Plywood adhesive development.

Edward J. Dowd

University of Louisville

Follow this and additional works at: https://ir.library.louisville.edu/etd

Part of the Chemical Engineering Commons

Recommended Citation
https://doi.org/10.18297/etd/2356
UNIVERSITY OF LOUISVILLE

PLYWOOD ADHESIVE DEVELOPMENT

A Thesis
Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Edward J. Dowd
1949
PLYWOOD ADHESIVE DEVELOPMENT

Edward J. Dowd

Approved by the Examining Committee:

R. C. Ernst
G. C. Williams
W. R. Barnes

June 1949
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>iv</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vi</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>vii</td>
</tr>
<tr>
<td>Abstract</td>
<td>ix</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Historical</td>
<td>3</td>
</tr>
<tr>
<td>Theoretical</td>
<td>7</td>
</tr>
<tr>
<td>Experimental</td>
<td>22</td>
</tr>
<tr>
<td>Straight Phenolic Resin Adhesives</td>
<td>28</td>
</tr>
<tr>
<td>Phenolic Resin Adhesives Modified with 1,3,5 Xylenol</td>
<td>33</td>
</tr>
<tr>
<td>Phenolic Resin Adhesives Modified with Resorcin</td>
<td>36</td>
</tr>
<tr>
<td>Phenolic Resin Adhesives Modified with 1,3,5 Xylenol and Resorcin</td>
<td>44</td>
</tr>
<tr>
<td>Rate of Temperature Change in Heated Plywood Panels</td>
<td>57</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>62</td>
</tr>
<tr>
<td>Appendix</td>
<td>65</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>80</td>
</tr>
<tr>
<td>Vita</td>
<td>83</td>
</tr>
<tr>
<td>Table</td>
<td>Title</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>I</td>
<td>Chronological Development of Adhesives in the United States</td>
</tr>
<tr>
<td>II</td>
<td>Reaction Rates of the Various Phenolics with Formaldehyde</td>
</tr>
<tr>
<td>III</td>
<td>Test Results of Panels Made with Phenolic Resins of Various Caustic Contents</td>
</tr>
<tr>
<td>IV</td>
<td>Test Results of Panels Made with 3% Caustic Catalyzed Phenolic Resins at Various Curing Times</td>
</tr>
<tr>
<td>V</td>
<td>Test Results of Panels Made with a Phenolic Resin Modified with Various Percentages of 1,3,5 Xylenol</td>
</tr>
<tr>
<td>VI</td>
<td>Test Results of Panels Made with 16.7% and 33.3% Resorcin Modified Phenolic Resins at Various Curing Times</td>
</tr>
<tr>
<td>VII</td>
<td>Test Results of Panels Made with 20% Resorcin Modified Phenolic Resins at Various Curing Times</td>
</tr>
<tr>
<td>VIII</td>
<td>Test Results of Panels Made with Phenolic Resins Modified with 10% Resorcin and 7.5% Xylenol</td>
</tr>
<tr>
<td>IX</td>
<td>Formulation of Spread Mix for Xylenol-Resorcin Modified Phenolic Resin PFXR-20</td>
</tr>
<tr>
<td>X</td>
<td>Formulation of Spread Mix for Xylenol-Resorcin Modified Phenolic Resin PFXR-16</td>
</tr>
<tr>
<td>XI</td>
<td>Formulation of Spread Mix for Xylenol-Resorcin Modified Phenolic Resins PFXR-18, PFXR-21</td>
</tr>
<tr>
<td>XII</td>
<td>Test Results of Panels Made with Phenolic Resins Modified with 15% Resorcin and 10% 1,3,5 Xylenol</td>
</tr>
<tr>
<td>XIII</td>
<td>Percentage of Wood Failure Required After Boiling</td>
</tr>
<tr>
<td>Table</td>
<td>Title</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>XIV</td>
<td>Minimum Shear Values Required After Boiling</td>
</tr>
<tr>
<td>XV</td>
<td>Material Cost of a 15% Resorcin, 10% 1,3,5 Xylenol Modified Phenolic Resin</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Equipment Used in Making Resins</td>
</tr>
<tr>
<td>2</td>
<td>Hot Press Used in Making Panels</td>
</tr>
<tr>
<td>3</td>
<td>Riehle Plywood Strip Shear Tester</td>
</tr>
<tr>
<td>4</td>
<td>Effect of Time on Spread Mix Viscosity of Resorcin Modified Phenolics PFR-4</td>
</tr>
<tr>
<td>5</td>
<td>Effect of Time on Spread Mix Viscosity of Xylenol-Resorcin Modified Phenolic PFXR-20</td>
</tr>
<tr>
<td>6</td>
<td>Effect of Time on Spread Mix Viscosity of Resorcin-Xylenol Modified Phenolic PFXR-16</td>
</tr>
<tr>
<td>7</td>
<td>Effect of Time on Spread Mix Viscosity of Resorcin-Xylenol Modified Phenolic PFXR-18 and PFXR-21</td>
</tr>
<tr>
<td>8</td>
<td>Change of Glue Line Temperature with Time for 3 Birch Panels</td>
</tr>
<tr>
<td>9</td>
<td>Change of Glue Line Temperature with Time for 3 Gum Panels</td>
</tr>
<tr>
<td>10</td>
<td>Change of Glue Line Temperature with Time for 2 Plywood Caus and 1 Gum or Birch Panel</td>
</tr>
<tr>
<td>11</td>
<td>Plywood Testing Specimen</td>
</tr>
</tbody>
</table>
The author wishes to acknowledge the kind assistance and helpful guidance who directed this research.
The author wishes to acknowledge the kind assistance and helpful guidance of Dr. R. C. Ernst who directed this research.
This study is primarily a study of various phenolic-based adhesive cures with varying amounts of resorcin, 1,3,5 xylanol, and resorcin. Both were evaluated by using 10% wood specimens in making panels. The phenolic was then tested for stress-rupture and bond durability, after a four-hour delay.

Proprietary and other factors led to testing of various straight phenolic resins and a combination with 1,3,5 xylanol or resorcin, or combinations of all of these accelerating resins.

The straight phenolic-1,3,5 xylanol-1,3,5 resorcin bonds, but the curing cycle was slower. The phenolics modified with 1,3,5 xylanol gave relatively short cures, but large quantities of this material were necessary. Modification of phenolic resins with resorcin gave very rapid cures, but the pot life of these resins was too short. The best cures were obtained with a combination of 1,3,5 xylanol and resorcin as modifying agents for the phenolic. Some of these three-component resin cures have sufficient pot life and produced ball-proof bonds during short curing cycles.
This thesis is primarily a study of two-step plywood adhesives made with varying amounts of phenol, 1,3,5 xylenol, resorcin, and formaldehydes. Each resin was evaluated by using it as the adhesive in making plywood. The plywood was then tested for shear strength and wood failure after a four hour boil.

Procedures are given for making and testing of various straight phenolic resins and resins modified with 1,3,5 xylenol or resorcin, or combinations of both of these accelerating resins.

The straight phenolic resins gave boil-proof bonds, but the curing cycle was too long. Those phenolics modified with 1,3,5 xylenol gave relatively short cures, but large quantities of this modifier were necessary. Modification of phenolic resins with resorcin gave very rapid cures, but the pot life of these resins was too short. The best compromise was obtained with a combination of 1,3,5 xylenol and resorcin as modifying agents for the phenolic. Some of these three-component resin adhesives had sufficient pot life and produced boil-proof bonds during short curing cycles.
The purpose of the investigation presented in this report was to develop a plywood adhesive capable of giving a fail-proof bond. This adhesive must be required to have a relatively short curing cycle and to have a cost within a given price range.

At present no commercial plywood adhesives meet the requirements of (a) fail-proof bond, (b) short curing cycle and (c) low cost. A phenol-formaldehyde resin is the basis for some adhesives, for its constituents are comparatively cheap and readily available. However, a straight phenol

INTRODUCTION

resin has a very long curing cycle which must be decreased to competitive economy in the mean from a production standpoint. It was believed that by incorporating small amounts of 1,3,5-xylene and methylene in a phenolic resin, a quick cure could be obtained at low price. Since adhesives at short storage life could be tolerated, this investigation was especially feasible.

The feasibility of developing an adhesive of the type described was suggested by the General Plywood Corporation of Louisville, Kentucky, and at their request the investigation was conducted in the University of Louisville Institute of Industrial Research.
The purpose of the investigation presented in this thesis was to develop a plywood adhesive capable of giving a boil-proof bond. This adhesive was required to have a relatively short curing cycle and to have a cost within a given price range.

At present no commercial plywood adhesives meet the requirements of (a) boil-proof bond, (b) short curing cycle and (c) low cost. A phenol-formaldehyde resin is the best base adhesive, for its constituents are comparatively cheap and readily available. However, a straight phenolic resin has a very long curing cycle which must be decreased to compete favorably with the fast setting ureas from a production standpoint. It was believed that by incorporating small amounts of 1,3,5 xylenol and resorcin in a phenolic adhesive, a quick cure could be obtained at low price. Since adhesives of short storage life could be tolerated, this investigation was especially feasible.

The desirability of developing an adhesive of the type described was suggested by the General Plywood Corporation of Louisville, Kentucky, and at their request the investigation was conducted in the University of Louisville Institute of Industrial Research.
As early as 1900 phenolic resins were used as molding materials, but major developments in the technology of the field began in 1908 with work by Beckman (1,2,4,5). He worked out a number of the conditions required for control such as the amount of catalyst, the temperature and pressure for final condensation, and the use of fillers to improve the physical characteristics of the finished plastic.

The first United States patent on the area of formaldehyde resins was issued in 1929 (6). Bollak (7) recognized the usefulness of these resins and set off a series of strong sales as accelerators. However, it was about 1930 when synthetic resin adhesives were used only on a laboratory scale.

HISTORICAL

The first mass production of plywood made with synthetic adhesives began in the early 1930's with the introduction of a phenol-formaldehyde film called "Tego". The plywood bond formed by this adhesive achieved world-wide acceptance, for it was extremely resistant to both water and heat. About 1937 the cheaper, but less water and heat resistant urea-formaldehyde adhesives were brought into commercial use. These urea adhesives are capable of very rapid cure at lower temperatures than those required for the phenolic
As early as 1900 phenolic resins were used as molding materials, but major developments in the technology of the field began in 1908 with work by Baekeland (1,2,3,4,5). He worked out a number of the conditions required for control such as the amount of catalyst, the temperature and pressure for final condensation, and the use of fillers to improve the physical characteristics of the finished plastic.

The first United States patent on the urea formaldehyde resins was issued in 1920 (6). Pollak (7) recognized the usefulness of the urea adhesives and salts of strong acids as accelerators. However, up to about 1930 synthetic resin adhesives were used only on a laboratory scale.

The first mass production of plywood made with synthetic adhesives began in the early 1930's with the introduction of a phenol-formaldehyde film called "Tego". The plywood bond formed by this adhesive achieved world-wide acceptance, for it was extremely resistant to both water and heat. About 1937 the cheaper, but less water and heat resistant urea-formaldehyde adhesives were brought into commercial use. These urea adhesives are capable of more rapid cures at lower temperatures than those required for the phenolic adhesives.

The basic patents of the resorcinol-formaldehyde reaction were taken out by Novotny in 1930 and 1932 (8,9,10).
About the same time, the substitution of part of a straight phenol-formaldehyde resin with resorcinol was also recognized as appreciably improving the rate of curing time (11). The commercial production and control of the resorcinol-formaldehyde reaction was worked out largely by Norton (12) about 1940. Rhodes (13) further improved the characteristics of the resorcin resin by using only enough formaldehyde to form a fusible resin, withholding all catalyst until the completion of the reaction.

