Wettability of southern pine veneers was judged by measuring the contact angles made by 36 phenol formaldehyde resins. Formulation of the resins was by factorial design, the molar ratios of sodium hydroxide to phenol being 0.4, 0.7, and 1.0, the levels of resin solids content in the reaction mixture 37, 40, and 43 percent, and the molar ratios of formaldehyde to phenol 1.6, 1.9, 2.2, and 2.5. As molar ratios of sodium hydroxide to phenol increased and ratios of formaldehyde to phenol decreased, the contact angle decreased. Contact angle was not correlated with solids content. Contact angle on earlywood was less than that on latewood, apparently because earlywood surfaces were rougher. Contact angle was positively correlated with glue bond quality as tested by wet shear strength, percent of wood failure, and percent of delamination. High contact angle of the resin—and low wetting of the veneer—may prevent excess glue penetration, which often causes poor bonds in southern pine plywood.

Freeman (1959) and Bodig (1962) demonstrated that wettability of wood as measured by the contact angle method is related to quality of glue bonds. Gray (1962) has reviewed the concept of equilibrium contact angle and the methods of measuring it on wood surfaces. More recently, Herczeg (1965) investigated the wetting of wood by liquids having various surface tensions and pointed out the probability that bond strength is closely dependent upon wetting, spreading, and surface tension of the adhesive. Bryant (1968) showed that bond quality is influenced by the wettability of wood by the resin, and by chemical interactions between the resin and the wood surface.

Most wettability measurements on wood have been performed with homogeneous liquids such as water. Only limited studies with resin have been reported (Herczeg 1965). This paper reports on the wettability of southern pine veneers by 36 exterior-grade phenolic resins having a wide range of physico-chemical properties. It discusses the effects of resin formulation on wettability as measured by contact angles as well as the relation between contact angle and bond quality.

**Procedure**

**Resin Preparation**

All phenol formaldehyde resins were prepared in the laboratory; formulation variables were as follows:
- Molar ratio of sodium hydroxide to phenol (NaOH/P)—0.4, 0.7, and 1.0.
- Molar ratio of formaldehyde to phenol (F/P)—1.6, 1.9, 2.2, and 2.5.
- Concentration of reaction mixture (percentage of weight of pure sodium hydroxide, phenol, and formaldehyde)—37, 40, and 43.

Thus, 36 resins were formulated; as each was replicated, 72 batches of resins were prepared. The detailed procedures for resin preparation have been described in a previous paper (Hse 1971a).

**Veneer Preparation**

All veneers were from mill-run southern pine bolts peeled at a plywood plant in Natchitoches, La. The 1/8-inch veneer was dried for 10½ minutes in a six-section jet dryer at temperatures ranging from 340 to 380°F. Final moisture content averaged less than 4 percent. The veneers were sawn to yield sufficient 12- by 12-inch pieces for gluing into 72 panels of three-ply plywood, i.e., one panel for each of two replications of 36 variables.
Specimens for measurement of contact angle were 1/2 inch by 1 inch in size; they were cut from pieces withdrawn at random from the pile of 12- by 12-inch stock. Changes in moisture content were minimized by sealing all specimens in polyethylene bags. A total of 720 earlywood and 720 latewood specimens were prepared, i.e., 10 specimens for each of two replications of 36 resins.

Contact Angle Measurement

Contact angles were measured with a microscope equipped with a goniometer eyepiece. The microscope tube was arranged horizontally. The veneer specimen rested on a bracket attached to the stage, and a small

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### Table 2. — CONTACT ANGLES AND GLUE BOND QUALITY.

<table>
<thead>
<tr>
<th>Solids Content (F/P ratio)</th>
<th>0.4 mole NaOH/mole phenol</th>
<th>0.7 mole NaOH/mole phenol</th>
<th>1.0 mole NaOH/mole phenol</th>
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</thead>
<tbody>
<tr>
<td>F/P ratio</td>
<td>Degrees</td>
<td>Average</td>
<td>Shear strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>37</td>
<td>1.6</td>
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<td>58</td>
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<td>1.9</td>
<td>55</td>
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<td>40</td>
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<td>66</td>
<td>70</td>
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<td>2.5</td>
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<tr>
<td>43</td>
<td>2.5</td>
<td>58</td>
<td>62</td>
</tr>
</tbody>
</table>

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1 F/P = molar ratio of formaldehyde to phenol.
2 EW and LW = earlywood and latewood. Each value is the average of 20 observations.

