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<https://doi.org/10.18297/etd/2038>

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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

Jesse R. Goza, Jr.
///

1948

PLYWOOD ADHESIVE DEVELOPMENT

Jesse R. Goza, Jr.

Approved by the Examining Committee:

Director

R. C. Ernst

G. C. Williams

W. R. Barnes

June 1948

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ACKNOWLEDGEMENTS

The author wishes to acknowledge
the kind assistance and helpful guidance
of Dr. R. C. Ernst
who directed this research

A B S T R A C T

This thesis presents a study in the formulation of plywood adhesives with phenol, 1,3,5 xyleneol, resorcin and formaldehyde. Each resin was evaluated by making and testing plywood with it as the adhesive.

Procedures are given for producing water-soluble phenol-formaldehyde adhesives. This type of adhesive was found to give "boil-proof" bonds on gum wood, but the curing cycle was too long for the ordinary commercial production of plywood.

A study was made of the use of 1,3,5 xyleneol as a modifier for phenol-formaldehyde resins. In the course of the investigation, "one-step" xyleneol adhesives were found to be impractical, and 1,3,5 xyleneol, alone, as a modifier, was found to be of doubtful value.

Resorcin as a modifier for phenol-formaldehyde adhesives was found to increase the curing rate of the adhesive greatly, and six minute cures were effected on birch wood.

Methods for formulating synthetic resin adhesives containing 1,3,5 xyleneol, resorcin, and phenol were studied and the results presented in the thesis. These three-component resins on birch wood produced boil-proof bonds when short curing cycles were used.

INTRODUCTION

The investigation presented in this thesis was undertaken in an attempt to develop an adhesive capable of giving a thoroughly water-proof bond (1). This adhesive was to be within a given price range and possess a very short curing cycle in the hot press.

No commercial plywood adhesive satisfactorily meets the requirements: (a) boil-proof bond, (b) very rapid cure, (c) low cost. It was thought possible to develop an adhesive, having these characteristics, by incorporating 1,3,5 xylenol and resorcin with phenol and formaldehyde. The percentage of modifiers would necessarily be small, but both resorcin and xylenol were known to react much faster with formaldehyde than phenol. The project seemed especially feasible, in view of the fact that shorter resin storage life could be tolerated than would be practicable with usual commercial materials.

The desirability of developing an adhesive of the type described was suggested by the General Plywood Corporation of Louisville, Kentucky. The research was carried out at their request.

HISTORICAL

The first commercial glue factory of which we have any record (2) was established in Holland in 1690. Shortly afterwards the English began commercial production, and established it as a permanent industry about 1700. Some hundred or so years later, in 1808, the first American glue plant was founded in Boston by Elijah Upton. In 1814 the first patent literature on glues and their production appeared in the United States. An apt presentation of adhesive development in the United States is given by Delmonte (3) in the form of a chronological table. This historical outline is given in Table I.

It was not until about 1875 that plywood or laminated wood, as it was then called, began to assume commercial importance. This new field opened bright horizons for the glue industry, and with the advent of the twentieth century and modern synthetic resins the golden age began. Prior to the twentieth century the art had changed little from the glues and techniques known to the Egyptians.

In the United States Baekeland and Thurlow (4) first recognized the possibilities of phenolic resin adhesives in plywood manufacture. This was in 1912 while the commercial production of phenolic resins was yet in its infancy. The commercial developments of phenolic resins actually date from Dr. L. T. Baekeland's patents and announcements (5)(6)(7)(8)(9) in 1909. However, it was not until

TABLE I. CHRONOLOGICAL DEVELOPMENTS OF ADHESIVES
IN UNITED STATES (3)

Year	Material
1814	Glue from Animal Bones (Patent)
1872	Domestic Manufacture of Fish Glues (Isinglass)
1874	First U.S. Fish Glue Patent
1875	Laminating of Thin Wood Veneers Attains Commercial Importance
1909	Vegetable Adhesives from Cassava Flour (F.G. Perkins)
1912	Phenolic Resin to Plywood (Bakeland-Thurlow)
1915	Blood Albumin in Adhesives for Wood (Haskelite Co.)
1917	Casein Glues for Aircraft Construction
1920-30	Developments in Cellulose Ester Adhesives and Alkyd Resin Adhesives
1927	Cyclized Rubber in Adhesives (Fischer-Goodrich Co.)
1928	Chloroprene Adhesives (McDonald-B.B. Chemical Co.)
1928-30	Soybean Adhesives (I.F. Lanchs Co.)
1930	Urea Formaldehyde Resin Adhesives
1930-35	Phenolic Resin Adhesive Films (Resinous Products & Chemical Co.)
1939	Polyvinyl Acetate Adhesives (Carbide & Carbon Chemicals Co.)
1940	Chlorinated Rubber Adhesives
1941	Melamine-Formaldehyde Resin Adhesives (American Cyanamid Corp.) and "Redux" by de Bruyne (Aero Research Ltd.)
1942	"Cycleweld" Mutual Adhesives (Saunders-Chrysler Corp.)
1943	Resorcinal-Formaldehyde Adhesives (Penn. Coal Products Co.)
1944	"Metlbond" Adhesives (Havens, Consolidated Vultee Aircraft Corp.)
1945	Furane Resin Adhesives (Delmonte, Plastics Inst.) and "Pliobond" (Goodyear Tire & Rubber Co.)

about 1920 that synthetic resins were used as adhesives on a laboratory scale, and at that time their cost seemed prohibitive (10). Also, their use generally required hot presses which for plywood were practically non-existent.

In the early 1930's, however, a phenol-formaldehyde resin film, "Tego", was introduced in Europe as a plywood bonding agent, and the unusual durability of the resulting plywood attracted world-wide interest. In 1935 "Tego" was introduced into American plywood industries by Resinous Products and Chemical Company of Philadelphia. Since that time, phenol-formaldehyde adhesives have found wide acceptance in liquid form as well as film form. About 1937 a less expensive resin, slightly below "Tego" in ultimate serviceability, was brought into commercial use. This resin was a "Urea-Formaldehyde" adhesive capable of rapid cures at lower temperatures than those ordinarily required for the phenolics.

In 1943 the Pennsylvania Coal Products Company in cooperation with A. J. Norton introduced commercially the resorcinol formaldehyde adhesive. The basic patents on the resorcinol-formaldehyde reaction were taken by Novotny in 1930, 1931, and 1932. Novotny claimed an improvement in the rate of cure of phenolic resins when modified with relatively small amounts of resorcinol (11). He reacted resorcinol successfully with less than 1/2 molar para formaldehyde,

adding other paraform to produce the final, insoluble stage (12).

Very little information on 1,3,5 xylenol adhesives can be found in the literature. Delmonte (13) states that 3,5 xylenol behaves similarly to resorcinol in reducing the curing time of phenol-formaldehyde resins. It is known that the Shell Development Company, making a study of 1,3,5 xylenol as a modifier for phenolic resins, found that incorporation even to a minor extent results in a marked increase in the rate of cure.

At the present time, synthetic resins, adaptable to the plywood adhesive program, fall into three general classes:

- (A) Phenol-aldehyde; this group includes the formaldehyde resins made with cresols, resorcinol, 3,5 xylenol, and "Cardanol" ($C_6H_4OH \cdot C_{14}H_{27}$), which is a phenolic constituent found in cashew nut shell liquid.
- (B) Urea-formaldehydes; included in this group are the melamines.
- (C) Vinyl and Acrylic group; the members of this group have a limited field of application since they are thermoplastic adhesives. Practically all commercial production employs a resin or combination of resins from class (A) or (B).

Synthetic resin adhesives are necessary items today in many processes and industries. Plywood bonded with synthetic resin adhesives is presently being used in the

manufacture of small boats, aircraft wings, fuselages, propellers and innumerable small items. Entire homes are now being constructed of plywood, and laminated wood arches over 100 feet in span are being used in building construction (14).

The phenolic type plywood adhesive has established itself as leader wherever conditions of severe exposure to rain and weather exist.

T H E O R E T I C A L

The theoretical aspects of the problem will be presented in two sections.

I. The Chemistry of Phenolic Resins

In 1872 Baeyer (15) discovered that phenols and aldehydes reacted to give resinous products. Between that date and the time of the work of Baekeland (16) in 1907 a number of workers experimented with this phenomenon, but the reaction was not brought under control until the arrival of Baekeland. Baekeland, not only showed how the reaction could be carried out, but that the final resinous product was invaluable to industry.

Though phenolic resin chemistry is largely controversial, there are a few points that are generally agreed upon: (a) phenols, cresols, xylenols, and related substances form resins with aldehydes; (b) of these materials, those which set readily to the infusible, insoluble condition are those in which the ortho and para position are open, e.g., phenol, 1,3,5 xylenol, m-cresol (17); (c) in general, the reaction rate with aldehydes decreases in the order - resorcinol, 1,3,5 xylenol, m-cresol, phenol, para cresol, o-cresol, etc. (18); (d) slightly different reactions take place in acid and in basic solution; (e) in any case, the reaction consists of a condensation with one mol of water being formed for each mol of formaldehyde reacted.

Xylenols, cresols and higher phenols can be considered as homologues of phenol; the reaction between formaldehyde and these substances can be illustrated by the reaction of phenol with formaldehyde. This general reaction is divided into three, not too well defined, stages. Baekeland called the material in these stages Resinoids A, B, and C.

Formation of Resinoid "A"

Formation of Resinoid "B"

Resinoid "C"

The three classifications "A", "B", and "C" are rather freely used, but in general the following terminology applies: Resinoid "A" - the low molecular weight, initial condensate; Resinoid "B" - the difficultly soluble, fusible, intermediate polymer; Resinoid "C" - the insoluble, infusible, final stage.