The methods of control and the reactivity of 1,3,5 xylenol are similar to resorcinol. However, the use of this compound as a modifying agent for phenol adhesives is new and only little work has been done with it.

Today the phenolic modified resins are strong competitors with the urea resins, and yield a superior bond at approximately the same cost.
### TABLE I. CHRONOLOGICAL DEVELOPMENTS OF ADHESIVES IN THE UNITED STATES BY DELMONTE (14)

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1814</td>
<td>Glue from Animal Bones (Patent)</td>
</tr>
<tr>
<td>1872</td>
<td>Domestic Manufacture of Fish Glues (Isinglass)</td>
</tr>
<tr>
<td>1874</td>
<td>First U. S. Fish Glue Patent</td>
</tr>
<tr>
<td>1875</td>
<td>Laminating of Thin Wood Veneers Attains Commercial Importance</td>
</tr>
<tr>
<td>1909</td>
<td>Vegetable Adhesives from Cassava Flour (F. G. Perkins)</td>
</tr>
<tr>
<td>1912</td>
<td>Phenolic Resin to Plywood (Baekeland-Thurlow)</td>
</tr>
<tr>
<td>1915</td>
<td>Blood Albumen in Adhesives for Wood (Haskelite Co.)</td>
</tr>
<tr>
<td>1917</td>
<td>Casein Glues for Aircraft Construction</td>
</tr>
<tr>
<td>1920-30</td>
<td>Developments in Cellulose Ester Adhesives and Alkyd Resin Adhesives</td>
</tr>
<tr>
<td>1927</td>
<td>Cyclized Rubber in Adhesives (Fischer-Goodrich Co.)</td>
</tr>
<tr>
<td>1928</td>
<td>Chloroprene Adhesives (McDonald-B. B. Chemical Co.)</td>
</tr>
<tr>
<td>1928-30</td>
<td>Soybean Adhesives (I. F. Laucks Co.)</td>
</tr>
<tr>
<td>1930</td>
<td>Urea Formaldehyde Resin Adhesives</td>
</tr>
<tr>
<td>1930-35</td>
<td>Specialty Pressure Tapes; Rubber Base (Drew-Minnesota Mining and Mfg. Co.)</td>
</tr>
<tr>
<td>1935</td>
<td>Phenolic Resin Adhesive Films (Resinous Products and Chemical Co.)</td>
</tr>
<tr>
<td>1940</td>
<td>Chlorinated Rubber Adhesives</td>
</tr>
<tr>
<td>1941</td>
<td>Melamine-formaldehyde Resin Adhesives (American Cyanamid Corp.) and &quot;Redux&quot; by de Bruyne (Aero Research Ltd.)</td>
</tr>
<tr>
<td>1942</td>
<td>&quot;Cycleweld&quot; Metal Adhesives (Saunders-Chrysler Corp.)</td>
</tr>
<tr>
<td>1943</td>
<td>Resorcinol-formaldehyde Adhesives (Pa. Coal Prod.)</td>
</tr>
<tr>
<td>1944</td>
<td>&quot;Metlbond&quot; Adhesives (Havers, Consolidated Vultee Aircraft Corp.)</td>
</tr>
<tr>
<td>1945</td>
<td>Furane Resin Adhesives (Delmonte, Plastics Inst.) and &quot;Fliobond&quot; (Goodyear Tire &amp; Rubber Co.)</td>
</tr>
</tbody>
</table>
The many factors that influence adhesive action may be broadly grouped as physical and chemical. The physical and chemical properties are closely interrelated and, in many instances, any distinct division between the two is impossible. An arbitrary division of the most important physical and chemical factors has been made as follows:

1. Physical Properties
   a. Characteristics of surface being bonded
   b. Physical properties of the adhesive film
   c. Thickness and viscosity of adhesive film
   d. Methods of application of adhesive

2. Chemical Properties
   a. Water characteristics
   b. Evaporation and diffusion of volatile free films
   c. Acidity and alkalinity of the glue line

THEORETICAL

Characteristics of Surface Being Bonded

Need is present in the case of that it has a tendency to capillarize into which the adhesive may flow. These capillaries will allow the solvent and other volatile materials of the adhesive to flow into the seal, disturbing the balance of the solute and solvent and the resultant weight distribution.
The many factors that influence adhesive action may be broadly grouped as physical and chemical. The physical and chemical properties are closely interrelated and in many instances, any distinct division between the two is impossible.

An arbitrary division of the most important physical and chemical factors has been made as follows:

1. Physical Properties
   a. Characteristics of surface being bonded
   b. Physical properties of the adhesive film
   c. Thickness and viscosity of adhesive film
   d. Methods of application of adhesive

2. Chemical Properties
   a. Polar characteristics
   b. Process of polymerization
   c. Evaporation and diffusion of volatiles from films.
   d. Acidity and alkalinity of the glue line

PHYSICAL PROPERTIES

Characteristics of Surface Being Bonded

Wood is porous in the sense that it has numerous capillaries into which the adhesive may flow. These capillaries will allow the smaller and more mobile materials of the adhesive to flow into the wood, disturbing the balance of the solute and solvent and the molecular weight distribution
of the polymers. Too rapid a flow into the wood results in poor bonding characteristics and the result is known as a starved glue line.

A moisture content of between 8 and 12 per cent, based on the weight of dry wood, is generally recommended for best results when using phenolic adhesives. Either above or below this percentage gives correspondingly poorer results. Moisture must also be evenly distributed throughout the material or there will be shrinkage or swelling which may lead to an over stressing of the glue line caused by extreme warping of the wood.

A series of tests by Sanborn (15) indicate that abnormal stresses are set up in plywood, if the moisture content of the wood is reduced below the original moisture content of the veneer when it was formed into plywood. There is little effect if the moisture content remains higher than that of the veneer before assembling, but delamination sometimes occurs if the moisture content is reduced below this point (16).

The presence of certain chemicals in the wood structure will also partially control the penetration of the adhesive (17). The concentration of these chemicals may be altered by the solvent in the adhesive and cause swelling and shrinking of the veneer. The partial delignification of the surface will remove some of these materials and improve penetration of the adhesive (18).
Physical Properties of Adhesive Film

The modulus of elasticity and the thermal coefficient of expansion are two of the more important physical factors of an adhesive film. The modulus of elasticity of the film should be comparable to the modulus of the material being bonded. This allows the load to be distributed from one surface to another with less chance of rupture of the film. Thermal coefficients of expansion of similar size likewise give better results, for under temperature variations, considerable stress is set up in the glue line.

Thickness of Adhesive Film and Its Viscosity

True adhesion is theoretically independent of the adhesive film thickness. According to Delmonte (19), the apparent strength of an adhesive containing no volatile matter will be independent of its glue line thickness. For the solvent type adhesive, however, the thinnest glue line gives the greatest strength. This was proved by Poletikan, who showed that joint strength is inversely proportional to the thickness of the glue line (20). Therefore, the most desirable condition for the production of plywood is the use of the thinnest glue line possible, for it not only reduces cost, but gives the greatest shear strength.

The viscosity of an adhesive is also a very important consideration, particularly from the standpoint of production.
With the use of high pressure in assembly of plywood, the viscosity of an adhesive is of little consequence in controlling of the glue line thickness. However, the viscosity of the glue is very important in its production application to the veneer. The average industrial glue spreader works most efficiently when the glue has a viscosity between 5 and 60 poises. Since the minimum pot life of a commercial adhesive should be at least two hours, the adhesive must be formulated in such a way that after the addition of the catalyst and accelerating resins, its viscosity after two hours will not be over 60 poises.

Methods of Application of Adhesives

Pressure, temperature, and time are the three variables which, in the application of adhesives, have a bearing on the strength of an assembly. The pressure determines the thickness of the glue line; the temperature and time determine whether the film has completely cured or not.

There is no general law that will permit the calculation of a pressure to be applied to the surface being bonded. Theoretically, zero pressure is sufficient if the surfaces are perfectly flat, but for normal application, a pressure of 150 to 200 psi. is necessary to bring the surfaces into intimate contact with each other. Pressure must be applied uniformly and steadily while the glue is setting. Too high a pressure
has a tendency to force the glue into the surface causing embrittlement of the fibers and a starved glue line. Too little pressure does not bring the surfaces in close enough contact with each other and gives poor strength.

Thermosetting resins must be either cured by heat or catalyst, or both. In the plywood industry, where large production is essential, hot presses are more practicable than curing by catalyst alone, because of the shorter curing cycle.

As in the case of pressure, there is no standard from which the curing time for a class of adhesives may be found. The curing time for various adhesives differs considerably with so many dependent factors, that each adhesive must be considered individually. However, on obtaining experimentally the minimum curing time of an adhesive in one panel at one temperature, the minimum curing time for any thickness of panels in the press at any temperature may be calculated (21).

The type of wood used as the veneer in the making of plywood is also important when considering curing time of an adhesive. Because of the differences in thermal conductivity of the wood, phenolic resins cure more slowly between gum veneer than between birch (22).

The curing temperatures (or platen temperatures) of plywood assemblies vary widely in industry, depending
on the desired curing cycle and properties of the individual
adhesives. Since phenolic resins are not susceptible to
deterioration at the higher temperatures, plywood made with
phenolic are generally cured between 275 and 325°F.

CHEMICAL FACTORS INFLUENCING ADHESION

Polar Characteristics

Wood is a strong polar material because of the
presence of free hydroxyl groups in the cellulose molecules.
Strong joints can never be made to a polar surface with a non
polar adhesive or vice versa (25). Substances with weak polar
groupings possess little adhesion, for polar groups are very
strongly absorbed. Thus, since wood also has an affinity for
water, a strongly polar, water-soluble adhesive, such as a
phenol resin, should give the best results. Hydrogen bonding
has also been proposed as a contributing factor (23). The
fact that smooth planed surfaces yield greater strength than
coarse sanded surfaces indicates that mechanical adhesion is
not the most important consideration.

Process of Polymerization

Generally speaking, the more reactive positions a
phenolic compound has, the easier the formation of a thermo-
setting polymer. Compounds such as the 1,2,4 and 1,2,6 xylenols,
which have but one reactive position, are incapable of forming
linear polymers with formaldehyde. Ortho and para cresol with two reactive positions favor the formation of long straight chain polymers containing from 5 to 12 phenolic nuclei called Novolaks. The cross-linked thermosetting polymer is most easily obtained by using compounds with three reactive positions such as phenol, meta cresol, 1,3,5 xylenol or resorcinol.

The comparative reactivity of the different phenols with formaldehyde was found in a series of experiments by Strung (27):

**TABLE II. REACTION RATIO OF VARIOUS PHENOLICS WITH FORMALDEHYDE**

<table>
<thead>
<tr>
<th>Phenol</th>
<th>Comparative Reactivity (Phenol = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,6 xylenol</td>
<td>.16</td>
</tr>
<tr>
<td>o-cresol</td>
<td>.26</td>
</tr>
<tr>
<td>p-cresol</td>
<td>.35</td>
</tr>
<tr>
<td>1,2,5 xylenol</td>
<td>.71</td>
</tr>
<tr>
<td>1,3,4 xylenol</td>
<td>.83</td>
</tr>
<tr>
<td>phenol</td>
<td>1.00</td>
</tr>
<tr>
<td>2,3,5 trimethylphenol</td>
<td>1.49</td>
</tr>
<tr>
<td>1,3,5 xylenol</td>
<td>7.75</td>
</tr>
<tr>
<td>m-cresol</td>
<td>7.88</td>
</tr>
</tbody>
</table>

Compounds such as resorcin and 1,3,5 xylenol, which have very high reactive rates, are often used to assist in the curing of phenolic resins. With the use of small percentages of resorcin and 1,3,5 xylenol, the curing time of a phenolic resin may be cut in half. Because of the extreme reactivities of these additives, a catalyst is not generally necessary when either is used in phenolic composition, and the resulting resin
is practically neutral. Neutral resins are not as detrimental to wood as the highly alkaline or acid resins.

