# Properties of Phenolic Adhesives As Related to Bond Quality In Southern Pine Plywood

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**Abstract**

Experimental panels of southern pine plywood were glued up with 72 phenolic resins (36 resins with replication) representing a wide range of properties. In the range tested, contact angle (57 to 105°), heat of curing reaction (95 to 235 cal./gm.), and glueline thickness (8 to 21 μm) were linearly and positively correlated with wet shear strength and percentage of wood failure. Resin shrinkage (11 to 21 percent) during cure also was linearly correlated with shear strength and percentage of wood failure, but the relationship was negative, *i.e.*, resins with the most shrinkage yielded the poorest bonds. Surface tension, time to cure, and pH were in general negatively correlated with wet shear strength and wood failure; the regression relationships were parabolic with maxima. The most effective bonding occurred when the resin wetted — but not over-penetrated — the veneer surfaces. For the formulations tested, this condition resulted when the resin had a high contact angle and a surface tension of approximately 68.4 dynes/cm. The optimum glue bonds were from resins with high chemical reactivities. Such resins appeared to produce a high degree of cross linking when cured and required short cure times.

ALTHOUGH THE TECHNOLOGY for formulating phenol formaldehyde resin adhesives for plywood manufacture is well established, it has for the most part been developed empirically. Consequently, there are few published data relating the basic properties of these resins to wood adhesion, even though the chemistry of the resins has been studied extensively. This paper reports data on the relationships between bond quality and some of the physical and chemical properties of the adhesives. If such relationships can be adequately defined, criteria for controlling both formulation and performance of the glues can eventually be developed.

## Procedure

### Resin Preparation and Characterization

All phenol formaldehyde resins were prepared in the laboratory; formulation variables were as follows:

1) Mole ratio of sodium hydroxide to phenol — 0.4, 0.7, and 1.0.
2) Mole ratio of formaldehyde to phenol — 1.6, 1.9, 2.2, and 2.5.
3) 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.

To prepare each resin, all of the phenol, formaldehyde, and water was placed in the reaction kettle. The sodium hydroxide was added, as a catalyst, in three steps, *i.e.*, 0.3 mole of sodium hydroxide per mole of phenol was added at the beginning, and the balance was divided into two equal parts, one of which was added 30 minutes after the reaction began and the other a half-hour later. To initiate the reaction, the mixture was quickly heated and maintained at 96-100°C. (reflux temperature). When viscosity of the mixture reached

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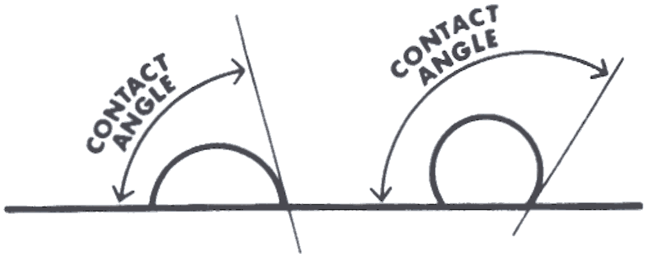

**Figure 1. — Definition of contact angle**

3.2 stokes (ASTM Method D 1545-63) the temperature in the kettle was reduced to 80°C. When viscosity reached 9.0 stokes the reaction was terminated by rapidly cooling the mixture to 25°C.

Each batch of resin was measured for contact angle (Fig. 1), surface tension, specific gravity, and curing properties. These properties were evaluated as the resin came from the reaction kettle. The pH of each resin was determined with a Beckman meter.

*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 droplet of resin (0.05 ml.) was placed on the specimen with a pipette. The contact angle was measured by rotating the 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 on the surface of the specimen. Each contact angle reported is the average for 20 droplets.

*Surface tension measurement.* — The surface tension of each resin was measured with a Du Nouy ring mounted on an Instron testing machine set at maximum sensitivity (10 grams full scale). Resin, contained in a beaker, was supported on the moving crosshead of the testing machine. Upward movement of the crosshead positioned the resin container at the starting point, *i.e.*, the suspended ring was immersed in the resin. The crosshead was then lowered at a speed of 0.1 inch per minute, and pull of the Du Nouy ring was recorded continuously. The maximum pull observed (at the instant of rupture of the ring from the resin surface) permitted calculation of surface tension from a calibration curve. All measurements were in a room maintained at 25°C. and with relative humidity held at 50 percent.

Correlation between maximum pull and surface tension was established by evaluating 11 liquids of known surface tension. The linear regression equation shown in Figure 2 accounted for 97 percent of the observed variation.

*Specific gravity.* — Specific gravity of the fresh resin was determined with a Hubbard-type pycnometer according to ASTM Method D 1963. To determine specific gravity after curing, resin was spread thinly on a watch glass and put in an oven held at 110°C. The resulting flake of cured resin was weighed to the nearest 0.1 mg. and its volume determined on a volumeter.

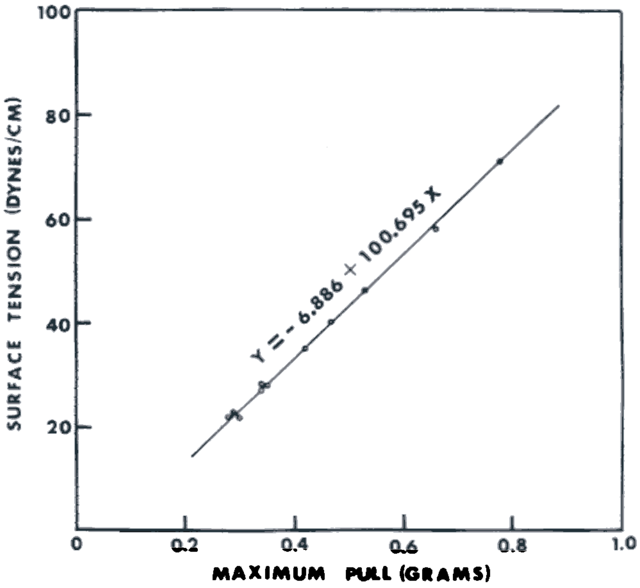

**Figure 2. — Relationship between maximum pull on Du Nouy ring and liquid surface tension.**

*Curing properties.* — A Perkin-Elmer DSC-1B differential scanning calorimeter was used for determination of curing properties in the temperature range from 40 to 160°C. Thermograms were obtained at the following instrument settings: range, 4 mcal./sec. at half-scale deflection; scan, 20°C./min.; slope, 330 to 370 adjusted as required to give the best baseline; and chart speed, 4 in./min. Procedural details for analyses of this type have been described by Watson *et al.* (1964).