Although the final polymer is very nearly the same, the course of the reaction is different in acid and basic media. The course of the reaction also depends upon the relative amounts of phenol and formaldehyde present.

When alkaline catalysts are employed, ortho and para hydroxy benzyl alcohols are formed from the initial reaction of phenol and formaldehyde.

Usually more than one mol of formaldehyde is used with a basic catalyst and poly alcohols may also be formed.

The ortho and para hydroxy benzyl alcohols have been isolated and positively identified, and it is claimed by Granger (19) that he has isolated the two dialcohols and the trialcohol.

Ordinarily reactions carried out in alkaline solution employ an excess of formaldehyde. The reaction is carried out by heating and can be stopped during the early stages simply by lowering the temperature. The soluble product is probably a resol; a typical resol is represented by the following formula:

The alkaline reaction product can be carried over to the final form at any subsequent time by the addition of heat. Even though the reaction is said to be stopped, it actually proceeds at an extremely slow rate, and this rate determines the storage life of the resins. As the reaction proceeds, the solubility of the resol decreases, as a result of the formation of cross linkages. When the molecular weight reaches 300-400 it approaches the difficultly soluble stage.

Alkaline "two-step" resins are frequently made. They are formulated with less than one mol of formaldehyde per mol of phenol and, therefore, require heat and additional formaldehyde to produce the final resin.

The alkaline "two-step" reactions take place at a slower rate and cannot be made to proceed further than Stage "B". There must be an addition of formaldehyde to increase the mol ratio to about 1 to 1 before it is possible for the reaction product to reach the final, insoluble, infusible stage. Usually, in practice with adhesive formulations the mol ratio of formaldehyde to phenol is brought into the range of 1.1-2.0 to 1.

Resinification under acid conditions leads initially to the formation of dihydroxy diphenyl methanes.

This differs from the alkaline reaction in that no alcohols can be isolated. Weith (20) has stressed this primary difference in the acid and basic reactions. In the two types of reactions represented by the equations

the first reaction is promoted by alkaline catalysts, which are very ineffective in causing the second reaction to take place. However, this second reaction is strongly accelerated by acid catalysts. Apparently the practical difference between the alkaline and acid processes is in the relative effectiveness of the two types of catalysts. Alcohols and poly-alcohols are, no doubt, formed in the acid reaction, but they are extremely short lived transition products and the tendency is towards the formation of longer linear molecules.

Because of the rapidity with which the reaction takes place, acid catalyzed reactions are carried out with less than the theoretical amount of formaldehyde. Mason and Manning (21) state that acid catalyzed resins are formed

three to three and one-half times as fast as those made with alkaline catalysts, provided the same amount of formaldehyde is used in each case.

As the resinification of the acid catalyzed resin continues beyond the diphenyl methane stage a resin form known as a "Novolak" is produced. This Novolak resin consists of a straight chain containing 5 to 7 phenolic residues.

Novolak Resin

However, Koebner (22) states that the molecular weights of Novolaks reach about 1200 before the resin becomes insoluble. Koebner also shows that the molecular weight of a Novolak varies according to the amount of phenol and formaldehyde in the original mixture.

In order to convert the fusible, soluble Novolak resin into the cross-linked, thermosetting stage, hexamethylenetetramine, sometimes called "hexa", is usually added. Aylsworth (23) is credited with the initial use of "hexa" as a catalyst. When heat is applied, hexamethylenetetramine decomposes to form both formaldehyde and ammonia. The ammonia accelerates the reaction and the required methylene groups are supplied by the formaldehyde. Cross linkages develop rapidly and transformation into stage "C" occurs.

A few acid catalysts which have been successfully employed are hydrochloric, sulfuric, phosphoric, formic, tartaric and aromatic sulfonic acids. Alkaline catalysts which have been found satisfactory are ammonia, sodium carbonate; sodium, calcium and potassium hydroxides. According to Mason and Manning (24) the concentration of a basic catalyst has little effect on the velocity of the resinification reaction, whereas if an acid catalyst is employed, the velocity of the reaction will be proportional to the concentration of the acid used.

The reactions which 1,3,5 xlenol and resorcin undergo with formaldehyde are analogous to those of phenol. They differ, however, in the rate at which these reactions occur and herein lies the basis for a large portion of the experimental work reported in this thesis. By incorporating these faster reacting components with phenol formaldehyde resins, a co-polymer can be obtained which will cure at a rate intermediate between that of either resin alone.

Sprung (25) studied the reaction of phenol and its homologues with paraformaldehyde in the absence of water by measuring the rate of disappearance of formaldehyde and found that the reaction was of the first order. The comparative reactivities of several phenols are given in the following table:

TABLE II. REACTION RATIO OF VARIOUS PHENOLS WITH FORMALDEHYDE

Phenol	Comparative Rate
1,2,6 xlenol	0.16
a-cresol	0.26
p-cresol	0.35
1,2,5 xlenol	0.71
1,3,4 xlenol	0.83
phenol	1.00
m-cresol	7.88
1,3,5 xlenol	7.75

A study of these results shows the probability of increasing the curing rate of a phenol-formaldehyde resin by modifying the resin with a more reactive phenolic compound.

II. The Theory of Adhesion

Until the 1920's little serious thought was given to the underlying causes of adhesion. Previously, the little known about the mysterious process of gluing was regarded as confidential knowledge of the trade. In 1929, Browne and Brouse (26) of the Forest Products Laboratory at Madison, Wisconsin, published one of the best of several pioneer articles. They classified the major factors of adhesion as "mechanical adhesion" and "specific adhesion".

"Mechanical adhesion" means that two substances are held together by a mechanical interlocking of the adhesive and

the adherent surface. After a glue has been applied to a wood surface, it gets its initial grip by flowing a small way into the wood; it usually cures before it gets very far and some of the strength possessed by the resulting joint is credited to the intertwining and interlocking of the two solids, wood and cured glue. For a long time this was thought to be the entire explanation, but actually it is only a part. The theory that mechanical adhesion alone is responsible can be disproved by the fact that two optically flat surfaces adhere strongly when placed together without any adhesive, whatsoever.

"Specific adhesion" may be defined as surface adhesion, independent of any protrusions of adhesive into the surfaces that are glued together. It is because of the existence of molecular and electrical forces. de Bruyne (27) has studied an important phase of this phenomenon. His investigations were concerned with the nature of the attractive forces between molecules and atoms, and especially with the secondary forces that exist between them. He emphasizes that strong joints can never be made to polar surfaces with non-polar adhesives or vice versa.

The phenolics, urea resins, and cellulose derivatives are formed of polar molecules and are therefore excellent for the gluing of wood. However, for non polar materials, such as metals, they are poor adhesives.

The relative importance of mechanical and specific

adhesion is a controversial subject. The adhesive research committee of the Department of Scientific and Industrial Research in London made a study of the nature of adhesion on wood surfaces. Their findings indicate that the adhesion is largely mechanical and only slightly specific (28). However, Browne and Brouse (26) concluded that the adhesion is mainly specific. The latter view is the more widely accepted today.

Undoubtedly both mechanical and specific adhesion are present in the gluing of wood. Regardless of which type is ultimately responsible, the effectiveness of the glue bond on wood is known to be influenced by such factors as moisture content of the wood, the porosity and smoothness of the wood surfaces, the pH of the glue, the glue spread, the solids content of the glue, the thickness of the glue line, the open and closed assembly times, and the pressure and the temperature used in curing the bond.

The moisture content of wood at the time of gluing is very important. High moisture content is completely undesirable and moderate moisture content, if uneven in the various members, will result in unequal swelling or shrinking, with subsequent warping and possible over stressing of the glue line. Also when gluing operations are carried out at temperatures above 212°F., heat is lost through the vaporization of water present in the wood. On the other hand, when the moisture content is too low proper flow is not obtained during bonding. The most general range of moisture content

recommended for wood bonding is 8 to 12 per cent. At a room temperature of 70°F., the equilibrium moisture content of wood is 8% when the relative humidity is 45% and 12% when the relative humidity is about 63% (29).

The porosity and smoothness of the wood is important for several reasons. The porosity of the wood determines to some degree the flow of the adhesive and excessive flow results in "starved" glue joints. If a surface is deeply scored, bubbles may be trapped in the glue line and weakness results. However, when smooth wood surfaces are properly bonded to form the thinnest glue joints, the resulting bonds possess the highest strength (30). It is generally recognized that a penetrating adhesive contributes little to the strength of the glue joint. On the contrary, an adhesive which remains at the glue line will probably produce the better bond.

The pH of a resin bond profoundly affects the life and strength of plywood (31). The lower and upper critical values of pH for phenol-formaldehyde seem to be 3.5 and 8 respectively; for urea-formaldehyde the values are pH 4 and about pH 6. In addition to the pH, the acid radical is important. At the same pH strong acids are more harmful than weak acids.

The glue spread determines to a large extent the thickness of the glue line and consequently the strength of the resulting joint. The spread is generally expressed as weight of glue per 1000 square feet of glue area and usual

spreads for hot pressed synthetic adhesives are 25-40 pounds. The thicker spreads are used on porous woods such as gum and the lighter spreads on non-porous woods such as birch. It is known that adhesives containing large amounts of volatiles work best with very thin glue lines and only the non-volatile adhesives such as the furan type are suited for very thick glue lines.

The open and closed assembly times allow for thickening of the glue, mainly through loss of volatiles by evaporation and diffusion into the wood structure. This operation is especially important in the gluing of porous woods where some thickening of the adhesive film nearly always is desired in order to minimize loss when pressure and heat are applied. The optimum assembly time depends upon the adhesive and the prevailing temperature.