The initial reaction of phenol and formaldehyde is the formation of saligenin (ortho-hydroxybenzyl alcohol)

\[
\begin{align*}
1) & \quad \text{OH} + HCHO \rightarrow \text{OH} \quad \text{CH}_2\text{OH} \\
2) & \quad \text{OH} \quad \text{CH}_2\text{OH} + \quad \text{OH} \rightarrow \quad \text{OH} \quad \text{CH}_2 \quad \text{OH} + H_2O \\
3) & \quad \text{OH} \quad \text{CH}_2\text{OH} + \quad \text{OH} \quad \text{CH}_2\text{OH} \rightarrow \quad \text{OH} \quad \text{CH}_2 \quad \text{CH}_2\text{OH} + H_2O
\end{align*}
\]

Saligenin is quite reactive and condenses with another molecule of phenol or a molecule of saligenin.

Both of the products formed in equations 2 and 3 may react with either a phenol or another molecule of formaldehyde forming the following polymer or one very similar to it (28)
The end groups of this polymer may be either methylole groups or phenolic rings depending on the relative amounts of phenol and formaldehyde. If there is less than 1 mol of formaldehyde for every mol of phenol, the end groups of the above polymer will be primarily phenolic nuclei. If there is more than one mol of formaldehyde, the end groups of the above polymer will tend to be methylole groups.

Since phenol also has a reactive para position, the hydrogen atom may form with formaldehyde and then with phenol to form a branch polymer, e.g.

[Diagram of molecular structures]
and finally to a cross-linked polymer, e.g.

![Polymer structures](image)

In early investigations on phenol-formaldehyde reactions, Baekeland proposed that the letters A, B and C be used to distinguish between the various stages of a resin. Stage A indicates a low molecular weight, initial condensate, of a polymer; stage B as the fusible, but difficultly soluble; and stage C as the infusible insoluble stage. Though these terms are still used, the distinction between the various stages is not precise.

According to Weith (29), the initial reaction polymers formed from phenol and formaldehyde with an alkaline catalyst favor a compound having methylole groups at each end, e.g.

![Polymer structures](image)
This type of polymer is readily formed when there is more than one mol of formaldehyde per mol of phenol in the presence of an alkaline catalyst. Furthermore polymers (similar to the one shown in 7) react with each other quickly, forming a complicated cross-linked molecule (30). These cross-linked polymers become insoluble much quicker than long straight chained polymers (novolaks) of the same molecular weight.

However, when an acid catalyst is used in the phenol-formaldehyde reaction, the end groups of the average novolak will be phenolic nuclei, e.g.

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_2 \\
\text{OH} \\
\text{CH}_2 \\
\text{....} \\
\text{OH}
\end{array}
\]

According the Koebner (31) the molecular weight of these compounds is approximately 700, increasing to 1400 in the first cross-linkage reaction and to over 2800 on the second. These polymers are formed by using less than 1 mol of formaldehyde per mol of phenol in the presence of an acid catalyst.

With a two-step alkaline catalyzed resin it is more difficult to verify the exact nature of the initial reactions. However, since most experiments in this investigation were with phenol-formaldehyde molal ratios of nearly 1 to 1 and
alkaline catalyzed, the initial polymers should be very similar to the one shown in Equation 7. Consequently a large amount of cross-linking between these polymers should be expected, rather than the formation of very long, straight chained molecules.

Evaporation and Diffusion of Volatiles from Adhesive Films

The presence of solvents in an adhesive contribute but little to the plywood bond. Solvents do, however, have such benefits as permitting better polar adjustment and molecular rotation on curing. Also, they allow the initial reaction to be carried out for a longer time and increase the pot and storage life of resins.

However the presence of solvents in adhesives may be detrimental to the bond formed on resinification. If the adhesives polymerize too quickly, small mechanical voids may be left in the adhesive film on evaporation of the solvent or some of the solvent may even be entrapped in the film. Both of these conditions are conducive to low bond strength.

There are a few polymerizable solvents such as furfuryl alcohol and furfuraldehyde that may be used as a solvent in phenolic resins. However, extreme care must be exercised in choosing them because the combined polymers formed may overshadow the characteristics of the original polymer.

Too large a percentage of volatile material in phenolic resins will increase the tendency of the resin to
flow into the pores of the wood. This causes a starved glue line and embrittlement of the fibers of the wood. Most phenolic resins contain at least 40% solid material, the rest being water, generally with some alcohol.

Acidity and Alkalinity of the Glue Line

For more rapid cures with phenolic resins either an acid or alkaline catalyst may be used. However, strong acid or alkaline catalysts are very detrimental to the wood. With a low glue line pH of about 3.5 or lower, there is an embrittlement of the wood resulting in low shear strength (32). Highly alkaline glue lines above a pH of about 8.5 not only deteriorate the wood, but also have the additional disadvantage of reducing the water resistance of the adhesive.

The use of a catalyst with an adhesive to help speed polymerization is widely used in the resin industry. One commonly used compound is hexamethylenetetramine. This compound decomposes to form formaldehyde, which supplies methylene groups, and ammonia, which catalyzes the reaction. The most common alkaline catalysts are sodium carbonate, ammonia and sodium hydroxide. Hydrochloric, sulfuric, formic, or aromatic sulfonic acids are generally used for catalyzing the final polymerization with acids.

According to Mason and Manning (33), resin prepared using phenol and formaldehyde with an acid catalyst form from
3 to 3.5 times faster than those made with alkaline catalysts, using the same amount of formaldehyde in each case. They further state that the velocity of resinification of an adhesive is proportional to the concentration of the acid used, but this velocity, using an alkaline catalyst, is largely independent of the concentration of the catalyst.
This investigation was undertaken in an attempt to formulate a bullet-proof adhesive of low cost with a relatively short curing cycle. Since only the phenolic type resins are known to give the desired bond and be economically feasible, the search was narrowed to a phenol formaldehyde resin with small amounts of 1,5,5 xylenol or resorcin as accelerating resins. Therefore the investigation was divided into four parts: the investigation of (1) a straight phenolic, (2) a phenolic modified with 1,5,5 xylenol, (3) a phenolic modified with resorcin, and (4) a phenolic modified with both 1,5,5 xylenol and resorcin.

EXPERIMENTAL

Four general pieces of apparatus were used in the making, pressing, and final testing of the various adhesives. These are the reaction apparatus, the constant humidity cabinet, the hot press and the sheer test machine.

The reaction apparatus consisted of a three-neck flask, condenser, stirrer, thermometer, and burner. The three-neck flask was usually a thousand cubic centimeters in volume. The stirrer was driven by a one-quarter horsepower motor with a reduction gear unit off the usual belt and pulley system. The r.p.m. range could be adjusted from about 30 to 1,500. A vapor seal was made by using porous impregnated asbestos packing around the submerging tube. A standard 19-blind

This investigation was undertaken in an attempt to formulate a boil-proof adhesive of low cost with a relatively short curing cycle. Since only the phenolic type resins are known to give the desired bond and be economically feasible, the search was narrowed to a phenol formaldehyde resin with small amounts of 1,3,5 xylenol or resorcin as accelerating resins. Therefore the investigation was divided into four parts: the investigation of (1) a straight phenolic, (2) a phenolic modified with 1,3,5 xylenol, (3) a phenolic modified with resorcin, and (4) a phenolic modified with both 1,3,5 xylenol and resorcin.

APPARATUS

Four general pieces of apparatus were used in the making, pressing, and final testing of the various adhesives. These are the reaction apparatus, the constant humidity cabinet, the hot press and the shear test machine.

The reaction apparatus consisted of a three-neck flask, condenser, stirrer, thermometer, and burner. The three-neck flask was usually a thousand cubic centimeters in volume. The stirrer was driven by a one-quarter horsepower motor with a reduction gear made of the usual belt and pulley system. The r.p.m. range could be adjusted from about 40 to 400. A vapor seal was made by using graphite impregnated asbestos packing around the stirring rod. A standard 12-inch
straight tube condenser, bunsen burner and 110\(^\circ\)C. thermometer were used in all cases.

The constant humidity cabinet consisted of a large, insulated and air-tight box. Various saturated salt solutions were placed in flat pans on perforated shelves. The center stock and faces of the wood were packed loosely over these saturated solutions. A fan was also placed in the box in such a position as to blow over the solutions and thus a constant humidity was obtained more quickly.

The pressing apparatus consisted of two 12-inch square platens, one stationary, the other driven by a 50 square inch hydraulic ram. The platens are electrically heated and thermostatically operated. When careful temperature control was desirable a copper-constantan thermocouple and a Leeds and Northrup potentiometer were used. The pressure on the hydraulic piston was read on a Bourdon gage reading from 0 to 2000 pounds per square inch. A total load of 50 tons was obtainable with this press.

The various plywood specimens were tested in a Riehle plywood strip-shear tester. This machine was adjusted so that a load of 600 to 1000 pounds per minute was applied to the specimen.

All viscosity measurements were taken with Gardner viscosity tubes, ranging from U to Z6.

All plywood panels were either from gum or birch.
Figure 1. Equipment Used in Making Resins
Figure 2. Hot Press Used in Making Panels
Figure 3. Richle Plywood Strip Shear Tester
wood. The birch wood was used exclusively where the strength of the bond was the primary consideration. Gum wood was used primarily in the determination of the suitability of the final adhesives for plywood manufacture. The center stock was approximately 5/32 of an inch and the face veneer 1/18 inch thick for both gum and birch wood.

The moisture content of veneer and center stock varied between 10 to 12 per cent (dry basis). Generally two 6 by 12 inch panels were pressed at a time, and they were always placed between two 12-inch square, 1/4 inch thick plywood cauls, to simulate production conditions. After being pressed, the panels were hot stacked from 12 to 20 hours before being cut for testing.

STRAIGHT PHENOLIC RESINS

The first consideration was a method of preparing a good phenolic resin suitable for later modification with accelerating resins. The most important factors involved in making such a phenolic resin were:

1. Initial mol ratio of phenol to formaldehyde
2. Type and amount of catalyst
3. Time of reflux
4. Amount of extender or filler
5. Final mol ratio of phenol to formaldehyde
6. Time and temperature of curing
Procedure

In making each resin, the formalin was weighed into a three-necked flask fitted with stirrer, reflux condenser, and thermometer. The phenol was then added, followed by the caustic, the mixture heated to reflux temperature, and at varying intervals of time a sample was removed. After the sample was cooled enough paraformaldehyde was added to change the phenol-formaldehyde mol ratio of 1 to 0.7 to 1 to 1.25. Walnut shell flour was added in the amount equal to twenty per cent of the solid content of the adhesive. The adhesive was then spread on gum veneer and center stock, pressed and tested. Results of these tests appear in Table III.

Conclusions

The results itemized in Table III indicate that the best phenolic resin is one which contains 3 to 4 per cent caustic based on the weight of phenol. The reflux time must be at least two hours with results improving as the reflux time is increased to three hours. The superiority of a three-hour reflux over the two and one-half hour one may be observed in Table IV. Good results were obtained for both final phenol-formaldehyde mol ratios of 1 to 1.25 and 1 to 1.5. The data give no indication that either mol ratio is superior to the other. The minimum curing time for a 3 per cent caustic catalyzed phenolic is in the order of 13 minutes with 300°F. platens.
In order to obtain data that could be correlated, all of the above factors were held constant with the exception of the time of reflux and the amount of catalyst.