To facilitate statistical analysis, it was necessary to transform the thermograms into numerical data.

A typical thermogram recorded during the curing of phenolic resins is shown in Figure 3. The abscissa provides a measure of both time and temperature. The ordinate indicates the differential energy required to keep both resin specimen and reference material at identical temperatures while the temperatures of both

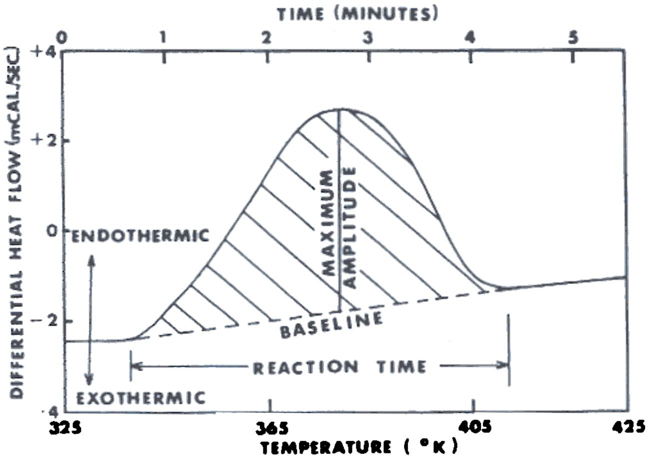

**Figure 3. — Differential scanning calorimeter thermogram for the curing of phenol formaldehyde resin. Shaded area shows heat of reaction. Amplitude of the curve indicates rate of heat absorption.**

were being increased at 20°C. per minute. Thus, the amplitude of the thermogram curve from the baseline is directly proportional to the rate of inflow or outflow of energy to the resin specimen. The area under the peak equals total reaction energy, and the time between the initial deflection of the curve from the baseline and its convergence with the baseline equals total reaction time.

Figure 3 depicts an endothermic reaction and gives no evidence of exothermic heat of curing. Probably the strong endotherm associated with water removal masked

Table 1. — INGREDIENTS OF THE GLUE MIXES.

| Ingredient | 37% Resin[1] | 40% Resin[1] | 43% Resin[1] |
|---|---|---|---|
| | | Percent | |
| Water | 15.0 | 20.0 | 25.0 |
| Furafil | 10.5 | 10.5 | 10.5 |
| Wheat flour | 1.5 | 1.5 | 1.5 |
| Caustic | 3.0 | 3.0 | 3.0 |
| Resin | 70.0 | 65.0 | 60.0 |
| Total | 100.0 | 100.0 | 100.0 |

[1] Percentage of solids in the reaction mixture.

Table 2. — PHYSICAL AND CHEMICAL PROPERTIES OF PHENOLIC RESINS AND GLUE BOND QUALITY (VALUES ARE AVERAGES OF 2 REPLICATES).

