INVESTIGATION OF THE RELATIONSHIPS BETWEEN LIGNIN STRUCTURE AND ITS MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Ten
A Progress Report

PULP MANUFACTURERS RESEARCH LEAGUE

July 30, 1969
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INVESTIGATION OF THE RELATIONSHIPS BETWEEN LIGNIN STRUCTURE
AND ITS MECHANICAL AND ADHESIONAL BEHAVIOR

SUMMARY

In pursuing studies in the adhesional phase of the program, a limited examination was made of the effects of reduced lignosulfonate surface tension on the bonding strength of southern pine plywood. The surface tension of electrodialyzed lignosulfonate (ELSA) was reduced from approximately 45 dynes/cm. to 34-35 dynes/cm. through incorporation of low levels of selected surface active agents. The low surface tension ELSA was utilized as the adhesive in preparing layups from veneer aged 2-3 weeks and having a critical surface tension of approximately 28 dynes/cm. A set of layup controls was prepared from "unmodified" ELSA which had been diluted to 37% solids in order to approach the solids and viscosity levels of the low surface tension materials. The bonding strength afforded by the low surface tension ELSA tended to be somewhat less than that provided by straight ELSA at 37% solids and this value, in turn, tended to be lower than that provided by 40% ELSA on the aged veneer. Cohesional failure using the low surface tension ELSA was estimated to be in excess of 95%. These results were interpreted in terms of preferential sorption of surfactant at the veneer—adhesive interface and in terms of reduced ELSA viscosity and increased penetration.

In the project area dealing with the cohesional strength of lignosulfonic acid adhesive materials for plywood, the use of lightweight paper for reeds for adhesive viscomechanical measurements was investigated, the measurement of the adhesive bond strength was established, and the correlation between loss tangent of the reed and the adhesive bond strength was observed.
As a means of increasing the sensitivity of the loss tangent of the reed to the behavior of the adhesive, lightweight papers were tested as substrates for the reeds. Under the usual conditions of ELSA adhesive cure, 310°F. at 150 p.s.i. for 30 min., kraft tissue (25 lb./TAPPI ream) cigarette paper, saturating rag stock (29 lb./TAPPI ream), glassine, and bleached kraft (45 lb./TAPPI ream) each became extensively charred and brittle making them useless for reed work. When the curing conditions were reduced to 310°F., at 28 p.s.i. for 5 min. or 260°F. at 28 p.s.i. for 5 min., the 45-lb. bleached kraft paper was not seriously degraded. Layups were made with this substrate using the latter curing conditions. For comparison purposes, the adhesives previously used were employed. In addition, a similar set of layups was prepared using the previously employed substrate, 149 lb./TAPPI ream kraft, at curing conditions of 310°F. at 150 p.s.i. for 30 min. to be used for adhesive bond strength measurements.

The loss tangent data previously obtained showed a fairly high scatter, therefore a comparison was made between the rapid two-point method previously used and the slower, more precise frequency vs. vibrational amplitude method. Vibrational data were obtained by the two methods on two reeds cut from one of the layups. The precision by the latter method for measuring the resonance band width, $\Delta \omega$, was better so all subsequent loss tangent data were determined by this slower method. The scatter of the loss tangent data from different reeds in a layup is due primarily to the variability in the layup.

Loss tangent data were obtained on reeds from the 45-lb. bleached kraft layups including the substrate alone. The range of these data (0.041-0.047) was very small with an accuracy of up to $\pm$ 20%. Thus, the lighter weight substrate still has a major influence on the viscomechanical behavior of the reed.
Of the two methods considered for measuring the adhesive bond strength to shear stress, the method employing a specimen with a kerf in the lamina on each side at a prescribed distance apart was used because it does not require a gluing step and it is convenient. Six 1-inch square specimens were tested from each layup with the span between kerfs fixed by the strength of a lamina (1/32 in. for 45 lb. and 1/8 in. for 149 lb. paper). The deviation of the six specimens about the average was high (up to +50%), again primarily due to the variability in a layup. In both the 45-lb. bleached kraft layups and the 149-lb. kraft layups, the average bond strengths ranged from 100-1000 lb./in.². Observations of the adhesive rupture zone showed that failure occurred in the region between the adhesive and the substrate indicating that the strength values represent lower limits of the cohesive strength of the adhesive.

Plots of loss tangent vs. bond strength showed that one increases with the other for the data from both the 45-lb. and the 149-lb. substrates. This correlation is apparent in spite of the large uncertainty of each datum and the limitation of the point of bond failure.

