycerin into synthetic fibers has been studied by Kermans (31) and found to proceed at a much slower rate than water. Kermans postulated that, in order for glycerin to penetrate cellulose, it was first necessary to swell the fiber structure with water. In the preparation of the glycerin-treated cotton
linters, the linters were soaked in glycerin solutions so that it was
possible for glycerin to enter well into the fiber structure.

PRESENTATION OF MOISTURE CONTENT DATA FOR GLYCERIN-TREATED ALPINE SHEETS

The moisture content data for glycerin-treated alpine sheets are
found in Table V. The relative humidity cycle employed was one of de-
creasing the relative humidity down to the dry condition, increasing it to
75.4 per cent, and, finally, returning to 55.2 per cent R. H. The moisture
content results are expressed on a glycerin-free dry fiber basis.

The trend in moisture content data obtained for glycerin-treated
alpine pulp sheets was the same as that for the treated cotton linters. At
11.1 per cent R. H., samples containing less than 21.5 per cent of glycerin
showed lower moisture contents than the untreated sheets. Sheets containing
2.95 per cent of glycerin had lower moisture contents up through 63 per
cent R. H. than the untreated sheets. These data give support to the con-
cclusion made on the basis of the moisture content of glycerin-treated
linters—that glycerin does not soften paper at low relative humidities
on the basis of its increasing the moisture content of the sheet.

Decrease in the hysteresis of the moisture contents of the
alpine sheets was found with an increasing glycerin content just as it was
found for the glycerin-treated cotton linters. This is readily seen by
comparing the moisture contents of the sheets at the same relative humidities.
For example, at 44.2 per cent R. H., sheets containing no glycerin
had 2.0% less water on desorption than the equilibrium desorption
content. However, sheets containing 21.5 per cent of glycerin had a
## Table V

<table>
<thead>
<tr>
<th>Glycerin Content</th>
<th>Relative humidity, %</th>
<th>Moisture content calculated on the basis of dry glycerin-free alpha paper, mg./g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.8</td>
<td>32.3</td>
<td>47.7 67.6 82.5 89.4 75.6</td>
</tr>
<tr>
<td>11.1</td>
<td>11.5</td>
<td>42.1 66.6 85.5 109.8 96.5</td>
</tr>
<tr>
<td>11.1</td>
<td>11.5</td>
<td>42.1 66.6 85.5 109.8 96.5</td>
</tr>
<tr>
<td>32.8</td>
<td>32.3</td>
<td>47.7 67.6 82.5 89.4 75.6</td>
</tr>
<tr>
<td>53.2</td>
<td>54.6</td>
<td>75.4 64.6 63.4 53.2 36.6</td>
</tr>
<tr>
<td>6.6</td>
<td>6.6</td>
<td>53.2 35.1 33.8 32.5 27.2</td>
</tr>
</tbody>
</table>

1 All sheets were conditioned at 50% R.H., before the cycle was started.
2 On total weight of sheet.
3 Calculated on the basis of dry glycerin-free alpha paper, mg./g.
4 Average of two determinations.

---

Difference of only 1.1 mg. of water in their equilibrium moisture contents when equilibrium was approached from the two different directions.

### Introduction of the Glycerin-Cotton Linters Cycle

Although it has been demonstrated that the moisture content of glycerin-treated cotton linters is lower than that of untreated linters at low relative humidities, the reason for this behavior remains to be explained. The decrease in the hysteresis of the moisture content of cotton linters affected by glycerin suggests that glycerin may be absorbed by cellulose. Shutt and Lack (17) reached the same conclusion in their study of glycerin-treated cellulose and cotton.
Storm (30) and Storm and Hansen (31) have studied the selective adsorption of salts and some organic compounds on wood from aqueous solutions. They concluded that adsorption could be measured by swelling, over these compounds which tended to displace the most sorbed water caused the greatest swelling. Storm (30) gave a table for the external volumetric swelling relative to that in water for cylinder white pine sections in various water-free organic liquids. Although the swelling power of glycerin is not given, it is seen that the monoalcohol alcohols up through ethyl alcohol cause some swelling of the wood sections and the swelling decreases with increasing chain length of the alcohol. Press and Diakowsky (32) studied the swelling of cellulose fibers in several organic liquids. They also found that monoalcohol alcohols up through ethyl alcohol swelled cellulose but, in addition, they found that ethylene glycol, although not as effective in swelling as water, was a better swelling agent than even methanol alcohol. It would seem likely that glycerol, with its three hydroxyl groups and polar nature, would also cause appreciable swelling of cellulose.

Another measure of adsorption is the heat evolved in wetting.
Theard and Newhouse (33) and Morrison, Campbell, and Maas (24) found that the total heat of wetting of cellulose by a series of normal aliphatic alcohols decreased with increasing chain length. The conclusion from this that alcohols are adsorbed by cellulose is in conformity with that obtained by swelling measurements and tends to support the theory that glycerin is adsorbed by cellulose.

The moisture content data for glycerin-treated cotton linters in Table III permit the investigation of the cellulose-glycerin-water system to
determine if the glycerin adsorption theory holds. The moisture content of untreated cotton linters, as well as the data for the treated linters, is given in Table I. The equilibrium moisture content of glycerin at various relative humidities, obtained from the International Critical Tables (35), is shown in Figure 1. If glycerin were not adsorbed by cellulose or in any way inactivated by it, both the glycerin and the cellulose would show their normal equilibrium moisture contents at any chosen relative humidity. The sum of the moisture contents of glycerin and untreated cotton linters at each relative humidity should then give the moisture content of the glycerin-treated cellulose. However, that there is a discrepancy between these calculated moisture contents and the observed moisture content is seen in Table VI.

In this table, the observed moisture content of the glycerin-treated cotton linters was subtracted from the calculated moisture content. The data are plotted in Figure 2. The points chosen were all adsorption points in the relative humidity cycle.

| TABLE VI |
| WEIGHT OF WATER HOLD BY GLYCERIN-TREATED COTTON LINTERS AT VARIOUS RELATIVE HUMIDITIES ON A 1 g. DRY FIBER BASIS IN MILLIRAMS |
| WEIGHT OF GLYCERIN IN SHEET, \( \% \), |
| 11.1% R.H. | 27.8% R.H. | 53.2% R.H. | 64.6% R.H. |
| 9.5 | 1.6 | 1.8 | 2.4 | 2.7 |
| 11.3 | 2.6 | 3.6 | 5.8 | 6.4 |
| 27.5 | 5.6 | 3.6 | 14.8 | 15.4 |
| 72.0 | 11.4 | 11.9 | 35.0 | 44.6 |
| 72.4 | 16.9 | 31.4 | 57.5 | 72.1 |
| 323 | 24.1 | 44.5 | 50.4 | 97.1 |

* 1 g. glycerin-free fiber basis
FIGURE 1

Moisture Content of Glycerol at Various Relative Humidities at 25° C.
FIGURE 2

Difference between Observed and Calculated Moisture Contents of Glycerin-Treated Cotton Linters at Various Relative Humidities

- 64.6% R. H.
- 53.2% R. H.
- 32.8% R. H.
- 11.1% R. H.

Glycerin content of cotton linters (dry glycerin-free basis), mg./g.
The increasing discrepancy with increasing glycerin content between the calculated moisture content of glycerin-treated cotton lint and the observed moisture content indicates that the glycerin or the cellulose or both are in some way being inactivated in the cellulose-glycerin-water system. One explanation might be that some of the glycerin is located in the cellulose micellar system in such a way that the relative size of the glycerin molecule and the size of the capillary structure of the cellulose might physically prevent the full moisture sorption of the cellulose and glycerin. Probably such a mechanism does not explain the moisture discrepancy very well. In consideration of the modern theory of molecular attraction, it would be expected that there would be some attraction between celluloseic and glycerin hydroxyl groups in the confined capillary regions. Very likely the glycerin molecules prevent moisture sorption because the glycerin molecules may occupy portions of the surface available for moisture sorption, but the glycerin molecules should not be considered to be inert particles in the cellulose capillaries.

