THE EFFECT OF ALKYL-SUBSTITUTED PHENOLIC ADHESIVES ON THE BONDING OF DOUGLAS FIR VENEER

By

John K. Guiher

A Thesis
Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science
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THE EFFECT OF ALKYL-SUBSTITUTED PHENOLIC ADDITIVES
ON THE BOILING OF [illegible] WATER

By

John H. Gruber

An Abstract

Submitted to the School of Graduate Studies of Michigan
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Approved Alexis J. Panshin

The purpose of this investigation was to determine the effect of four variables on the shear strength of southern pine plywood. These variables were: 1) variation in phenolic resin adhesive formulations, 2) addition of adhesives of walnut shell flour in different concentrations, 3) influence of specific gravity of veneer, and 4) effect of three intervals between bonding and testing plywood.

Sliced veneer, one-eighth inch in thickness, was used in this experiment. The veneer was conditioned in a lumber dry kiln to an average moisture content of seven percent and cored into four by five inch sheets. The green veneer sheets were divided into four equal portions, each to be assigned the variable to be bonded into plywood with each of the four phenolic type resins used in this study. The veneer sheets in every lot were separated into four specific gravity groups.

The adhesives used in this experiment were four reacting with formaldehyde, alkyl-substituted phenol components obtained from commercial sources. The catalyst used in the reaction was ammonium hydroxide. The resins tested included phenol-formaldehyde, resorcinol-formaldehyde, 2,4-dimethyl phenol-formaldehyde, and p-ethyl-phenol-formaldehyde. These resins were reduced to 46 percent resin solids content, and then divided into equal portions. Portion one of each resin was not modified. Walnut shell flour in percentages of 5, 10, 15, and 20 was mixed with portions two, three, four, and five, respectively, of each resin.

The analysis of variance indicated that the highest plywood strength was obtained with p-cresol-formaldehyde resin, followed by phenol-formaldehyde and p-ethylphenol-formaldehyde resins. Plywood bonded with 3,5-dimethyl phenol-formaldehyde resin showed the lowest strength.

The statistical analysis of strength data of plywood bonded with all resins used in this investigation showed that the higher the specific gravity of veneer, the greater are the bonds their strength. Walnut shell flour added to three of the resins increased their bonding strength when it was used in the proportion of 10 to 15 percent of the resin solids content. The shear strength of plywood bonded with p-cresol-formaldehyde resin showed no significant increase due to the addition of walnut shell flour. Plywood bonded with three of the resins showed significant reduction in bond strength after 4 hours to 16 days after bonding. Plywood bonded with 3,5-dimethyl phenol-formaldehyde resin showed strength in dry test a significant decrease in strength after 16 days due to progressive cracking of the resin.

The following are the main conclusions reached:

1. The shear strength of Douglas fir plywood bonded with p-cresol-formaldehyde resin, phenol-formaldehyde resin, p-ethyl phenol-formaldehyde resin, and 3,5-dimethyl phenol-formaldehyde resin decreased in the order named.

2. Plywood strength increased with the increase in the specific gravity of veneer.

3. Shear strength increased with the addition of walnut shell

flour in amounts of 10 to [illegible] percent of the resin solids content.

4. Maximum glycol strength was reached in nine to 15 days after bonding.

TABLE OF CONTENTS

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I. INTRODUCTION

The use of synthetic resin adhesives for the bonding of wood is relatively recent. Their use in the United States dates back to 1934, when a phenol-formaldehyde resin film adhesive was introduced. This period, a total of about 18 years, appears especially short if one considers that the art of gluing wood has been practiced for more than 35 centuries, having had its start in early Egypt.

Up to the time of the introduction and use of synthetic resin adhesives for wood bonding, most of the wood glues were of animal or vegetable origin. Examples of these are animal glue, which is obtained from the hides and bones of animals, starch glue, mainly originating from the roots of the cassava plant, casein glue from the curd of milk, soybean glue, made from soybean meal, and blood albumin from the blood of animals. All of these glues produced acceptable dry wood bonds but were not water resistant.

The advent of the synthetic resins as wood adhesives had a marked effect on commercial wood gluing. These adhesives were found to be extremely water resistant. Urea-formaldehyde adhesives showed some tendency toward hydrolyzing on contact with water, but the phenolic resin adhesives approached the point of being waterproof, and were not attacked by molds or fungi. This allowed the use of glued-wood products in water and under conditions where the bonded construction was exposed to adverse weather. Glued, laminated boats, for example, exposed to fresh or salt water for long periods of time gave highly

satisfactory performances. Many other weather and water resistant wood products can be made with synthetic resin adhesives. For instance, phenolic resins are used in the production of exterior type Douglas fir plywood which gives the plywood an excellent reputation in the building industry.

The synthetic resin adhesives that usually are in use for plywood manufacture are the so-called thermosetting resins; these include phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, and resorcinol-formaldehyde resin types. These resins usually are cured by heat and pressure, or by the addition of a catalyst into infusible and insoluble films in the glue line of a bonded wood construction. The term thermosetting refers then to a resin which becomes irreversibly infusible and insoluble on application of heat or catalyst. In contrast, the term thermoplastic refers to a resin, for example polystyrene or polyvinyl acetate, which is hard when cool but will soften when heated to particular temperatures, becoming hard again on cooling below its softening point.