| Percent solids content (1) | Mole[1] ratio NaOH/P (2) | Contact angle (3 | Surface tension (4) | Specific gravity<br>Resin solution (5) | Specific gravity<br>Cured resin (6) | Time to cure (7) | Heat of reaction (8) | Rate of heat absorption (9) | Shear strength (10) | Wood failure (11) | Glueline thickness (12) | Cure shrinkage (13) | Resin weight loss (14) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Degrees | Dynes/cm. | | | Min. | Cal./gm. | Mcal./sec. | P.s.i. | Percent | μm | Percent | |
| 1.6 mole formaldehyde/mole phenol | | | | | | | | | | | | | |
| 37 | 0.4 | 89.4 | 69.8 | 1.118 | 1.281 | 2.61 | 155 | 6.17 | 266 | 76 | 19.3 | 14.6 | 64.3 |
| 37 | 0.7 | 79.0 | 76.3 | 1.139 | 1.327 | 2.69 | 122 | 4.01 | 154 | 30 | 17.3 | 16.6 | 58.1 |
| 37 | 1.0 | 60.8 | 76.5 | 1.149 | 1.355 | 3.09 | 122 | 3.14 | 255 | 50 | 12.0 | 18.0 | 52.0 |
| 40 | 0.4 | 88.1 | 70.3 | 1.128 | 1.289 | 2.63 | 180 | 6.90 | 306 | 60 | 17.8 | 14.2 | 61.5 |
| 40 | 0.7 | 80.8 | 76.2 | 1.152 | 1.347 | 2.90 | 110 | 3.60 | 245 | 50 | 13.7 | 16.8 | 58.3 |
| 40 | 1.0 | 61.8 | 76.9 | 1.171 | 1.386 | 3.03 | 123 | 3.51 | 216 | 50 | 10.3 | 18.4 | 50.9 |
| 43 | 0.4 | 88.0 | 71.1 | 1.141 | 1.308 | 2.64 | 184 | 6.53 | 303 | 69 | 19.0 | 14.6 | 59.8 |
| 43 | 0.7 | 80.1 | 76.4 | 1.168 | 1.342 | 2.88 | 104 | 3.37 | 246 | 61 | 14.2 | 14.9 | 52.2 |
| 43 | 1.0 | 63.0 | 77.3 | 1.183 | 1.378 | 3.00 | 140 | 3.31 | 244 | 62 | 11.7 | 16.4 | 50.2 |
| 1.9 mole formaldehyde/mole phenol | | | | | | | | | | | | | |
| 37 | 0.4 | 89.5 | 70.2 | 1.120 | 1.293 | 2.51 | 192 | 6.01 | 290 | 75 | 16.8 | 15.4 | 63.7 |
| 37 | 0.7 | 80.9 | 76.2 | 1.141 | 1.362 | 2.83 | 129 | 3.65 | 159 | 38 | 13.9 | 19.3 | 59.9 |
| 37 | 1.0 | 64.7 | 78.3 | 1.156 | 1.362 | 3.07 | 120 | 3.36 | 168 | 25 | 10.1 | 17.9 | 51.7 |
| 40 | 0.4 | 89.7 | 71.5 | 1.128 | 1.291 | 2.66 | 211 | 6.43 | 290 | 82 | 17.3 | 14.6 | 62.4 |
| 40 | 0.7 | 80.9 | 75.5 | 1.149 | 1.371 | 2.73 | 118 | 3.96 | 248 | 66 | 13.5 | 19.3 | 55.4 |
| 40 | 1.0 | 57.7 | 77.9 | 1.170 | 1.389 | 3.01 | 127 | 3.67 | 223 | 65 | 10.1 | 18.7 | 53.0 |
| 43 | 0.4 | 91.5 | 71.3 | 1.140 | 1.282 | 2.54 | 184 | 6.53 | 289 | 75 | 15.2 | 12.2 | 60.9 |
| 43 | 0.7 | 78.5 | 75.3 | 1.164 | 1.373 | 2.76 | 181 | 3.87 | 258 | 63 | 13.3 | 17.9 | 53.3 |
| 43 | 1.0 | 63.8 | 77.1 | 1.187 | 1.396 | 2.91 | 122 | 3.22 | 233 | 45 | 11.0 | 17.5 | 47.0 |
| 2.2 mole formaldehyde/mole phenol | | | | | | | | | | | | | |
| 37 | 0.4 | 97.6 | 68.9 | 1.118 | 1.277 | 2.57 | 207 | 6.69 | 259 | 79 | 15.9 | 14.2 | 64.6 |
| 37 | 0.7 | 83.8 | 77.7 | 1.143 | 1.378 | 2.72 | 114 | 3.93 | 150 | 30 | 13.9 | 20.5 | 60.7 |
| 37 | 1.0 | 67.4 | 79.1 | 1.152 | 1.373 | 3.03 | 116 | 3.62 | 157 | 28 | 12.2 | 19.3 | 50.9 |
| 40 | 0.4 | 93.3 | 70.8 | 1.132 | 1.280 | 2.62 | 214 | 7.32 | 279 | 75 | 16.4 | 13.1 | 62.7 |
| 40 | 0.7 | 82.9 | 77.1 | 1.149 | 1.375 | 2.74 | 106 | 4.23 | 197 | 51 | 14.1 | 19.7 | 56.6 |
| 40 | 1.0 | 67.8 | 78.0 | 1.180 | 1.388 | 3.01 | 116 | 3.71 | 220 | 58 | 9.4 | 17.6 | 51.7 |
| 43 | 0.4 | 98.9 | 71.7 | 1.147 | 1.326 | 2.47 | 194 | 3.86 | 268 | 76 | 17.4 | 15.6 | 61.1 |
| 43 | 0.7 | 85.3 | 77.4 | 1.158 | 1.370 | 2.76 | 108 | 3.77 | 264 | 66 | 15.3 | 18.3 | 54.9 |
| 43 | 1.0 | 61.8 | 76.7 | 1.177 | 1.381 | 2.89 | 125 | 3.56 | 262 | 58 | 11.4 | 17.3 | 51.5 |
| 2.5 mole formaldehyde/mole phenol | | | | | | | | | | | | | |
| 37 | 0.4 | 100.7 | 71.9 | 1.122 | 1.300 | 2.37 | 222 | 6.77 | 286 | 71 | 16.6 | 15.3 | 64.9 |
| 37 | 0.7 | 90.1 | 79.1 | 1.133 | 1.349 | 2.73 | 132 | 3.98 | 176 | 27 | 12.9 | 19.1 | 62.7 |
| 37 | 1.0 | 63.6 | 79.2 | 1.154 | 1.392 | 3.03 | 115 | 3.44 | 160 | 21 | 11.1 | 20.6 | 52.9 |
| 40 | 0.4 | 93.9 | 70.6 | 1.127 | 1.317 | 2.46 | 203 | 7.14 | 267 | 78 | 17.0 | 16.3 | 64.1 |
| 40 | 0.7 | 90.5 | 78.1 | 1.145 | 1.353 | 2.61 | 147 | 3.59 | 213 | 48 | 13.9 | 18.2 | 60.4 |
| 40 | 1.0 | 70.9 | 78.4 | 1.166 | 1.372 | 2.99 | 102 | 3.52 | 252 | 55 | 12.3 | 17.7 | 54.8 |
| 43 | 0.4 | 102.9 | 72.7 | 1.139 | 1.303 | 2.28 | 200 | 7.11 | 273 | 64 | 17.0 | 14.4 | 61.6 |
| 43 | 0.7 | 90.3 | 76.4 | 1.156 | 1.353 | 2.60 | 158 | 4.12 | 238 | 54 | 13.3 | 17.1 | 57.2 |
| 43 | 1.0 | 60.2 | 75.6 | 1.178 | 1.386 | 2.90 | 127 | 3.53 | 246 | 57 | 10.9 | 17.7 | 50.5 |

[1] NaOH means sodium hydroxide; P means phenol.

the exothermic heat. The total heat of reaction, which corresponds to the sum of endothermic and exothermic reactions, is the value of practical importance. Three curing properties were determined from each thermogram:

1) Time to cure — represented by total reaction time, minutes.
2) Maximum rate of heat absorption — corresponding to maximum amplitude of the curve, millicalories per second (1 mcal. = $10^{-3}$ calories).
3) Heat of reaction — area under the peak calibrated to a standard, calories per gram.

### Preparation and Evaluation of the Plywood

All veneers were from mill-run southern pine bolts peeled at a plywood plant in Natchitoches, Louisiana. The 1/8-inch veneer was dried for 10-1/2 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 12- by 12-inch clear pieces. These pieces were randomly chosen for gluing into 3-ply panels.

Furafil and wheat flour were added to all resins 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 pounds per 1,000 square feet of double glueline and the veneers were immediately assembled into three-ply panels. All panels were given 20 minutes of closed assembly time. They were then pressed for 6-1/2 minutes at a temperature of 285°F., and a specific pressure of 175 psi. As the panels were removed, they were placed in a hot-stack box where they remained overnight.

Twenty standard shear specimens were cut from each panel. Wet shear strength and wood failure were evaluated by the vacuum-pressure cycle for exterior gluelines (PS-1-66).

## Results and Discussion

The 36 resins described in Table 2 exhibited a wide range of physical and chemical properties. Ranges for all 72 batches were: contact angle, 56.9 to 105.4°; surface tension, 68.4 to 80.0 dynes/cm.; specific gravity of resin solution, 1.118 to 1.191; specific gravity of cured resin, 1.275 to 1.398; time to cure, 2.23 to 3.12 min.; heat of reaction, 95 to 235 cal./gm.; rate of heat absorption, 2.83 to 7.51 mcal./sec.; and pH 10.5 to 12.1. As expected, bond quality as evaluated by shear strength and percentage of wood failure also varied widely. The values for wet shear ranged from 114 to 315 psi, and percentage of wood failure from 9.9 to 85.9 percent.