A more plausible explanation for the discrepancy in moisture content is that of glycerin adsorption by cellulose and, therefore, prevention of the normal quantity of moisture adsorption. The increasing discrepancy with increasing glycerin content would mean that more glycerin was being adsorbed. The curves level off with increasing glycerin concentration, probably because the cellulose adsorbing surface becomes saturated with glycerin. The polar and hydrogen nature of both cellulose and glycerin suggests adsorption, and the literature references cited above also substantiate this concept. Discrepancies between observed and calculated moisture contents were also found for glycerin-treated lime sheets.
Apparently, the adsorbed glycerin is replaced, partially by water because water may be a better swelling agent and, therefore, more strongly adsorbed on cellulose than is glycerin. Also with increased moisture content, the equilibrium of the whole glycerin-water-cellulose system is changed. This system is a two-phase, three-component one whose composition is determined by quantitative relationships at equilibrium. The quantity of moisture held by the cellulose is determined by the water-vapor pressure in the surrounding atmosphere. The quantity of moisture held by the free glycerin is also fixed by the water-vapor pressure in the surrounding atmosphere.

The quantity of glycerin held by the cellulose is dependent on the concentration and quantity of glycerin solution in contact with the cellulose.

SUMMARY

It was found that both glycerin-treated cotton linters and alpha
nyl sheets had lower moisture contents than the untreated linters and
sheets at the same low relative humidities. Therefore, the hygroscopicity
concept of softening cannot explain the softening mechanism of glycerin.
This observation seems to be but a part of the generalization that, at all
relative humidities, glycerin-treated cellulose has a lower moisture content
than can be calculated by summing the moisture content of untreated cellulose
and the equilibrium moisture content of the glycerin in the linters if it
were considered free. The concept that glycerin in adsorbed by cellulose
seems to agree well with the observed behavior of the glycerin-water-
cellulose system.
The softening of paper or with plasticizers has been attributed to a lubrication of the fibers in the sheet by Hildebrand and Nadelson. According to their idea, if a sheet were lubricated, the fibers would slide over one another easily on flexure and impart a feeling of softness to the paper. However, in consideration of the structure of a sheet of paper, it would seem that the slipage distance could only be very small. If gross slipage did occur, the fibers would no longer hold together in a sheet because the bonding between fibers would be destroyed. Therefore, the relative motion between fibers must be very small in flexing or crumpling a piece of paper.

In order to consider how fiber lubrication can be measured, a piece of paper may be thought of as a beam. When a beam is made to vibrate and the force is released, the beam will continue to vibrate until the energy is transformed through friction to heat. This friction is attributable to the viscosity of the medium in which the vibration occurs and to internal friction in members which are deformed. In the case of paper, the internal friction could be the result of friction between or within the fibers. The internal friction might be decreased by some lubrication action, wherein lubricant molecules decreased the force of attraction between fiber surfaces or micelles in the fiber. It is known that friction between surfaces in contact increases with an increase in the force which holds them together. The adhesion of glycerin on fiber surfaces might cause a separation of the surfaces and give a form of boundary lubrication so that the internal friction would be decreased without affecting enough adhesion to cause a
mixture of the sheet. It would seem, therefore, that a measurement of the internal friction of glycerin-treated paper might be used to study the lubricating action of glycerin in paper. Van den Akker (36) has shown that internal friction in paper may be measured by use of a torsion pendulum (see Figure 3).

Since the mathematical theory underlying Van den Akker's (36, 36) torsion pendulum method for measuring internal friction in paper has been discussed only briefly, it is developed below.

Under the stress of shear, Newtonian liquids exhibit strain at once, and it is an experimental fact that the stress is proportional to the velocity gradient:

$$\tau = \eta \frac{dv}{dz},$$

where $$\tau$$ is the shearing force,

$$A$$ is the area over which the shearing force acts,

$$\frac{dv}{dz}$$ is the velocity gradient in the liquid caused by shear, and

$$\eta$$ is the coefficient of viscosity of the medium;

or

$$\tau = \eta \frac{dv}{dz}.$$

In a visco-elastic solid, in which frictional stress is proportional to the rate of strain, the frictional force on a volume element $$dV$$ is

$$d F = C (\varepsilon)(d\varepsilon/dt),$$

where $$C$$ is the coefficient of internal friction and $$\varepsilon$$ is the instantaneous strain of the material (see Figure 3a).
FIGURE 3

TORSION PENDULUM
The instantaneous power \( \delta P \) expended in effecting deformation in the element is

\[ \delta P = \mathbf{v} \delta \mathbf{E}, \]

where \( \mathbf{v} \) is the instantaneous velocity of deformation along the \( z \) axis.

The instantaneous velocity may be given by

\[ \mathbf{v} = \frac{d}{dt} \frac{\delta z}{\delta t} = \left( \frac{\Lambda \delta z}{\Lambda t} - \Lambda \delta z \right) / \Delta t, \]

\[ \lim_{\Delta t \to 0} \]

The instantaneous strain experienced by the material varies with time:

\[ \varepsilon = \Delta \frac{\delta z}{\delta z}; \quad \varepsilon = \Delta \frac{\delta z}{\delta z}, \]

or, when \( \Delta t \to 0 \),

\[ \mathbf{v} = \left( \frac{\delta z}{\delta t} - \frac{\delta z}{\delta t} \right) / \Delta t = (\Delta e / \Delta t) \delta z \]

and

\[ \mathbf{v} = \left( \frac{\delta e / \delta t}{\delta e / \delta t} \right) \delta z. \]

Substituting this expression for \( \mathbf{v} \) in the equation for power expended in causing deformation,

\[ \delta P = C \left( \frac{\delta e / \delta t}{\delta e / \delta t} \right) \delta z \left( \delta x \delta y \right) \delta e / \delta t \]

\[ = C \left( \frac{\delta e / \delta t}{\delta e / \delta t} \right)^2 \delta x \delta y \delta z \]

and, in the limit,

\[ dP = C \left( \frac{\delta e / \delta t}{\delta e / \delta t} \right)^2 \delta x \delta y \delta z. \]

The type of torsion pendulum which has been used to measure internal friction is shown in Figure 3b. This figure gives a top view of the essential parts of the pendulum. Rod \( \mathbf{A} \) carries two masses whose distance from the center, \( \mathbf{B} \), may be varied. Clamps \( \mathbf{C} \) is rigidly connected to the rod and the assembly is hung on a fine wire having a small torsion constant. The sample strip is clamped at one end and at the other end of the strip is cemented to a roller which can move in the arc of a circle and is also free to rotate on its axis. The sample is thus allowed lateral motion but no
vertical rotation in flexure. To a hree, the pendulum is given a small
displacement and is released, and its period, \(T\), is measured with a stop
watch. The initial and final displacements after \(n\) swings are also observed.

The strain \(e\) in a beam at any point \(y\) distance from the neutral
surface (see Figure 3a) is given by
\[
e = \frac{y}{R}.
\]
Differentiating with respect to time,
\[
\frac{de}{dt} = (-\frac{y}{R^2})(\frac{dR}{dt})
\]
Therefore, the expression for strain energy in a volume element during
flexion of the beam becomes
\[
\frac{dF}{dx} = C(\frac{y^2}{R^4}) \cdot (\frac{dR}{dt})^2 \, dy \, dx \, dz.
\]
In integration with respect to \(x\) and \(y\), the expression becomes
\[
\frac{dF}{dx} = \left(\frac{bR^3}{12}\right) \cdot \left(\frac{dR}{dt}\right)^2 \, dy \, dz,
\]
where \(b\) is the width of the beam and \(w\) is the thickness.