The investigation herein described has to do with phenol-formaldehyde and other phenolic type resins. There has been considerable research done on the use of phenol-formaldehyde resins for plywood bonding, particularly with one-sixteenth inch yellow birch. However, most of this research has been conducted with phenolic resins for which the resin production data are not available. Consequently, if in conducting research on synthetic resin adhesives information on composition of the adhesive is desired, the investigator is forced to produce his own resin. In the experiment described in this thesis, the

phenolic resin adhesives used were made in the laboratory since it was desired to produce alkyl-substituted phenolic resins for which manufacturing conditions were known.

The formulation and use of various phenolic resins has been examined quite extensively in the case of molding and laminating materials. To a limited extend adhesive qualities of phenol-formaldehyde resin and cresol-formaldehyde resin have also been studied. It appears, however, that there is no published information on the adhesive properties of alkyl-substituted phenolic resins in general. It was proposed, therefore, that four phenolic resins, including phenol-formaldehyde resin be prepared and that these resins be used in the bonding of one-eighth inch Douglas fir veneer into three-ply plywood.

II. STATEMENT OF THE PROBLEM

The purpose of this study was to determine the effective bond strength of Douglas fir plywood as related to different phenol-formaldehyde resin adhesives. The adhesives were formed by reacting phenolic compounds, that had certain alkyl groups substituted in the meta positions of the phenolic rings, with formaldehyde. These alkyl-substituted phenols were obtained from commercial sources and were reacted with formaldehyde using a small amount of ammonia as a catalyst. The plywood produced using these resin adhesives was then tested for shear strength, using the standard plywood shear test procedure (42).

The resins prepared for this study included those formed from phenol and formaldehyde, and three alkyl-substituted resins formed from m-cresol and formaldehyde, 3,5-dimethylphenol and formaldehyde, and m-ethylphenol and formaldehyde. These resins were produced in the laboratory to assure that each of the alkyl-substituted phenolic resins was reacted with formaldehyde for a length of time that corresponded to the length of reaction time used for the phenol-formaldehyde resin.

It was proposed further that whereas a portion of each resin would be used in an unmodified form, another portion would be used with different percentages of walnut shell flour, to find how a given quantity of flour would affect bond strength. The use of the flour retards resin flow into the wood and also minimizes squeeze-out of resin from the glue line during the bonding operation. It should be mentioned that there is an increase in bond strength if a certain amount of

adhesive goes into the wood. However, it is obvious that if too much adhesive penetrates into the wood, the amount of adhesive retained in the glue line may be inadequate, resulting in a "starved" glue joint.

The Douglas fir veneer pieces used in the investigation were standardized as much as possible. All the pieces of veneer were conditioned to the same moisture content before they were used. The gluing surfaces of the veneer were sanded to obtain comparable surfaces. The veneer was selected and cut so that the grain direction was parallel to the sides of the pieces. The specific gravity of each piece of veneer was determined and the veneer was divided into four specific gravity groups. This preliminary processing of the veneer tended to reduce variability.

A theory was proposed regarding the effect of alkyl substitution on the aromatic rings of the phenolic resins as related to the strength of Douglas fir plywood bonded with these resins. The theory suggested that phenol-formaldehyde resin bonded plywood would show the highest shear strengths since there are no alkyl groups on the phenolic ring to hinder polymerization of this resin. It was further theorized that plywood strength would decrease in the following order—m-cresol-formaldehyde resin bonded plywood, 3,5-dimethylphenol-formaldehyde resin bonded plywood, and m-ethylphenol-formaldehyde resin bonded plywood. This order was suggested because m-cresol-formaldehyde resin has only one methyl group on the aromatic ring, 3,5-dimethylphenol-formaldehyde resin has two separated methyl groups, and m-ethylphenol-formaldehyde has a two-carbon ethyl group which extends farther from the phenolic ring and perhaps would have more effect in hindering good glue bonds.

III. DISCUSSION OF BACKGROUND TOPICS

Phenolic Type Resins

Development of phenolic type resins. In view of the fact that this thesis deals with phenolic type resins it seems fitting that a brief historical and theoretical background be presented concerning the development of these resinous products. Only the points which are pertinent to the development of the phenolic resins in general will be presented.

It is of interest to note that the basic raw materials for the production of phenolic resins, namely phenol and formaldehyde, were not known early in chemical history. Phenol was identified in 1834 by Runge some 38 years before the first published reference to phenolic resins. Formaldehyde was prepared by Hofman in 1868, a scant four years before Baeyer conducted his experiments on the preparation of phenolic resins.

Previous to 1872, many chemists had discovered that some reactions which they had carried out resulted in a resinous substance as a product. These new substances were not all appreciated since they could not be analyzed. They had no definite melting points and could not be crystallized. Consequently, at that time, they represented undesirable reactions and such products were discarded without further thought. The value of resins is definitely recognized today.

The first work of any consequence in the study of phenolic resins

was conducted by Baeyer (6) in 1872. He produced several colorless resins and published the results of his investigations. He evidently did not visualize any particular uses for the resins he produced, but he did report that his investigations indicated that the reaction between phenol and aldehydes was a general reaction.

The first research work which provided any information of importance on the way the phenol-formaldehyde condensation reaction took place was conducted by Lederer (33) and Manasse (34). These two investigators, working separately, isolated ortho-hydroxybenzyl alcohol and para-hydroxybenzyl alcohol, the former being known as saligenin. These phenol alcohols were shown to be the simplest products formed in the phenol-formaldehyde resin reaction. The work of these two men was the basis for all later investigations involving the resinification of phenol with formaldehyde. It is recognized today that phenol alcohols are probably the first products formed in the phenol-formaldehyde reaction.