The relationships between individual resin properties and gluebond quality were evaluated by regression analysis. All equations are of the form: $y = b_0 + b_1x + b_2x^2$, where $y$ is a dependent variable (*i.e.*, shear strength or wood failure); $b_i$ is a regression coefficient; and $x$ is an independent variable (*e.g.*, surface tension, contact angle, and time to cure). Deviation from a linear regression was detected by variance analysis. All relationships were tested at the 95-percent level of probability, and all curves drawn are significant at that level.

### Contact Angle

One of the most interesting results of the study is the relationship between contact angle and glue bond quality. In the range of the data, the shear strength and percent of wood failure increased as contact angle increased (Fig. 4). These results seem to contradict the general impression that a low contact angle — with accompanying ability of the glue to wet and spread — is highly desirable. Considering the interactions between wood properties and resin properties, however, 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 bonds. A resin with a high contact angle does not penetrate excessively and may give the best compromise of wetting, spreading, and penetration.

To ascertain whether variability in the veneer substrate might have caused the observed relationship between contact angle and bond quality, a test was made of critical surface tension for wetting each veneer. This was done for all 72 batches of resin. Critical surface tension is an empirical parameter for estimating the specific surface free energy of the veneer.

In Figure 5, critical surface tension was defined by the intersection of cosine of contact angle = 1 and

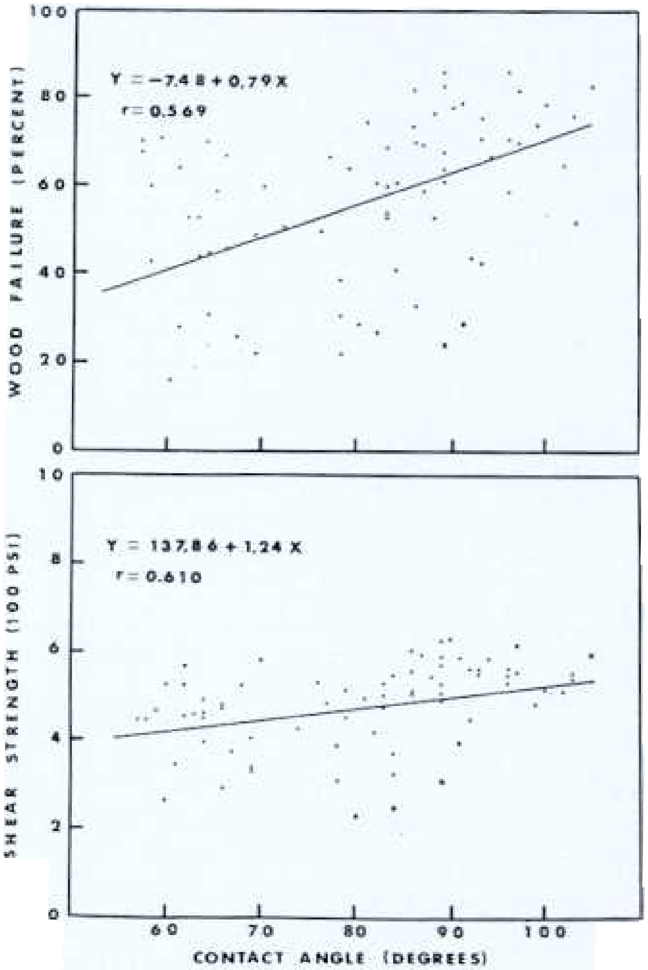

Figure 4. — Relationship of contact angle to wood failure (top) and wet shear strength (bottom).

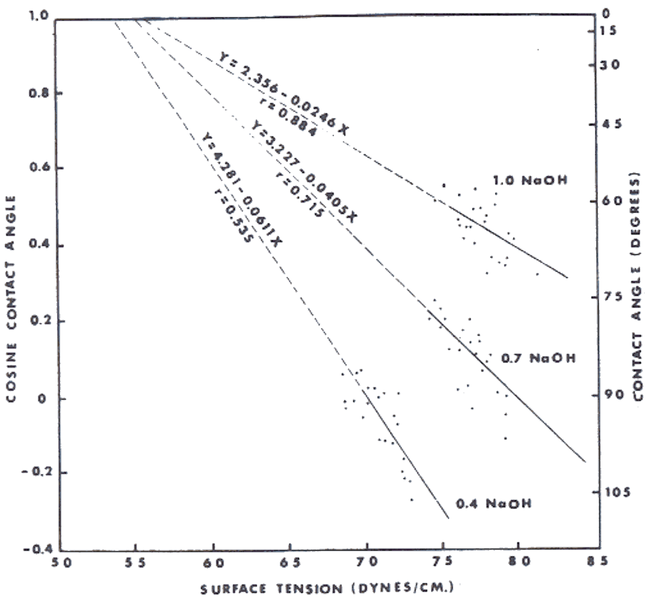

Figure 5. — Relationship of cosine of contact angle to surface tension for three resins with different mole ratios of sodium hydroxide to phenol.

the extrapolated plot of the linear regression of contact angle cosine on surface tension of the resin (Zisman 1963). The data fell into three distinct groupings corresponding to the mole ratio of sodium hydroxide to phenol. The linear relationship between the cosine of the contact angle and surface tension is evident, and the critical surface tensions (53.70, 54.99, and 55.12 dynes/cm.) are remarkably close — an indication that the veneers differed only slightly in specific surface free energy. The result confirms that the veneers provided uniform chemical surfaces and that the relationship between contact angle and glue bond quality was attributable to the resin and not to the veneer.

### Penetration of Glue and Glueline Thickness

In view of the relationships shown in Figure 4, an attempt was made to evaluate the effect of glue penetration. Depth of penetration is difficult to observe directly, but the volume of glue penetrating is readily calculated if glueline thickness, amount of spread, and density of cured resin are known. In this study, spread was constant, variation in resin density was much less than the variation in glueline thickness, and conditions of gluing and panel preparation were the same for each resin. Hence, it seemed reasonable to assume that penetration was inversely proportional to glueline thickness.