The bending moment for a beam, \(M\), is related to the flexural
rigidity, \(EI\), in the following manner:
\[
\frac{1}{R} = \frac{M}{EI}
\]
and, for any point on a beam \(y\) distance from the clamped end (see Figure 3d), this
expression becomes
\[
\frac{1}{R} = \frac{y}{EI} = (1-y) \frac{F}{EI}.
\]

By differentiating and squaring,
\[
\left(\frac{1}{R^2} \frac{dR}{dt}\right)^2 = \left(\frac{(1-y)^2}{y^2} \frac{y^2}{R^2} \frac{dF}{dt}\right)^2
\]
and substituting into the expression for instantaneous power consumed during
plastic flow or flexure,
\[
\frac{dP}{dx} = \left(\frac{bdw^3}{12}\right) \cdot \frac{(1-y)^2}{y^2} \cdot \left(\frac{dF}{dt}\right)^2 \cdot \frac{dF}{dx} \, dx.
\]
Integrating with respect to $r$, 

$$ P = \left( \frac{bdx^3}{36r^2} \right) (dx/dr)^2. $$

but for this type of bending at point $m$ where the force is applied, 

$$ P = 3\pi E_{m} L^{3}. $$

For small angles $\Delta t \approx L$, approximately 

and 

$$ (\Delta t/dr)^2 \approx L^2 \omega^2, $$

where $\omega$ is the angular velocity of the end limb.

Then, 

$$ (\Delta t/dr)^2 = (gE^{2}2/16)(da/da)^2 $$

$$ = (gE^{2}2/16)w^2, $$

so that the expression for instantaneous power becomes, 

$$ P = \left( \frac{bdx^3}{4L} \right) w^2. $$

However, the power consumed in damped vibration of a torsion

and limb is given by

$$ P = gw^2 $$

where $g$ is the torsional damping constant—i.e., the frictional torque, 

$$ g = gw \quad \text{and} \quad P = gw. $$

Then 

$$ g = \frac{bdx^3}{4L}. $$

By experiment, the vibration was found to decrease in logarithmic

fashion so that the logarithmic decrement, $\lambda$, may be used:

$$ \lambda = \left( \frac{g_{o} + g}{1} \right)/2L, $$

where $g_{o}$ is the torsional damping constant of the system without the

specimen in place, 

$g$ is the torsional damping constant of the system with the specimen included, 

$L$ is the period of one complete vibration, and 

$L$ is the dynamic moment of inertia of the vibrating system.
Then \[ a + a_0 = 2I \lambda /T \]
or \[ bT^2/4 = 2I \lambda /T - a_0. \]

For the logarithmic decrement,
\[ \lambda = (1/n) \ln \left( \theta_0 / \theta_n \right) \]
where \( \theta_0 \) is the initial angular displacement in degrees, and
\( \theta_n \) is the final angular displacement after \( n \) complete vibrations.

Hence,
\[ c = \left( L / b^3 \right) \left[ \left( 4.6L / nT \right) \log_{10} \left( \theta_0 / \theta_n \right) - a_0 \right] \]
or \[ c = \left( 6.4L / b^3 \right) \left[ \log_{10} \left( \theta_0 / \theta_n \right) / nT - \log_{10} \left( \theta_0 / \theta_n \right) / b^2 T^2 \right] \]
where \( \theta_0, \theta_n, a_2, T_0 \) are values with no units in place.

The dimensions of \( c \) are poises or grams per centimeter-seconds.

The dynamic moment of inertia can be determined by finding the period of oscillation for the pendulum without a sample and adding equal masses of known dimensions to the connecting rod, \( dd' \), of Figure 3b re-determining the period of oscillation.

The dynamic moment of inertia is then given by
\[ I = \left( mT^2 + mT'^2 / T \right) / T^2 - 1 \]
where \( I \) is the dynamic moment of inertia of the pendulum in \( cm^2 \),
\[ (76.26 cm^2 \text{ for the pendulum used}), \]
\( m \) is the combined mass of the added masses in grams,
\( l \) is the distance from the center of the pendulum to the center of added mass in grams,
\( d \) is the diameter of weights in centimeters,
\( T' \) is the period of the pendulum with the added mass, and
\( T \) is the period of the pendulum with no added mass.
The torsion pendulum used to make internal friction and molecular viscosity measurements is shown in Figure 3. Rod 4 carries two markers whose distance from the center may be varied to give the desired period. Clamp 6 is rigidly connected to the rod, and the assembly is hung on a fine wire, S, having a small torsion constant. The sample strip of paper, T, is clamped at one end in Clamp 7 and the other end is cemented to pin V, which is free to rotate. Pin F is fastened to post C and the pin T is allowed lateral motion because the coulumbic assembly, H, is free to rotate on pin P. This arrangement allows the paper free lateral motion in flexing but keeps it from swaying or moving in the vertical direction. Assembly II can be rotated by lever I so that the paper may be held closer for slight flexure. The whole assembly II may be raised or lowered by loosening screw J and adjusting post C to the desired height. Post F is used to support the torsion pendulum device. To zero the instrument, lever I is rotated. This causes the torsion wire and, therefore, the whole pendulum to change its rest position. To prevent clamp 5 from oscillating when a sample is being inserted, clamp 7 is raised to the position indicated in Figure 3. Clamp 7 is moved down on shaft K when the pendulum is made to vibrate.

To determine the period of the pendulum, clamp P is lowered and rod 4 is displaced. Then the whole pendulum vibrates and the time for any number of oscillations is measured with a stopwatch. The blank is determined for the pendulum in the absence of a paper specimen. To determine the damping for internal friction measurements, clamp P is lowered and rod 4 is brought to a zero reading on scale T. The rod is then rotated to some other reading on the scale and allowed to oscillate. After the desired number of
swings, the scale reading is again observed. The blank is determined by
measuring the dam,ing without a paper sample in place. In order to obtain
greater accuracy, a beam of light is directed on mirror \( B \) on Clamps \( C \) which
rotates. The reflected light falls on a circular scale about 10 inches from
the center of rotation and displacement readings are observed on the scale.

**PROCEDURE FOR OBTAINING INTERNAL FRICTION**

Sheets containing up to 42 per cent of glycerin were prepared for
the internal friction measurement by the method described on pages 21 and 22.
The sheets contained 0, 2.8, 5.7, 15.7, and 32.6 per cent of glycerin as
determined by the periodate oxidation method. Five or six specimens were
taken for the internal friction measurement at each relative humidity in
order to obtain suitable average values. The untreated sheets were not
given a soaking in water when the other sheets were soaked in the glycerin
baths because the water-soaked sheets had a tendency to cockle on drying,
whereas the glycerin-containing sheets did not. In order to determine the
effect of soaking, one comparison of internal friction was made at 42 per
cent R. H. in which sheets resoaked in water and carefully dried on the
noble and good drier were compared with untreated alpha sheets that were not
resoaked.

**TRYING OF SHEETS AT VARIOUS RELATIVE HUMIDITIES**

The internal friction of glycerin-treated sheets was measured at
several relative humidities in order to determine the effect of moisture on
this property. Water of itself is an effective softener and it is of value
to determine how it affects fiber internal friction as measured by internal
friction. The moisture contents of glycerin-treated sheets have been determined over a wide range of glycerin contents in connection with the study of the hygroscopicity concept of softening and are found in Table IV.