For a given resin, the molecular weight is a function of reflux time. Since curing time is inversely proportional to molecular size, the longest possible reflux time is desirable. However, the length of reflux is limited, for after a certain period of time, the resin molecules become so large they separate from the solution. This is undesirable because mixing is very difficult, and flow characteristics are poor.

A practical compromise must also be made on the amount of catalyst. Since only alkaline resins were made, most experiments were done using caustic soda. Too little caustic fails to keep the resin molecules in solution. Too much caustic gives poor bonds because of its greater affinity for water, thus causing delamination.

Experiments were made using 1, 2, 3, and 4 per cent caustic and varying the time of reflux from 1/2 hour to as much as 5 hours. The initial mol ratio of phenol to formaldehyde was held constant at 1 to 0.7. Amount of filler, final mol ratios, curing time, temperature, and pressure were held constant for the first few experiments. The percentage of caustic added to the phenol and formaldehyde was based on the weight of the phenol.
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Per Cent Caustic</th>
<th>Total Reflux Time Hrs.</th>
<th>Final Phenol to Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Flatten Temp. °F.</th>
<th>Time in Press Min.</th>
<th>Shear Strength psi.</th>
<th>Per Cent Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-17A</td>
<td>1</td>
<td>1:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PF-17B</td>
<td>1</td>
<td>2:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PF-17C</td>
<td>1</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>185</td>
<td>70</td>
</tr>
<tr>
<td>PF-17D</td>
<td>1</td>
<td>4:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PF-17E</td>
<td>1</td>
<td>5:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>165</td>
<td>70</td>
</tr>
<tr>
<td>PF-18A</td>
<td>2</td>
<td>2:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PF-18B</td>
<td>2</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PF-16A</td>
<td>3</td>
<td>1:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>335</td>
<td>55</td>
</tr>
<tr>
<td>PF-16B</td>
<td>3</td>
<td>2:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>290</td>
<td>55</td>
</tr>
<tr>
<td>PF-16C</td>
<td>3</td>
<td>2:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>360</td>
<td>95</td>
</tr>
<tr>
<td>PF-16D</td>
<td>3</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>285</td>
<td>70</td>
</tr>
<tr>
<td>PF-19A</td>
<td>4</td>
<td>1:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>310</td>
<td>90</td>
</tr>
<tr>
<td>PF-19B</td>
<td>4</td>
<td>2:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>320</td>
<td>100</td>
</tr>
<tr>
<td>PF-19C</td>
<td>4</td>
<td>2:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td>340</td>
<td>100</td>
</tr>
<tr>
<td>PF-19D</td>
<td>4</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Constants: Pressure - 200 psi.
Spread - 40 lbs. adhesive per 1000 square feet of surface

x Indicates all specimens delaminated during the 1/4 hour boil
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Time in Press Min.</th>
<th>Total Reflux Time Hrs.</th>
<th>Final Phenol to Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Platen Temp. °F. @ 45°</th>
<th>Boil Test Results</th>
<th>Shear Strength psi.</th>
<th>Per Cent Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-21A</td>
<td>18</td>
<td>2:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>290</td>
<td>205</td>
<td>75</td>
</tr>
<tr>
<td>PF-21B</td>
<td>15</td>
<td>2:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>200</td>
<td>360</td>
<td>95</td>
</tr>
<tr>
<td>PF-21C</td>
<td>13</td>
<td>2:30</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>320</td>
<td>270</td>
<td>70</td>
</tr>
<tr>
<td>PF-21D</td>
<td>18</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>360</td>
<td>360</td>
<td>90</td>
</tr>
<tr>
<td>PF-21E</td>
<td>15</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>250</td>
<td>210</td>
<td>15</td>
</tr>
<tr>
<td>PF-21F</td>
<td>13</td>
<td>3:00</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>305</td>
<td>305</td>
<td>100</td>
</tr>
<tr>
<td>PF-21G</td>
<td>18</td>
<td>2:30</td>
<td>1-1.5</td>
<td>20</td>
<td>300</td>
<td>215</td>
<td>215</td>
<td>80</td>
</tr>
<tr>
<td>PF-21H</td>
<td>15</td>
<td>2:30</td>
<td>1-1.5</td>
<td>20</td>
<td>300</td>
<td>230</td>
<td>230</td>
<td>15</td>
</tr>
</tbody>
</table>

Constants: Pressure - 200 psi., Spread - 40 lb. adhesive per 1000 sq. ft. surface.

x Indicates 1 specimen delaminated during the 4 hour boil.
PHENOLIC RESINS MODIFIED WITH 1,3,5 XYLENEOL

Since the curing cycle of a straight phenolic adhesive was too long, it was decided to reduce this cycle by modifying with a faster polymerizing resin. 1,3,5 xylenol seemed to be a logical choice for it is extremely reactive with formaldehyde and costs less than one-half as much as resorcin.

Procedure:

Experiments were made using 8.3, 16.7 and 33 per cent 1,3,5 xylenol as the modifying agent in a two step 3 per cent caustic catalyzed, phenolic resin. The percentages of 1,3,5 xylenol were based on the total phenol and xylenol content of the resin.

To a two step, 3 hour refluxed, phenolic resin was added enough 1,3,5 xylenol to give the desired percentage. For each mol of 1,3,5 xylenol, 0.7 mol of (36%) formalin was added. The entire mixture was then refluxed with constant stirring for various intervals of time ranging from 15 minutes to 45 minutes.

A 1,3,5 xylenol resin was also made separately, rather than with a phenolic resin. This xylenol resin was refluxed one hour with a 3 per cent caustic catalyst and a ratio of 1 mol xylenol to 0.7 mol formaldehyde. The resulting resin, however, was insoluble in water and so viscous that
handling on a production scale would be very difficult.

Data and Results

In the formulation of adhesives for panels, enough paraformaldehyde was added to change the phenol (or xylenol)-formaldehyde ratio from 1 to 0.7 to 1 to 1.25. Walnut shell flour was added to the extent that it was 20 per cent of the solid content of the resin. All panels were made of birch veneer and center stock, pressed at 200 psi. with the platen temperatures approximating 300 F. Results appear in Table V.

Conclusions

Results of panels made with the lower percentages of xylenol (8.3 and 16.7) were poor and inconsistent. Panels made with adhesives containing 33 per cent xylenol and a small percentage of ethyl alcohol met boil test specifications using a curing cycle of 8 minutes or longer. The addition of some solvent to this adhesive seems to be a necessity, for otherwise spreading is extremely difficult and results very poor. Throughout these experiments it was noted that 1,3,5 xylenol seemed to increase the water resistance of an adhesive, but failed to decrease the curing time as much as expected. Further it was noticed that improved adhesives were obtained by increasing the reflux time of the 1,3,5 xylenol resin. Best results were obtained after a reflux of about 45 minutes.
### TABLE V. TEST RESULTS OF PANELS MADE WITH A PHENOLIC RESIN MODIFIED WITH VARIOUS PERCENTAGES OF 1,3,5 XYLENOL

<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Per Cent Xylenol</th>
<th>Reflux Time of Phenol Hrs.</th>
<th>Reflux Time of Xylenol Hrs.</th>
<th>Final Phenol to Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Platen Temperature °F. ±5°</th>
<th>Curing Time Min.</th>
<th>Shear Strength psi.</th>
<th>Per Cent Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFX-1A</td>
<td>8.3</td>
<td>3</td>
<td>20 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>295</td>
<td>10</td>
<td>200</td>
<td>15</td>
</tr>
<tr>
<td>PFX-2B</td>
<td>16.7</td>
<td>3</td>
<td>20 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>295</td>
<td>10</td>
<td>295</td>
<td>30</td>
</tr>
<tr>
<td>X-1A</td>
<td>8.3</td>
<td>3</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>315</td>
<td>10</td>
<td>280</td>
<td>0</td>
</tr>
<tr>
<td>X-1B</td>
<td>16.7</td>
<td>3</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>315</td>
<td>10</td>
<td>270</td>
<td>30</td>
</tr>
<tr>
<td>PFX-2A</td>
<td>33.0</td>
<td>3</td>
<td>15 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>360</td>
<td>95</td>
</tr>
<tr>
<td>PFX-3A</td>
<td>33.0</td>
<td>3</td>
<td>25 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>360</td>
<td>95</td>
</tr>
<tr>
<td>PFX-2B</td>
<td>33.0</td>
<td>3</td>
<td>15 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PFX-3B</td>
<td>33.0</td>
<td>3</td>
<td>25 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>175</td>
<td>0</td>
</tr>
<tr>
<td>PFX-4A</td>
<td>33.0</td>
<td>3</td>
<td>35 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>270</td>
<td>0</td>
</tr>
<tr>
<td>PFX-5A</td>
<td>33.0</td>
<td>3</td>
<td>45 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>230</td>
<td>0</td>
</tr>
<tr>
<td>PFX-4B</td>
<td>33.0</td>
<td>3</td>
<td>35 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>320</td>
<td>85</td>
</tr>
<tr>
<td>PFX-5B</td>
<td>33.0</td>
<td>3</td>
<td>45 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>410</td>
<td>100</td>
</tr>
</tbody>
</table>

Panels X-1A and X-1B - the phenolic and xylenol resins were made separately. PFX-4B and PFX-5B - contain 16% ethyl alcohol based on solid content of resin.

Constants: Pressure - 200 psi.; Spread - 40 lb. per 1000 square feet.
PHENOLIC RESINS MODIFIED WITH RESORCIN

Since the use of comparatively large quantities of 1,3,5 xylenol needed for short curing cycles would be uneconomical, a study was made using a resorcin resin as the modifier for phenol-formaldehyde adhesives. Although resorcin is more expensive than 1,3,5 xylenol, it was thought that it might be possible to use much smaller amounts.

Procedure

Experimentation on resorcin modified phenolic resins was divided into two parts: in one part the phenol and resorcin were copolymerized; in the other the phenolic and the resorcin resins were made separately, then mixed.

In the copolymerization of phenol and resorcin resins, adhesives were made with as low as 7.5 per cent resorcin, based on the total resorcin and phenol, to as high as 33 per cent. The caustic soda was increased from 3 to 4 per cent based on the amount of phenol, and the initial phenol-formaldehyde ratio was also changed from 1 to 0.7 to 1 to 0.92 in some of the later experiments. The figure 0.92 was chosen, for beyond this point the two-step phenolic becomes a one-step resin. The use of a larger quantity of formalin was advantageous, for it decreased the amount of paraformaldehyde (about twice as costly as formalin) needed to form the thermosetting polymer and increased the pot life of the adhesive.
The first experiment consisted of making a 33.3 per cent resorcin modified phenolic, in one operation. The regular 3 per cent caustic catalyzed phenolic with a 1 to 0.7 phenol-formaldehyde ratio was allowed to reflux for 2 hours and 30 minutes. At this point, the resorcin and additional formaldehyde (1 mol of resorcin to 0.7 mol of formaldehyde) were added and the mixture allowed to reflux 30 minutes longer. A sample of the resin was then removed and cooled. The remaining mixture was refluxed for 30 minutes longer before removing the final sample.

The boil test results on panels made with the above resin appear in Table VI. Also some panels were made by diluting the 33 per cent resorcin modified phenolic with straight phenolic resin to decrease the resorcin content to 16.7 per cent.