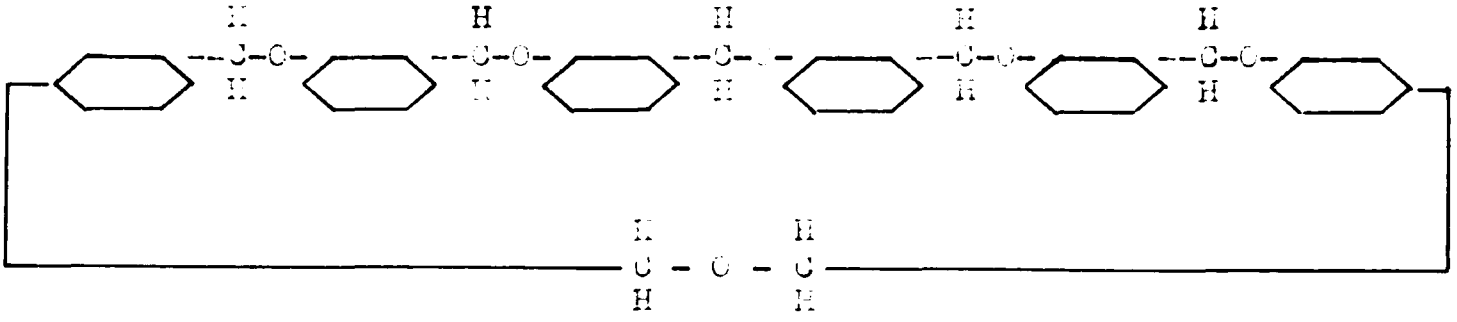
Up to 1900, research on phenolic resins consisted mainly in preparing the resinous products or in the examination of the initial products of the phenol-formaldehyde condensation reaction. In 1900, research began which had as its purpose an examination of the resins obtained in the phenol-formaldehyde reaction to see what could be done with them. In the same year phenolic resins were proposed as an electrical insulating material. Phenolic resins as a substitute for shellac were also suggested and work was actually done toward this goal in 1902 to 1904. Also at this time, in 1901, the first suggested uses

of phenolic resins as an adhesive for bonding wood appeared in a British patent issued to Societè Derepas Frères (50). There is no evidence that a successful adhesive resin was actually developed in that year.

Baekeland (4) introduced a theory of resin formation. He considered the reaction of phenol and formaldehyde as a condensation-polymerization reaction having three steps or stages. In the first part or A stage of the reaction, the resin, called a resol, was formed. It was considered to be of low molecular weight, having the form of a liquid, solid, or semisolid. During this stage the resin was soluble in acetone, alcohol, or toluene. In the second part of the reaction or B stage, the resin, called a resitol, was formed. This resin was considered to be a solid insoluble in acetone but swollen by this solvent. The resin could be softened by heating a limited number of times before it was converted to the final stage. The final stage or C stage produced an insoluble, infusible substance called a resite. These stages are recognized today.

Baekeland explained resin formation on the basis of the products of three resinification reactions. He reacted saligenin with phenol in one reaction. The product of this reaction was a soluble, fusible resin. Saligenin was then heated with varying amounts of formaldehyde which indicated that one-sixth of a molecular portion of formaldehyde was necessary to produce an insoluble and infusible resin. Smaller amounts of formaldehyde always gave a resin that was soluble and fusible and which was attacked by organic solvents. He then reacted

phenol and formaldehyde in sealed tubes with a small amount of base as a catalyst. Stage A resin was marked by a certain amount of water being eliminated. The elimination of additional water indicated stage B. The further reaction from stage B to stage C did not produce any eliminated water. Baekeland suggested that the final stage was addition polymerization. He explained that saligenin, formed in the early stages of the reaction, condensed with itself through intermolecular reaction of phenolic and aliphatic hydroxyl groups and since one-sixth of a molecular portion of formaldehyde must be added to convert saligenin into the final C stage, the C stage resin must be made up of units represented by the following molecular structure:

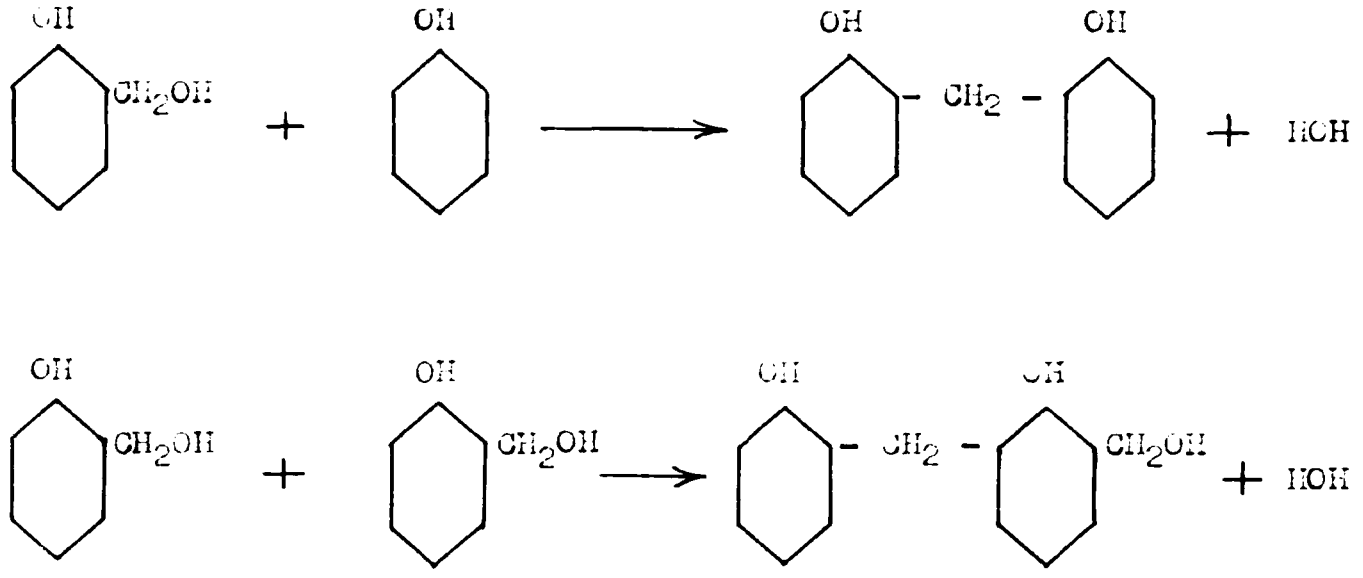


This reaction, through phenolic hydroxyl groups, is not recognized today.

Baekeland also reacted phenol with formaldehyde using a small quantity of hydrochloric acid as a catalyst. The product was a soluble fusible resinous mass. The reaction was carried out using an excess of phenol. His third resinification reaction showed that in the presence

of an alkaline catalyst, the reaction gave an insoluble, infusible product even with an excess of phenol.

Raschig (45) did not like Baekeland's ether linkage and suggested that phenol alcohols could react in two ways. The alcohols could react either with more phenol to produce diphenololmethanes or could react with themselves to form alcohols of diphenylolmethanes.



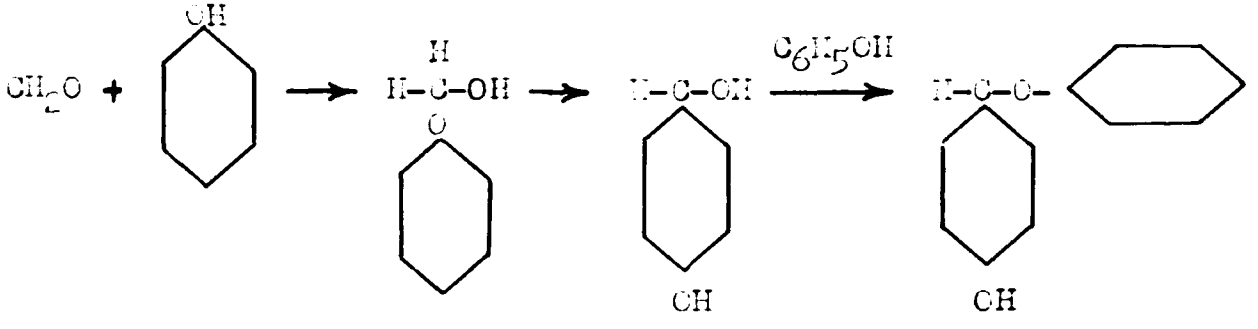
Raschig's reaction scheme for the formation of phenol-formaldehyde resins was then either the first initial reaction, alcohols reacting with more phenol, or phenol alcohols reacting with themselves to form an insoluble, infusible resin product.

Raschig, in considering his data, pointed out that in phenol-formaldehyde resin reactions, soluble fusible resin products are obtained when one, or less than one, mole of formaldehyde is reacted with one mole of phenol. When the molar portion of formaldehyde is greater than

one mole, the molar portion of phenol being one, insoluble products are obtained. According to Raschig, where less than one mole of formaldehyde reacted with one mole of phenol diphenololmethanes are favored, whereas with excess formaldehyde, products of early stages of the reaction are phenol alcohols and diarylmethanes. Final products in the latter case are referred to as resinous mixtures having great complexity.

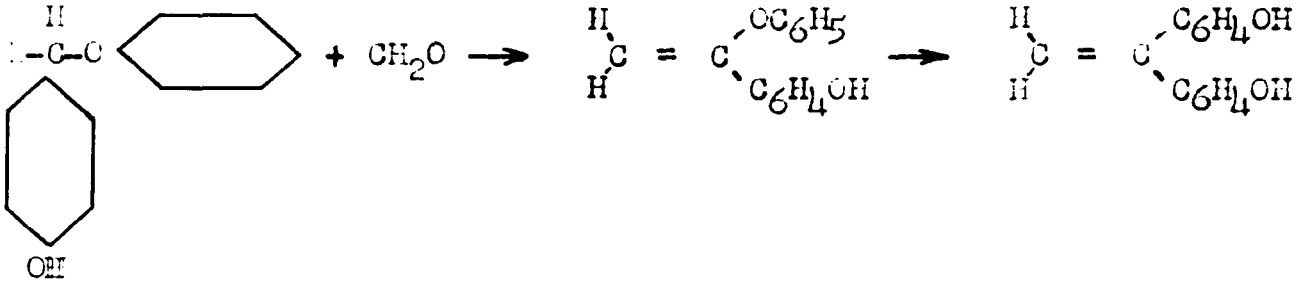
Thirteen years later, Baekeland and Bender (5), reviewed past theories, and after some experimental work developed a new hypothesis which still retained the idea of the ether linkage. Three chemical steps in the condensation reaction were recognized. The following equations represent these three steps.

In the first step, two molecular portions of phenol combine with one molecular portion of formaldehyde to give an unsymmetrical ether, o-hydroxyphenylphenoxymethane. It was stated that this compound was the important component of the initial, or the A stage resin.