A relative humidity range of 75 per cent down to the driest condition obtainable was desired for making the internal friction measurements in order to discover how internal friction might vary with moisture content. A cabinet was designed and constructed for the purpose of providing a test chamber at a known relative humidity. The design of the cabinet is shown in Figure 4.

The cabinet was made from sheet metal and was provided with a close top so that all testing operations could be seen from above. The bottom and sides of the cabinet were constructed from galvanized iron. The joints were soldered. Conditioned air was passed into the chamber through a tube at B and could be exhausted at X. Rubber sleeves 1/2 inch long were inserted on the air holes at 4. The rubber sleeves were made from rubber dental dam held together with rubber cement. An entrance for inserting or removing specimens and equipment was provided at G. A glass plate was used to cover this entrance. A moisture barrier was obtained around this entrance and between the top plate and its flange by closing the gaps with modeling clay. When not in use, the air holes were sealed with glass plates clamped tightly against the rubber sleeves. A small hole, Y, closed with a cover glass, was provided to allow light to enter the chamber and shine on the mirror on the torsion pendulum. The torsion pendulum and scale were arranged in the cabinet so that light reflected from the pendulum would appear on the circular scale and thus permit the deflections to be read easily from above.
FIGURE 4
Relative Humidity Cabinet
It was necessary to wear rubber nitrile gloves when the hands were inserted into the cabinet to manipulate the torsion pendulum. The rubber gloves and sleeves prevented the rapid transfer of moisture vapor from the hands and arms into the cabinet at low relative humidities, and also prevented loss of moisture from the cabinet at high relative humidities.

The constant humidity cabinet was kept in a room in which the temperature was held at 75 ± 10°F. In order to maintain desired relative humidity conditions, the air passing into the chamber was conditioned to give the desired relative humidity by bubbling compressed air through three gas washing bottles containing the respectively saturated salt solution. The air was bubbled through the solutions slowly to insure proper moisture content. For the low relative humidity, the first washing bottle was filled with anhydrous calcium chloride because the air from the compressed air line tended to be saturated with water vapor. In order to obtain dry conditions in the cabinet, phosphorous pentoxide was put into strikers within the cabinet and the entering air was passed through anhydrous calcium chloride and anhydrous traps.

The relative humidity in the cabinet was determined with electric hygrometers as described by Van der Vler (17). The actual humidity determination of the relative humidity within the internal friction measurements in the cabinet was carried out at a certain scale. When variation of ± 1% occurred, the testing was discontinued until the desired value was attained. The variation in relative humidity was caused by passage of water vapor from the hands and arms through the rubber gloves and sleeves. Further check on the relative
humidity was provided by keeping samples of alpha paper in the chamber. These samples could be removed and weighed at any time and the moisture content checked against the moisture data reported in Table V. At 6.5 percent R.H., the electric hygrotherm was not used because the practicality of this device at this relative humidity has not been proven. Therefore, the weighing method was employed to determine the relative humidity.

MEASUREMENT OF SHEET THICKNESS

The thickness of all test sheets was required for internal friction calculations. TAPPI Standard T 411 M-84 was employed. However, the Federal compressibility gauge was used instead of the usual caliper because it gave readings to 0.00001 inch. The weight employed gave seven pounds per square inch pressure, which comes within the TAPPI specifications. Five measurements of thickness were made on each sheet following the internal friction measurement at each relative humidity.

PREPARATION AND GRAPHING OF INTERNAL FRICTION DATA

The internal friction data for the glycerin-treated alpha sheets are found in Table VII and the average values are graphed in Figure 5. Maximum, minimum, and average internal friction values, as well as the standard error, are included in the table. The standard error or the standard deviation of the mean is given by

\[ \sigma = \left[ \frac{d_1^2 + d_2^2 + \ldots + d_n^2}{n} \right]^{1/2} \]

where \( d_1, d_2, \ldots, d_n \) are deviations from the arithmetic mean and \( n \) is the number of readings.
### TABLE VII

**Internal Friction of Glycerin-Tin Alloy Sheets at Various Relative Humidity**

<table>
<thead>
<tr>
<th>Glycerin content (at 50°F. R. H.), %</th>
<th>75.4</th>
<th>63.2</th>
<th>52.8</th>
<th>41.1</th>
<th>6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Relative Humidity, %</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximum</td>
<td>270</td>
<td>218</td>
<td>202</td>
<td>227</td>
<td>211</td>
</tr>
<tr>
<td>minimum</td>
<td>208</td>
<td>188</td>
<td>194</td>
<td>153</td>
<td>165</td>
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<tr>
<td>average</td>
<td>230</td>
<td>207</td>
<td>201</td>
<td>188</td>
<td>183</td>
</tr>
<tr>
<td>standard error</td>
<td>10.7</td>
<td>3.3</td>
<td>19.3</td>
<td>10.9</td>
<td>11.7</td>
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<td>2.7</td>
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<td></td>
</tr>
<tr>
<td>maximum</td>
<td>264</td>
<td>249</td>
<td>286</td>
<td>303</td>
<td>233</td>
</tr>
<tr>
<td>minimum</td>
<td>228</td>
<td>191</td>
<td>214</td>
<td>236</td>
<td>185</td>
</tr>
<tr>
<td>average</td>
<td>251</td>
<td>217</td>
<td>247</td>
<td>256</td>
<td>211</td>
</tr>
<tr>
<td>standard error</td>
<td>8.7</td>
<td>12.4</td>
<td>8.9</td>
<td>13.9</td>
<td>10.2</td>
</tr>
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<td>9.2</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximum</td>
<td>274</td>
<td>311</td>
<td>307</td>
<td>306</td>
<td>286</td>
</tr>
<tr>
<td>minimum</td>
<td>237</td>
<td>291</td>
<td>174</td>
<td>209</td>
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<tr>
<td>average</td>
<td>257</td>
<td>287</td>
<td>221</td>
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<td>263</td>
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<td>standard error</td>
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<td>13.6</td>
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<td>18.7</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximum</td>
<td>146</td>
<td>331</td>
<td>337</td>
<td>286</td>
<td>304</td>
</tr>
<tr>
<td>minimum</td>
<td>129</td>
<td>167</td>
<td>161</td>
<td>207</td>
<td>212</td>
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<td>average</td>
<td>139</td>
<td>167</td>
<td>187</td>
<td>230</td>
<td>253</td>
</tr>
<tr>
<td>standard error</td>
<td>3.1</td>
<td>12.4</td>
<td>10.1</td>
<td>12.7</td>
<td>11.9</td>
</tr>
<tr>
<td>41.4</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>maximum</td>
<td>126</td>
<td>123</td>
<td>155</td>
<td>178</td>
<td>195</td>
</tr>
<tr>
<td>minimum</td>
<td>81</td>
<td>140</td>
<td>113</td>
<td>159</td>
<td>154</td>
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<td>average</td>
<td>103</td>
<td>113</td>
<td>134</td>
<td>169</td>
<td>170</td>
</tr>
<tr>
<td>standard error</td>
<td>6.1</td>
<td>4.8</td>
<td>5.3</td>
<td>2.4</td>
<td>7.7</td>
</tr>
</tbody>
</table>

At all relative humidities, the internal friction was found to increase initially and then decrease with glycerin content. If only a lubricating action were involved, a decrease in internal friction would be expected. That the increase in internal friction is significant is evident from the magnitude of the standard errors. Therefore, it would seem that, for low glycerin contents, some factor other than lubrication causes a change in the internal friction.
Internal Friction of Glycerin-Treated Alpha Sheets at Various Relative Humidities

- 75.4% R. H.
- 53.2% R. H.
- 32.2% R. H.
- 11.1% R. H.
- 6.5% R. H.