Pressure affects the ultimate adhesive strength because it determines largely the amount and thickness of the adhesive film. Actually, no pressure is necessary in the gluing of materials if the surfaces to be joined are perfectly flat. However, for porous substances such as wood, pressure is very desirable until the adhesive has developed sufficient strength to keep the assembly together. For certain operations specific pressures have been said to be optimum, but actually pressure is not extremely critical in the bonding operation. Generally, pressures employed in the bonding of

plywood are about 125 to 150 psi for basswood and Douglas Fir, 150 to 175 psi for poplar and gum, and 200 to 250 psi for birch and maple (32).

Temperature and time influence the adhesive strength only in the sense that they determine when the glue is cured. The rate of cure of the resin adhesive increases rapidly with increasing temperature; therefore, curing time and temperature are inversely proportional. No standard curing time, at a given temperature, can be set for a class of glues. This curing time depends on so many factors that it remains an individual matter with each adhesive. However, most phenolics are cured at high temperatures, i.e., in the range 275-325°F.

EXPERIMENTAL

This work was undertaken in an attempt to find an economical adhesive, suitable for the mass production of plywood, and capable of giving a boil-proof bond. Because of the nature of this objective, the search was narrowed to an investigation of the phenolic resins. Special consideration was given to means of increasing the curing rate of phenol-formaldehyde adhesives by the addition of resorcinol and 3,5 xyleneol.

Apparatus:

The equipment used in making all resins is shown in Figure 1. Usually, the resins were made in a 1000 ml, three-necked, round-bottomed flask, fitted with a centigrade thermometer, mechanical stirrer and water condenser. Heat was supplied by a Bunsen burner, with only an asbestos gauze between the burner and the flask.

Measurements of resin viscosity were made with a Gardner Bubble Viscometer, range U to Z-6.

All weighing was made on a standard triple-beam laboratory balance, accurate to 0.1 gram.

A hand-operated hydraulic press having thermostatically operated, electrically heated platen was used to make experimental panels. This press is shown in Figure 2. It was made by the Charles E. Francis Company, Rushville, Indiana, has platens one foot square, and a piston area of 50 square inches. The press has a pressure gauge reading

from 0 to 2000 lbs. per square inch hydraulic pressure and is graduated in 40 lb. increments. It is possible to obtain up to 50 tons total load on this press.

Wood sawing operations were carried out using a small, power operated circular saw with an 8 inch blade.

Shear tests were performed on the standard Riehle Test Machine shown in Figure 3. This machine was set to apply load at a rate of approximately 800 pounds per minute.

Platen temperatures were taken with copper-constantan thermocouples used in conjunction with a Leeds and Northrup Potentiometer Indicator which gave direct readings in °F.

The moisture content of wood stock was maintained at 10-12% by storing the wood in a tight compartment where a saturated solution of ammonium chloride was kept exposed to the air.

Procedure:

The method of resin preparation, and the formulation of glue mixes for spreading, differ for the several divisions of the experimental work and are described in these subsections.

The method of test panel preparation and subsequent testing was the same throughout: Panels were prepared from birch or gum wood containing approximately 10-12% moisture. They were assembled by weighing a definite amount of glue mix

onto a piece of center stock, spreading the glue with a spatula, adding the face veneer, and repeating the process on the reverse side, forming a 3 ply assembly ready for the hot press. Most of the test panels were made 6" by 12", in order that two test pieces could be made during one pressing operation. The assembled panels were pressed at 225 psi or some lower specified pressure, and the platen temperature was held as closely as possible to 300°F. Before insertion of the panels, and during the pressing operation, the platen temperatures were observed by means of a thermocouple. In order that plant conditions might be closely simulated, panels were pressed between 1/4" gum plywood cauls. A short study was made and reported herein of the relative rates of heat transfer through these cauls and through uncured panels of the same thickness.

After being pressed, the panels were stacked and allowed to stand for 12-20 hours before being cut for testing. The standard plywood strip shear test was used exclusively. A description of the test sample preparation and the four-hour boil test is given in Appendix II.

Usually, half the test samples from each panel were tested dry and the others subjected to the four-hour boil test.

Figure 1
Equipment Used in Making Resins

Figure 2
Equipment Used in Making Panels

Figure 3

Riehle Shear Test Machine

Unmodified Phenol-Formaldehyde Resin Adhesives

The literature investigation, which preceded experimental work on this problem showed that unmodified phenol-formaldehyde adhesives probably would not be suitable. However, it was thought expedient to gain a working knowledge of these straight phenolic resins before attempting the manufacture of the modified resins.

Procedure:

The preparation of these resins is described as follows: One mol of phenol, 1.5 or 1.25 mols of formaldehyde (37% formalin), and caustic, as specified in Table III, were introduced into the reaction apparatus. These contents were then brought to boil over a bunsen burner and refluxed at atmospheric pressure for a definite time. The resin was then cooled rapidly with cold water. No water was removed from these resins, and in only one case was alcohol added. The variables in this process are given in Table III.

These resins were tested as outlined in the general procedure. The spread-mix was prepared by adding walnut shell flour in the amount of 20% of the solids content of the resin. Most of these early panels were made one foot square out of gum, 5/32" centerstock and 1/18" face veneer.

Data and Results:

A number of preliminary experiments were made before a resin suitable for testing was obtained. Beginning with PF10 (Phenol-Formaldehyde Number 10) the resins were tested. In Table III the make-up variables are fixed for these resins and certain descriptive statements made about them.

Shear test results for the resins in Table III are shown in Table IV and Table V. Panels made from the first nine resins in Table III were pressed at a constant time of 18 minutes with both short and long open assembly periods. These results are recorded in Table IV. Thereafter the best resins produced were evaluated at several different curing times and a constant short assembly period. The results of these tests are given in Table V.

Several attempts were made to shorten these rather long curing cycles by using acidic accelerators. A number of panels were made using a 12 minute pressing cycle and acid catalyzed glues, but delamination occurred in all cases during the boil test. A list of accelerators used and observations made is given in Table VI.

TABLE VI. EFFECT OF ACCELERATORS ON WATER SOLUBLE PHENOLIC RESINS

Accelerator	Per Cent Used	Observation
Oxalic Acid	1.5	Precipitated resin from solution
HCl	1.0	Precipitated resin from solution
Hexamethylene Tetramine	2.0	Caused excessive flow
Phthalic Anhydride	2.0	Insoluble in resin
Ammonium Chloride	2.0	Precipitated resin from solution

TABLE III. PHENOLIC RESIN FORMULATIONS AND CHARACTERISTICS

Resin No.	Mol Ratio Formaldehyde to Phenol	Per Cent Caustic*	Minutes Reflux	Product Viscosity	Water Solubility	Approximate per cent solids
Pf 10	1.5-1	9.6	75	High	No	53
Pf 13	1.5-1	4.3	80	Medium	Yes	53
Pf 12	1.5-1	4.3	105	High	No	53
Pf 15	1.5-1	2.0	30	Very low	Yes	53
Pf 16	1.5-1	2.0	60	Low	Yes	53
Pf 17	1.5-1	2.0	75	Medium	Yes	53
Pf 14	1.5-1	2.0	90	High	No	53
Pf 18	1.5-1	3.0	90	Medium	Yes	53
Pf 19	1.5-1	4.0	90	Medium	Yes	53
Pf 20	1.5-1	6.0	90	High	Yes	53
Pf 21 A	1.25-1	3.0	90	Low	Yes	56
Pf 21 B	1.25-1	3.0	120	Medium	Yes	56

* Based on the weight of phenol

TABLE IV. SHEAR TEST RESULTS ON PHENOLICS AFTER 4 HOUR BOIL TEST
(CONSTANT CURING TIME)

Resin Used	5 to 10 Minutes Assembly		30-40 Minutes Assembly	
	Shear Strength psi*	Per cent Wood Failure*	Shear Strength psi*	Per cent Wood Failure*
Pf 10	x	-	x	-
Pf 13	205	75	265	100
Pf 12	270	10	240	95
Pf 15	x	-	x	-
Pf 16	x	-	x	-
Pf 17	300	40	180	80
Pf 14	280	100	235	95
Pf 18	not tested	-	185	100

Constants: (1) Temperatures of platens: 300°F. ± 50
 (2) Pressures: 225 psi
 (3) Curing Time: 18 minutes
 (4) Spread: 35#/1000 ft.² of glue line
 (5) Distance to deepest glue line: approximately 5/16"

* Average of at least four samples

x Samples delaminated

TABLE V.

SHEAR TEST RESULTS ON PHENOLICS AFTER 4 HOUR BOIL TEST
(CURING TIMES VARIED)

Resin Used	Minutes in Press	Shear Strength* psi	Per cent Wood Failure*
Pf 17	25	300	100
Pf 18	25	340	100
Pf 19	25	280	70
Pf 20	25	265	100
Pf 21 A	25	160	10
Pf 21 B	25	300	100
Pf 17	20	225	100
Pf 18	20	220	100
Pf 19	20	140	100
Pf 20	20	245	100
Pf 17	18	300	40
Pf 18	18	315	100
Pf 19	18	195	100
Pf 20	18	255	100
Pf 21 A	18	290	20
Pf 21 B	18	305	65
Pf 17	15	x	-
Pf 18	15	410	70
Pf 19	15	215	95
Pf 20	15	410	100
Pf 21 A	15	x	-
Pf 21 B	15	x	-

TABLE V. (contd.)