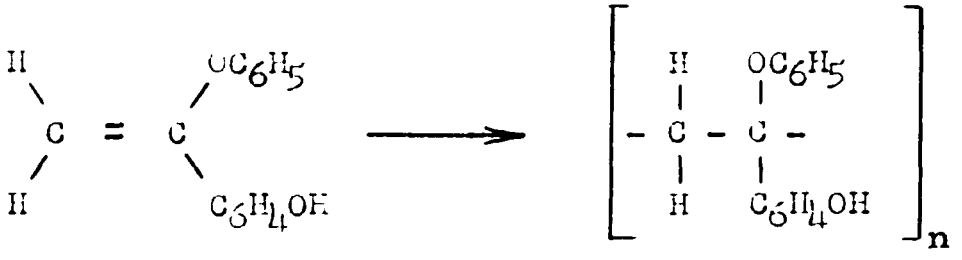


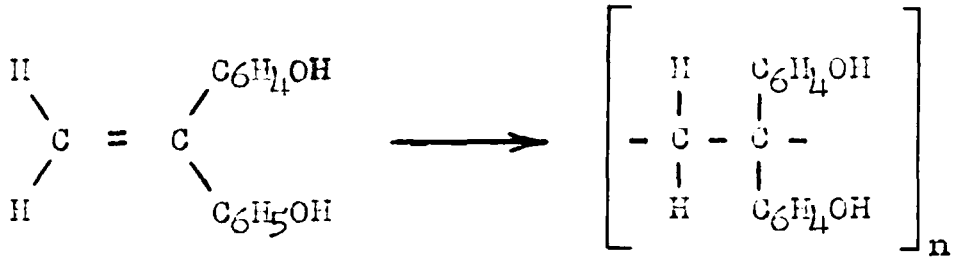
In the B stage it was thought that another molecule of formalde-

hyde condensed with the ether to form unsaturated compounds.



The final C stage was thought to be brought about gradually by addition polymerization.





Up to about 1930 both the theories of Baekeland and Raschig were accepted. However, during the 1930's the condensation polymerization reaction between phenol and formaldehyde was reviewed by several researchers and the hypothesis of Raschig was declared essentially valid. Robitschek and Lewin (47) considered that this point in the advancement of knowledge concerning the phenol-formaldehyde resins brought the development to present-day thinking.

Present concepts of phenol-formaldehyde resin reaction. The review of present-day thinking on the concept of the phenol-formaldehyde resin reaction will include only the more important general ideas concerning this reaction. It must be emphasized that the ideas presented will be general in nature since phenol-formaldehyde reactions can assume all manner of variations due to variation of reaction conditions, which are especially important when phenolic compounds are reacted with formaldehyde. Changes in temperature conditions, in the type and amount of catalyst, in the phenol-formaldehyde ratio, and in the manner of dehydration of the resin are a few of the variables which have a marked effect on the type of resin produced. The phenol-formaldehyde reaction appears to be more sensitive to minor changes than many other chemical reactions; this fact accounts for considerable lack of agreement in the data produced by different investigators. These facts must be borne in mind when the phenol-formaldehyde reaction is under discussion.

One of the classical concepts of organic chemistry which has been

known and accepted for many years is that a hydroxyl group on a benzene ring activates those positions on the ring which are ortho and para to the hydroxyl group*. It is considered that the hydroxyl group on the benzene ring is necessary in the reaction of phenolic compounds with formaldehyde and if the hydroxyl group is acetylated or methylated, the reaction between the phenolic compound and formaldehyde takes place with great difficulty. This concept of reactive positions on the benzene ring leads to the theory of functionality for phenolic compounds.

As indicated in Table 1, phenolic compounds can be divided into trifunctional, bifunctional, and monofunctional types. As can be seen, the functionality of the phenolic compound is determined by the number of available reactive positions on the benzene ring. Formaldehyde is bifunctional and can thus form bridges between phenolic nuclei. In view of this a trifunctional phenolic compound would be expected to form cross-linked macromolecules, a bifunctional phenolic compound would be expected to form only linear chain molecules, and a monofunctional phenolic compound would not form large molecules when the compounds are reacted with formaldehyde. Exceptions to the theory of functionality have been found. A notable exception is that both ortho and para cresols,

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* A convenient diagram of the benzene ring to show its nomenclature is as follows (17):