Glycerin content (at 50% R. H.), %
For sheets containing no glycerin but increasing amounts of water (because of increase in relative humidity), the internal friction was found to increase with the moisture content. The increased internal friction could be the result of increased motion between fibers because, in this way, more energy would be expended. An increase in the motion between fibers would be expected if the forces holding them together were weakened. One indication of the weakening of fiber bonds is found in Table VIII, in which the thicknesses of the test sheets are given for various relative humidity and glycerin content conditions. It is seen that the thickness of the sheets is increased both with moisture and glycerin. The swelling of cellulose with water is a well-known phenomenon and the swelling with glycerin was to be expected. Water is not an intramicellar swelling agent and, therefore, the swelling must occur between micelles or fibers. An increase in these distances would cause a weakening of the fiber bonds or micellar bonds and, thus, allow greater movement of the fibers or micelles when under stress. It is shown in a later section that the fiber bonds are weakened but that individual fiber strength is retained on increasing the glycerin and moisture content. In view of the swelling information, it would seem that the initial increase in internal friction is to be expected. To illustrate, it can be shown that cloth in which fibers are not bonded together has a very high internal friction coefficient because of the motion between fibers. As the cloth is starched and the fibers are bonded together, the internal friction is decreased.

With large amounts of glycerin in the paper, however, the internal friction was found to decrease. This indicates that, even though the relative motion between fibers is increased, some sort of lubricating action...
## Table VIII

Volatility of Glycerin-Derived from Hydrate to at Various Relative Humidities

<table>
<thead>
<tr>
<th>Glycerin Content (at 50° B.°)</th>
<th>75.4</th>
<th>55.2</th>
<th>32.8</th>
<th>11.1</th>
<th>6.5</th>
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</thead>
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<tr>
<td>Thickness, 0.001 in.</td>
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<td></td>
<td>4.73</td>
<td>4.65</td>
</tr>
<tr>
<td>19</td>
<td>5.00</td>
<td>4.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td>4.35</td>
<td>4.27</td>
<td>4.27</td>
<td>4.12</td>
</tr>
<tr>
<td>32</td>
<td>4.96</td>
<td>4.36</td>
<td>4.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>5.06</td>
<td>5.00</td>
<td>4.95</td>
<td>4.95</td>
<td>4.93</td>
</tr>
<tr>
<td>39</td>
<td>5.08</td>
<td>5.05</td>
<td>5.00</td>
<td>4.97</td>
<td>5.00</td>
</tr>
</tbody>
</table>
must be involved. Possibly the fiber surfaces are spread further apart so that glycerin molecules and water molecules form a fairly continuous layer and serve as lubricating agents. That water, as well as glycerin, is effective as a lubricant is seen from the decrease in internal friction with increasing relative humidity for an oil containing larger amounts of glycerin. It has been shown previously that glycerin is adsorbed by cellulose and the adsorption of water is well known. Boundary lubricants show the phenomenon of adsorption and, therefore, both glycerin and water should be good boundary lubricants for paper fiber lubrication. The distance between well lubricated and swollen fibers must be small in order to maintain fiber structure and strength on stressing, so that possibly boundary lubrication is required for paper fibers.

The relation between fiber lubrication and softness has not been discussed, since the lubrication concept seems to be tied in closely with the concept of weakening of fiber bonds. It is discussed in a following portion of this thesis which deals with weakening of fiber bonds.

In the experiment to determine the effect of soaking an internal friction of untreated alpha sheets, no significant difference was found between the runaked and unrunaked sheets. This experiment was made to determine whether the untreated alpha sheets needed to be runaked in a water bath to give a suitable blend because the glycerin was put into the sheets by a solute procedure. The results are found in Table II.
Internal Friction Coefficient, megapoisces

<table>
<thead>
<tr>
<th></th>
<th>Boweot</th>
<th>Not Boweot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>295</td>
<td>269</td>
</tr>
<tr>
<td>Minimum</td>
<td>215</td>
<td>138</td>
</tr>
<tr>
<td>Average</td>
<td>212</td>
<td>202</td>
</tr>
<tr>
<td>Standard error</td>
<td>33.8</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Currently, the sheet structure is not altered considerably in the rewetting of untreated bleached sheets and it is not necessary to rewet the sheet in water to obtain a suitable blank.

**Summary**

The internal friction coefficient of glycerin-treated sheets was found to increase with glycerin content up to about 10 per cent of glycerin and the internal friction coefficient decreased with increasing glycerin concentration. For untreated sheets, the internal friction increased with moisture content. This effect was explained on the basis of fiber swelling and weakening of fiber bonds followed by fiber lubrication at the higher glycerin concentrations. As the bonds become weaker because of increased distance between fibers, the fibers are allowed more relative motion when the sheet is flexed. It is thus the increased freedom of motion results in increased friction. However, at higher glycerin and water contents, the fibers become lubricated and less friction is developed. The lubrication may be a form of boundary lubrication because the distance between bonded fibers in a sheet of paper are probably very small in order to hold the paper together. Too thick layer of lubricant could not be built up between the fibers without dispersing the fibers and greatly reducing the sheet strength.
The decrease in strength of fiber-to-fiber bonds has been found to
explain plasticizing action for cellulose derivatives. This concept has not
been used previously to explain the softening of paper but seemed worthy of
investigation in view of its usefulness in explaining the plasticizing of
cellulose derivatives. Richter and Khler (38) mentioned that glycerin-
treated sheets had lower wet and dry strengths than the untreated sheets.
A decrease in either individual fiber strength or bonding strength between
fibers would explain the decrease in over-all sheet strength.

Clark (39-42) has reviewed and discussed several methods for
determining bonding strength in paper. He (39) stated that the adhesion
between fibers in a sheet of paper is dependent upon "the extent of the
surface of the fibers in mutual contact, the strength per unit area of the
joints, and the flexibility of the joints."

The normal tensile test is not wholly satisfactory for measuring
fiber bonding, for, according to Clark (39), "[I]t is clearly influenced by
factors other than adhesiveness. For instance, the normal tensile test...is
influenced by the length of the fibers, which allows a better working of the
fibers into the sheet structure. A short fiber may be pulled out of a sheet
more easily than a longer one, although both may have the same degree of
adhesion." However, for a comparison of the bonding strength in sheets
whose only difference is in plasticizer content, the tensile test should be
of value.

Clark's measurements of "zero gram" tensile strength of paper which
give a value approaching the fiber strength of individual fibers, were higher
than the normal tensile strength of the sheets (39). Park (45), from the forces required to break the C-C, C-N, and C-O bonds in a cellulose fiber, calculated that, if primary valence forces were continuous, the fiber would have a strength much greater than that observed for paper sheets. Mihlemann (44) directly measured the tensile strengths of between 50 and 150 fibers of each of 14 sprucewood pulps and found that their individual tensile strengths were much greater than their tensile strength in sheet form. In his study of the tensile strength of individual cotton hairs, Mann (45) found that the breaking strength increased slightly with increasing relative humidity.

In order to determine whether glycerin weakened fiber bonds in paper, it would be necessary to make tensile strength measurements of glycerin-treated papers and also of individual fibers which contained glycerin.

DETERMINATION OF TENSILE STRENGTH OF INDIVIDUAL FIBERS

Individual cotton hairs selected from cotton linters were chosen for the tensile strength measurements. Because only a comparison rather than an accurate measurement of tensile strength of glycerin-treated and untreated fibers was desired, this method seemed satisfactory. It was decided that the longer cotton linter hairs would be more suitable specimens than the pulp fibers for obtaining individual fiber tensile strengths with the puller instrument. It seemed likely that, if glycerin decreased individual fiber tensile strength of cotton linters, it would act similarly with all hemp fibers.