SHEAR TEST RESULTS ON PHENOLICS AFTER 4 HOUR BOIL TEST
(CURING TIMES VARIED)

Resin Used	Minutes in Press	Shear Strength* psi	Per cent Wood Failure*
Pf 17	12	x	-
Pf 18	12	x	-
Pf 19	12	210	50
Pf 20	12	240	50
Pf 21 A	12	x	-
Pf 21 B	12	x	-

Constants: (1) Temperature of platens: 300°F. $\pm$ 5°

(2) Pressure: 225 psi

(3) Spread: 35#/1000 ft. of glue line

(4) Distance to deepest glue line: approximately
5/16"

* Average of at least four samples

x Samples delaminated

Conclusions:

Table IV shows that for the type of adhesives studied, the assembly time is not significant, as long as it is kept within reasonable limits, e.g., one hour. For moderate percentages of caustic, as the amount is decreased, the solubility of the resin in water is likewise decreased. This can be seen in a study of Table III. The transformation into the water insoluble stage occurs after about 100 minutes reflux for the 4% caustic catalyzed resins, and after about 85 minutes for the 2% caustic catalyzed resins.

Faster cures may be obtained by using larger percentages of caustic, but glues with high pH values are known to be detrimental to wood. In Table V it is seen that 12-minute cures may be obtained with both 4% and 6% caustic catalyzed resins. Acid accelerators are particularly unsuccessful with these resins, chiefly because they precipitate the resin from the water solution and because the resin is difficult to handle in an emulsion form.

For the production of a practical one step phenol-formaldehyde plywood adhesive, the best percentage of caustic is in the range of 3 to 4% based on the weight of phenol. The reflux time of this water soluble resin should be about one and one-half hours. Good results may be obtained with a formaldehyde to phenol ratio of 1.5-1.

1,3,5 Xylenol as a Modifier

Since the curing cycle of the straight phenolic adhesive was too long the next logical step was to incorporate a faster reacting component. It was decided to investigate first 1,3,5 xylenol because it was less expensive than resorcin. The xylenol was a grade (manufactured by Barrett Chemicals) with a setting point of 60° C.

Procedure:

A one step 1,3,5 xylenol-formaldehyde resin (XF1) was made by reacting one mol of xylenol with 1.25 mols of formaldehyde (37 per cent formalin) in the presence of 1 per cent caustic soda (based on the weight of xylenol). The product was refluxed for 15 minutes and then cooled rapidly with cold water.

A straight two-step xylenol (XF2) was made by reacting 1 mol of 3,5 xylenol with 0.7 mol of formaldehyde, using a 2% caustic catalyst based on the weight of xylenol. The reactants were refluxed for 30 minutes, then 40 parts of alcohol were added to give a workable resin.

Several copolymerized phenol-xylenol-formaldehyde resins were made as follows: 1 mol of phenol, 1.5 mols of formaldehyde (37% formalin), and 3 per cent or 4 per cent caustic soda (based on the weight of phenol), were introduced into the reaction apparatus. These contents were refluxed for about 1 hour, at which time the reflux was

stopped momentarily so that 1,3,5 xlenol and additional formaldehyde could be added. Reflux then was resumed for a short period after which the resin was cooled rapidly. In this investigation the per cent xlenol was varied from 10% to 30% (based on the weight of xlenol plus the weight of phenol). The 37% formalin was added in amounts such that the mol ratio of formaldehyde to xlenol was 1.25 to 1.

The spread-mix was prepared by extending the glue with walnut shell flour in the amount of 20% of the solids content.

Data and Results:

The straight xlenol reaction with formaldehyde took place rather rapidly at around 95-100°C. The reaction, once begun, was exothermic and might be difficult to control commercially. The reaction product was observed to reach the water insoluble stage after about 5 minutes of reflux. After 15 minutes of reflux, the reaction was stopped by cooling rapidly with cold water. The resulting product (XF1) was a brown solid, practically insoluble in alcohol, acetone, and ether.

The two-step xlenol resin was black and moderately viscous, but easily handled. The reaction was relatively mild and simple to control. This resin was not used in this investigation.

A number of experiments were made in an attempt to copolymerize 1,3,5 xyleneol with phenol and formaldehyde. The reaction can be better controlled in this manner, and the xyleneol can be kept in solution for longer periods of reflux, but on the whole all the resins produced in this manner were failures as adhesives. In order to keep the resin in water solution, the xyleneol reaction was necessarily stopped at some very early stage in its polymerization, and when the modified resin was applied to wood, then pressed, the xyleneol contributed greatly to the flow of the resin.

One 1,3,5 xyleneol-modified phenolic resin (MP5), made in the manner described above, was evaluated at several different pressing cycles and is presented as an example of this phase of the investigation. For this resin, the phenol and formaldehyde were refluxed for 1 hour, with 4% caustic catalyst; then 1,3,5 xyleneol and additional formaldehyde were added and reflux continued for 10 minutes. The amount of the added xyleneol was sufficient to make the resin 30% xyleneol and 70% phenol; the formaldehyde was added in the mol ratio of 1.25 mols to 1 mol of xyleneol. The resulting product was dark and moderately viscous.

Resin MP5 was tested using a glue spread of 30 lb. per 1000 square feet and birch veneer. The three ply panels were pressed between 1/4" plywood cauls and short assembly periods of 5 to 15 minutes were used. Test results are given

in Table VII. In an attempt to achieve better cures, hexamethylene-tetramine was added in two cases; however, the results were not as good as those obtained without the catalyst.

Conclusions:

One step 1,3,5 xylenol resins are impractical; two-step xylenols are rather easily made, but their value is not known at present. It is possible, however, to make a copolymerized xylenol-phenol-formaldehyde resin with a storage life of several weeks, by reacting phenol and excess formaldehyde for about 1 hour, then adding 1,3,5 xylenol (up to 30% of total phenols) and a slight molar excess of formaldehyde. A water soluble reaction product is obtained after about 10 to 15 minutes additional reflux. However, the minimum curing time obtained was about 15 minutes, too long to be useful. The 1,3,5 xylenol contributed greatly to resin flow and to water resistance.

Resorcin as a Modifier

Since 1,3,5 xylenol failed to lower the curing time sufficiently, a study was made as to the effectiveness of resorcin as a modifier for phenol-formaldehyde adhesives.

Procedure:

First, a series of resins was made in the following manner: two one-step straight phenolic resins were made using

TABLE VII. TEST RESULTS ON 1,3,5 XYLENOL MODIFIED PHENOLICS

Panel No.	Minutes in press	Accelerator	Dry		After 4 Hour Boil	
			Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP5-1	8	none	x	x	x	x
MP5-2	15	none	390	100	440	100
MP5-3	10	none	200	5	325	5
MP5-4	10	4% Hexa	x	x	x	x
MP5-5	15	none	265	75	385	100
MP5-6	15	4% Hexa	260	45	x	x

Constants: (1) Temperature of platens: 300°F. $\pm$ 5°

(2) Pressure: 225 psi

(3) Distance to deepest glue line: approximately 5/16"

x Samples Delaminated

xx Figures given are the average of several values (usually four)

the formulas and procedures for PF18 and PF20. (These two resins are alike except for the percentages of caustic used in their manufacture; PF18 is a 3%, and PF20 a 6%, caustic catalyzed resin.) To these base resins resorcin was added, at room temperature, in amounts varying from 10% to 30% of the weight of phenol plus resorcin.

Three resins were made using PF18 as a base resin and three more using PF20 as a base resin. Immediately before use 1.1 mols of paraformaldehyde were added for each mol of resorcin present; then the resin was extended with walnut shell flour in the amount of 20% of the solids content. The formulation data and the test results for these resins are given in Table VIII.

Secondly, a two-step resorcin-formaldehyde was made and this resin used to modify PF18. The two-step resorcin (RF1) was made by reacting 1 mol of resorcin with 0.7 mol of formaldehyde (37% formalin) in the presence of 1.3% caustic catalyst, based on the weight of resorcin. The reaction product was allowed a 20 minutes reflux. During the first 15 minutes, the 37% formalin was added slowly from a separatory funnel, then the caustic was added and the resin refluxed for 5 minutes longer.

Formulation data on RF1 - PF18 are given in Table IX. To form the spread-mix, enough paraform was added to give a mol ratio of formaldehyde to resorcin of 1.25 to 1 and walnut

shell flour was added to give a 20% extension based on resin solids. Test results are recorded in Table X.

Thirdly, several copolymerized phenol-resorcin-formaldehyde resins were made as follows: phenol was reacted with formaldehyde (the ratio being 1 to 1.5 mols) for about one hour, then resorcin was added with formaldehyde (the ratio being 1 to 0.7 mols) and reflux resumed for an additional, but shorter time. The reaction was catalyzed by 3.5% caustic soda, based on the weight of phenol alone. The variables for the various resins are shown in Table IX. The spread-mix was prepared by adding paraformaldehyde in sufficient amount to bring the mol ratio of formaldehyde to resorcin to 1.25 to 1; this mix was then extended with walnut shell flour in the amount of 20% of resin solids. Test results are shown in Table X.

Birch wood was used in making all panels with these modified adhesives. The centerstock averaged slightly more than $1/8$ " in thickness, and the face veneer averaged about $1/20$ ". The panels were pressed between $1/4$ " plywood cauls.

Data and Results:

Make up data and test data for the resorcin modified phenolics are shown in Tables VIII, IX and X.

Table VIII gives the composition and test results of the various resins made by modifying straight phenolic resins with raw resorcinol. These resins were all thin and easily spread. The life of the adhesive was short after the

TABLE VIII. TEST RESULTS ON RAW RESORCIN MODIFIED PHENOLICS

Panel No.	% Caustic	Phenolics Ratio Phenol-Resorcin	Minutes in press	Dry*		After 4 hr. boil*	
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP6-1	3	70-30	8	330	60	400	100
MP6-2	3	70-30	9	310	55	440	100
MP10-1	3	80-20	8	295	35	375	80
MP10-2	3	80-20	10	330	100	410	100
MP10-3	3	80-20	6	225	5	420	55
MP11-1	3	90-10	10	300	50	390	100
MP11-2	3	90-10	8	285	0	345	95
MP11-3	3	90-10	6	x	x	x	x
MP12-1	6	70-30	10	270	75	360	70
MP12-2	6	70-30	8	290	100	430	80
MP12-3	6	70-30	6	250	75	390	100
MP12-4	6	70-30	6	250	10	435	100
MP13-1	6	80-20	10	220	0	x	x
MP13-2	6	80-20	8	270	85	380	100
MP13-3	6	80-20	6	205	5	x	x

TABLE VIII. TEST RESULTS ON RAW RESORCIN MODIFIED PHENOLICS (contd.)