It is recommended that the program now focus on the cohesive strength properties of the adhesive isolated from the substrate. This will include the role of insolubilization on these properties.
INTRODUCTION

By way of review, in order for a liquid adhesive to form a strong bond with a solid surface, the chemical theory of adhesion requires that the liquid wet the solid surface with essentially a zero contact angle or, in other words, the attractive forces between the surface molecules of the adhesive film and the solid surface should be equal to, or greater than, the force of cohesion between the adhesive molecules themselves. These forces are frequently expressed in terms of surface tension and, in order to fulfill the aforementioned requirements, the surface tension of the adhesive must approach or equal the solid or critical surface tension ($\gamma_s$) of the adherend.

The approach taken in the adhesional phase of the program has been one of measuring the liquid surface tension of ELSA and fractions thereof, the critical surface tension of southern pine veneer, and then relating these properties to the bonding strength of layups formed from the veneer utilizing unmodified ELSA and a formulated adhesive containing ELSA. Results given in Progress Report Nine revealed that the critical surface tension of the pine veneer declined as a function of aging at 73°F. and 50% R.H. reaching a level of approximately 28 dynes/cm. after two weeks. Subsequent bonding strength values utilizing the ELSA adhesives with liquid surface tensions of 44-45 dynes/cm. showed a tendency to decline as the veneer surface was aged prior to layup formation. Of the two adhesives, the formulated product provided substantially higher bonding strength and a much greater percentage of wood failure.

The present report describes results obtained to date in utilizing surface active agents to reduce the ELSA surface tension and promote adhesion. Theoretically, it would be necessary to reduce the ELSA surface tension to 28 dynes/cm. in order to provide complete wetting of the aged veneer surface. However, since the maximum
work of adhesion usually occurs at low but finite contact angles and since Herczeg
(1) found significantly reduced bonding strength when a surfactant was used to adjust
the surface tension of a plywood adhesive below the critical surface tension of the
veneer, it was decided to adjust the ELSA surface tension to 30-35 dynes/cm. for
the present work.

EXPERIMENTAL

Lowering of ELSA Surface Tension

A total of seven commercial surfactants were examined for their effectiveness in lowering the surface tension of ELSA. These products were selected on the basis of available information concerning surface activity at low concentrations, stability in acid media, and foaming tendencies. A description of the agents is provided in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Product</th>
<th>Class or Composition</th>
<th>Type</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton QS-44</td>
<td>Phosphate ester</td>
<td>Anionic</td>
<td>Rohm &amp; Haas Co.</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Octyl phenoxy polyethoxy ethanol</td>
<td>Nonionic</td>
<td>Rohm &amp; Haas Co.</td>
</tr>
<tr>
<td>Igepal CO-610</td>
<td>Nonyl phenoxy polyethoxy ethanol</td>
<td>Nonionic</td>
<td>General Aniline &amp; Film Corp.</td>
</tr>
<tr>
<td>Igepal CO-630</td>
<td>Same as Igepal CO-610</td>
<td>Nonionic</td>
<td>General Aniline &amp; Film Corp.</td>
</tr>
<tr>
<td>PC-176</td>
<td>Fluorochemical</td>
<td>Nonionic</td>
<td>3M Co.</td>
</tr>
<tr>
<td>PC-134</td>
<td>Fluorochemical</td>
<td>Cationic</td>
<td>3M Co.</td>
</tr>
<tr>
<td>PC-173</td>
<td>Fluorochemical</td>
<td>Anionic</td>
<td>3M Co.</td>
</tr>
</tbody>
</table>
In an effort to conserve the supply of the reference ELSA (No. 66-2, Run 38), preliminary surface tension measurements were made in dilute sulfuric acid at pH 0.6, the pH of the unmodified ELSA. Stock solutions of all surfactants were prepared at a 0.1% active content in distilled water. This relatively low solids level was adopted because of the limited solubility of one of the fluorochemicals and because it afforded greater accuracy in preparing very low concentrations. The stock solutions were then utilized to prepare known concentrations in the range of 0.0001 to 0.05% in dilute sulfuric acid. The surface tension of the acid solutions was measured at 73°F. with a du Nouy Interfacial Tensiometer and the readings were adjusted for Harkins-Jordan correction factors (2). The results of these measurements are recorded in Table II. It was found, in the course of this work, that several of the fluorochemicals were adsorbed on glass and metal surfaces at low concentrations and, hence, fresh solutions of these agents were prepared in polyethylene beakers.

Based on the results in Table II, concentrations of surfactants were selected which provided a surface tension of 30-35 dynes/cm. However, when the specified amounts were incorporated into ELSA, the resulting surface tension was somewhat higher than anticipated, and therefore, increased amounts of surfactant were required to produce the desired surface tension level. The ELSA surface tension data are included in Table II and the surface tension - concentration relationships are shown graphically in Fig. 1.