Purified cotton linters were soaked in glycerin and dried by the method used to prepare them for the moisture equilibrium studies. The
Linters were found to contain 7.23% or cent of glycerin at 90 or cent R. H. Fifty cotton hairs of an average fiber length of 5/8 inch were selected for the tensile test. The fibers ranged from 5/8 inch to 1 inch in length. The fibers were divided into two groups of 25 each, so that the precision of the measurements could be checked. In the same fashion, fifty cotton hairs of the same average length and length were selected from the untreated linters.

The tensile strength of each fiber was determined with the full single fiber tester. The breaking load was reported to the nearest gram. The loads were increased by one-gram increments until the fiber broke. The reading recorded was one gram lower than the load necessary to break the fiber. The average distance between the jaws of the tester was 1.1 cm.

The tensile strengths of glycerin-treated linters were determined at two relative humidities—50 and 6.5% or cent. The tensile strengths were determined at 50 or cent R. H. to investigate the effect of glycerin under standard conditions. Further tests were made at 6.5 or cent R. H. in the humidity chamber in order to obtain data in which the effect of water was minimized. The tensile tests were made according to Textile Standard 254-45 for eight sheets at each of the levels of glycerin content. At 6.5% or cent R. H., the tensile tests were made in the relative humidity chamber described in the previous section. A small portable cotton fiber tensile tester was used to make the tensile measurements at the two relative humidities. The distance between the jaws of the tensile tester was set at 2 inches in both cases.
The values obtained with the portable tester in the tensile strength range for the sheets tested were about 11 per cent lower at 50 per cent R. H. than those made with the larger standard tester. However, accurate values for tensile strength were not absolutely necessary, because it was desired to compare tensile values within each relative humidity range.

The tensile strengths of glycerin-treated and untreated cotton hairs are found in Table II.

<table>
<thead>
<tr>
<th>Glycerin Content</th>
<th>No. of Tests</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Max.</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>5.7</td>
</tr>
<tr>
<td>7.0</td>
<td>25</td>
<td>6.0</td>
</tr>
<tr>
<td>7.2</td>
<td>25</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The data indicate that the tensile strength of individual fibers containing up to 7.2 per cent of glycerin is not decreased by glycerin. Corn (25) has made tensile measurements on cotton hairs at several relative humidities and found that moisture actually increases the tensile strength slightly. These experiments indicate that glycerin and water do not weaken the bonding strength within individual cotton fibers. As a corollary, it might be expected that the strength of wood fibers would not be decreased by glycerin and water, because both wood and cotton fibers are supposedly held together in the same general fashion.
The tensile strengths of glycerin-treated alpha sheets at 50 and 6.5 per cent R. H. are found in Table VI.

TABLE VI

AVERAGE TENSILE STRENGTH OF GLYCERIN-TREATED SHEETS AT 50 AND 6.5% R. H.

<table>
<thead>
<tr>
<th>Glycerin Content, %</th>
<th>50% R. H.</th>
<th>6.5% R. H.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5 lb./15 mm. width</td>
<td>9.0</td>
<td>12.7</td>
</tr>
<tr>
<td>9.2</td>
<td>7.4</td>
<td>11.5</td>
</tr>
<tr>
<td>12.7</td>
<td>5.7</td>
<td>10.0</td>
</tr>
<tr>
<td>18.7</td>
<td>3.2</td>
<td>8.0</td>
</tr>
<tr>
<td>42.4</td>
<td>0.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The data of Table VI indicate that the tensile strength of alpha sheets is decreased by glycerin. Even at 6.5 per cent R. H., where the moisture content of the glycerin-treated sheets is less than that of the untreated sheets (except for the sheets containing 42.6% per cent of glycerin), the tensile strength of the sheets decreased with increasing glycerin content. Although different tensile testers were used at the two relative humidities, the one used at 6.5% per cent R. H. was found to give results about 11 per cent lower than the standard tester. Thus it is seen that moisture also decreases tensile strength. Therefore, it is concluded that glycerin and water decrease sheet strength by weakening fiber bonding, for they do not decrease individual fiber tensile strength. It remains to be demonstrated that a weakening of fiber bonds results in increased softness of the sheet.

THE USE OF Glycerin TREATMENTS

The use of plasticizers in rendering liable film of cellulose
derivatives has been discussed in the historical portion of this thesis. The softening effect was attributed to a weakening of the bonds between the chains of the cellulose derivative by plasticizer molecules. The weakening effect of glycerin on the fiber bonds in cellulose sheets has been demonstrated in the previous section. In order to show how this weakening of bonding strength might cause a softening effect, it is necessary to measure the softness of glycerin-treated sheets. Although there is no method for measuring softness that is accepted throughout the paper industry, the flexural rigidity of the sheets was taken as the measure of softness and has been shown to correlate with TFI softness. This property is important in text concepts of softness.

Flexural rigidity was measured by the use of the torsion pendulum of Figure 3 and its use is described by van den Thillart (46). This type of instrument was used for measuring flexural rigidity of paper at the Institute of Paper Chemistry in a study of the Clark softness tester (28). The equation for the flexural rigidity of a strip of paper of standard width is:

\[ E = \left( \frac{4h^2 T^3}{b^3} \right) \cdot \left[ \left( \frac{1}{T_1} \right)^2 - \left( \frac{1}{T_2} \right)^2 \right] \]

where

- \( E \) is the flexural rigidity in dynes cm\(^2\),
- \( T \) is the dynamic moment of inertia of the pendulum in g cm\(^2\),
- \( b \) is the length of the sample between clamps in centimeters,
- \( T_1 \) is the period of oscillation with the sample in place (in seconds), and
- \( T_2 \) is the period of oscillation of the pendulum with no sample (in seconds).

The flexural rigidity is divided by the cube of the caliper or thickness to reduce the results to a unit thickness basis. This is called the flexural rigidity factor and the units become dynes per centimeters.
The numerical values were divided by 10^6 to put them on a more convenient basis.

The sheets used for measuring flexural rigidity were the same as those for which internal friction was determined in a previous section. Measurements were made at 75.4, 53.2, 32.8, 11.1, and 6.5 percent R.H.

The flexural rigidity factor data are given in Table XII and are plotted in Figures 6 and 6a. The values are the averages of 5 or 6 determinations.

**Table XII**

<table>
<thead>
<tr>
<th>Glycerin Content (at 50°F R.H.)</th>
<th>75.4</th>
<th>53.2</th>
<th>32.8</th>
<th>11.1</th>
<th>6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td></td>
<td>Flexural Rigidity Factor x 10^6, dynes/cm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 average</td>
<td>3286</td>
<td>1920</td>
<td>5374</td>
<td>5540</td>
<td>7840</td>
</tr>
<tr>
<td>maximum</td>
<td>3920</td>
<td>4390</td>
<td>6360</td>
<td>5860</td>
<td>8500</td>
</tr>
<tr>
<td>minimum</td>
<td>2870</td>
<td>2890</td>
<td>4320</td>
<td>5000</td>
<td>7000</td>
</tr>
<tr>
<td>3.7 average</td>
<td>3124</td>
<td>3518</td>
<td>5176</td>
<td>5360</td>
<td>6960</td>
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<tr>
<td>maximum</td>
<td>3330</td>
<td>4200</td>
<td>5980</td>
<td>6260</td>
<td>7540</td>
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<tr>
<td>minimum</td>
<td>2870</td>
<td>2326</td>
<td>4360</td>
<td>4950</td>
<td>5980</td>
</tr>
<tr>
<td>9.2 average</td>
<td>2800</td>
<td>2872</td>
<td>4160</td>
<td>4260</td>
<td>4368</td>
</tr>
<tr>
<td>maximum</td>
<td>3170</td>
<td>3700</td>
<td>4580</td>
<td>5300</td>
<td>5350</td>
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<tr>
<td>minimum</td>
<td>2880</td>
<td>2570</td>
<td>3660</td>
<td>3620</td>
<td>5640</td>
</tr>
<tr>
<td>13.7 average</td>
<td>1960</td>
<td>1668</td>
<td>2290</td>
<td>3240</td>
<td>4066</td>
</tr>
<tr>
<td>maximum</td>
<td>1226</td>
<td>1960</td>
<td>2560</td>
<td>3360</td>
<td>4380</td>
</tr>
<tr>
<td>minimum</td>
<td>878</td>
<td>1568</td>
<td>2120</td>
<td>2780</td>
<td>3780</td>
</tr>
<tr>
<td>47.1 average</td>
<td>588</td>
<td>868</td>
<td>750</td>
<td>1158</td>
<td>1158</td>
</tr>
<tr>
<td>maximum</td>
<td>740</td>
<td>1260</td>
<td>936</td>
<td>1280</td>
<td>1340</td>
</tr>
<tr>
<td>minimum</td>
<td>462</td>
<td>484</td>
<td>664</td>
<td>956</td>
<td>962</td>
</tr>
</tbody>
</table>
FIGURE 6