A 20 per cent resorcin modified phenolic was also made changing the initial phenol-formaldehyde ratio from 1 to 0.7 to 1 to 0.92. The caustic content was also increased to 4 per cent of the total resorcin and phenol. The phenol, caustic and formaldehyde were refluxed for two hours. The resorcin and additional formaldehyde (a mol ratio of 1 to 0.67) were then added and the entire mixture refluxed for 45 minutes. After sampling the remaining mixture was refluxed for 15 minutes more before taking the final sample. The boil test results on panels made with this resin appear in Table VII.
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Per Cent Resorcin</th>
<th>Reflux Time of Phenol</th>
<th>Reflux Time of Resorcin</th>
<th>Final Phenol to Formaldehyde Ratio</th>
<th>Per Cent</th>
<th>Walnut Shell Flour</th>
<th>Curing Time °F. -5°</th>
<th>Shear Strength psi.</th>
<th>Per Cent Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFR-1A</td>
<td>16.7</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>9</td>
<td>310</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PFR-1B</td>
<td>16.7</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>7.5</td>
<td>340</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>PFR-1C</td>
<td>16.7</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>340</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PFR-1D</td>
<td>33.3</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>9</td>
<td>310</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>PFR-1E</td>
<td>33.3</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>320</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>PFR-1F</td>
<td>33.3</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>7</td>
<td>350</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PFR-1G</td>
<td>33.3</td>
<td>2:30</td>
<td>30 min.</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>330</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>PFR-1H</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>5.5</td>
<td>320</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>PFR-2A</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>9</td>
<td>380</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PFR-2B</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>340</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PFR-2C</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>7</td>
<td>350</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>PFR-2D</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>340</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PFR-2E</td>
<td>33.3</td>
<td>2:30</td>
<td>1 hr.</td>
<td>1-1.25</td>
<td>20</td>
<td>5.5</td>
<td>240</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Constants: Temperature of Platens - 300° ±5°F.; Pressure - 225 psi.; Wood - Birch
## TABLE VII. TEST RESULTS OF PANELS MADE WITH 20 PER CENT RESORCIN MODIFIED PHENOLIC RESINS AT VARIOUS CURING TIMES

<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Final Phenol to Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Per Cent Water or Isopropyl Alcohol</th>
<th>Total Reflux Time Hrs., Min.</th>
<th>Curing Time Min.</th>
<th>Boil Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFR-5A</td>
<td>1-1.25</td>
<td>20</td>
<td>5 Iso.</td>
<td>3:00</td>
<td>6</td>
<td>260</td>
</tr>
<tr>
<td>PFR-4A</td>
<td>1-1.25</td>
<td>20</td>
<td>10 Iso.</td>
<td>2:45</td>
<td>8</td>
<td>230</td>
</tr>
<tr>
<td>PFR-4B</td>
<td>1-1.25</td>
<td>20</td>
<td>10 Iso.</td>
<td>2:45</td>
<td>7</td>
<td>330</td>
</tr>
<tr>
<td>PFR-4C</td>
<td>1-1.25</td>
<td>20</td>
<td>10 Iso.</td>
<td>2:45</td>
<td>6</td>
<td>220</td>
</tr>
<tr>
<td>PFR-4D</td>
<td>1-1.25</td>
<td>20</td>
<td>4O H2O</td>
<td>3:00</td>
<td>8</td>
<td>x</td>
</tr>
<tr>
<td>PFR-5B</td>
<td>1-1.25</td>
<td>20</td>
<td>4O H2O</td>
<td>3:00</td>
<td>7</td>
<td>270</td>
</tr>
<tr>
<td>PFR-5C</td>
<td>1-1.25</td>
<td>20</td>
<td>4O H2O</td>
<td>3:00</td>
<td>6</td>
<td>x</td>
</tr>
<tr>
<td>PFR-5D</td>
<td>1-1.25</td>
<td>20</td>
<td>15 H2O 7.5 Iso.</td>
<td>3:00</td>
<td>8</td>
<td>210</td>
</tr>
<tr>
<td>PFR-5E</td>
<td>1-1.25</td>
<td>20</td>
<td>15 H2O 7.5 Iso.</td>
<td>3:00</td>
<td>7</td>
<td>260</td>
</tr>
<tr>
<td>PFR-5F</td>
<td>1-1.25</td>
<td>20</td>
<td>15 H2O 7.5 Iso.</td>
<td>3:00</td>
<td>6</td>
<td>150</td>
</tr>
</tbody>
</table>

Constants: Temperature - 300° ±5°F.; Pressure - 150 psi.; Wood - Gum
The percentages of water and isopropyl alcohol are based on the weight of resin used.

A number of experiments were made in which the phenolic and resorcin resins were made up separately. The phenolic resins were made up with an initial phenol-formaldehyde ratio of 1 to 0.92. The caustic content was four percent of the weight of phenol. A sample of resin was removed after 2 hours and 20 minutes of reflux, followed by the removal of another sample every 20 minutes up to a total time of 3 hours and 40 minutes.

In the make-up of the resorcin resin a resorcin-formaldehyde ratio of 1 to 0.67 was used. Half of the formalin was added to the resorcin, and the mixture was then heated to reflux temperature. After about ten minutes the remaining formalin was slowly added over a period of ten minutes. Then 1.2% caustic based on the weight of resorcin was added. The resin was allowed to reflux ten minutes longer, making a total reflux time of 30 minutes, before cooling.

These two resins, the straight phenolic and the straight resorcin were mixed together so that for 0.9 parts of phenol there was one-tenth of a part of resorcin. The three-hour phenolic was chosen as the best of the straight phenolics. Isopropyl alcohol was added to the extent of 16 per cent of the weight of the phenolic resin in an attempt to increase the pot life and decrease the viscosity. 20 per
cent walnut shell flour, based on the solids content, was added with varying amounts of paraformaldehyde. Viscosity curves, indicative of the pot life, of these resins with the varying mol ratios of phenol to formaldehyde appear in Figure 4.

Data and Results

The panel formulation and test results of the resorcin modified phenolics are shown in Tables VI and VII. Table VI gives the results of 16.7 and 33% resorcin modified phenolic resins. The results from tests on these copolymerized adhesives were excellent, but their pot life is much too short, being less than an hour. The resin using 33.3 per cent resorcin is too expensive because of the large amounts of resorcin and paraformaldehyde. This cost was reduced in the following adhesive where only 20 per cent resorcin was used and an initial mol phenol-formaldehyde ratio of 1 to 1 reduced the quantity of paraformaldehyde necessary. The panel formulation and test results of this resin appear in Table VII. The pot life of this adhesive is less than an hour.

The variation of viscosity with time for those adhesives in which the resorcin and phenolic resins were made separately are shown in Figure 4. In all curves the resorcin content is 10 per cent of the weight of the total phenolics present. The final phenolic formaldehyde ratios were varied, curve 1 has a final ratio of 1 to 1.25, curve 2 a final ratio
Curve 1 - Para., Phenol-Formaldehyde Ratio 1 to 1.25
Curve 2 - Para., Phenol-Formaldehyde Ratio 1 to 1.1
Curve 3 - Para., Phenol-Formaldehyde Ratio 1 to 1
Curve 4 - Hexa., Phenol-Formaldehyde Ratio 1 to 1.25

Figure 4. Effect of Time on Spread Mix Viscosity of Resorcin Modified Phenolic PFR-4
of 1 to 1.1, and curve 3 a ratio of 1 to 1. In curve 4, hexamethylenetetramine was used in place of paraformaldehyde, having a final phenol-formaldehyde ratio of 1 to 1.25.

Conclusions

The test results of those adhesives using 16.3 and 33.3 per cent resorcin were excellent, and good cures were obtained in as little as 6 minutes. Their pot life of less than an hour, however, is too short to make them practical in the plywood industry.

In trying to reduce the cost and, at the same time, increase the pot life of the adhesive containing 20 per cent resorcin, test results were poor. On reducing the solids content of adhesives used in making panels PFR-4D, PFR-4E, and PFR-4F from about 55 per cent to 42 per cent with water, a pot life of about two and one-half hours was obtained. However, these panels failed to pass the shear strength and wood failure requirements after being boiled 4 hours. When trying to increase the pot life by the addition of a smaller amount of water and a little isopropyl alcohol, the pot life was increased to a little over one hour, but the curing cycle must be at least 7 or 8 minutes.

The procedure for making the phenolic and resorcin resins separately gave adhesives of very short pot life. The pot life was increased to about an hour by changing the phenol-formaldehyde ratio to 1 to 1, but even this is too
short and the panels were of poor quality. Though Figure 4 presents curves of resins containing 10% resorcin, various other percentages of resorcin were tried, and the results were similar. The use of hexamethylenetetramine instead of paraformaldehyde gave a pot life of many hours, but the decomposition of hexa was so slow that the curing cycle was too long.

In general, quick cures can be obtained by copolymerization of resorcin and phenolic resins, but the pot life of such adhesives is too short. Undoubtedly the pot life of these resorcin modified phenolics could be increased by the removal of part of the water under vacuum and replacing it with some solvent such as ethyl alcohol, but the cost of the additional equipment and alcohol would make such an adhesive very expensive.

**PHENOLIC RESINS MODIFIED WITH 1,3,5 XYLENOL AND RESORCIN**

Modification of phenolic resins with 1,3,5 xylenol was found to give adhesives that were somewhat slow curing but of good pot life. Resorcin modified phenolics gave short cures, but unfortunately the pot life also was too short. The next step of the investigation was a study of phenolics modified with both 1,3,5 xylenol and resorcin in an effort to combine the short cures obtained with the resorcin with the longer pot life of the adhesives made with 1,3,5 xylenol.
Procedure

The procedure for making a phenolic adhesive modified with 1,3,5 xylenol and resorcin was as follows unless otherwise stated: the phenol, formalin (36%), and the caustic were added together and heated to reflux temperature. The initial phenol-formaldehyde ratio was 1 to 0.92 with 4% caustic based on the weight of phenol. This mixture was generally allowed to reflux for a period of two hours. The resin was then cooled slightly, whereupon the 1,3,5 xylenol and additional formalin were added to the phenolic. A xylenol-formaldehyde ratio of 1 to 0.67 generally was used. The entire mix was then heated to reflux for a period of 15 minutes after which the resorcin and a further quantity of formalin were added using the same formaldehyde ratio as for the 1,3,5 xylenol. The entire resin was then cooked for 45 minutes longer, making a total of 3 hours altogether.

To prepare the adhesive for spreading, the resin was extended with walnut shell flour (about 20% of the solid content). Paraformaldehyde was added to change the final phenolic-formaldehyde ratio to about 1 to 1.15 or 1 to 1.25. Water and isopropyl alcohol were sometimes added to increase the pot life and decrease the viscosity.

A slightly different method of attack was used in this section. Throughout this investigation the major trouble had been that of obtaining an adhesive with a pot life long.
enough for commercial usage. Short cures were obtained in many cases, but the pot life was insufficient. These two factors are very closely interrelated, but with the right combination of solvent, accelerating resins, and paraformaldehyde, it was felt that satisfactory pot life and short curing cycles could be obtained. In this section, most of the work consisted of taking the viscosity of an adhesive at various intervals of time to determine the pot life. If the pot life was satisfactory the adhesive was used in making a panel for testing; otherwise no panels were made.

Data and Results

Since a relatively large number of these three-component resins were made and tested to find the approximate percentages of the accelerating resins necessary, the presentation of the complete set of data would make this section voluminous. Therefore viscosity curves and some test data for the two most important adhesives appear in this section. The formulation and test data of those adhesives for which test panel data were obtained appear in Appendix IV.