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### Table 1. — INGREDIENTS OF THE GLUE MIXES.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>37% Resin</th>
<th>40% Resin</th>
<th>43% Resin</th>
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<tr>
<td>Water</td>
<td>15.0</td>
<td>20.0</td>
<td>25.0</td>
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<tr>
<td>Furfuryl</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>Wheat flour</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Caustic</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Liquid resin</td>
<td>70.0</td>
<td>65.0</td>
<td>60.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

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1 Percentage of solids in the reaction mixture.
droplet of resin (0.05 mL) was placed on the specimen with a pipette. The contact angle was measured by rotating the goniometer eyepiece so that the hairline passed through the point of contact between droplet and veneer and was tangent to the droplet at that point. All measurements were made 5 seconds after the resin had been dropped. Each contact angle reported is the average for 20 droplets, *i.e.*, two droplets measured on each of the 10 specimens per resin.

Gluing

All resins were mixed with Furafil and wheat flour to achieve 26-percent resin solids in the final mix. Ingredients of the glue mixes are shown in Table 1.

Glue was spread at 75 lbs./1,000 sq. ft. of double glueline. The veneers were assembled into three-ply panels immediately after the cores were spread. All panels were given 20 minutes' closed assembly time. The panels were then pressed for 6½ minutes in a two-opening hot press at a temperature of 285°F., and a specific pressure of 175 psi. As the panels were removed, they were immediately placed in a hot-stack box where they remained overnight.

After the panels were fabricated, 20 standard shear specimens were cut from each. Wet shear strength and wood failure were evaluated following the vacuum-pressure cycle for exterior gluelines (PS-1-66).

In addition to the standard shear specimens, two-ply, cross-laminated specimens of all earlywood or all latewood were prepared as described in a previous report (Hse 1968). Delamination was measured on these specimens at the end of 3 months of exterior exposure and was expressed as a percentage of total glue-line area.

Results and Discussion

<table>
<thead>
<tr>
<th>Variables</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of NaOH to phenol</td>
<td>Earlywood</td>
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<tr>
<td>0.4</td>
<td>92</td>
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<tr>
<td>0.7</td>
<td>81</td>
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<tr>
<td>1.0</td>
<td>61</td>
</tr>
<tr>
<td>Molar ratio of formaldehyde to phenol</td>
<td>Earlywood</td>
</tr>
<tr>
<td>1.6</td>
<td>75</td>
</tr>
<tr>
<td>1.9</td>
<td>75</td>
</tr>
<tr>
<td>2.2</td>
<td>80</td>
</tr>
<tr>
<td>2.5</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 3. — EFFECT OF RESIN FORMULATION VARIABLES ON CONTACT ANGLE.

Results and Discussion

Table 2 summarizes contact angles and glue bond qualities as evaluated by shear strength, percent of wood failure, and percent of delamination. Individual values of contact angle varied widely, ranging from 53 to 109°.

Variance analysis indicated (Table 3) that the contact angle differed significantly (0.05 level) with three of the four primary variables, *i.e.*, NaOH/P ratio, type of wood substrate (earlywood or latewood), and F/P ratio. The significant interactions involved NaOH/P ratio with solid content and with F/P ratio (Figs. 2 and 3).

As Table 3 shows, contact angle decreased as NaOH/P ratio increased and as F/P ratio decreased. Level of solid content had no significant effect.

Contact angles on latewood were significantly greater (average 82.43) than those on earlywood (average 78.20). As Leney (1960) and Nearn (1965) have shown, earlywood fractures across the cell wall when cut with a veneer knife, thus exposing its large lumens; in contrast, latewood fractures within and between cell walls to expose a relatively smooth, tight surface with few lumen openings. Consequently, the surface roughness and possibly the surface chemical properties of earlywood differ from those of latewood; these differences may affect the contact angle.

As shown by Wenzel (1936) and Dettre and Johnson (1964), the apparent or measured contact angle may differ from true contact angle whenever the surface departs from a true plane. An equation derived by Wenzel is:

\[
\cos \theta = \frac{\cos \theta'}{R}
\]

where the roughness factor, *R*, is defined as the ratio of the true (daylit) surface to the apparent surface (*i.e.*, that

Table 4. — EFFECT OF SURFACE ROUGHNESS ON CONTACT ANGLE MEASUREMENT.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Roughness Factor</th>
<th>Apparent Contact Angle</th>
<th>True Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earlywood</td>
<td>2.11</td>
<td>78.2</td>
<td>84.5</td>
</tr>
<tr>
<td>Latewood</td>
<td>1.20</td>
<td>82.4</td>
<td>83.6</td>
</tr>
</tbody>
</table>

Figure 1. — Definition of contact angle.
Figure 2. — Contact angle as related to molar ratios of sodium hydroxide to phenol and percent of solid resin in reaction mixture.