Flexural Rigidity Factor of Treated Alpha Sheets at Various Relative Humidities

- 75.4% R. H.
- 53.2% R. H.
- 32.8% R. H.
- 11.1% R. H.
- 6.5% R. H.

Glycerin content (at 50% R. H.), %
FIGURE 6a
Flexural Rigidity Factor of Glycerin-Treated Alpha Sheets at Various Relative Humidities

- 0% glycerin
- 2.7% glycerin
- 9.2% glycerin
- 18.7% glycerin
- 42.4% glycerin

Relative humidity, %
At all relative humidities, the flexural rigidity factor of glycerin-treated sheets decreased with increasing glycerin content. Even at the low relative humidities, where the moisture content of glycerin-treated sheets was less than that of the untreated sheets, the flexural rigidity factor was less for the treated sheets. With decreasing relative humidity, the flexural rigidity factor was found to increase. This increase was found for all the sheets tested. Therefore, both water and glycerin are effective in reducing the flexural rigidity factor of paper. This conclusion is not new, but the generalization for a wide relative humidity range merits a better understanding of how flexural rigidity is affected by moisture and glycerin.

A logarithmic relation was found to hold roughly for describing mathematically the behavior of glycerin in softening paper. In Figure 7, the logarithm of the flexural rigidity factor is plotted against the glycerin content. Straight lines were obtained of approximately the same slope and by orienting these lines, the curve except in the area of the highest glycerin concentrations.

In fundamental law could arise to explain the reasons for this logarithmic relationship. It would seem reasonable that all the glycerin in the sheet was effective in softening fiber bonds, because a large portion of the glycerin is available within the fiber. It is likely that only a portion of the glycerin in such sheets is held in such a way as to reduce fiber bonds and, hence, increase flexural rigidity.

In order to find the relation between softness and a percentage of fiber bonds, the flexural rigidity factor of glycerin-treated sheets was
Figure 7
Logarithm of Flexural Rigidity Factor for Glycerin-Treated Alpha Sheets at Various Relative Humidities

- 75.4% R.H.
- 53.2% R.H.
- 32.8% R.H.
- 11.1% R.H.
- 6.5% R.H.

Glycerin content (at 50% R.H.), %
plotted against the tensile strength (Figure 6). A straight line relation seems to hold for the data at both 6.5 and 5.5 per cent R. B. It can be felt that, even though the tensile tests were made at 50 per cent R. B. and the flexural rigidity measurements were made at 55 per cent R. B., results could be compared because of the usual tolerance of approximately 2 per cent in relative humidity conditions.

The tensile test and the flexural rigidity test differ in that, in the former, the sheet is destroyed and the value obtained is for failure of the sheet, whereas, in the latter, the sheet is flexed but not ruptured. The tensile test largely depends on the ultimate strength of fiber bond, whereas the rigidity test depends on their strength under less creasie conditions. The straight line relation between the flexural rigidity factor and tensile strength does show, however, that both properties are dependent on the same factor—i.e., fiber-to-fiber bonding strength.

In general, the mechanism by which glycerin and water weaken the fiber bond is probably that of increasing the distance between bonds or fiber surfaces by absorption of water and glycerin. The force between bonds is known to decrease rapidly with distance. The volumetric swelling of the sheet causes, as measured by increase in thickness with increasing glycerin and water content, should not be considered to be the result of increasing the fiber-to-fiber distance alone. Rather, the whole fiber structure is swollen. Any increase in distance between fibers would be small in comparison to that, although over-all swelling indicates an increase in fiber-to-fiber distance, it is not a direct measure of it. The decrease in systems of relative cohesion with increasing glycerin content is further
FIGURE 8
Flexural Rigidity Versus Tensile Strength of Glycerin-Treated Sheets

Tensile strength (per 15 mm. width), lb.

- 50% R. H.
- 6.5% R. H.
evidence that glycerin increases the distance between fiber surfaces. Glycerin molecules remain in the sheet at low relative humidities and prevent the collapse of the fiber structure to the point where irreversible bonds are formed between fibers. It seems evident that the action of glycerin in softening paper is analogous to the action of plasticizers in plastics in that it increases the fiber bonding distances.

RELATION OF FIBER LUBRICATION TO STRENGTH OF FIBER BONDS

In a previous section, it was suggested that the fiber lubrication concept of softening was but a portion of the weakening of fiber bonds concept. The tensile and flexural rigidity data showing the weakening of fiber-to-fiber bonds with both glycerin and water fits in well with the explanation for the initial increase in internal friction found for glycerin-treated sheets. The fiber bonds are weakened by increasing their distances and, therefore, allow more motion of the fibers so that internal friction is increased. For the sheets of greater glycerin content, the decrease of internal friction correlates with the decrease in flexural rigidity and tensile strength. The decrease in internal friction has been explained by fiber lubrication. However, it would not be expected that fiber lubrication could explain the decrease in flexural rigidity. Rather, it would seem that fiber lubrication was obtained by forcing the fibers apart with glycerin and water and thereby increasing the amount of lubricant between them. Probably the internal friction within the individual fibers is not of great importance to the overall internal friction, because it was found that the tensile strength of individual fibers increased with glycerin addition, and, therefore, the weakening and relative motion in the sheet was in the bonded portions of the fiber.
In consideration of the molecules of fiber bonds concept for the softening of paper, it might be concluded that glycerin and water involve the same mechanism in softening. Therefore, one might well be as effective as another. One set of equations to determine the effectiveness is that based on the number of hydroxyl groups available for sorption, because it is this sorption phenomenon which causes a swelling of the cellulose structure. It has been shown in work done at the Institute of Paper Chemistry [47] that mineral oils (whose molecular size is large) do not decrease sheet strength.
The reason for this is that the oil molecules are probably not adsorbed by cellulose and therefore cannot weaken fiber bonds. In a picture of absorbed glycerin might be found one, two, or three of its hydroxyl groups in interaction with cellulose.

In order to compare the effectiveness of water and glycerin in softening, or, the flax ray rigidity factor of glycerin-treated flax sheets was plotted against moisture content plus the effective glycerin content. This was done on a weight basis with the assumption that one molecule of glycerin was equivalent to one, two, and three molecules of water. The best correlation was found for the case in which one molecule of glycerin is equivalent to two molecules of water. The plots are found in Figures 5, 10, and 11. In Figure 3 the points for each relative humidity are best distributed on either side of the resistant curve and the distance of points from the curve is not exact, so that, as a rough approximation, the two to one ratio was thought to be the most satisfactory.
FIGURE 9

Flexural Rigidity Factor as a Function of Combined Glycerin and Water Contents in Paper. 1 Mole of Glycerin is Equivalent to 2 Moles of Water.