A number of panels were made using an adhesive containing 10% resorcin, 7.5% 1,3,5 xylenol, and the rest phenol. The mixture was refluxed for a total of three hours. The spread mix of the adhesive prepared for panel testing contained a final phenolic-formaldehyde ratio of 1 to 1.25.
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Initial Phenol-Formaldehyde Ratio</th>
<th>Final Phenol-Formaldehyde Ratio</th>
<th>Per Cent Walnut</th>
<th>Per Cent Shell</th>
<th>Per Cent Ethyl Flour</th>
<th>Alcohol</th>
<th>Time in Press 300°F</th>
<th>Type of Wood</th>
<th>Shear Strength psi</th>
<th>% Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFXR-20A</td>
<td>1-0.92</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>300</td>
<td>8</td>
<td></td>
<td>Gum</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-20B</td>
<td>1-0.92</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>300</td>
<td>6</td>
<td></td>
<td>Gum</td>
<td>275</td>
<td>65</td>
</tr>
<tr>
<td>PFXR-16A</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>8</td>
<td></td>
<td>Birch</td>
<td>410</td>
<td>80</td>
</tr>
<tr>
<td>PFXR-16B</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>7</td>
<td></td>
<td>Birch</td>
<td>350</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-16C</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>6</td>
<td></td>
<td>Birch</td>
<td>340</td>
<td>80</td>
</tr>
<tr>
<td>PFXR-16D</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>8</td>
<td></td>
<td>Gum</td>
<td>170</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-16E</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>7</td>
<td></td>
<td>Gum</td>
<td>170</td>
<td>90</td>
</tr>
<tr>
<td>PFXR-16F</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>6</td>
<td></td>
<td>Gum</td>
<td>150</td>
<td>70</td>
</tr>
</tbody>
</table>

Constants:  
- Pressure - 175 psi.  
- Spread - 30 lb./1000 square feet  
- Total Reflux Time - 3 hrs.  
- Initial xylenol (or resorcin) formaldehyde ratio - 1 to 0.67

x Percentage alcohol based on the weight of resin
The results on panels made from this adhesive appear in Table VIII.

Since tests show that short cures can be obtained with adhesives containing 10% resorcin and 7.5% 1,3,5 xylenol, the effect of time on the spread mix viscosity was determined using different percentages of solvent. By doing this it could be established whether a satisfactory pot life could be obtained while still maintaining these short cures.

Figure 5 shows a number of these curves using various solvents with resin PFXR-20. The amount and type of each solvent is shown in Table IX.

**TABLE IX. FORMULATION OF SPREAD MIX FOR 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLIC RESINS**

<table>
<thead>
<tr>
<th>Curve</th>
<th>Parts of Resin</th>
<th>Parts of Formalin (F) or para (P)</th>
<th>Parts of Walnut Shell Flour</th>
<th>Parts of Water</th>
<th>Parts of Isopropyl Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>6 P</td>
<td>11.6</td>
<td>10.7</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>16.7 F</td>
<td>11.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>6 P</td>
<td>11.6</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>16.7 F</td>
<td>11.6</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>6 P</td>
<td>11.6</td>
<td>10.7</td>
<td>6.7</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>16.7 F</td>
<td>11.6</td>
<td>-</td>
<td>6.7</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>16.7 F</td>
<td>11.6</td>
<td>10</td>
<td>6.7</td>
</tr>
</tbody>
</table>

The final phenol-formaldehyde mol ratio was 1 to 1.25 in all cases. Walnut shell flour was used in the amount
Curve 1 - Para., 10.7% water
Curve 2 - Formalin
Curve 3 - Para., 24% water
Curve 4 - Formalin, 13.3% water
Curve 5 - Para., 10.7% water, 6.7% Iso. alcohol
Curve 6 - Formalin, 6.7% Iso. alcohol
Curve 7 - Formalin, 10% water, 6.7% Iso. Alcohol

Percentages are based on weight of Resin Phenol-Formaldehyde Mol Ratio, 1-1.25
20% Walnut Shell Flour Based on Solids

Figure 5. Effect of Time on Spread Mix
Viscosity of Xylenol-Resorcin Modified Phenolic PFXR-20
of 20% of the total solids content. For a good comparison between curves 1 and 2, 3 and 4, and 5 and 6, in Figure 5 the solid content of those using paraformaldehyde and those using formalin were kept the same. Panels were made of the same mix as represented by curves 5, 6 and 7 of Figure 5, but they were of poor quality and could be easily pulled apart.

Using the same adhesive (10% resorcin and 7.5% xylenol), but with an initial phenol-formaldehyde mol ratio of 1 to 1 (resin PFXR-16), more runs were made to show the effect of time on the viscosity. The formulation of each adhesive is shown in Table X. Figure 6 shows the viscosity curves.

As in the previous case, panels were made from the adhesives whose pot life are represented by curves 3 and 4 in Figure 6. The samples were poor showing a starved glue line.

Since the desired pot life with quick cures was not obtained with a resin containing 10% resorcin and 7.5% 1,3,5 xylenol, the resorcin and the xylenol were increased to 15 and 10 per cent respectively. This resin was identical to the previous one in reflux time and with an initial phenol-formaldehyde mol ratio of 1 to 0.92. The initial xylenol or resorcin-formaldehyde ratio was 1 to 0.67.

Viscosity curves were made using various percentages of solvents and are shown in Figure 7. Table XI shows the amount of solvent in each of the resins.
<table>
<thead>
<tr>
<th>Curve</th>
<th>Parts of Resin</th>
<th>Final Phenol-Formaldehyde Ratio</th>
<th>Parts of Paraformaldehyde</th>
<th>Parts Walnut Shell Flour</th>
<th>Parts Isopropyl Alcohol</th>
<th>Parts Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1-1.25</td>
<td>4.67</td>
<td>11.3</td>
<td>-</td>
<td>13.3 acetone</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1-1.20</td>
<td>4.0</td>
<td>10.6</td>
<td>-</td>
<td>20 acetone</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>1-1.25</td>
<td>4.67</td>
<td>11.3</td>
<td>10</td>
<td>12 water</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1-1.20</td>
<td>4.0</td>
<td>10.6</td>
<td>23.3</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 6. Effect of Time on Spread Mix Viscosity of Resorcin Xylenol Modified Phenolic PFXR-16
Curve 1 - Phenol-Formaldehyde Ratio, 1 to 1.2, 20% Iso. Alcohol
Curve 2 - Phenol-Formaldehyde Ratio, 1 to 1.15, 10% Iso. Alcohol, 18.7% Water
Curve 3 - Phenol-Formaldehyde Ratio, 1 to 1, 20% Iso. Alcohol
Curve 4 - Phenol-Formaldehyde Ratio, 1 to 1.25, 15% Water

Figure 7. Effect of Time on Spread Mix Viscosity of Resorcin Xylenol Modified Phenolic PFXR-18 and PFXR-21
TABLE XI. FORMULATION OF SPREAD MIX FOR XYLENOl-RESORCIN MODIFIED PHENOLIC RESINS PFXR-18, PFXR-21

<table>
<thead>
<tr>
<th>Curve</th>
<th>Parts of Resin</th>
<th>Final Phenol Ratio</th>
<th>Parts of Formaldehyde</th>
<th>Parts of para</th>
<th>Parts of Walnut</th>
<th>Parts of Isopropyl Alcohol</th>
<th>Parts of Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1 to 1.2</td>
<td>6</td>
<td>11.3</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>1 to 1.15</td>
<td>3.6</td>
<td>10.5</td>
<td>10</td>
<td>18.7</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>1 to 1</td>
<td>1.67</td>
<td>10</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1 to 1.25</td>
<td>6.75</td>
<td>9</td>
<td>-</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

Panels were made of the same mix as represented by curves 2, 3, and 4 in Figure 7. Those made of the resin represented by curve 3 were poor. The other two resins, however, gave good results which are presented in Table XII. Adhesive number PFXR-18 is the same composition as curve 4 and adhesive number PFXR-21 has the same formulation as curve 2 of Figure 7.

Conclusions

Test results on the adhesive containing 10% resorcin and 7.5% 1,3,5 xylenol show that short cures may be obtained provided the quantity of solvent is small. However, if enough solvent is added to give these adhesives a practical working pot life, they fail to meet requirements using the short curing cycles.

Results also indicate from Figure 5 that the rate of polymerization is slower when formalin is used in place
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Final Phenol Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Per Cent Isopropyl Alcohol</th>
<th>Per Cent Waterlof Water Temp. +50</th>
<th>Type of Wood</th>
<th>Time in Press</th>
<th>Shear Strength psi.</th>
<th>Per Cent Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFXR-18A</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>18.7</td>
<td>Birch</td>
<td>10</td>
<td>370</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-18B</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>18.7</td>
<td>Birch</td>
<td>8</td>
<td>330</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-18C</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>18.7</td>
<td>Birch</td>
<td>6</td>
<td>350</td>
<td>40</td>
</tr>
<tr>
<td>PFXR-21A</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Birch</td>
<td>10</td>
<td>370</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-21B</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Birch</td>
<td>8</td>
<td>330</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-21C</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Birch</td>
<td>6</td>
<td>370</td>
<td>10</td>
</tr>
<tr>
<td>PFXR-21D</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Gum</td>
<td>10</td>
<td>210</td>
<td>80</td>
</tr>
<tr>
<td>PFXR-21E</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Gum</td>
<td>8</td>
<td>220</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-21F</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Gum</td>
<td>7</td>
<td>240</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-21G</td>
<td>1-1.15</td>
<td>20</td>
<td>10</td>
<td>18.7</td>
<td>Gum</td>
<td>6</td>
<td>300</td>
<td>40</td>
</tr>
</tbody>
</table>

Constants: Pressure - 175 psi. 
Spread - PFXR-18, 30#/1000 ft.²; PFXR-21, 25#/1000 ft.²

1. Percentage of alcohol and water based on the weight of the resin alone
of paraformaldehyde, both resins having the same solid content. Another advantage in the use of formalin is that its price is only about half as much as paraformaldehyde, considering both on a 100% formaldehyde basis. However, the formaldehyde molecule is in a more volatile state in formalin solution, producing a stronger and more irritating smell than paraformaldehyde. Working around large quantities of resins in which formalin solution had been added would be difficult without a very good ventilating system. For this reason the use of formalin solution for the final polymerization was abandoned.

Adhesives containing 15% resorcin and 10% 1,3,5 xylenol gave the best combination of suitable pot life and short cures of any tried. Adhesive PFXR-13, containing a large amount of water, has a pot life of about 3 hours. This resin will cure in 7 to 8 minutes with 300°F platens. PFXR-21 has a usable pot life of about 1 hour and 45 minutes and gave good cures in a 7 minutes curing cycle, with most specimens passing after 6 minutes in the press.

This adhesive, PFXR-21, gave the best combination of properties that has been found in this investigation. A pot life of about one hour and forty-five minutes is sufficient for normal production, although this time provides only a small margin of safety in case of a shut-down. A curing cycle of 6 to 7 minutes will, in most cases, allow an increase in production. The cost of materials for this adhesive is
approximately $2.75, spreading 25 pounds of glue per 1000 square feet of surface.

RATE OF TEMPERATURE CHANGE IN HEATED PLYWOOD PANELS

Throughout this investigation, one square foot of plywood was found to be more than sufficient for testing purposes. So in order to eliminate making any more plywood than necessary and yet simulate production conditions, two plywood cauls were used with each pressing. Several experiments were then run to determine the relative rate of heat transfer through the cured cauls and uncured panels.