Thickness data are shown in Column 12 of Table 2; each entry is the average of 20 measurements made with a microscope. A significant regression (Fig. 6) showed that glueline thickness increased as contact angle increased. If the relationship between glueline thickness and penetration is inverse, greatest penetration could be expected from the resin with the lowest contact angle.

By regression analysis, wet shear strength and percentage of wood failure increased as glueline thickness

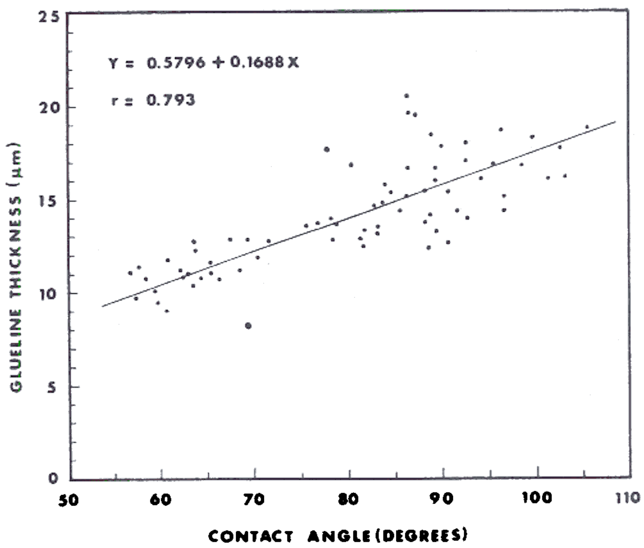

Figure 6. — Relationship of contact angle to glueline thickness.

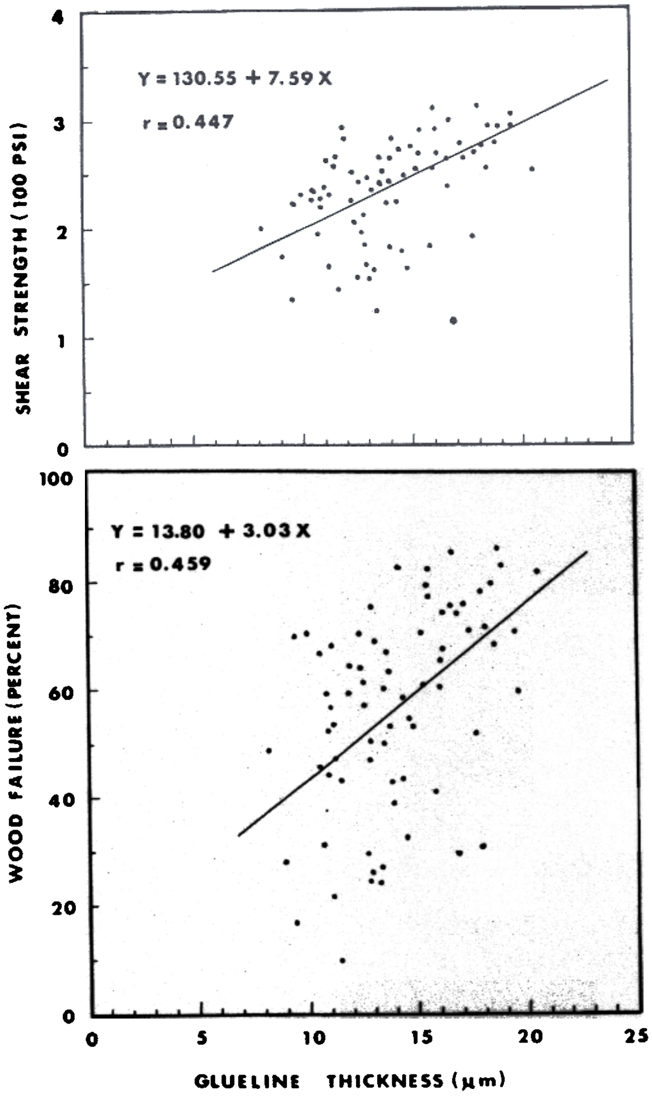

Figure 7. - Relationship of glueline thickness to wood failure (bottom) and wet shear strength (top).

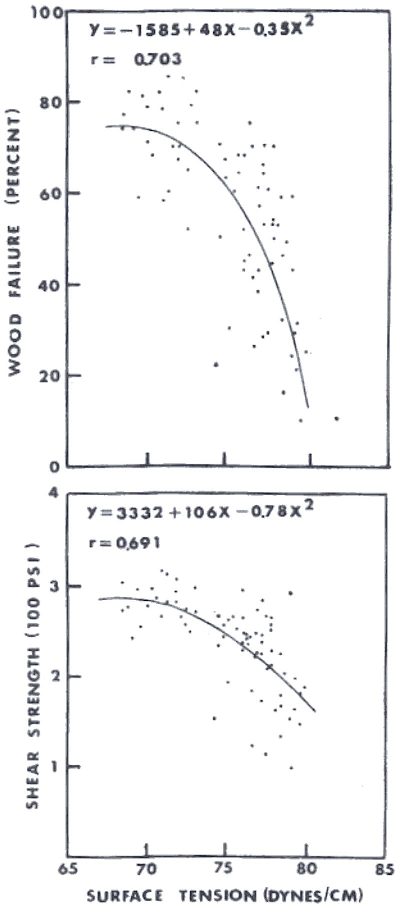

Figure 8. — Relationship of surface tension to wood failure (top) and wet shear strength (bottom).

increased (Fig. 7). While this result appears to contradict Poletika's findings (1943), it is in agreement with Rice's data (1965) on urea formaldehyde resin. The average glueline thickness was 14 μm (a micrometer is $10^{-6}$ meter); this value approximates the thicknesses reported by Rice, but is far below those of Poletika. It is possible that the contradictory results are attributable to the range of thicknesses studied. In this study, the observed relationship between glueline thickness and bond quality may be explained by the fact that a thin glueline is likely to develop discontinuities or defective spots if penetration is excessive.

## Surface Tension

Surface tension of the resin proved to be curvilinearly related to wet shear strength and percentage of wood failure (Fig. 8). This result is a confirmation of Zisman's (1964) theoretical derivation of relationships between adhesion and critical surface tension.

Differentiation of the equations shown in Figure 8 indicated that maximum wet shear strength and percentage of wood failure were associated with resin surface tensions of 68.0 and 68.8 dynes/cm. These values are close to the minimum observed in the 72 resin batches, but it appears from the equation that further reductions in surface tension would not improve the bond. Therefore, the lower portion of the observed range of surface tensions approximates the optimum.