Panel No.	% Caustic	Phenolics Ratio Phenol-Resorcin	Minutes in press	Dry*		After 4 hr. boil*	
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP14-1	6	90-10	10	250	45	345	40
MP14-2	6	90-10	8	235	20	330	75
MP14-3	6	90-10	6	x	x	x	x

Constants: (1) Spread: 30#/1000 ft.²

(2) Temperature of platens: 300°F. $\pm$ 5°

(3) Pressure: 225 psi

(4) Distance to deepest glue line: approximately 5/16"

* Values are the average of four samples

x Signifies delamination of panel

TABLE IX. FORMULATION DATA ON RESORCIN MODIFIED PHENOLICS

Resin No.	Weight Ratio of Phenol to Resorcin	Minutes Reflux Phenol - Resorcin	% Caustic*	Per Cent Solids	Per cent Alcohol
MP21	85-15	60-30	3.5	55	0.0
MP22	85-15	60-40	3.5	49	10.0
MP23	85-15	75-25	3.5	45	17.4
	Combination of				
MP20	85-15	PF18-RF1	3.5	47	5.7

* Per cent is based on the weight of phenol

TABLE X. TEST RESULTS ON RESORCIN-MODIFIED PHENOLICS

Panel No.	Minutes in press	Spread #/1000 ft ²	Dry*		After 4 hr. boil*	
			Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP21-1	10	30	290	15	325	100
MP21-2	8	30	340	95	400	100
MP21-3	6	30	275	0	x	x
MP21-4	6	25	215	0	x	x
MP22-1	10	30	350	85	420	95
MP22-2	8	30	290	0	385	70
MP22-3	6	30	275	15	x	x
MP22-4	6	25	250	50	x	x
MP23-1	10	30	275	20	360	30
MP23-2	8	30	260	40	300	60
MP23-3	6	30	320	60	350	80
MP20-1	10	30	325	80	345	100
MP20-2	8	30	290	5	330	100
MP20-3	6	30	325	90	410	100

TABLE X. TEST RESULTS ON RESORCIN-MODIFIED PHENOLICS (Contd.)

Constants: (1) Temperature: 300°F. $\pm$ 5°

(2) Pressure: 225 psi

(3) Assembly Period: 5-15 minutes

(4) Distance to deepest glue line: approximately 5/16"

* Values are the average of 4 samples

x Samples delaminated

addition of paraform (several hours), but until the paraform was added the resins seemed to have suitable storage life.

In Table IX is given descriptive data about the other resorcin modified resins made. The test results for these same resins are given in Table X.

The storage life of these copolymerized resins is relatively short, probably several weeks, and the pot life is about 2 hours.

Conclusions:

A combination one-step phenolic and a mixture of resorcin forms a suitable adhesive when paraform is added in a ratio of 1.1 mols of paraform to 1 mol of resorcin. This unique combination gave satisfactory results at 8 minute cures, down to 20% resorcin, 80% phenol. The best results were obtained when using the 3% caustic catalyzed phenol-formaldehyde resin, and 30% resorcin. In these proportions of 30% resorcin, 70% phenol, six minute panels passed the 4 hour boil test. However, these same panels gave doubtful dry tests. Panels made with this type resin possess great resistance to water; in many cases where previous experience indicated almost certain delamination during the boil test, the cures were advanced and greater strength obtained.

The copolymerized resorcin-modified phenolics (15% resorcin-85% phenol) are suitable for 6 minute cures on birch wood, provided the phenol is refluxed about 75 minutes and the

resorcin about 25 minutes. Alcohol is necessary to make this resin workable, but the data indicate the improbability of obtaining a 6 minute cure with a completely water soluble resin. The lower limit for the water soluble resins is about 8 minute cures.

Modification With 1,3,5 Xylenol and Resorcin

Phenolic resin adhesives modified with 15% resorcin were found to give 8 and 6 minute cures on birch wood. The next step in the investigation was an attempt to lower the percentage of resorcin by adding 1,3,5 xylenol in small amounts.

There were two general methods by which this modification could be carried out. The phenolic resin, 1,3,5 xylenol resin, and resorcin resin can be made separately and later mixed in the desired proportions, or the three can be made together. Although the latter method requires more technique in the manufacturing process, it needs less equipment and was chosen for this work.

Procedure:

The general reaction for the manufacture of the copolymerized three component resins was the same throughout; the variables being ratio of phenolics by weight, per cent of caustic based on the weight of the phenol, mol ratio of formaldehyde to phenolics and reaction times with one, two, and three components present.

The general procedure was as follows: into the reaction apparatus was introduced 1 or more mols of phenol, depending on the size batch desired. Then, 1.5 or 1.25 mols of formaldehyde (36% or 37% formalin) were added for each mol of phenol, followed by the caustic catalyst (3% or 4% based on the weight of phenol). The contents were brought to boil and refluxed for a time; reflux was stopped and 1,3,5 xlenol added in proper amount plus enough formalin to give a formaldehyde to xlenol mol ratio of about 0.7 to 1. Reflux was resumed for a short time, then halted again in order that resorcin plus enough formalin to give a formaldehyde to resorcin mol ratio of about 0.7 to 1 could be added. The reaction was completed by an additional short period of reflux, and the reaction product cooled rapidly to room temperature by means of a cold water bath. In most cases alcohol was then added to bring the resin into solution and lower its viscosity into a practical range of 5 to 15 poises.

Spread mixes were prepared by extending the resins with walnut shell flour (about 20% of solids content) and adding paraform. In some cases enough paraform was added to change the mol ratio of formaldehyde to xlenol and resorcin to 1.25 to 1, and in others to change the mol ratio of formaldehyde to phenol, xlenol and resorcin to 1.5 to 1.

Three-ply panels were made with these resins out of birch centerstock and veneer. These panels were then cut into standard shear test specimens and evaluated both dry and after

the four hour boil test. A number of the latter resins made were tested in like manner on gum veneer.

Data and Results:

Since a relatively large number of three component phenolic resins were made and tested, the complete data were voluminous. Formulation data and test data are presented here for the best resin produced. Formulation data and test data for the other resins produced are given in Appendices IV, V and VI.

The most successful resin had a phenolic composition of 82.5%, 7.5% xylenol and 15% resorcin; the phenol was refluxed 80 minutes, the phenol and xylenol 20 minutes, and the phenol, xylenol, and resorcin refluxed 35 minutes. The mol ratio of formaldehyde to phenol was 1.25 to 1 and the mol ratio to xylenol and resorcin was 0.7 to 1. Four per cent caustic, based on the weight of phenol was used to catalyze the reaction and alcohol was added to the reaction product until the resin solids content was 53%. This final resin was then 9.4% alcohol. The reference number given this resin was MP32.

Resin MP32 was used to make plywood test panels with both birch and gum veneer. The test results obtained with birch wood are shown in Table XI and the results from gum panels are given in Table XII.

In some cases the data are erratic; 8 minutes cures, or even 6 minute cures appear better than the 10 minute cures. These discrepancies are explained on the basis of the small number of samples, 4 or 5 in most cases. In order to show a definite reasonable trend, a much larger number of samples would have to be made and tested.

In the case of both birch and gum, a final mol ratio of formaldehyde to phenolics of 1.5 to 1 produces better results than a 1.25 to 1.

It can be seen in Table XI that boil-proof bonds are definitely obtainable with resin MP32 on birch wood at curing times of 10 minutes, 8 minutes and 6 minutes. Also, a 25 pound spread is sufficient.

Examination of Table XII shows resin MP32 to be much less effective on gum than on birch. The same pressure (225 psi) was used for birch and gum, which is a possible explanation of this fact. This pressure, though appropriate for birch, is higher than the recommended bonding pressure for gum. Ten minute cures and eight minute cures are inconsistent and no panels cured for 6 minutes passed the boil test. It is not known at this time why this type of resin produces suitable bonds on birch and fails on gum.

An important factor relative to the possible commercial use of resin MP32, or any of the similar resins produced is its "storage life" and "pot life". A record of viscosity

change with storage time was kept for MP32 and four other representative resins. Viscosities were taken with a Gardner Bubble Viscometer and the data are recorded in Table XIII and the results are shown graphically in Figure 4. Resin MP21 is a resorcin modified phenolic (85% phenol-15% resorcin) and is listed in Table IX; MP25, MP26, MP29 and MP32 are all 1,3,5 xylenol-resorcin modified phenolics. These three component resins differ only in reflux times and amounts of alcohol added; the formulations and make-up procedures for these resins, other than MP32, are given in Appendix IV.

Resin MP25 is seen to possess the best storage life, but it proved inferior to MP32 as a plywood adhesive. Resin MP32 has a storage life of about three weeks.

The pot life of several representative adhesive mixes was determined by recording viscosity change with time. Viscosity readings were taken using a Gardner Bubble Viscometer. Only apparent values could be obtained since the material being studied was heterogeneous. In order to obtain a smooth mix, the ingredients were vigorously stirred for fifteen minutes before any readings were taken. The data are given in Table XIV and graphically shown in Figure 5. The mixes were made with resins MP35 and MP26 (data on resins MP35 and MP26 are given in Appendix IV). These adhesive mixes were prepared by adding walnut shell flour and paraform to the resin. Walnut shell flour was added in the amount of 20% of resin solids;

TABLE XI.