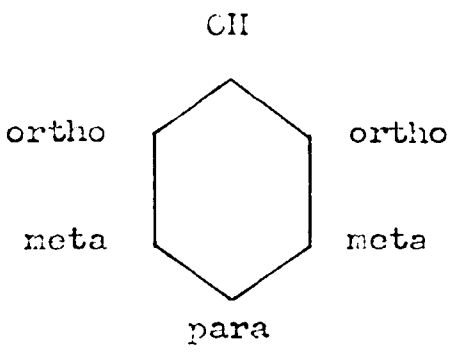
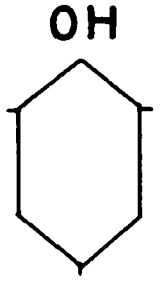
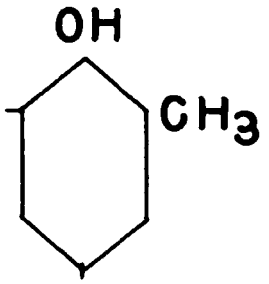
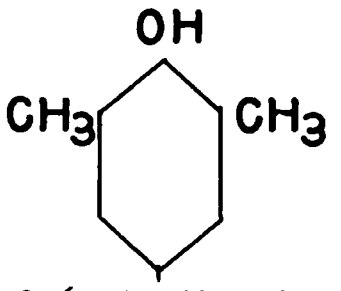
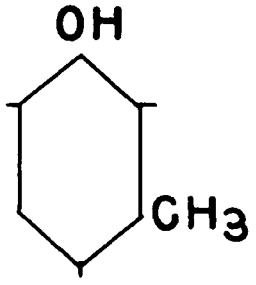
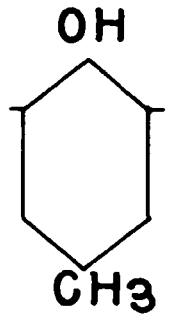
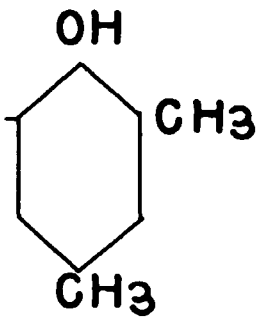
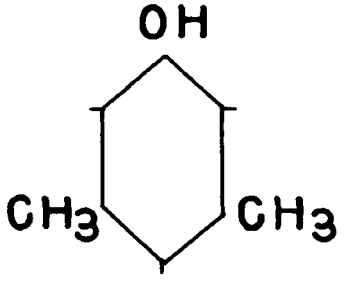
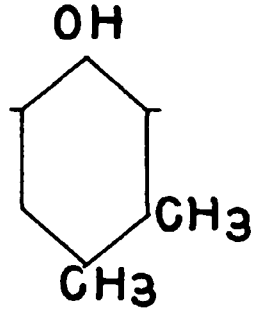
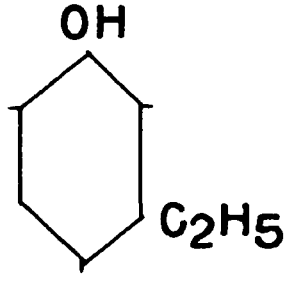


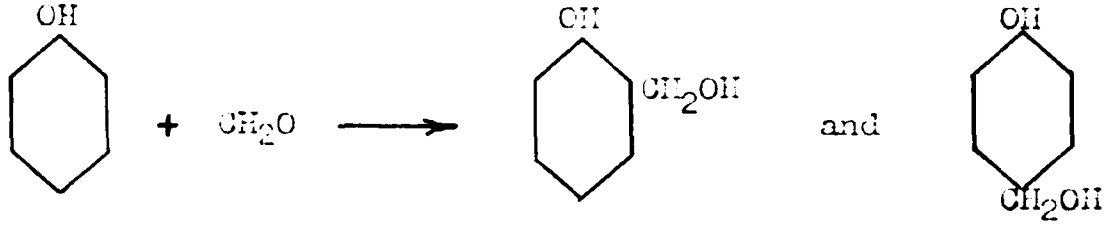
TABLE I. THE FUNCTIONALITY OF PHENOLIC COMPOUNDS

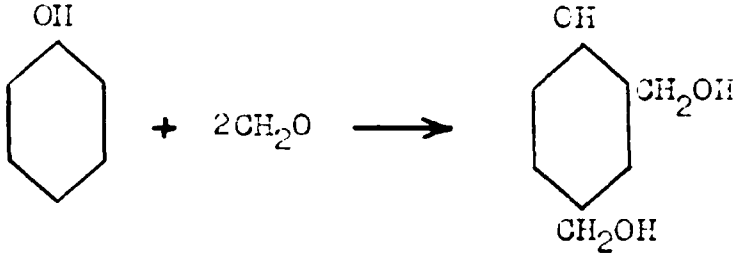
Trifunctional Phenols	Bifunctional Phenols	Monofunctional Phenols
 phenol	 o-cresol	 2,6-dimethylphenol
 m-cresol	 p-cresol	 2,4-dimethylphenol
 3,5-dimethylphenol	 3,4-dimethylphenol	
 m-ethylphenol		

- reactive position

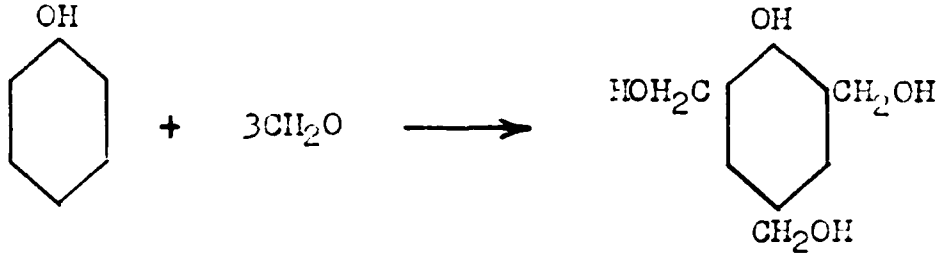
although being classed as bifunctional will, if reacted for a long enough period of time with formaldehyde, form insoluble and infusible resinous material. A bifunctional phenolic compound usually would be expected to form only soluble and fusible resins. Thus these two compounds when reacted with formaldehyde act somewhat like trifunctional compounds which give rise to insoluble and infusible resins. The monofunctional compounds do not form resins.