Two sets of curves are apparent in Fig. 1; one for the fluorinated materials and the other for the nonfluorinated products. On the basis of the low surface tension provided by the fluorinated materials, it was decided to utilize these products and to include one nonfluorinated product in layup preparations.
TABLE II
THE SURFACE TENSION OF ELSA IN THE PRESENCE OF SELECTED SURFACTANTS

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration, %</th>
<th></th>
<th>Surface Tension, dynes/cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In sulfuric acid at pH 0.6</td>
<td>In ELSA</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.0050</td>
<td>40.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0080</td>
<td>--</td>
<td>43.9</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>33.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0200</td>
<td>--</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>0.0500</td>
<td>31.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0800</td>
<td>--</td>
<td>35.3</td>
</tr>
<tr>
<td>Igepal CO-610</td>
<td>0.0010</td>
<td>39.8</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0025</td>
<td>33.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>32.0</td>
<td>45.9</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>31.4</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>0.1000</td>
<td>--</td>
<td>36.6</td>
</tr>
<tr>
<td>Igepal CO-630</td>
<td>0.0010</td>
<td>44.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0020</td>
<td>36.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>32.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>32.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0400</td>
<td>--</td>
<td>40.7</td>
</tr>
<tr>
<td></td>
<td>0.1000</td>
<td>--</td>
<td>37.0</td>
</tr>
<tr>
<td></td>
<td>0.1500</td>
<td>--</td>
<td>34.7</td>
</tr>
<tr>
<td>FC-176</td>
<td>0.0025</td>
<td>31.7</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>20.2</td>
<td>34.5</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>20.1</td>
<td>31.6</td>
</tr>
<tr>
<td>FC-134</td>
<td>0.0001</td>
<td>70.4</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>23.7</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>22.4</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>--</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>--</td>
<td>29.0</td>
</tr>
<tr>
<td>FC-173</td>
<td>0.0010</td>
<td>52.7</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>41.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0075</td>
<td>--</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>36.8</td>
<td>26.4</td>
</tr>
<tr>
<td>Triton QS-44</td>
<td>0.0010</td>
<td>45.7</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0050</td>
<td>36.7</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>32.9</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>0.0200</td>
<td>--</td>
<td>42.5</td>
</tr>
<tr>
<td></td>
<td>0.1000</td>
<td>--</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
<td>0.1200</td>
<td>--</td>
<td>34.4</td>
</tr>
</tbody>
</table>

Note: The surface tension values listed above represent the average of two determinations.
Figure 1. Surface Tension – Concentration Relationships for Selected Surfactants in ELSA
Preparation and Testing of Plywood Layups

Layups were prepared from hot-peeled clear southern pine veneer which had been sanded and then aged for 2-3 weeks at 73°F. and 50% R.H. The fluorochemicals were incorporated into unmodified ELSA to provide surfactant concentrations in the range of 0.006 to 0.009% (60-90 p.p.m.); Triton QS-44 was utilized at 0.12% (1200 p.p.m.). The surface tension of ELSA was measured immediately after blending in the surfactant and the adhesive was then used in preparing layups. Since incorporation of surfactant solutions reduced the effective ELSA concentration, a set of reference controls was included in which the ELSA was diluted to 37% solids with distilled water. The procedures used in preparing and testing the layups were identical to those described in Progress Report Nine. The bonding strength results along with pertinent surface tension and viscosity data are summarized in Table III. (Note: Table III includes results previously reported for freshly generated and aged surfaces.)

DISCUSSION OF RESULTS

It is readily apparent from the results in Table III that reducing the ELSA surface tension through incorporation of surfactants has, thus far, lead to reduced bonding strength. The reasons for this may be several. First of all, in spite of the low concentrations of surfactant used in three of four cases, these materials may have been preferentially sorbed at the veneer - adhesive interface causing a reduction rather than an increase in adhesion. As indicated earlier, there is evidence to suggest that some of the fluorinated materials are rapidly sorbed on solid surfaces. Secondly, incorporation of surfactants at low solids content reduced the effective concentration and viscosity of the ELSA, resulting in greater penetration into the wood. The role of viscosity on penetration is shown by the idealized rate of penetration equation

\[
\frac{dl}{dt} = \frac{yr \cos \theta}{4\eta l}
\]
FUTURE WORK

Laboratory work of immediate interest in the adhesional phase of the program will be concerned with the effects of increased ELSA viscosity on penetration and bonding strength in southern pine plywood. Increased viscosity may be achieved by increasing the solids content or by incorporating small percentages of selected polymers. In conjunction with this work it would also be desirable to examine further the effects of surface tension. One possibility which has not been explored involves enriching ELSA with the low molecular weight fraction previously found to be of low surface tension. The combination of higher viscosity and reduced surface tension should provide for moderate penetration and an adequate supply of ELSA to fill the surface voids.
MECHANICAL PROPERTIES OF LIGNOSULFONIC ACIDS

INTRODUCTION

The ability of an adhesive to withstand an applied stress depends upon stress distribution within the adhesive. Internal stress redistribution is accomplished through molecular relaxation, a property which is manifest in the viscoelastic behavior of the adhesive (3). The most convenient measure of this relaxation is the loss tangent, which is the ratio of energy lost to energy stored in a periodic application of stress (i.e., the ratio of the imaginary to the real component of the complex modulus of the viscoelastic material).