TEST RESULTS FOR 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOL (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft ²	Final mol ratio of Formaldehyde to Phenolics	Dry*		After 4 hr. boil*	
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP32-1	10	30	1.5-1	390	100	335	95
MP32-2	8	30	1.5-1	360	100	360	100
MP32-3	8	30	1.25-1	310	80	320	90
MP32-4	6	30	1.5-1	350	90	390	40
MP32-5	6	25	1.5-1	390	85	415	100
MP32-6	6	30	1.25-1	275	5	255	5

Constants: (1) Platen temperature: 300°F. $\pm$ 50

(2) Pressure: 225 psi

(3) Per cent walnut shell flour based on solids content: 20%

(4) Short assembly periods: 5-15 minutes

(5) Distance to deepest glue line: approximately 5/16"

* Average of four samples

TABLE XII. TEST RESULTS FOR 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLIC (GUM WOOD)

Panel No.	Minutes in press	Spread #/1000 ft ²	Final mol ratio Formaldehyde to Phenolics	Dry*		After 4 hr. boil*	
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP32-7	10	30	1.5-1	270	40	220	30
MP32-8	10	30	1.5-1	235	90	145	10
MP32-9	10	35	1.5-1	325	85	x	x
MP32-10	8	30	1.5-1	295	100	245	80
MP32-11	8	30	1.5-1	275	90	x	x
MP32-12	8	35	1.5-1	355	100	350	75
MP32-13	8	30	1.25-1	200	40	160	90
MP32-14	7	30	1.5-1	210	15	x	x
MP32-15	6	30	1.5-1	160	0	x	x
MP32-16	6	30	1.5-1	185	5	x	x
MP32-17	6	30	1.25-1	200	40	x	x

* Average of four samples

x Samples delaminated

TABLE XII (contd.)

Constants:

- (1) Platen temperatures: 300°F. $\pm$ 5°
- (2) Pressure: 225 psi
- (3) Per cent walnut shell flour based on solids content: 20%
- (4) Short assembly periods: 5-15 minutes
- (5) Distance to deepest glue line: approximately 5/16"

TABLE XIII. CHANGE IN RESIN VISCOSITY WITH STORAGE TIME

Time in Days	Resin No.	Viscosity in Poises	Time in Days	Resin No.	Viscosity in Poises
0	MP25	3	7.5	MP32	10
0	MP26	14	8	MP26	20.5
1	MP32	7.1	8	MP29	32
1	MP21	10	10	MP32	11.2
1	MP26	15	10	MP26	21
1	MP29	16.3	13	MP21	46.2
2	MP26	15.5	14	MP32	13.6
3	MP25	4	14	MP21	55
3	MP21	13.2	14	MP29	80
4	MP21	15	16	MP26	26
4	MP26	18.1	17	MP26	29
5	MP21	18	21	MP32	19.6
7	MP26	20	23	MP26	56.4
7	MP21	24	26	MP25	20
7	MP29	31.2			

TABLE XIV
CHANGE OF ADHESIVE VISCOSITY WITH POT TIME

Pot Time in Hrs.	Resin No.	Viscosity in Poises
0.25	MP32	31.2
0.25	MP35	44.8
0.25	MP26	46.5
0.75	MP32	36
0.75	MP35	54.9
0.75	MP26	58
1.50	MP26	72
1.75	MP32	54.8
1.75	MP35	72.6
2.50	MP26	87.0
2.75	MP35	85
3.00	MP26	94.8
3.50	MP32	99
3.75	MP35	95.7

Figure 4
Effect of Time on
Resin Viscosity

Figure 5
Effect of Time on
Spread Mix Viscosity

paraform was added to MP26 and MP35 to give a final mol ratio of formaldehyde to total phenolics of 1.25 to 1; paraform was added to MP32 to give a ratio of 1.5 to 1.

The initial viscosity of the spread-mix is shown in Figure 5 to be several times the viscosity of the resin used. The addition of the walnut shell flour and the paraform causes the resin viscosity to become double or triple its initial value. Also, the additional formaldehyde used with MP32 reversed the slope of the viscosity curve. In any case, the pot life is about 2 hours at 75°F.

Conclusions:

Phenolic resins consisting of 82½% phenol, 10% resorcin and 7½% 1,3,5 xyleneol (based on the total phenolic weight) serve as suitable adhesives for the preparation of birch plywood. The reaction should be carried to the water insoluble stage and the reaction product taken into solution with alcohol in order to obtain rapid cures. The best total reaction time seems to be about 2 hours and 15 minutes, consisting of 80 minutes phenol reflux, 20 minutes phenol and xyleneol reflux, and 35 minutes phenol, xyleneol and resorcin reflux. Cures may be effected on birch wood in 6 minutes with three 1/4" plywood panels in the press opening and a platen temperature of 300°F. The resulting bonds are boil-proof.

These same adhesives are much less effective, at the same bonding pressure (225 psi), in producing boil-proof bonds on gum wood. The minimum curing time is about 10 minutes under the same conditions as listed for birch. Good results are obtained on gum at 8 minute cures when the samples are tested dry, but the water resistance is low. Better results were obtained on both birch and gum wood when enough formaldehyde was added to the adhesive mix to increase the mol ratio of formaldehyde to phenolics from 1.25-1 to 1.5 to 1.

The maximum "storage life" of the type resin produced is about 2 weeks at an average room temperature of 75°F. The resin is not a loss after this time, however, but can be further diluted with alcohol to reduce the viscosity.

The "pot-life" of the adhesive mix is about 2 hours, but here also, the adhesive can be made usable after this time by the addition of small amounts of alcohol.

Rate of Temperature Change in Heated Plywood Panels

In order to determine something about the relative rates of heat transfer through cured cauls and uncured panels, several experiments were run.

Procedure:

First, three 1/4" birch plywood assemblies, one foot square were prepared using an adhesive mix made with resin MP32.

The assemblies were of standard 3-ply construction and the wood contained about 8% moisture. Averaging thermocouples (in parallel) were placed in glue lines 1 & 6 (outermost), 2 & 5 (intermediate), and 3 & 4 (innermost). The uncured panels were placed in the hot press (300°F.), and pressure applied (225 psi). Temperature readings were taken at regular intervals for a period of twenty minutes. These readings are recorded in Appendix VII and the results are graphically presented in Figure 6.

Second, the same procedure was repeated, using three 1/4", uncured gum panels of about 9% moisture content. The temperature readings are given in Appendix VIII, and the results are presented graphically in Figure 7.

Third, one 1/4" uncured birch panel was prepared, thermocouples inserted in the two glue lines, and the panel pressed between two cured 1/4" gum cauls. Temperature readings were taken for twenty minutes and these readings are recorded in Appendix IX. The glue line temperature change is shown graphically in Figure 8.

Fourth, the above procedure was repeated with one 1/4" uncured gum panel between two 1/4" cured gum cauls. The record of temperature change is given in Appendix IX, and the curves representing these data are shown in Figure 8.

Figure 6
Change of Glue Line Temperature with Time -
3 Birch Panels in Hot Press

Figure 7
Change of Glue Line Temperature with Time -
3 Gum Panels in Hot Press

Figure 8
Change of Glue Line Temperature with Time -
1 Panel, 2 cured Cauls in Hot Press

Conclusions:

Temperature rise is seen to be faster in gum wood than in birch, especially for the first 6 minutes in the press. The effect is even more pronounced when the cauls are used. In runs where the cauls were used, the temperature of the gum glue lines remained about 100F. above the temperature of the birch glue lines throughout the run.

Comparison of the relative rates of temperature rise through cured cauls and uncured panels shows the glue line temperature of the panels between cauls to remain about 100F. higher for both birch and gum. This difference would probably result in about a one minute longer curing cycle for three uncured panels in the press, in comparison with one uncured panel between two cured cauls.

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A P P E N D I X

APPENDIX I

GLOSSARY

Assembly: the collection and placing together in proper order of the layers of veneer, with the adhesive, ready to be pressed and bonded into plywood. As a noun, "Assembly" refers to these layers of veneer and glue, ready for pressing.

Assembly Time: the time which elapses after the glue is spread and until the pressure becomes effective.

Bond: the grip of the adhesive on the wood, at the time of its application.

Cauls: additional sheets of material used to sandwich plywood assemblies during the pressing operation. They are generally used for protection of plywood faces or to facilitate loading.

Centerstock: a term used to indicate the middle veneer in three-ply plywood construction. It is usually thicker than the face veneer and may be a cheaper wood.

Cure: the process of condensation and polymerization by which the resin adhesive changes over to the final insoluble form. This is generally brought about by heat.

Extender or Filler: an additional substance, sometimes combined in adhesive resins to provide body, reduce costs, or impart some desirable quality such as flow control.

Moisture Content: this term is used to express the amount (by weight) of water in wood, and is computed as a percentage on the bone dry weight of the wood.

Panel: this term refers to a sheet or piece of plywood.

Platens: the heat-bearing plates of the hot press.

Ply: a sheet or layer of veneer

Plywood: an assembled product, made of layers of veneer, the chief characteristic of which is the alternate cross layers, distributing the longitudinal wood strength.

Pot Life: the period during which an adhesive remains suitable for spreading, before hardening in the receptacle or commencing to jell.

Pressing Cycle: the time which an assembly is kept in the hot press.

Spread: the amount of adhesive, in pounds of liquid mixture, that is applied per thousand square feet of single adhesive joint.

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

Storage Life: that time which an adhesive remains suitable for use, while in storage.

Veneer: a thin sheet or layer of wood, sliced, rotary cut or sawn from a log.

Veneer (face): the outside ply in an assembly. It is usually thin and of a better grade than those below.

APPENDIX II

SAMPLE PREPARATION AND TESTING PROCEDURES

Samples were prepared and subsequently tested in accordance with "Hardwood Plywood Commercial Standard CS35-47" (1). Appropriate paragraphs are abstracted from this publication.