75.4% R. H.
53.2% R. H.
32.8% R. H.
11.1% R. H.

Combined glycerin and water content per gram of paper:

\[ (\text{mg. H}_2\text{O} + \text{mg. glycerin} \times \frac{2 \times 18}{92}) \]
FIGURE 10

Flexural Rigidity Factor as a Function of Combined Glycerin and Water Contents in Paper. 1 Mole of Glycerin is Equivalent to 1 Mole of Water.

- O 75.4% R.H.
- ☐ 53.2% R.H.
- O 32.8% R.H.
- ☒ 11.1% R.H.

Combined glycerin and water content per gram of paper

(mg. H₂O + mg. glycerin x 18)
FIGURE 11

Flexural Rigidity Factor as a Function of Combined Glycerin and Water Contents in which 1 Mole of Glycerin is Equivalent to 3 Moles of Water

Combined glycerin and water content per gram of paper (mg. H₂O + mg. glycerin x \( \frac{3}{42} \))
The fact that one curve can be used to relate flexural rigidity and various combinations of glycerin and moisture strengthens the argument that glycerin and water act similarly in their softening mechanisms. A more thorough study of the softening mechanism would involve the determination of the relative adsorption of water and glycerin on cellulose, the measurement of distances between fibers, and a consideration of the molecular sizes of water and glycerin.

The equivalence of two molecules of water to one of glycerin in affecting softness of paper seems to be reasonable on the basis of the configuration of the cellulose units. Because of the spatial configuration of hexose units in cellulose, it seems unlikely that all three hydroxyl groups of glycerin would be attracted to corresponding cellulosic hydroxyl groups. On the other hand, the cellulosic surfaces must be very close together in order to have attractive forces hold the fibers together in a sheet of paper. It would seem improbable that, on the average, only one hydroxyl group would be attracted to the cellulosic surface in such limited space. From such considerations there is some justification for the rough equivalence of one molecule of glycerin to two of water. The equivalence is probably a statistical average.

Internal friction is plotted in Figure 12 as a function of softener content in which 1 mole of glycerin is equivalent to two of water. The agreement is not as good as with the flexural rigidity data, but the increase followed by a decrease with softener content is found so that water and glycerin must show a similar action in affecting flexural rigidity.

If the logarithm of the total softener content is plotted against
FIGURE 12

Internal Friction as a Function of Combined Glycerin and Water Contents in which 1 Mole of Glycerin is Equivalent to 1 Mole of Water.

- 75% R. H.
- 53% R. H.
- 33% R. H.
- 11% R. H.

Combined Glycerin and water content per gram of paper

\( (\text{mg. } H_2O + \text{mg. } \text{glycerin} \times \frac{2 \times 18}{92} ) \)
the flexural rigidity factor, a straight line results (Figure 13). Only two points at the low relative humidities diverge from this line and this might be expected since the measurements of flexural rigidity at low relative humidities are difficult because of buckling of the samples.

The expression relating flexural rigidity to softener content over the range of softener contents studied becomes log (weighted glycerin plus water content) =

\[ \log c = -k(x + k_1) \]

and

\[ c = 10^{-k(x + k_1)} \]

This type of equation is to be expected, because the stiffness of the sheet with no moisture or glycerin content would not be expected to be infinite. Rather, the stiffness of the fiber units themselves would limit the stiffness. On adding an excess of water or glycerin, the stiffness would not be expected to be zero, because no further swelling of the cellulose occurs after the fiber saturation point is reached, and glycerin and water are not sufficiently strong dispersing agents to disrupt sheet structure at any concentration.

The strength of alpha sheets was found to decrease with increasing glycerin content and increasing moisture content as measured by tensile tests. However, the tensile strength of individual cotton fibers was found to increase slightly with glycerin addition so that the weakening of glycerin-treated sheets is ascribable to a weakening of fiber bonding.
FIGURE 13

Logarithm of Softener Content Versus Flexural Rigidity Factor of Glycerin-Treated Alpha Sheets

Logarithm of softener content per gram of dry paper

\[
\text{Log} (m_p \cdot H_2O + m_p \cdot \text{glycerin} \cdot \frac{2 \times 18}{92})
\]
Both water and glycerin were found to decrease the flexural
rigidity factor of all the papers. A linear relationship was found between
tensile strength and the flexural rigidity factor at two relative humidities
for sheets of varying glycerin content. Therefore, the softening of paper
as measured by flexural rigidity was concluded to be dependent on fiber
bonding strength. When one mole of glycerin was considered to be equivalent
to two moles of water, the flexural rigidity factor data could be plotted
against a calculated softener content to give one straight line. It was
concluded that both glycerin and water soften paper by the same mechanism—
i.e., by weakening fiber bonding strength.
"As a result of these investigations of the various cases for softening with glycerin, the basic mechanism of softening seems to be better understood. The action of glycerin is one in which glycerin is absorbed by cellulose. A portion of the glycerin is absorbed at the fiber surface where it forces them apart and thus weakens the fiber bond strength. The decrease in fiber bond strength results in lower sheet strength and in a lower flammability factor with increasing glycerin content. Water has the same effect as glycerin and, as a rough approximation, two molecules of water are as effective as one of glycerin. With glycerin contents above 10 per cent, one of glycerin seems to be held between the fibers to act as a lubricant. From the work in this thesis, the basic mechanism of softening seems to be, at least in part, one involving weakening of fiber bond. In general, it seems likely that any substance which might be adsorbed by cellulose and cause its swelling would show some softening action."
C. EXP. DORS

1. Glycerin does not exert a, or at low relative humidities by virtue of its hygroscopic nature alone. Cotton linters containing up to 6.1 per cent of glycerin and sheets containing up to 3.1 per cent of glycerin had lower moisture contents than the corresponding untreated sheets for relative humidities up to 72 per cent. At 112 per cent R. H., sheets and cotton linters containing up to 3.1 per cent of glycerin had lower moisture contents than the untreated materials.

2. At all relative humidities, glycerin-treated sheets and cotton linters contained less moisture at equilibrium than could be calculated from the moisture content data for the cellulose and glycerin.

3. The data are in conformity with the view that glycerin is absorbed by cellulose.

4. The fact that, at low relative humidities, glycerin-treated sheets hold less moisture than the untreated is but a corallary of the general rule stated in 2 above. At low relative humidities, enough glycerin is absorbed by cellulose so that the equilibrium moisture content of the glycerin and cellulose free to absorb water is lower than that of the untreated cellulose.

5. Glycerin causes a decrease in the sheet strength by weakening fiber bonding.

6. Glycerin effects a substantial decrease in the flexural rigidity of the sheets at all relative humidities.
7. Glycerin causes a swelling of alpha sheets as determined by thickness measurements.

8. Glycerin first causes an increase in internal friction with increasing glycerin content (up to about 18 per cent) by weakening fiber bonds and allowing more fiber motion. At higher glycerin contents, glycerin decreases the internal friction by fiber lubrication. Fiber lubrication alone does not explain the softening of paper.

9. Glycerin softens paper (as measured by the decrease in flexural rigidity) by weakening the fiber-to-fiber bonds. The fibers are moved further apart by the adsorption and swelling action of glycerin so that the attractive forces between them are decreased.

10. Water softens paper in a similar fashion. As an approximation, two water molecules are as effective as one glycerin molecule in softening alpha paper to any given degree.
LITERATURE CITED


47. The Institute of Paper Chemistry. Unpublished work, 1946.