It is the goal of the cohesional phase of this project to relate the viscoelastic properties of lignosulfonic acid materials to their adhesive strength, particularly in plywood operations. Greater understanding of the relationship will aid significantly the development of adhesive formulations.

Previous work (4) has shown that the potentially adaptable vibrating reed method of measuring viscoelastic properties of adhesives by means of their loss tangent, was possible when a porous substrate such as paper was used for the reed. This method allows the adhesive to be put through a normal curing process of high temperature and pressure. However, the limited sensitivity of the system to the loss tangent of the adhesive may have been caused by the heavy paper (149 lb./TAPPI ream) first examined.

The work presented in this report covers (1) the examination of lighter weight papers for reed substrates and the resultant loss tangent, (2) the measurement of the adhesive bond strength, and (3) the relationship between the loss tangent and the bond strength.
EXPERIMENTAL

Testing Lightweight Paper Substrates

The papers selected were tested by (1) immersing a 6 by 6-inch sheet in adhesive 65-24-R44 (a sodium-based, heat-treated ELSA with a concentration of 37% solids); (2) removing it after 5 min.; (3) plotting it gently; (4) placing it between 0.015-inch thick aluminum foil; and (5) putting this on heated platens at a selected temperature, pressure, and time to effect an adhesive cure. The conditions previously used (310°F. at 150 p.s.i. for 30 min.) were first tested but these were subsequently reduced to 310°F. at 28 p.s.i. for 5 min. and, likewise, to 260°F. at 28 p.s.i. for 5 min. After the curing period, the sheet was removed from the platens, cooled under conditions of 73°F. and 50% relative humidity, and examined for potential use in reed measurements. The following papers were examined:

(1) glassine
(2) bleached kraft M.F., 45 lb./TAPPI ream
(3) saturating rag stock, 29 lb./TAPPI ream
(4) cigarette paper
(5) kraft tissue, 25 lb./TAPPI ream.

Layups were made as previously described (4) using the 29 lb. rag stock and 45 lb. bleached kraft papers. A No. 8 Meyer rod was used with the above adhesive and the curing conditions were 260°F. at 28 p.s.i. for 5 min. to minimize substrate degradation.

Testing Methods of Measuring the Resonance Band Width, Δω

Two methods of measuring Δω were described by Rieman and Kurath (5). (1)

The two-point method involves measuring the vibrational amplitude at the resonance frequency, setting the traveling telescope at $1/\sqrt{2}$ times this maximum amplitude, and measuring the vibrational frequencies on either side of the resonance frequency which have this calculated amplitude. The difference in these frequencies is Δω. This
is the method employed in this work up to the present time. (2) The amplitude vs. frequency method involves measuring the vibrational amplitude at a number of frequencies, plotting the amplitude vs. the frequency, and determining from the plot the difference in the frequencies, $\Delta \omega$, at $1/\sqrt{2}$ of the maximum amplitude. This second method is slower but potentially more accurate.

To compare these two methods, two 2.0 x 0.25-inch reeds were cut from the 45-lb. bleached kraft layup made using 65-25-R44 adhesive cured at 260°F. at 28 p.s.i. for 5 min. The vibrational measurements of the reeds were obtained as described in Progress Report Nine (4) by use of an audiooscillator coupled through an amplifier to a recording head (vibration transducer) with input voltage to the head held constant at 3.6 volts. The vibrational amplitude was measured by means of a traveling telescope.

Preparation of Layups

Layups, 6 by 6 inches in size, were prepared as described in Progress Report Nine (4) with the 45-lb. bleached kraft paper for substrate and curing conditions of 260°F. at 28 p.s.i. for 5 min., and also with the previously (4) used 149-lb. kraft liner board for substrate and curing conditions of 310°F. at 150 p.s.i. for 30 min. For reasons of comparison, the adhesives previously (4) employed were used, namely:

1. 65-24-R44, a sodium-base, electrodialized, heat-treated whole liquor, 37% solids.
3. 67-36-R2, an ammonium-base, whole liquor, 39% solids.
4. 66-2-R38, an ammonium-base, electrodialized, whole liquor, 40% solids. (For 30% solids the Brookfield viscosity at 25°C. and 12 r.p.m. is 4.0 centipoise.)
(5) Phenolformaldehyde resin, 50% solution, CR 9357, Catalin Corp. of America, Chicago, Illinois. (The Brookfield viscosity at 22°C. and 12 r.p.m. is 4.7 centipoise.)