The explanation for these results can probably be found in the spreading behavior of the resin. According to Zisman (1963), spontaneous spreading occurs when the surface tension of a liquid is less than the critical surface tension of the solid substrate. The average surface tension of the phenolic resins in the study was 75.3 dynes/cm., which is far greater than the average critical surface tension of the veneer (estimated at 54.6 dynes/cm. from Fig. 5). Therefore, the differences in surface tension affect the tendency of the resins to spread spontaneously. At surface tensions greater than about 68.4 dynes/cm., decreases in surface tension as a result of increased glue temperature during hot pressing may not be sufficient to achieve optimum spreading prior to curing. At surface tensions less than 68.4 dynes/cm., however, the decrease during hot pressing may cause excess penetration of the resin. Either condition could lead to less than optimum bond quality.

Another possible explanation of the poor bond quality of resin having high surface tension was evident from observation of glue on a standard cure plate maintained at 285°F. Unlike resins of low surface tension,

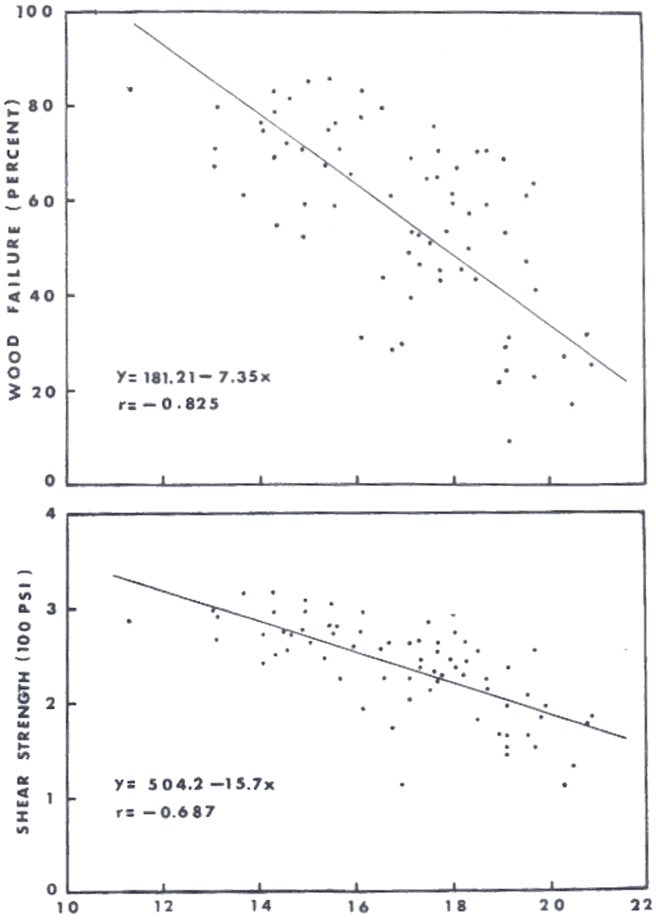

Figure 9. — Relationship of cure shrinkage to wood failure (top) and wet shear strength (bottom).

resin having high surface tension tended to form an impervious skin; further contraction accompanying condensation during curing took place inside the skin. The resulting voids, if formed between glued veneers, might weaken the bond. It is also possible that the skin retards heat penetration and prevents the removal of water from the resin, thus prolonging curing.

### Cure Shrinkage of Resin and Time to Cure

The specific gravities of liquid or cured resin appeared to exert no significant effect on glue bond qualities. It was noted, however, that the specific gravities of cured resins were consistently higher than those of liquid resins, primarily because of shrinkage during curing. The difference between the specific gravity of liquid and cured resin — expressed as a percentage of the liquid resin specific gravity — was therefore used as an indicator of cure shrinkage (Table 2, Col. 13).

Both wet shear strength and percentage of wood failure decreased as cure shrinkage of resin increased (Fig. 9). This is to be expected, because cure shrinkage causes internal stresses, and several studies have shown that such stresses weaken glue bonds (Marian *et al.* 1958, Pillar 1966, and Hse 1968).

Time to cure the resin (as determined by thermal analysis, see Fig. 3) proved to be negatively correlated with wet shear strength and percentage of wood failure (Fig. 10); bond quality decreased sharply with increased time required to cure the resin. It is possible that a slow rate of cure results in an incomplete cure and less than optimum cross-linkage. Chow and Hancock (1969) studied phenolic resins by analysis of ultraviolet spectra and then related the degree of cure to shear strength and percentage of wood failure. The trend evident in Figure 10, if attributable to incomplete cure, is in agreement with their results.

It is also possible that resins requiring a long time to cure penetrate excessively during the press cycle. Analysis of plywood made from the 72 batches of resin indicates that this is so, *i.e.*, glueline thickness was negatively correlated with time to cure (Fig. 11).

### Heat of Reaction

Heat of reaction was positively related to both wet shear strength and percentage of wood failure (Fig. 12). That is, resins that yielded thermograms with large areas under endothermic curves (Fig. 3, shaded area) produced good bonds. The total heat of reaction measured in this study was the sum of the heat evolved by the curing reaction (exothermic) and the heat absorbed to remove water from the glue during curing (endothermic). While a large heat of reaction may be caused by a small exothermic as well as a large endothermic reaction, small exothermic reactions are generally related to incomplete curing and weak bonds. For reasons to be discussed, heats of reaction seem largely determined by amount of heat required to remove water of condensation.

The amount of condensation water depends on the degree of polymerization and is difficult to measure. It is reasonable, however, to assume that the total weight loss of the resin during cure equals the total amount of water removed (including the water present in liquid resin as well as the water from the condensation reaction). For this reason the initial resin samples and the final cured samples were weighed at the time of calorimetric measurement; the total weight loss was then expressed as a percentage of the weight of the initial resin sample and considered indicative of the amount of water removed (Table 2, Col. 14).