It is now generally believed that the first products formed in the phenol-formaldehyde reaction are phenol alcohols. As indicated previously these are simple compounds which have been isolated in crystal form; they are water soluble. These alcohols may be mono- or dihydric alcohols. The scheme of their formation may be represented by the following equations:

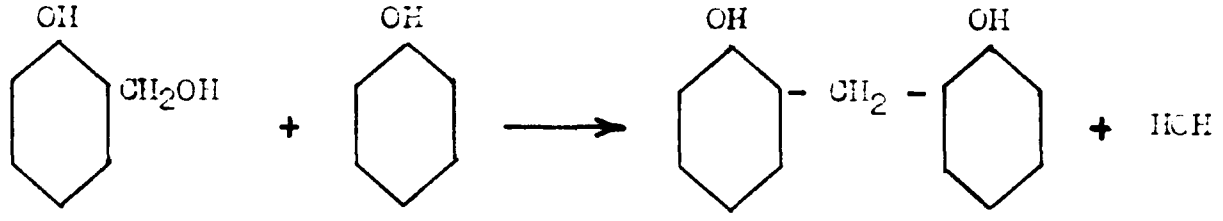




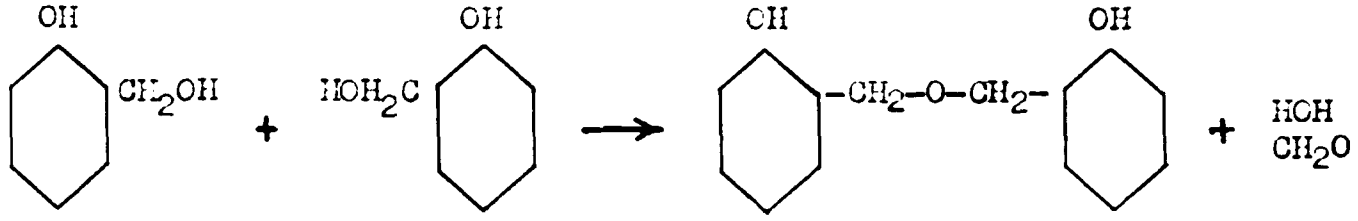
In addition to mono- and dihydric alcohols it has been suggested that trihydric alcohols are also formed (20)(22). Their formation may be shown by the following reaction scheme:



The growth of the phenol-formaldehyde molecule can take place from the alcohol stage in two ways; either by the elimination of a molecule of water, formed by the uniting of a molecule of phenol alcohol and a molecule of phenol between which a methylene bridge is formed as in the following equation,



or by elimination of a molecule of water when two molecules of phenol alcohol unite to form a methylene ether bridge.



Two points should be made concerning the last two equations. In the first place these equations must be considered general in nature since usually either acid or alkaline catalysts are used which will determine the type reaction that will occur. In the second place these equations represent a condensation polymerization reaction in which some simple compound such as water or alcohol is eliminated in the reaction. This is in contrast to addition polymerization in which the reaction takes place through the unsaturation caused by double or triple bonds in a chemical compound. There are no eliminated compounds in the addition polymerization reaction.

In connection with the use of catalysts, the phenol-formaldehyde ratio must be considered. It is accepted that when the phenol to formaldehyde ratio is below one, that is, when the number of moles of phenol in a reaction are fewer than the number of moles of formaldehyde, an insoluble and infusible resin can result. On the other hand, when the number of moles of phenol exceeds the number of moles of formaldehyde, or when the phenol-formaldehyde ratio is greater than one, a permanently soluble and fusible resin results. This is a basic concept

and an important factor underlying the use of catalysts. In order to obtain a hardenable resin it is necessary that the reaction mixture contains a greater number of moles of formaldehyde at the start of the reaction, or else an additional quantity of formaldehyde must be added after the reaction has proceeded to some extent. The addition of more formaldehyde can take place at the time the resin solution is used for some operation such as for molding or as an adhesive.

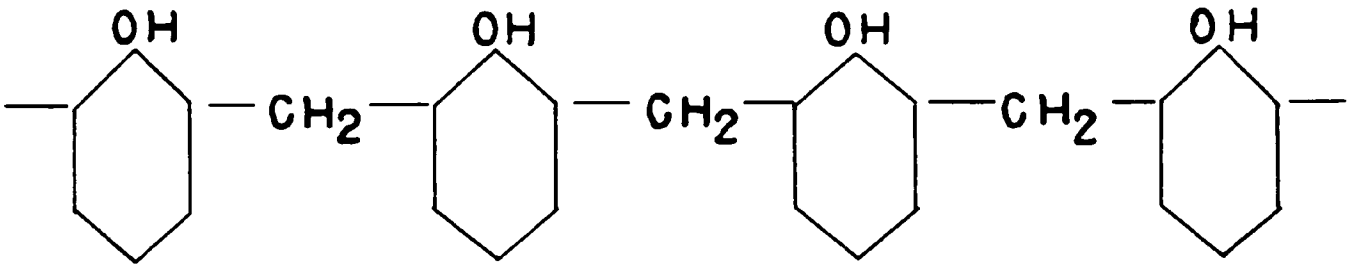
In the presence of an acid catalyst, if the phenol-formaldehyde ratio is greater than one, only permanently soluble and fusible resins can be obtained. However, if the formulation is such that the phenol-formaldehyde ratio is changed to a ratio which is less than one, the resin obtained will be capable of hardening into an insoluble resin. This is the effect obtained when an acid catalyst is used in the preparation of a phenol-formaldehyde resin used as an adhesive.

With an acid catalyst it is belived that chain molecules are formed in which phenolic rings are joined by methylene bridges. The product of such reaction is represented by A in Figure 1. If more formaldehyde is added later, a hardened resin is produced. This resin may be represented by formula B in Figure 1.