(6) Best formulation of Holderby, Olson, and Wegener (6); 30% ELSA solids (Sample 66-2-R38 used here) — 100 parts, 50% phenolformaldehyde — 24 parts, 200-mesh wood flour — 15 parts, freshly prepared and used immediately. (The Brookfield viscosity at 27°C. and 12 r.p.m. is 450 centipoise.)

In addition, layups were made using sulfuric acid of pH = 0.3 (a pH similar to the adhesive tested) as the "adhesive" for a control of the effect of acid on the substrate.

Reeds, 2.0 x 0.25 inch were cut from each layup as described in Progress Report Nine (4). Vibrational amplitude vs. frequency data were determined for reed numbers 1, 5, and 9 of the 45-lb. layups.

Measurement of Adhesive Bond Strength

Two methods were considered for measuring the adhesive bond strength to a shear force. The first method is to place equal size specimens glued symmetrically between three metal pulls, as:

so that stress applied to the pulls by means of the tensile tester (i.e., the Instron instrument) assures uniform shear stress to the specimens. The second method is to apply a tensile stress directly to a single specimen that has a kerf in the substrate on each side so that the cuts are parallel to each other while being perpendicular to the direction of stress and at a specific distance apart, as:
thus, the stress applied to the specimen by means of the tensile tester provide, to the adhesive region, a stress which is approximately a shear. The second method was selected as it does not involve the uncertain effects of gluing to pulls and, with care in cutting, it is conveniently applicable.

It would be most desirable to determine the bond strength of the actual reeds used for the vibration measurements. However, their narrow size precludes either gluing or cutting, so that other specimens of each layup were tested for bond strength. Six specimens from each layup, 1.0 x 1.0 inch in size, were cut from the side pieces remaining from the reed cutting operations. The kerf in the lamina on each side of the specimen was made by placing the sample on a metal bar with a groove filled the width of the specimen and the depth of the thickness of a lamina (0.0035 inch for the 45-lb. bleached kraft and 0.007 inch for the 149-lb. kraft). A metal guide was placed on top of the sample and a kerf was made by carefully cutting the top lamina with a new razor blade until the blade touched the top of the metal bar. The guide assures a straight cut perpendicular to the edge of the sample and at a set distance from the end of the sample. The sample was then turned over and the process repeated using a new razor blade and another metal guide to assure a fixed distance between kerfs. Some preliminary experiments were performed varying the distance between kerfs. If the kerfs were too far apart the specimen failed by breaking a lamina rather than by shear rupture of the adhesive region. For the 45-lb. bleached kraft the maximum useful distance between kerfs was found to be 1/32 inch and for the 149-lb. kraft it was 1/8 inch.
The specimen with kerfs was placed in line clamps of the Instron Tensile Tester and the stress was recorded while the sample was strained at the rate of 0.002 inch per min. until rupture occurred. The maximum stress is the adhesive bond strength. The sample was then observed by means of a hand lens for the place of failure.

RESULTS AND DISCUSSION

In order to maximize the sensitivity of the loss tangent of the reed to the behavior of the adhesive, lightweight papers were examined as substrate for reeds. When the ELSA adhesive was cured at the usual conditions of 310°F. at 150 p.s.i. for 30 min., each of these papers was severely degraded as evidenced by becoming brittle and charred making reed work impossible. In the absence of ELSA, the papers were unaffected by these conditions, suggesting that the acid conditions are at fault. When the curing conditions for the ELSA were reduced to 310°F. at 28 p.s.i. for 5 min., the degradation of the 29-lb. rag stock and the 45-lb. bleached kraft was reduced. Likewise, by reducing the curing temperature to 260°F., substrate degradation for these two papers was further reduced, particularly for the 45-lb. bleached kraft, making reed work feasible. Subsequent layups were made with the 45-lb. bleached kraft paper and curing conditions of 260°F. at 28 p.s.i. for 5 min.

Since the precision of the resonance band width, \( \Delta \omega \), measured by the two-point method is rather low (4), a comparison was made with \( \Delta \omega \) measured by the more accurate vibrational amplitude vs. frequency method. A typical plot of these resonance peak data is shown in Fig. 2 and is similar to those given by Rieman and Kurath (5). The finite "amplitude" at the base line of the resonance peak is a result of the thickness of the reed. Table IV lists the results of resonance frequency, \( \omega_0 \), and \( \Delta \omega \) determined by the two different methods on two reeds cut from a layup made with 45-lb. bleached kraft, 65-24-R44 cured at 260°F. at 28 p.s.i. for 5 min. (See Appendix I for
Figure 2. Vibrational Amplitude vs. Frequency for Reed No. 2
the basic data.) The amp. vs. freq. measurements were done twice on reed Number 1.

The precision of $\Delta \omega$ by the amp. vs. freq. method was much better than by the two point method and the average values were somewhat different. However, the variation of the loss tangent between reeds is probably due to the variation of the regions in the layup. Measurements on the subsequent layups were made by the more precise but slower amp. vs. freq. method.