Section 7, paragraph 61. Shear Test:

"Shear tests shall be conducted on specimens of the form shown in Figure 9. The ends of the specimen shall be gripped in the jaws of the test machine and the load applied at a rate of 600 to 1000 pounds per minute."

FIG. 9 SPECIMEN

Section 7, Paragraph 62b. Boil Test:

"Specimens of the form shown in Figure 6 shall be cut from each sample and submerged for four hours in boiling water. They shall then be removed from the boiling water,

placed in cold water until at approximately room temperature and while still wet, tested to failure in the shear test machine. Specimens shall meet the requirements of Tables XV and XVI. There shall be no separation of plies at the glue line."

TABLE XV. PERCENTAGE OF WOOD FAILURE

Average Shear Strength psi	Minimum Wood failure %	Average Wood Failure %
under 250	25	50
250-350	10	30
above 350	10	15

TABLE XVI. MINIMUM SHEAR VALUES (psi) REQUIRED FOR BOIL TESTS

Density of Veneers	Strength (Wet)
High	290
Medium	210
Low	120

In order to obtain a comparison, dry tests were performed on nearly all samples, in accordance with paragraph 61.

APPENDIX III

SAMPLE CALCULATIONS

The calculations were purely routine throughout. To exemplify the methods used, the calculations needed in the production and mix preparation of Resin MP32 are presented.

(1) Formulation:

It was desired to produce a resin batch containing two mols of phenol (188 g), and having a phenolics composition of 82.5% phenol, 7.5% 1,3,5 xyleneol and 10% resorcin.

188 g phenol

$$\frac{188}{0.825} = 228 \text{ g total phenolics}$$

$$228 \times 0.075 = 17.2 \text{ g 1,3,5 xyleneol}$$

$$228 \times 0.10 = 22.8 \text{ g resorcin}$$

Four per cent caustic based on the weight of phenol is: $188 \times 0.04 = 7.5$ g caustic soda. The required mol ratios of formaldehyde to phenolics are: 1.25 to 1 (phenol), 0.7 to 1 (xyleneol) and 0.7 to 1 (resorcin)

$$\frac{188}{94} \times \frac{30}{0.37} \times 1.25 = 203 \text{ g of 37\% formalin to be added with the phenol and caustic.}$$

$$\frac{17.2}{122} \times \frac{30}{0.37} \times 0.7 = 8.0 \text{ g of 37\% formalin to be added with the 1,3,5 xyleneol}$$

$$22.8 \times \frac{30}{0.37} \times 0.7 = 11.8 \text{ g of 37\% formalin to be added with the resorcin}$$

(2) Calculation of Per cent Solids:

$$188 + 22.8 + 17.2 = 228.0 \text{ g total phenolics}$$

$$203 + 8 + 11.8 = 222.8 \text{ g } 37\% \text{ formalin}$$

$$7.5 \text{ g} = \text{total caustic soda}$$

$$458.3 \text{ g} = \text{total batch weight}$$

Of this 458.3 g, the weight of water present after the completion of the reaction may be calculated.

$$222.8 \times 0.63 = 140.5 \text{ g water added with formaldehyde in formalin solution}$$

$$\frac{222.8 \times 0.37}{30} \times 18 = 49.5 \text{ g water formed during reaction.}$$

$$\text{Total water} = 190.5 \text{ g}$$

$$\% \text{ Water} = \frac{190.5}{458.3} \times 100 = 41.6\%$$

$$\% \text{ Solids} = 100 - 41.6 = 58.4\%$$

In most cases alcohol was added to lower the resin viscosity, and this changed the per cent solids correspondingly.

$$47 \text{ g alcohol added} - \text{resulting batch weight} = 505.3 \text{ g}$$

$$\text{resulting solids content} = \frac{458.3 \times 0.584 \times 100}{505.3} = 53\%$$

(3) Preparation of the Adhesive Spread Mix:

The first step in the preparation of the spread mix was to calculate the final percentages of the three phenolics based on the total batch weight.

$$100 \times \frac{188}{505} = 37.3\% \text{ phenol}$$

$$100 \times \frac{17.2}{505} = 3.41\% \text{ 1,3,5 xyleneol}$$

$$100 \times \frac{22.8}{505} = 4.52\% \text{ resorcin}$$

Two mixes were generally prepared, one with a formaldehyde to phenolics ratio of 1.5 to 1 and the other 1.25 to 1.

(a) 1.5 to 1 mix:

100 g MP32

$100 \times 0.53 \times 0.20 = 10.6$ g walnut shell flour

(20% of the weight of solids content)

$\frac{100 \times 0.373}{94} \times 30 \times 0.25 = 2.98$ g paraform to change

the formaldehyde to phenol ratio to 1.50 to 1

$\frac{100 \times 0.0341}{122} \times 30 \times 0.8 = 0.67$ g paraform to change

the formaldehyde to xlenol ratio to 1.5 to 1

$\frac{100 \times 0.0452}{110} \times 30 \times 0.8 = 0.99$ g paraform to change

formaldehyde to resorcin ratio to 1.5 to 1

The total paraform added was then $2.98 + 0.67 + 0.99 = 4.6$ g (to the nearest tenth gram)

(b) 1.25 to 1 mix:

100 g MP32

$100 \times 0.53 \times 0.20 = 10.6$ g walnut shell flour

$\frac{100 \times 0.0341}{122} \times 30 \times 0.55 = 0.46$ g paraform necessary

to change the formaldehyde to xlenol ratio to 1.25 to 1.

$\frac{100 \times 0.0452}{110} \times 30 \times 0.55 = 0.68$ g paraform necessary

to change the formaldehyde to resorcin ratio to 1.25 to 1

The total paraform added was then 1.1 g

APPENDIX IV. FORMULATION DATA ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS

Resin No.	Wt. Ratio Phenol-Xylenol Resorcin	Minutes Reflux Ph-Xy-Re	Per Cent Caustic*	Per Cent Alcohol	Per Cent Solids (calc'd)	Initial Viscosity Poises
MP15	70-20-10	45-15-30	3.0	10.7	51	--
MP18	82.5-10-7.5	30-10-10	3.5	0.0	55	--
MP19	82.5-10-7.5	45-10-15	3.5	0.0	55	--
MP24	82.5-7.5-10	60-10-20	4.0	0.0	59	--
MP25	82.5-7.5-10	60-15-30	4.0	6.5	55	3
MP26	82.5-7.5-10	75-15-30	4.0	6.5	55	14
MP28	82.5-7.5-10	60-30-30	4.0	3.8	56	7.6
MP29	82.5-7.5-10	75-30-30	4.0	4.6	56	16
MP31	83-7-10	90-30-30	4.0	9.5	52	9.5
MP32	82.5-7.5-10	80-20-35	4.0	9.4	53	7.1
MP33	82.5-7.5-10	75-15-35	4.0	5.0	55	11
MP34	82-8-10	75-30-30	4.0	10.0	52	12
MP35	82-8-10	80-20-30	4.0	8.5	53	7

* Based on the weight of phenol

Constants: (1) The make up mol ratio of Formaldehyde to Phenolics (phenol-xylenol-resorcin) was 1.25-0.7-0.7, except for the first three resins (MP15, MP18, MP19) where it was 1.5-0.7-0.7.

APPENDIX V

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft. ²	Per cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
					Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP15-1	10	30	20	1.5-1	270	40	300	90
MP15-2	8	30	20	1.5-1	290	90	410	100
MP15-3	6	30	20	1.5-1	245	30	x	x
MP18	10 min., 8 min., and 6 min. panels delaminated dry							
MP19	10 min., 8 min., and 6 min. panels delaminated dry							
MP24-1	10	30	20	1.5-1	345	100	420	100
MP24-2	10	25	20	1.5-1	300	80	335	100
MP24-3	8	30	20	1.5-1	295	30	350	90
MP24-4	8	25	20	1.5-1	270	40	320	100
MP24-5	6	30	20	1.5-1	270	15	x	x
MP24-6	6	25	20	1.5-1	255	0	x	x
MP25-1	10	30	20	1.25-1	320	60	310	100
MP25-2	8	30	20	1.25-1	300	10	360	100

APPENDIX V (contd.)

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft.2	Per Cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
					Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP25-3	6	30	20	1.25-1	290	0	245	5
MP25-4	7	30	20	1.25-1	360	15	260	0
MP25-5	10	30	20	1.25-1	295	100	355	100
MP26-1	10	30	20	1.25-1	375	80	340	100
MP26-2	8	30	20	1.25-1	350	35	365	100
MP26-3	6	30	20	1.25-1	330	30	325	95
MP26-4	7	30	20	1.25-1	270	5	260	80
MP26-5	10	30	15	1.5-1	330	30	370	100
MP26-6	8	30	15	1.5-1	340	85	430	100
MP26-7	6	30	15	1.5-1	300	25	380	65
MP26-8	6	25	15	1.5-1	260	35	240	25
MP28-1	10	30	20	1.25-1	300	30	370	100
MP28-2	10	25	20	1.25-1	275	35	300	100
MP28-3	8	30	20	1.25-1	265	5	340	5

APPENDIX V (contd.)

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft.2	Per Cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
					Shear Strength #/in	% Wood Failure	Shear Strength #/in	% Wood Failure
MP28-4	8	25	20	1.25-1	250	0	x	x
MP28-5	7	30	20	1.25-1	260	0	330	10
MP28-6	7	25	20	1.25-1	260	10	290	50
MP28-7	6	30	20	1.25-1	200	0	x	x
MP28-8	6	25	20	1.25-1	220	0	300	5
MP28-9	10	30	15	1.5-1	350	100	360	100
MP28-10	10	25	15	1.5-1	340	100	345	100
MP28-11	8	30	15	1.5-1	300	90	380	100
MP28-12	8	25	15	1.5-1	310	80	330	100
MP28-13	7	30	15	1.5-1	280	20	320	15
MP28-14	7	25	15	1.5-1	250	5	350	30
MP28-15	6	30	15	1.5-1	240	5	335	45
MP28-16	6	25	15	1.5-1	300	50	370	35
MP29-1	10	30	20	1.5-1	290	15	385	100

APPENDIX V (contd.)