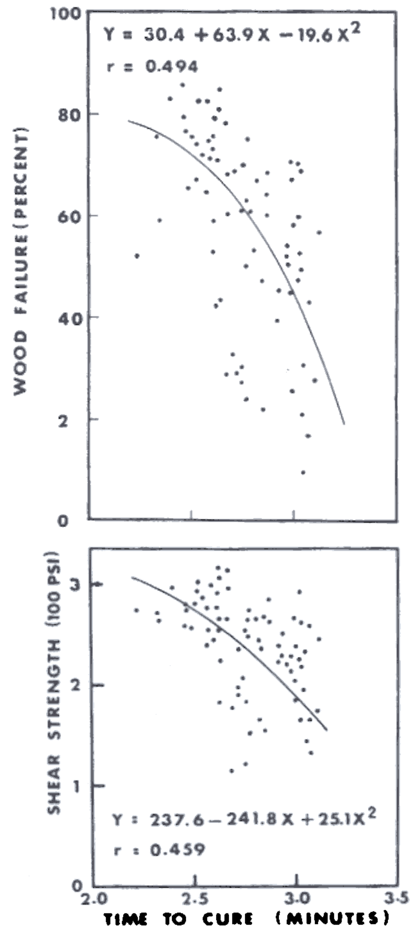

**Figure 10.** — Relationship of time to cure and wood failure (top) and wet shear strength (bottom).

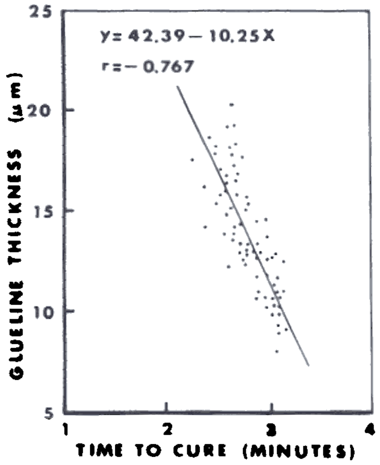

**Figure 11.** — Relationship of time to cure and glueline thickness.

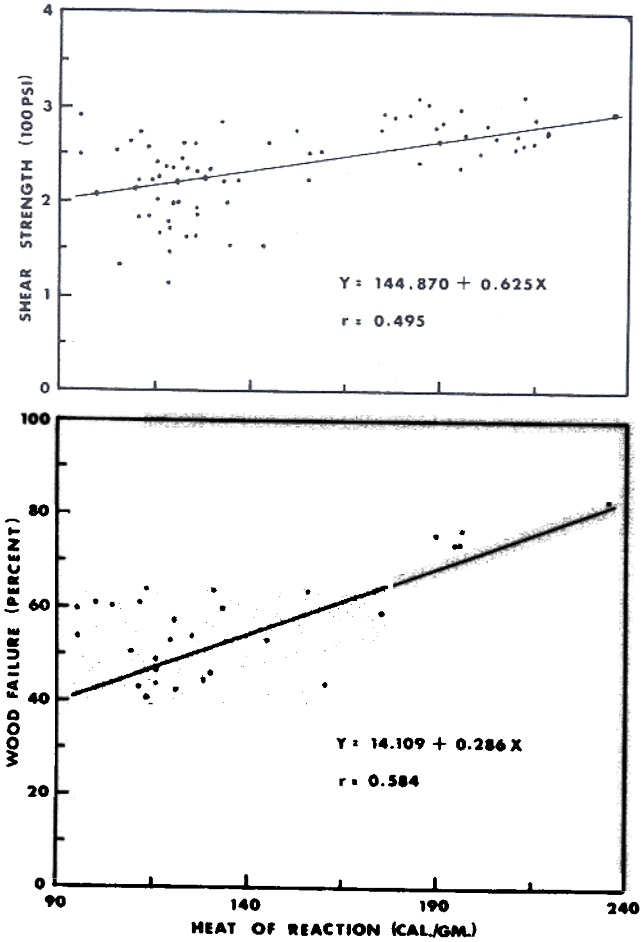

Figure 12. — Relationship of heat of reaction to wet shear strength (top) and wood failure (bottom).

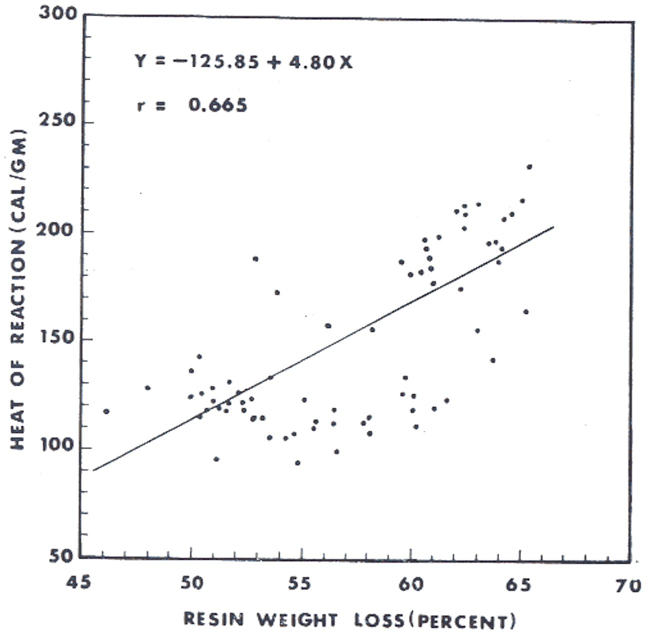

Figure 13. — Relationship of resin weight loss to heat of reaction.

There was a significant positive correlation between percentage of weight loss and heat of reaction (Fig. 13), an indication that the amount of water removed accounted for the major differences in the heat of reaction. By analysis of variance, the proportions of pure sodium hydroxide, phenol, and formaldehyde in each resin had no effect on percentage weight loss; it thus appears that the water in the liquid resin as formulated at various concentrations did not significantly contribute to the percentage weight loss of the resin. Heats of reaction must therefore have been largely accounted for by water resulting from polymerization. Large quantities of water of condensation indicate high degrees of polymerization and, in turn, good bonds.

This explanation is supported by the fact that time to cure was negatively correlated with both rate of heat absorption (defined in Fig. 3) and heat of reaction (Fig. 14). The resins with the greatest chemical reactivity, *i.e.*, those that took least time to cure, tended to yield high heats of reaction, high rates of heat absorbed, and good glue bonds.

It has been mentioned that resins having high surface tension tended to form impervious skins that may have retarded heat penetration and water removal. This possibility is supported by Figure 15, which shows that resins of high surface tension had low heats of reaction and required several minutes to cure.