**TABLE IV**

**COMPARISON OF METHODS FOR LOSS TANGENT MEASUREMENTS OF REEDS**

<table>
<thead>
<tr>
<th>Method</th>
<th>$\omega_0$, c.p.s.</th>
<th>$\Delta \omega$, c.p.s.</th>
<th>$\Delta \omega/\omega_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reed No. 1</td>
<td>Reed No. 2</td>
<td>Reed No. 1</td>
</tr>
<tr>
<td>Two point</td>
<td>36.0</td>
<td>33.8</td>
<td>2.5, 2.5, 2.0</td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>34.0</td>
<td>0.045 0.051</td>
</tr>
<tr>
<td>Amp. vs. Freq.</td>
<td>37.7</td>
<td>1.66 1.72</td>
<td>0.044</td>
</tr>
</tbody>
</table>

The adhesives previously tested (4) were examined again for comparison purposes using the 45-lb. bleached kraft paper for reed substrate. The loss tangent data of these systems are listed in Table V and the reed vibration data used to obtain these results are listed in Appendix I. The deviation about the average of the loss tangent data for three reeds from the same layup (up to $\pm 20\%$) is higher than the precision of a measurement for a single reed ($< \pm 10\%$). Thus, the deviation reflects the statistical variation of behavior within a layup. The range of average loss tangent data is very small, indicating that the loss tangent property of the reed with lightweight paper is still dominated by the substrate behavior. Since this 45-lb. paper was usable only with drastic reduction of curing conditions, in future work the adhesive will have to be isolated in order to improve the measurement of its loss tangent.
**TABLE V**

**ADHESIVE BOND STRENGTH AND LOSS TANGENT DATA**

<table>
<thead>
<tr>
<th>Span</th>
<th>Sample Identification</th>
<th>Substrata a</th>
<th>Adhesive b</th>
<th>Specimen Readings</th>
<th>Loss Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 2 3 4 5 6 av.</td>
<td>1 5 9 av.</td>
</tr>
<tr>
<td>1/32&quot;</td>
<td>H5 1lb. bl. kraft</td>
<td></td>
<td>R-44 W.L.</td>
<td>5.8 7.8 2.2 1.7 6.6 8.7 5.5</td>
<td>0.047 .057 .046 .039 .047</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-44 conc.</td>
<td>1.5 3.3 2.8 2.7 3.3 5.4 3.2</td>
<td>0.035 .044 .044</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-38</td>
<td>6.7 3.4 3.5 5.3 8.6 -- 5.5</td>
<td>0.042 .042 .048 .044</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-2</td>
<td>27.5 11.5 16.2 40.0 38.0 -- 29.9</td>
<td>0.043 .054 .044</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phenol</td>
<td>4.5 7.1 10.1 3.6 -- -- 6.3</td>
<td>0.051 .044 .042</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Formulation</td>
<td>24.0 23.0 21.0 16.5 17.5 18.0 20.0</td>
<td>0.048 .047 .047</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>None</td>
<td>-- -- -- -- -- -- --</td>
<td>0.043 .040 .059</td>
</tr>
<tr>
<td>1/8&quot;</td>
<td>H49 1lb. urbl. kraft</td>
<td></td>
<td>Phenol</td>
<td>109.0 46.0 125.0 104.0 88.0 111.0 97.2</td>
<td>-- -- -- .050</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-2</td>
<td>23.5 55.0 51.0 28.0 50.0 -- 41.3</td>
<td>-- -- -- .034</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Formulation</td>
<td>50.0 62.0 28.0 77.0 29.0 20.0 44.0</td>
<td>-- -- -- .045</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-38</td>
<td>37.5 14.0 16.3 7.7 50.0 33.3 26.5</td>
<td>-- -- -- .038</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-44 conc.</td>
<td>60.9 21.2 43.2 47.5 69.7 58.5 48.0</td>
<td>-- -- -- .041</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-44, W. L.</td>
<td>58.1 24.8 20.7 26.0 37.7 33.2 33.5</td>
<td>-- -- -- .025</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-80</td>
<td>11.0 16.0 12.7 8.3 17.1 -- 13.0</td>
<td>-- -- -- .024</td>
</tr>
</tbody>
</table>

a The H5-1lb. bleached kraft paper system was cured at 260°F for 5 min. at 28 p.s.i. and the H49-1lb. kraft paper system was cured at 310°F for 30 min. at 150 p.s.i.

b The adhesive descriptions are given on p. 15.