Figure 3. — Contact angle as related to molar ratios of sodium hydroxide to phenol and formaldehyde to phenol.

Figure 4. — Relationship of cosine of contact angle to surface tension for three resins with different molar ratios of sodium hydroxide to phenol. \( \gamma_c \) means critical surface tension.

projected to the cutting plane). The measured contact angle is defined in Figure 1. According to Wenzel's equation, the effect of surface roughness is to make the apparent contact angle less than the true contact angle if the true angle is less than 90°, and vice versa when the true angle is more than 90°.

The value of \( R \) was estimated (Hse 1971b) to be 2.11 for earlywood of southern pine and 1.20 for latewood. Table 4 summarizes the results of substituting these values in Wenzel's equation.

Compared to latewood, the greater roughness of earlywood resulted in a large difference between actual and apparent contact angle; the small difference in true contact angle between earlywood and latewood—after correction for roughness effect—suggests that differences in surface roughness account for most of the differences in apparent contact angle.

Chemical differences between earlywood and latewood were not evaluated. Although a higher percentage of lignin and extractives (i.e., alcohol-benzene, ether, and water-soluble) and a lower percentage of cellulose exist in earlywood than in latewood of southern pine (Ritter and Fleck 1926), the degree to which the differences influenced wettability is impossible to decide at this stage.

The NaOH/P ratio interacted with solids content to affect contact angle (Fig. 2). As solids content increased, the contact angle curve changed from concave at 0.4 mole of sodium hydroxide per mole of phenol to convex at 1.0 mole. At 0.7 mole the contact angle remained nearly constant as solids content increased.

The interaction of NaOH/P ratio with F/P ratio is shown in Figure 3. The contact angle increased rapidly between F/P ratios of 1.9 to 2.2 for all three NaOH/P ratios. In this part of the range, therefore, slight changes in the molar ratio appear to have significant effects on the wetting and spreading properties of a resin. In the range between F/P ratios of 2.2 to 2.5, however, contact angle decreased with NaOH ratio of 1.0.

Zisman (1963) indicated that a general linear relationship can be found between the cosine of the contact angle and the surface tension of a liquid. Surface tensions of the 36 resins had been determined in a prior study (Hse 1971a), but regression analysis failed to detect a correlation with contact angle when the three
Critical surface tension is an empirical parameter that estimates specific surface free energy of solid substrates. The close grouping of critical surface tension values in Figure 4 indicates that the veneers differed only slightly in specific surface-free energy. The different slopes of the curves are an indication that some fundamental chemical property of the resins may be strongly affected by the NaOH/P ratio. Such effects are expectable, since by the Cannizzaro reaction the conversion of formaldehyde to methanol and formic acid under alkaline conditions increased as concentration of sodium hydroxide increased (Martin 1958). The chemical properties of resins may differ according to the extent of the Cannizzaro reaction. Although the additions of sodium hydroxide were made in three steps to minimize the conversion of formaldehyde, the results indicate that the 30-minute intervals between steps were not sufficient to control the reaction.

Simple regression analyses were made of the relation between contact angle and glue bond quality as evaluated by shear strength, percent of wood failure, and percent of delamination; all three relationships were significant at the 0.05 level. As shown in Figure 5, shear strength increased, wood failure increased, and delamination decreased as contact angle increased. These results seem to contradict the general impression that a low contact angle is desirable because of its favorable effect on wetting and spreading. However, considering the interactions between wood properties and resin properties, the results are reasonable. Southern pine is known for its high permeability, and excess penetration is one of the most important causes of poor glue bond quality. A resin with a high contact angle does not penetrate excessively, and may give the best compromise conditions of wetting, spreading, and penetration.

NaOH/P ratios were pooled. However, the data fell into three distinct groups corresponding to the NaOH/P ratio, and an analysis was made for each of the three molar ratios. In Figure 4, the linear relationship between the cosine of the contact angle and surface tension is evident; also the critical surface tensions (e.g., 52.65, 54.00, and 54.60 dyne/cm.) obtained by the method of Zisman (1963) are remarkably close.
Although the contact angle of latewood was higher than that of earlywood, the delamination of latewood-to-latewood bonds was significantly higher than that of earlywood-to-earlywood bonds (Fig. 6). Apparently differences in wood properties other than wettability caused the observed results. It is interesting to note, nevertheless, that the relationships between contact angle and percentage of delamination were similar for the two types of substrate, although at different levels.

The significant correlations between contact angle and glue bond quality demonstrate that contact angle is a useful index of glue effectiveness. Furthermore, the results indicate that interactions between the physico-chemical characteristics of resin and the properties of the wood substrate may strongly affect bond quality.

__Literature Cited__