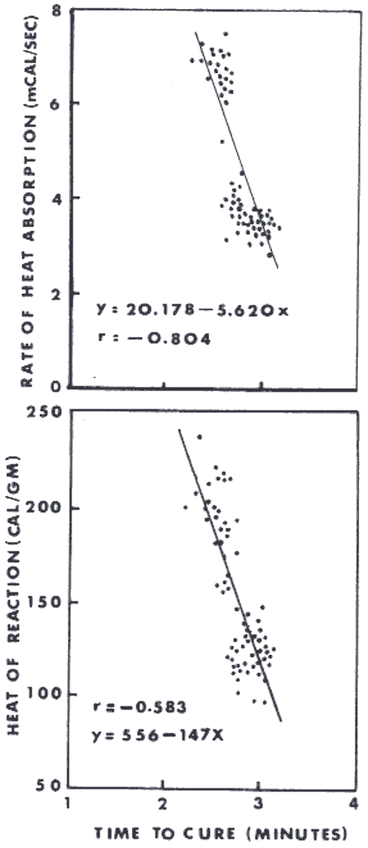

Figure 14. — Relationship of time to cure and rate of heat absorption (top) and heat of reaction (bottom).

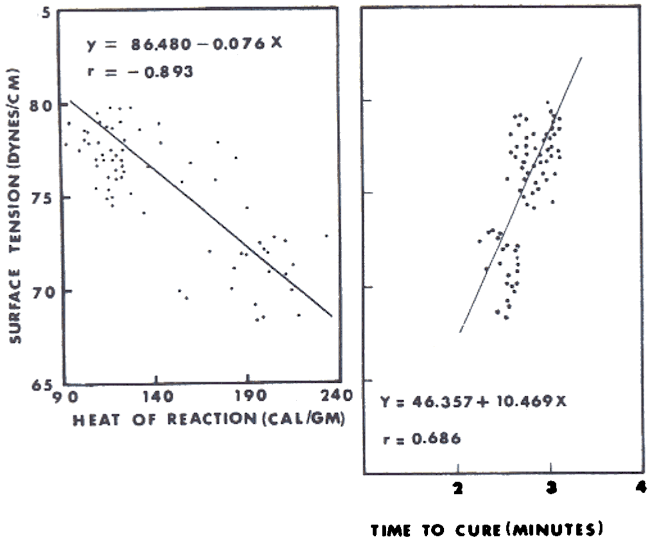

**Figure 15.** Relationship of surface tension to heat of reaction (left) and time to cure (right).

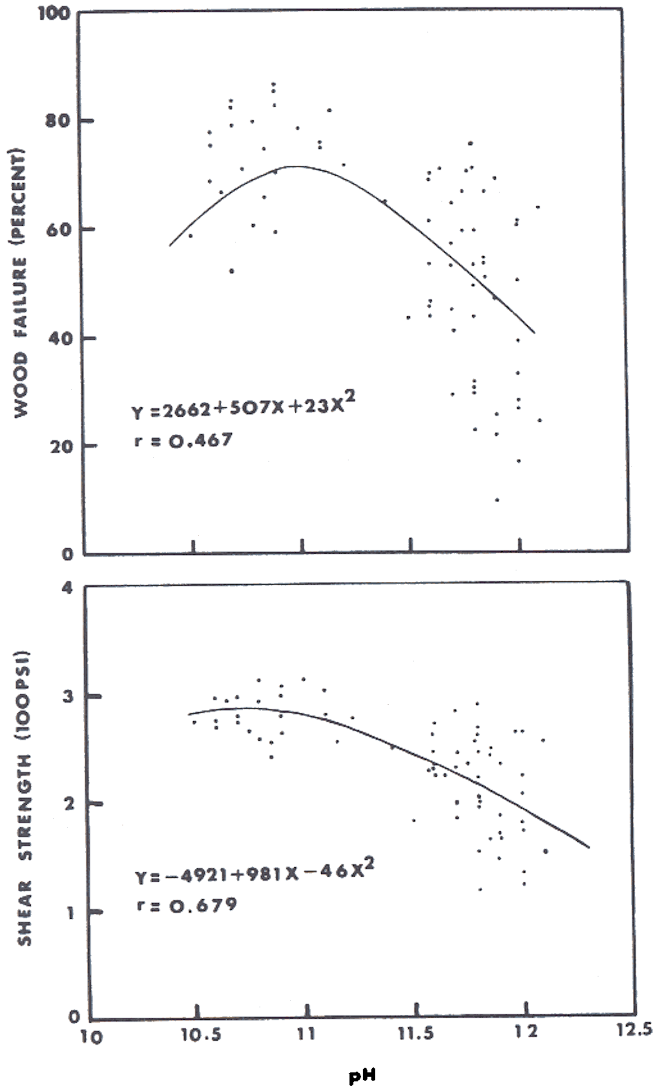

**Figure 16.** Relationship of pH to wood failure (top) and wet shear strength (bottom).

## Alkalinity of Resins

The relationships of pH to shear strength and wood failure were parabolic with a maximum (Fig. 16). This result was somewhat surprising. Because of the great buffering characteristic of phenolic resin, it is improbable that the acidity of southern pine veneer would neutralize the sodium hydroxide catalyst sufficiently to influence the degree of polymerization. Neither is resin pH likely to alter the wood substrate sufficiently to influence the quality of bonding.

Examination of the data showed that resin pH was positively correlated with surface tension (r = 0.814), negatively correlated with contact angle (r = −0.678), negatively correlated with rate of heat absorption (r = −0.888), negatively correlated with heat of reaction (r = −0.981), and positively correlated with time to cure (r = 0.930). The relationships indicated in Figure 16 presumably reflect the combined effect of all these resin properties.

As pH was largely dependent on the amount of sodium hydroxide added to the reaction mixture, the results may be attributed to the effects of this catalyst.

Sodium hydroxide exerts a strong catalytic effect not only on the additional reaction of phenol and formaldehyde (Sprung 1941, Debing *et al.* 1952) but also on the subsequent condensation reaction.[1] The effects are further complicated by the Cannizzaro reaction — conversion of formaldehyde to methanol and formic acid under alkaline conditions. Although the extent of these interactions is not yet completely understood, there are strong indications that the effects of sodium hydroxide on resin properties are far more important than has been realized.

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[1] Freeman, J. H. 1967. Kinetics of the formation of hydroxydiphenylmethanes for trimethylolphenol in alkali; effect of pH. Paper presented at the 153rd National Meeting of the Amer. Chem. Soc., Division of Organic Coatings and Plastic Chemistry. Miami, Fla. April 11, 1967.