c The loss tangent averages for the H49-1lb. kraft system are based on samples previously reported in Progress Report Nine (4).
The adhesive bond strength in shear stress of these 45-lb. layups and of 
149-lb. layups with the same adhesives but cured at the usual conditions of 310°F. 
at 150 p.s.i. for 30 min., are listed in Table V. The 149-lb. layups are a duplication 
of those reported in Progress Report Nine (4) for which two-point method loss tangent 
data are thus available for correlation assessments. The deviation from the average 
bond strength (up to ± 50%) is high reflecting the variable behavior within a layup. 
When placed on a unit area basis, the two sets of layups fall in the same range 
(100-1000 lb./in.²). It is interesting to note that the usually good adhesive, phenol-
formaldehyde, has a low bonding value for the 45-lb. paper. This unexpected result may 
be due to the low curing pressure and temperature (28 p.s.i. and 260°F. compared to 
the more favorable 150 p.s.i. and 310°F. used with the 149-lb. paper). This would 
limit the penetration of the adhesive into the substrate, thus reducing mechanical 
bonding. It is also interesting to note that sulfuric acid, pH = 0.3, alone caused 
some bonding of the 149-lb. paper, possibly through moisture effects and/or charring 
reactions.

Microscopic observations of the rupture zone in all cases showed that 
failure occurred in the region between the adhesive and the substrate. The exposed 
adhesive interface always contained scattered fibers and the adhesive appeared to 
be within a discrete layer (this would probably not be the case on a more porous 
wood surface). Since the bond failure was not within the adhesive layer, the 
strength data represent minimum values of the cohesive strength of the adhesives.

Plotted in Fig. 3 and 4 are the loss tangent vs. bond strength data for 
the 45-lb. bleached kraft layups and the 149-lb. kraft layups, respectively. In 
spite of the large uncertainty of each datum and the limitation of the point of 
bond failure, there seems to be a correlation of the loss tangent and adhesive bond
strength, one increasing with the other. The loss tangent is thus a potentially useful parameter in studies of adhesive behavior.

FUTURE WORK

Because of (1) the large scatter of the loss tangent and strength data of the bonded system due to the heterogeneity of the wood or paper substrate, and (2) the bond failure commonly observed to be in the substrate, it is recommended that the program now focus on the cohesive strength properties of the adhesive isolated from the substrate. Such a focus could also include the role of insolubilization which has never been measured but which is ultimately important in testing the adhesive.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Gerald R. Hoffman and Norman L. Colson for their help in obtaining the experimental data presented in this report. Appreciation also goes to members of the staff of the Pulp Manufacturers Research League for their help in preparing the adhesive formulation.
LITERATURE CITED


THE INSTITUTE OF PAPER CHEMISTRY

Joseph J. Becher, Research Assoc.

Dale G. Williams, Research Assoc.

John W. Swanson, Director
Division of Natural Materials & Systems
APPENDIX I

BASIC DATA ON THE LAYUPS AND THE VIBRATING REEDS

The basic data on the layups using the 45-lb. bleached kraft paper with the adhesive cured at 260°F. at 28 p.s.i. for 5 min., and on the layups using the 49-lb. kraft paper with the adhesive cured at 310°F. at 150 p.s.i. for 30 min. are given in Table VI. The basic vibrating reed data from these 45-lb. bleached kraft paper layups are given in Table VII and the resulting data needed to calculate the loss tangents are given in Table VIII.
## TABLE VI

### DATA ON THE LAYUPS

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Type a</th>
<th>Conc., % solid</th>
<th>6x6-Inch Two Ply, uncoated</th>
<th>Layup Weight, g. coated</th>
<th>Adhesive Weight, g.</th>
<th>Coating Rod</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>45 lb./TAPPI Ream Bleached Kraft</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65-24-R44</td>
<td>37.0</td>
<td>3.0111</td>
<td>3.2192</td>
<td>0.2081</td>
<td>Mayer No. 8</td>
<td></td>
</tr>
<tr>
<td>65-24-R44</td>
<td>37.0</td>
<td>3.0000</td>
<td>3.4311</td>
<td>0.4311</td>
<td>Mayer No. 12</td>
<td></td>
</tr>
<tr>
<td>concentrated</td>
<td>38.7</td>
<td>2.9770</td>
<td>3.4427</td>
<td>0.4657</td>
<td>Mayer No. 10</td>
<td></td>
</tr>
<tr>
<td>66-2-R38</td>
<td>30.0</td>
<td>3.0264</td>
<td>3.428</td>
<td>0.4018</td>
<td>Mayer No. 12</td>
<td></td>
</tr>
<tr>
<td>67-36-R2</td>
<td>39.1</td>
<td>3.0422</td>
<td>3.5498</td>
<td>0.5076</td>
<td>Mayer No. 10</td>
<td></td>
</tr>
<tr>
<td>Phenol-formaldehyde</td>
<td>50.0</td>
<td>3.0369</td>
<td>3.5541</td>
<td>0.5172</td>
<td>Mayer No. 8</td>
<td></td>
</tr>
<tr>
<td>Formulation</td>
<td>0.3M</td>
<td>3.0332</td>
<td>3.0064</td>
<td>(0.0268)</td>
<td>Mayer No. 8</td>
<td></td>
</tr>
</tbody>
</table>