Procedure

The first run was on three 1/4" birch plywood assemblies one foot square. The moisture content of the wood was about 8%. A phenolic resin modified with resorcin and 1,3,5 xylentol was used as the adhesive. Averaging thermocouples were placed in the two outermost, intermediate and intermost glue lines. The platen temperatures were held as close to 300°F. as possible, and a pressure of 225 psi. was used. Temperature readings were then taken at various intervals of time for a period of twenty minutes. These readings are graphically presented in Figure 8. The glue lines are numbered consecutively from top to bottom; the two outermost being 1 and 6, the intermediate 2 and 5, and the intermost 3 and 4.
The same procedure was repeated using gum panels and results appear in Figure 9. Then using two cured gum caulks, readings were taken of glue line variation in one uncured gum panel and in one uncured birch panel. These results are presented in Figure 10.

Conclusions

Results indicate that the temperature rise is faster in gum than in birch wood, giving a small margin of safety when pressing 3 birch assemblies. However, it was found that the use of plywood caulks gave a glue line temperature of approximately 100°F, higher than when 3 uncured assemblies were used. This difference would probably result in a half minute longer curing cycle for three uncured panels in the press. Therefore all resulting curing times made in this investigation should be increased about one-half a minute for plywood production.
Figure 8. Change of Glue Line Temperature with Time for 3 Birch Panels
Figure 9. Change of Glue Line Temperature with Time for 3 Gum Panels
Figure 10. Change of Glue Line Temperature with Time for 2 Plywood Cauls and 1 Gum or Birch Panel
<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Journal</th>
<th>Volume</th>
<th>Issue</th>
<th>Pages</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Beeckland, L. M.</td>
<td>Ind. Eng. Chem.</td>
<td>1</td>
<td>356</td>
<td>(1909)</td>
<td>abstract</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Beeckland, L. M.</td>
<td>U. S. Patent 999,966</td>
<td>(Nov. 16, 1909)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>Noyes, N. Y., U. S. Patent 1,077,796</td>
<td>(June 21, 1913)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>Noyes, N. Y., U. S. Patent 1,078,199</td>
<td>(March 15, 1913)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>Noyes, N. Y., U. S. Patent 1,092,590</td>
<td>(April 22, 1914)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>Noyes, N. Y., U. S. Patent 1,092,591</td>
<td>(April 22, 1914)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>Noyes, N. Y., U. S. Patent 1,092,570</td>
<td>(Sept. 25, 1914)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>Noyes, N. Y., U. S. Patent 1,092,505</td>
<td>(Sept. 25, 1914)</td>
<td>(abstract)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Schne, O. and Schne, E.</td>
<td>Trans. A.I. A., 68, 915 (1953)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
LITERATURE CITED

(2) Baekeland, L. H., U. S. Patent 939,966 (Nov. 16, 1909) (abstract)
(8) Novotny, E., U. S. Patent 1,776,366 (Sept. 23, 1930) (abstract)
(9) Novotny, E., U. S. Patent 1,767,696 (June 24, 1930) (abstract)
(10) Novotny, E., U. S. Patent 1,849,109 (March 15, 1932) (abstract)
(11) Novotny, E., U. S. Patent 1,802,390 (April 28, 1931) (abstract)
(18) Luce, F., Mech. Eng., 66, 654 (1944)
(19) Delmonte, J., Pacific Plastics, 2, 14 (1944)
(23) de Bruyne, N. A., Aircraft Engineer, 18, No. 12, 51 (1939) (abstract)
(24) Wlasey, W., Wood Products, 50, 22 (1945)
(28) Koebner, British Plastics, 14, 100, 1942 (abstract)
(31) Koebner, British Plastics, 14, 100 (1942) (abstract)
Glossary

Assembly line: the line on which workers remove the squeaking of the adhesive and the applying of pressure.

Bond: the grip of the adhesive on the wood.

Collar: thin sheets of material on which the plywood assembly is laid during the pressing operation. These thin sheets facilitate loading and protect these.

Center stock: refers to the thick middle veneer in unveneered plywood.

Gum: the polymerization of the adhesive to the final insensible, infusible form.

 härden or Filler: a finely divided material added to adhesives to provide body, reduce cost and control flow.

Face: the outside ply of an assembly.

Moisture Content: the per cent of water in wood based on the dry weight.

Face: a sheet of plywood.

Flap: the last hoarding plates of a hull press.

Fly: a wrack of veneer.
GLOSSARY

Assembly time: the time which elapses between the spreading of the adhesive and the applying of pressure.

Bond: the grip of the adhesive on the wood.

Cauls: thin sheets of material on which the plywood assembly is laid during the pressing operation. These thin sheets facilitate loading and protect faces.

Center stock: refers to the thick middle veneer in three ply plywood.

Cure: the polymerization of the adhesive to the final insoluble, infusible form.

Extender or Filler: a finely divided material added to adhesives to provide body, reduce cost and control flow.

Face: the outside ply of an assembly.

Moisture Content: the per cent of water in wood based on the dry weight.

Panel: a sheet of plywood.

Platens: the heat bearing plates of a hot press.

Fly: a sheet of veneer.
Pot life: that period of time during which an adhesive remains suitable for spreading. An adhesive is generally considered spreadable till it reaches a viscosity of about 60 poises.

Pressing cycle: the number of minutes an assembly remains in the hot press.

Spread: the amount of adhesive expressed in pounds that is applied to one thousand square feet of veneer.

Starved glue line: an expression used to indicate an inadequate amount of adhesive in a cured glue line.

Storage life: the period of time an adhesive remains usable while in storage at room temperature.

Veneer: a thin layer of wood, sliced, rotary cut or sawn from a log.
APPENDIX II
SAMPLE PREPARATION AND TESTING PROCEDURES

Samples were prepared in accordance with "Hardwood Plywood Commercial Standard CS35-47". For three-ply plywood each specimen was $3\frac{1}{2}$ inches long and 1 inch wide. An area of 1 square inch was cut in the center of each specimen by two $1/8$ inch groves, cut 2/3 through the center stock.

Figure 11. Plywood Testing Specimen

Each specimen was submerged in boiling water for a period of four hours. They were then removed from the boiling water and brought to room temperature by placing in cold water. While still wet the specimen was gripped between the jaws of the testing machine and a load of 600
to 1000 pounds per minute applied until failure took place. Specimens must meet the following requirements.

TABLE XIII. PERCENTAGE OF WOOD FAILURE REQUIRED AFTER BOILING

<table>
<thead>
<tr>
<th>Average Shear Strength psi.</th>
<th>Minimum Wood Failure %</th>
<th>Average Wood Failure %</th>
</tr>
</thead>
<tbody>
<tr>
<td>under 250</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>250-350</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>above 350</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

TABLE XIV. MINIMUM SHEAR VALUES REQUIRED AFTER BOILING

<table>
<thead>
<tr>
<th>Density of Veneers</th>
<th>Strength (wet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>290</td>
</tr>
<tr>
<td>Medium</td>
<td>210</td>
</tr>
<tr>
<td>Low</td>
<td>120</td>
</tr>
</tbody>
</table>
APPENDIX III

SAMPLE CALCULATIONS

As an example of the calculations made throughout this investigation, the procedure for the formulation, preparation of the adhesive mix and determination of cost are presented for Resin PFXR-21.

(1) Formulation of Resin

PFXR-21 contains 15 per cent resorcin, 10 per cent xylenol and 75 per cent phenol. The initial mol phenol-formaldehyde was 1 to 0.92 with a xylenol and resorcin-formaldehyde ratio of 1 to 0.67.

\[ 232 \text{ g. of phenol (3 moles)} \]
\[ \frac{232}{0.75} = 376 \text{ g. total phenolic content} \]
\[ 376 \times 10\% = 37.6 \text{ g. of 1,3,5 xylenol} \]
\[ 376 \times 15\% = 56.4 \text{ g. of resorcin} \]

Four per cent caustic based on the weight of the total phenolic equals \[ 376 \times 4\% = 15 \text{ g. caustic} \]

\[ \frac{232}{94} \times \frac{30}{0.36} \times 0.92 = 230 \text{ g. of 36\% formalin to be added with the phenol and caustic} \]

\[ \frac{37.6}{122} \times \frac{30}{0.36} \times 0.67 = 17.2 \text{ g. of 36\% formalin to be added with the 1,3,5 xylenol} \]

\[ \frac{56.4}{110} \times \frac{30}{0.36} \times 0.67 = 28.7 \text{ g. of 36\% formalin to be} \]
added with the resorcin.

(2) Preparation of the Final Mix

A final phenolic formaldehyde ratio of 1 to 1.15 is to be used with 20 per cent of the solid content of the resin being walnut shell flour.

Total formalin solution = 230 + 17.2 + 28.17 = 275.9 g.

275.9 x 0.36 = 99.3 g. of formaldehyde

Total solids without considering water formed in the reaction is

\[ 282 + 99.3 + 37.6 + 56.4 + 15 = 490.3 \text{ g.} \]

\[ \frac{282}{94} \times 18 \times 1.15 = 62.1 \text{ g. water formed from phenol and formaldehyde.} \]

\[ \frac{282}{122} \times 18 \times 1.15 = 6.4 \text{ g. water formed from 1,3,5 xylenol and formaldehyde.} \]

\[ \frac{56.4}{110} \times 18 \times 1.15 = 10.5 \text{ g. water formed from resorcin and formaldehyde.} \]

Total water formed in the reaction:

\[ 62.1 + 6.4 + 10.5 = 79 \text{ g. water} \]

Total formaldehyde necessary to give a final phenolic formaldehyde ratio of 1 to 1.15:

\[ \frac{282}{94} \times 30 \times 1.15 = 103.4 \text{ g. total formaldehyde for phenol.} \]
37.6 \times 30 \times 1.15 = 10.6 \text{ g. total formaldehyde for xylenol}.

\frac{56.4}{110} \times 30 \times 1.15 = 17.7 \text{ g. total formaldehyde for resorcin.}

Formaldehyde already added to the resin

230 \times 0.36 = 82.8 \text{ g. formaldehyde to phenol}
17.2 \times 0.36 = 6.2 \text{ g. formaldehyde to xylenol}
28.7 \times 0.36 = 10.3 \text{ g. formaldehyde to resorcin}

Amount of paraformaldehyde that must be added

103.4 - 82.8 = 20.6 \text{ g. paraformaldehyde for phenol}
10.6 - 6.2 = 4.4 \text{ g. paraformaldehyde for xylenol}
17.7 - 10.3 = 7.4 \text{ g. paraformaldehyde for resorcin}

Total paraformaldehyde that must be added

20.6 + 4.4 + 7.4 = 32.4 \text{ g. paraformaldehyde}

Total solid content

\frac{490.3 - 79.0 + 32.4}{125} = \frac{443.7}{g. total solids}

125 \text{ g. water and 66.7 g. isopropyl alcohol were added to decrease the viscosity and increase the pot life.}

The total weight of the entire resin, paraformaldehyde, water, and alcohol is:

282 \text{ g. (phenol) + 275.9 g. (formalin) + 15 g. (caustic)}
+ 37.6 \text{ g. (xylenol) + 56.4 g. (resorcin) + 125 g. (water) + 66.7 g. (alcohol) + 32.4 g. (para) = 891 g.}
Percentage of solids

\[ \frac{143.7}{289} = 49.8\% \text{ solids} \]

For 100 grams of resin, the amount of paraformaldehyde to be added is

\[ \frac{100}{289} = \frac{x}{32.4} \]

\[ x = 3.64 \text{ g.} \text{ paraformaldehyde for 100 g. resin} \]

For 100 grams of resin, the amount of walnut shell flour to be added is

\[ 100 + 3.64 = 103.64 \text{ g.} \]

\[ 103.64 \times 20\% \times 49.8\% = 10.3 \text{ g. walnut shell flour for 100 g. resin} \]

(3) Calculation of Material Cost Based on Approximate Prices Taken from the Chemical Engineering News of June 21, 1948

Total walnut shell flour is

\[ 43.7 \text{ g. (total solid content) x 20\% = 88.7 g. walnut shell flour} \]

The resorcin price is for 94\% resorcin.