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Dry** After 4 hr. boil**

Panel No.	Minutes in Press	Spread #/1000 ft. ²	Per Cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP29-2	8	30	20	1.5-1	300	55	405	100
MP29-3	6	30	20	1.5-1	300	15	395	100
MP29-4	6	25	20	1.5-1	305	5	380	95
MP29-5	8	30	15	1.25-1	330	70	305	100
MP29-6	7	30	15	1.25-1	310	35	345	25
MP29-7	6	30	15	1.25-1	370	10	425	10
MP29-8	6	25	15	1.25-1	385	0	x	x
MP29-9	8	30	20	1.25-1	390	100	370	100
MP29-10	7	30	20	1.25-1	330	55	345	80
MP29-11	6	30	20	1.25-1	440	20	380	45
MP29-12	6	25	20	1.25-1	405	25	330	5
MP31-1	8	30	20	1.5-1	340	70	325	50
MP31-2	6	30	20	1.5-1	355	20	x	x
MP31-3	8	30	20	1.25-1	340	60	345	55

APPENDIX V (contd.)

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft. ²	Per Cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
					Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP31-4	6	30	20	1.25-1	320	15	x	x
MP31-5	6	25	20	1.25-1	330	15	340	30
MP31-6	6	25	20	1.5-1	325	20	350	70
MP33-6	10	30	20	1.5-1	370	50	340	85
MP33-7	8	30	20	1.5-1	405	15	360	15
MP33-8	6	30	20	1.5-1	340	60	300	90
MP33-9	6	25	20	1.5-1	375	25	335	15
MP34-1	10	30	20	1.5-1	475	40	405	25
MP34-2	8	30	20	1.5-1	320	25	300	0
MP34-3	6	30	20	1.5-1	300	5	340	5
MP34-4	6	25	20	1.5-1	340	20	345	40
MP34-5	10	30	20	1.25-1	370	95	335	100
MP34-6	8	30	20	1.25-1	340	95	325	75
MP34-7	6	30	20	1.25-1	380	0	310	10

APPENDIX V (contd.)

TEST RESULTS ON 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (BIRCH WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft. ²	Per Cent Walnut Shell Flour*	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
					Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP34-8	6	25	20	1.25-1	355	75	365	65
MP35-1	10	30	20	1.5-1	330	40	370	50
MP35-2	8	30	20	1.5-1	345	0	360	25
MP35-3	7	30	20	1.5-1	360	10	325	15
MP35-4	6	30	20	1.5-1	410	15	270	15
MP35-5	10	30	20	1.25-1	335	100	325	100
MP35-6	8	30	20	1.25-1	365	40	345	15
MP35-7	7	30	20	1.25-1	330	5	300	15
MP35-8	6	30	20	1.25-1	295	0	x	x

* Based on the weight of phenol

** Values are the average of four samples

x Samples delaminated

Constants: (1) Temperature: 300°F. 150
 (2) Pressure: 225 psi
 (3) Assembly period: 5-15 minutes
 (4) Distance to deepest glue line: approximately 5/16"

APPENDIX VI

TEST RESULTS FOR 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (GUM WOOD)

Panel No.	Minutes in Press	Spread #/1000 ft ²	Final Mol Ratio Formaldehyde to Phenolics	Dry**		After 4 hr. boil**	
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP33-1	10	30	1.5-1	230	75	175	15
MP33-2	8	30	1.5-1	260	20	x	x
MP33-3	6	30	1.5-1	180	0	x	x
MP33-4	8	35	1.5-1	310	55	x	x
MP33-5	10	35	1.5-1	240	10	x	x
MP34-9	10	30	1.5-1	205	65	195	45
MP34-10	8	30	1.5-1	280	75	x	x
MP34-11	10	30	1.25-1	270	100	250	55
MP34-12	8	30	1.25-1	250	95	x	x
MP35-9	10	35	1.5-1	300	100	255	100
MP35-10	8	35	1.5-1	270	100	x	x
MP35-11	7	35	1.5-1	280	70	x	x
MP35-12	6	35	1.5-1	285	65	x	x

APPENDIX VI (contd.)

TEST RESULTS FOR 1,3,5 XYLENOL-RESORCIN MODIFIED PHENOLICS (GUM WOOD)

Panel No.	Minutes In Press	Spread #/1000 ft ²	Final Mol Ratio Formaldehyde to Phenolics	Dry**	After 4 hr. boil**		
				Shear Strength #/in ²	% Wood Failure	Shear Strength #/in ²	% Wood Failure
MP35-13	10	35	1.25-1	270	60	x	x
MP35-14	8	35	1.25-1	175	10	x	x
MP35-15	7	35	1.25-1	200	15	x	x
MP35-16	6	35	1.25-1	280	5	x	x

** Values are the average of 4 samples

x Samples delaminated

Constants: (1) Temperature: 300°F. ± 5°

(2) Pressure: 225 psi

(3) Per cent Walnut shell flour based on solids content: 20%

(4) Short Assembly periods: 5-15 minutes

(5) Distance to deepest glue line: approximately 5/16"

APPENDIX VII

CHANGE OF GLUE LINE TEMPERATURE WITH TIME IN HOT PRESS*

THREE UNCURED 1/4" BIRCH PANELS

Time (Min.)	Glue Lines 1 & 6, °F.	Time (Min.)	Glue Lines 2 & 5, °F.	Time (Min.)	Glue Lines 3 & 4, °F.
0	68	0	68	0	68
1.4	240	1	128	1.2	96
2.4	248	2	164	2.2	134
3.4	254	3	187	3.2	162
4.4	263	4	202	4.2	181
5.4	270	5	215	5.2	198
6.4	277	6	226	6.2	213
7.4	280	7	232	7.2	223
8.4	283	8	238	8.2	226
9.4	284	9	240	9.2	228
10.4	285	10	245	10.2	230
11.4	284	11	247	11.2	234
12.4	286	12	252	12.2	238
13.4	289	13	254	13.2	239
14.4	290	14	255	14.2	242
15.4	292	15	258	15.2	244
16.4	292	16	260	16.2	247
17.4	294	17	263	17.2	250
18.4	294	18	266	18.2	252
19.4	-	19	268	19.2	256

* Average Platen Temperature: 300°F.

APPENDIX VIII

CHANGE OF GLUE LINE TEMPERATURE WITH TIME IN HOT PRESS*

THREE UNCURED 1/4" GUM PANELS

Time (Min.)	Glue Lines 1 & 6, °F.	Time (Min.)	Glue Lines 2 & 5, °F.	Time (Min.)	Glue Lines 3 & 4, °F.
0	72	0	72	0	72
1	230	.6	107	.8	80
2	250	1.6	152	1.8	113
3	267	2.6	180	2.8	150
4	279	3.6	204	3.8	180
5	282	4.6	221	4.8	207
6	283	5.6	230	5.8	217
7	283	6.6	236	6.8	221
8	283	7.6	240	7.8	224
9	283	8.6	244	8.8	226
10	283	9.6	246	9.8	228
11	286	10.6	250	10.8	232
12	286	11.6	253	11.8	235
13	288	12.6	255	12.8	239
14	292	13.6	259	13.8	242
15	293	14.6	261	14.8	246
16	292	15.6	263	15.8	250
17	290	16.6	267	16.8	253
18	292	17.6	267	17.8	256
19	292	18.6	270	18.8	258
20	292	19.6	274	19.8	263

* Average Platen Temperature: 300°F.

APPENDIX IX

CHANGE OF GLUE LINE TEMPERATURE WITH TIME IN HOT PRESS*

ONE 1/4" PLYWOOD PANEL BETWEEN 1/4" GUM PLYWOOD CAULS

Birch		Gum	
Time (Min.)	Glue Lines 3 & 4, °F.	Time (Min.)	Glue Lines 3 & 4, °F.
0	68	0	72
1	84	1.5	110
2	128	2.5	142
3	160	3.5	182
4	185	4.5	212
5	204	5.5	226
6	222	6	235
7	230	7	238
8	234	8	242
9	236	9	247
10	239	10	252
11	241	11	256
12	246	12	259
13	248	13	262
14	250	14	264
15	254	15	268
16	258	16	272
17	260	17	276
18	264	18	279
19	266	19	281
20	270	20	282

* Average Platen Temperature: 300°F.

ACKNOWLEDGEMENT

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

V I T A

Jesse Rubel Goza, Jr. was born in West Point, Mississippi, on September 29, 1922, the son of Jesse Rubel Goza and Helen Frances Cantrell Goza. He received his primary education at McCondy High School, McCondy, Mississippi, and his secondary education at Prairie High School, Prairie, Mississippi. He attended East Mississippi Junior College for one year (1941-42) before entering Mississippi State College in September, 1942. His study there was interrupted in February, 1944, when he entered the U. S. Army Air Force.

Mr. Goza spent 27 months in service including 14 months in Europe as radio operator and control tower operator with the air force. After his return to the United States in 1946, he completed his work at Mississippi State College obtaining his B.S. degree in Chemical Engineering. He graduated with honors in May, 1947; and in June, 1947, he married Mary Lucille Lynch of Aberdeen, Mississippi.

Mr. Goza 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 1947-48. He received the degree of Master of Chemical Engineering in June, 1948.

He is a member of the Masonic Order and a junior member of the American Institute of Chemical Engineers.