| **149 lb./TAPPI Ream Kraft** |
| Phenol-formaldehyde | 50.0   | 9.6982         | 10.2900                     | 0.5918                 | Mayer No. 8        |
| 67-36-R2          | 39.1   | 9.7144         | 10.0567                     | 0.3423                 | Mayer No. 10       |
| Formulation       | Appr. x.| 9.7343        | 10.2290                     | 0.4947                 | Mayer No. 14       |
| 66-2-R38          | 30.0   | 9.7150         | 10.1342                     | 0.4192                 | Mayer No. 12       |
| 65-24-R44         | 38.7   | 9.6695         | 9.8950                      | 0.2255                 | Mayer No. 10       |
| concentrated      |        |                |                            |                        |                     |
| 65-24-R44         | 30.0   | 9.7761         | 9.9160                      | 0.1399                 | Mayer No. 12       |
| whole liquor      | 0.3M   | 9.7876         | 9.0534                      | (0.7342)               | Mayer No. 8        |
| H₂SO₄             |        |                |                            |                        |                     |

aSee p. 15 for descriptions.
bThis layup was used to make the reeds for the comparison of Aw methods.
### TABLE VII

DATA ON THE VIBRATING REEDS FROM 45-LB. BLEACHED KRAFT PAPER

<table>
<thead>
<tr>
<th>Reed No. 1</th>
<th>Reed No. 1 (verum)</th>
<th>Reed No. 2</th>
<th>Reed No. 2 (verum)</th>
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<tbody>
<tr>
<td>33.6</td>
<td>0.1861</td>
<td>38.9</td>
<td>0.1839</td>
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<td>34.1</td>
<td>0.1788</td>
<td>38.4</td>
<td>0.1670</td>
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<td>34.6</td>
<td>0.1569</td>
<td>37.9</td>
<td>0.1453</td>
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<td>35.1</td>
<td>0.1371</td>
<td>37.4</td>
<td>0.1297</td>
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<tr>
<td>36.5</td>
<td>0.0844</td>
<td>35.9</td>
<td>0.0951</td>
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<tr>
<td>37.1</td>
<td>0.1235</td>
<td>35.4</td>
<td>0.1166</td>
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<tr>
<td>37.2</td>
<td>0.0980</td>
<td>35.9</td>
<td>0.1308</td>
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<tr>
<td>37.2</td>
<td>0.0989</td>
<td>41.8</td>
<td>0.1207</td>
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<tr>
<td>37.2</td>
<td>0.0815</td>
<td>41.9</td>
<td>0.1207</td>
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<tr>
<td>37.7</td>
<td>0.0748</td>
<td>42.4</td>
<td>0.1039</td>
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### 65-2L-R44 Concentrated

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<th>Reed No. 5</th>
<th>Reed No. 9</th>
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<td>34.0</td>
<td>0.2216</td>
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<td>33.5</td>
<td>0.1887</td>
<td>35.7</td>
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<td>0.1526</td>
<td>35.2</td>
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<td>34.5</td>
<td>0.1355</td>
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<td>35.0</td>
<td>0.1120</td>
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<td>35.5</td>
<td>0.1027</td>
<td>33.7</td>
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<td>36.0</td>
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<td>34.2</td>
<td>0.2084</td>
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<td>34.7</td>
<td>0.1920</td>
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<td>0.1198</td>
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<td>36.7</td>
<td>0.1124</td>
<td>36.7</td>
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<td>37.2</td>
<td>0.1022</td>
<td>39.2</td>
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### 66-2-R38

<table>
<thead>
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<th>Reed No. 9</th>
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<td>33.3</td>
<td>0.2015</td>
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<td>33.8</td>
<td>0.2096</td>
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<td>46.7</td>
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<td>0.1182</td>
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<td>35.3</td>
<td>0.1065</td>
<td>38.2</td>
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<td>36.3</td>
<td>0.0923</td>
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<td>33.3</td>
<td>0.2228</td>
<td>35.7</td>
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<td>36.3</td>
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<td>30.1</td>
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<td>30.3</td>
<td>0.0875</td>
<td>32.7</td>
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</tbody>
</table>

*These reeds were used for the comparison of the Aw method.*
## TABLE VII (Continued)

DATA ON THE VIBRATING REEDS FROM 45-LB. BLEACHED KRAFT PAPER

### 67-36-82

<table>
<thead>
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<th>Amp., cm.</th>
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<td>0.1991</td>
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<td>38.4</td>
<td>0.0716</td>
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<th>Amp., cm.</th>
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</thead>
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### Phenolformaldehyde

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### Formulation

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### No Adhesive, Single Lamina

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