The xylenol price is for 60\%, setting 1,3,5 xylenol.

<p>| TABLE XV. MATERIAL COST OF A 15% RESORCIN, 10% 1,3,5 XYLENOL MODIFIED PHENOLIC RESIN |
|---------------------------------|-------------|----------------|
| Phenol                          | 282.0       | .1325          | 37.40        |
| Formalin                        | 275.9       | .042           | 11.60        |
| Caustic                         | 15.0        | .0235          | .43          |
| Xylenol                         | 37.6        | .30            | 11.30        |</p>
<table>
<thead>
<tr>
<th>Material</th>
<th>Pounds</th>
<th>Price in Dollars per lb.</th>
<th>Total cost in dollars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcin</td>
<td>56.4</td>
<td>.55</td>
<td>31.00</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>66.7</td>
<td>.077</td>
<td>5.13</td>
</tr>
<tr>
<td>Walnut shell flour</td>
<td>88.7</td>
<td>.035</td>
<td>3.11</td>
</tr>
<tr>
<td>Paraformaldehyde</td>
<td>32.4</td>
<td>.24</td>
<td>7.78</td>
</tr>
<tr>
<td>Water</td>
<td>125.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>TOTALS</strong></td>
<td><strong>979.7</strong></td>
<td></td>
<td><strong>$107.75</strong></td>
</tr>
</tbody>
</table>

Cost per pound for complete resin

\[
\frac{107.75}{979.7} = $0.1097
\]

With a spread of 25 pounds of adhesive per 1000 square feet of surface, the cost for the adhesive is

\[
$0.1097 \times 25 = $2.74 \text{ per 1000 square feet.}
\]
## APPENDIX IV

### TEST RESULTS OF PHENOLIC RESINS MODIFIED WITH VARIOUS PERCENTAGES OF 1,3,5 XYLENOL AND RESORCIN

<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Per Cent of Resorcin</th>
<th>Per Cent of Xylenol</th>
<th>Initial Phenol-Formaldehyde Ratio</th>
<th>Final Phenol-Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Platen Temp. of F. ±5°</th>
<th>Time in Press</th>
<th>Shear Strength psi</th>
<th>% Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFXR-3A</td>
<td>5</td>
<td>7.5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>350</td>
<td>40</td>
</tr>
<tr>
<td>PFXR-3B</td>
<td>5</td>
<td>7.5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>7</td>
<td>260</td>
<td>40</td>
</tr>
<tr>
<td>PFXR-3C</td>
<td>5</td>
<td>7.5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6.5</td>
<td>390</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-3D</td>
<td>5</td>
<td>7.5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6</td>
<td>220</td>
<td>3</td>
</tr>
<tr>
<td>PFXR-4A</td>
<td>7.5</td>
<td>5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>390</td>
<td>90</td>
</tr>
<tr>
<td>PFXR-4B</td>
<td>7.5</td>
<td>5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>7</td>
<td>290</td>
<td>30</td>
</tr>
<tr>
<td>PFXR-4C</td>
<td>7.5</td>
<td>5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6.5</td>
<td>330</td>
<td>50</td>
</tr>
<tr>
<td>PFXR-4D</td>
<td>7.5</td>
<td>5</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6</td>
<td>310</td>
<td>30</td>
</tr>
<tr>
<td>PFXR-2A</td>
<td>7.5</td>
<td>10</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-2B</td>
<td>7.5</td>
<td>10</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>360</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-2C</td>
<td>7.5</td>
<td>10</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>7</td>
<td>380</td>
<td>70</td>
</tr>
<tr>
<td>PFXR-2D</td>
<td>7.5</td>
<td>10</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6.5</td>
<td>420</td>
<td>100</td>
</tr>
<tr>
<td>PFXR-2E</td>
<td>7.5</td>
<td>10</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6</td>
<td>430</td>
<td>100</td>
</tr>
</tbody>
</table>
### APPENDIX IV (CONT'D.)

<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Per Cent of Resorcin</th>
<th>Per Cent of Xylenol</th>
<th>Initial Phenol-Formaldehyde Ratio</th>
<th>Final Phenol-Formaldehyde Ratio</th>
<th>Per Cent Walnut Shell Flour</th>
<th>Platen Temp. °F. ±5°</th>
<th>Time in Press</th>
<th>Shear Strength psi.</th>
<th>% Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFXR-1A</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>12</td>
<td>340</td>
<td>25</td>
</tr>
<tr>
<td>PFXR-1B</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>10</td>
<td>390</td>
<td>25</td>
</tr>
<tr>
<td>PFXR-1C</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>8</td>
<td>400</td>
<td>80</td>
</tr>
<tr>
<td>PFXR-1D</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>7</td>
<td>370</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-1E</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6.5</td>
<td>340</td>
<td>60</td>
</tr>
<tr>
<td>PFXR-1F</td>
<td>10</td>
<td>15</td>
<td>1 to 0.7</td>
<td>1 to 1.25</td>
<td>20</td>
<td>300</td>
<td>6</td>
<td>300</td>
<td>70</td>
</tr>
</tbody>
</table>

**Boil Test Results**

**Constants:**

1. Spread - 30#/1000 ft.²
2. Pressure - 200 psi.
3. Wood - Birch
4. Total Reflux Time - 3 hr.; xylenol, 45 min.; Resorcin, 30 min.
<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Total Reflux Time</th>
<th>Initial Phenol-Formaldehyde Ratio</th>
<th>Final Phenol-Formaldehyde Ratio</th>
<th>Final Per Cent Shell Oil</th>
<th>Final Per Cent Ethyl Alcohol</th>
<th>Flaten Time in Min.</th>
<th>Shear Strength psi.</th>
<th>% Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFXR-5A</td>
<td>2:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>300</td>
<td>10</td>
<td>340</td>
</tr>
<tr>
<td>PFXR-5B</td>
<td>2:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>300</td>
<td>7</td>
<td>350</td>
</tr>
<tr>
<td>PFXR-5C</td>
<td>2:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>6</td>
<td>300</td>
<td>6</td>
<td>340</td>
</tr>
<tr>
<td>PFXR-6A</td>
<td>2:00</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>PFXR-6B</td>
<td>2:00</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>7</td>
<td>320</td>
</tr>
<tr>
<td>PFXR-6C</td>
<td>2:00</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>5</td>
<td>300</td>
<td>6</td>
<td>320</td>
</tr>
<tr>
<td>PFXR-7A</td>
<td>1:45</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>1</td>
<td>300</td>
<td>10</td>
<td>380</td>
</tr>
<tr>
<td>PFXR-7B</td>
<td>1:45</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>1</td>
<td>300</td>
<td>7</td>
<td>290</td>
</tr>
<tr>
<td>PFXR-7C</td>
<td>1:45</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>1</td>
<td>300</td>
<td>6</td>
<td>310</td>
</tr>
<tr>
<td>PFXR-8A</td>
<td>1:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>300</td>
<td>10</td>
<td>320</td>
</tr>
<tr>
<td>PFXR-8B</td>
<td>1:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>300</td>
<td>7</td>
<td>x</td>
</tr>
<tr>
<td>PFXR-8C</td>
<td>1:30</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>-</td>
<td>300</td>
<td>6</td>
<td>x</td>
</tr>
</tbody>
</table>
APPENDIX V (CONTD.)

Constants: (1) Pressure - 150 psi.; Wood - Birch; Initial Mol ratio of xylenol (or resorcin) to formaldehyde - 1 to 0.7; Spread - 30#/1000 ft.²

(2) Total Reflux Time 2:30; xylenol :45, resorcin :30
                   2:00; xylenol :45, resorcin :30
                   1:45; xylenol :30, resorcin :15
                   1:30; xylenol :45, resorcin :30
## APPENDIX VI

**TEST RESULTS OF PHENOLIC RESINS MODIFIED WITH 7.5% RESORCIN AND 7.5% 1,3,5 XYLENOl WITH VARIOUS PHENOL-FORMALDEHYDE RATIOS**

<table>
<thead>
<tr>
<th>Adhesive and Panel No.</th>
<th>Total Reflux Time Hrs.</th>
<th>Initial Phenol/Formaldehyde Ratio</th>
<th>Final Phenol/Formaldehyde Ratio</th>
<th>Per Cent Walnut Flour</th>
<th>Per Cent Ethyl Alcohol</th>
<th>Time in Platen Temp. Press 15° Min.</th>
<th>Boil Test Results</th>
<th>% Wood Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PXR-9A</td>
<td>3</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>10</td>
<td>370</td>
</tr>
<tr>
<td>PXR-9B</td>
<td>3</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>7</td>
<td>400</td>
</tr>
<tr>
<td>PXR-9C</td>
<td>3</td>
<td>1-1</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>6</td>
<td>330</td>
</tr>
<tr>
<td>PXR-10A</td>
<td>3</td>
<td>1-0.9</td>
<td>1-1.25</td>
<td>20</td>
<td>7.5</td>
<td>300</td>
<td>10</td>
<td>410</td>
</tr>
<tr>
<td>PXR-10B</td>
<td>3</td>
<td>1-0.9</td>
<td>1-1.25</td>
<td>20</td>
<td>7.5</td>
<td>300</td>
<td>7</td>
<td>370</td>
</tr>
<tr>
<td>PXR-10C</td>
<td>3</td>
<td>1-0.9</td>
<td>1-1.25</td>
<td>20</td>
<td>7.5</td>
<td>300</td>
<td>6</td>
<td>320</td>
</tr>
<tr>
<td>PXR-11A</td>
<td>3</td>
<td>1-0.95</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>10</td>
<td>400</td>
</tr>
<tr>
<td>PXR-11B</td>
<td>3</td>
<td>1-0.95</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>7</td>
<td>360</td>
</tr>
<tr>
<td>PXR-11C</td>
<td>3</td>
<td>1-0.95</td>
<td>1-1.25</td>
<td>20</td>
<td>8</td>
<td>300</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

**Constants:**

1. Pressure - 150 psi.; Wood - Birch; Initial Mol Ratio of xylenol (or resorcin) to formaldehyde - 1 to 0.7
2. Total reflux time - 3:00; xylenol 1:00, resorcin :45

---

83
Acknowledgments

This research was made possible through a fellowship grant from
The University of Louisville Institute of Industrial Research
as a portion of contracted research with
General Plywood Corporation
This research was made possible through a fellowship grant from The University of Louisville Institute of Industrial Research as a portion of contracted research with General Plywood Corporation
The author wishes to acknowledge
the assistance of
Jesse R. Goza, Jr.
who worked concurrently on the project
VITA
Edward Joseph Dowd was born in Louisville, Kentucky, on January 9, 1924. He received his secondary education at Campion High School, Prairie du Chien, Wisconsin. Upon graduating from high school, he entered the College of Engineering at the University of Notre Dame in September, 1941. He enlisted in the U. S. Army Air Forces in May, 1943.

Mr. Dowd attended the San Marcos Navigation School, where he was commissioned a year later after qualifying in dead reckoning, pilotage, radio, and celestial navigation. He was then assigned to a heavy bombardment group in the 15th Air Force in Italy, where he flew 63 missions over Europe. With the ending of the war, he returned to the United States and was discharged.

Mr. Dowd completed his work at the University of Notre Dame obtaining his B. S. degree in Chemical Engineering in June, 1947. He entered the graduate school of the University of Louisville in July, 1947, and worked under a research fellowship at the Institute of Industrial Research during the year 1947-1948. He received the degree of Master of Chemical Engineering in June, 1949.