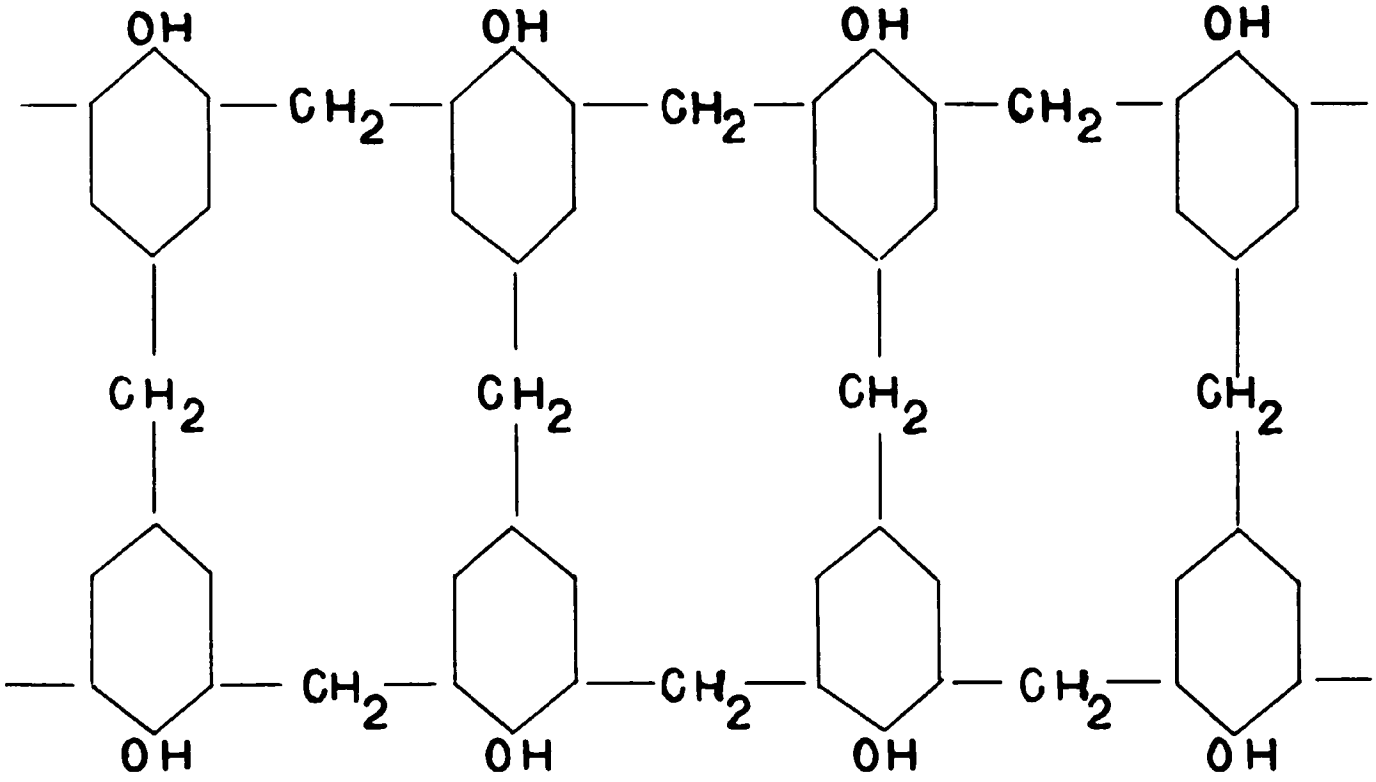
When an alkaline catalyst is used under the usual conditions of a less-than-one phenol-formaldehyde ratio, a resin capable of being hardened is formed. In the initial stages of the reaction, polyhydric alcohols are formed; these alcohols will form even if the phenol-formaldehyde ratio is greater than one, in which case a quantity of phenol remains unreacted. If the unreacted phenol along with the water intro-

duced with the formaldehyde is removed by distillation, the remaining solution consists mainly of polyhydric alcohols having sufficient formaldehyde groups for subsequent cross-linking into an insoluble and infusible resin. On the other hand, if the free phenol is allowed to remain in the solution and if the phenol-formaldehyde ratio is greater than one, a permanently fusible and soluble resin can be formed. The phenol reacts with the polyalcohols present.

With an alkaline catalyst, both methylene bridges, as formed with an acid catalyst, and methylene-ether bridges are formed. A branched chain molecule, as shown in A of Figure 2, results due to the growth of the molecule from polyhydric alcohols. It is believed that both types of bridges are formed up to a temperature of 160° C. The methylene-ether bridge is unstable at higher temperatures, and between 130° C. and 200° C. the methylene-ether bridge is transformed into a methylene bridge as represented by equation B in Figure 2. At temperatures between 170° C. and 220° C., the methylene-ether bridge is transformed into the quinone methide. Chapman (14) suggested that the quinone methide monomer may be formed from a phenol alcohol with the elimination of a molecule of water. The transformation of a phenol alcohol structure is shown in A of Figure 3. The transformation of a molecule of dihydroxydibenzyl ether to the quinone methide structure is shown in B of Figure 3. If the quinone methide does take part in the phenol-formaldehyde reaction, then it can be concluded that a part of the phenol-formaldehyde reaction is an addition polymerization reaction, it being fairly well established that a condensation polymeriza-



A



B

Figure 1. A. Representation of the phenol-formaldehyde reaction product when acid catalyst is used in the reaction and the phenol to formaldehyde ratio is greater than one.

B. Representation of the phenol-formaldehyde reaction product when acid catalyst is used in the reaction and the phenol to formaldehyde ratio is less than one.

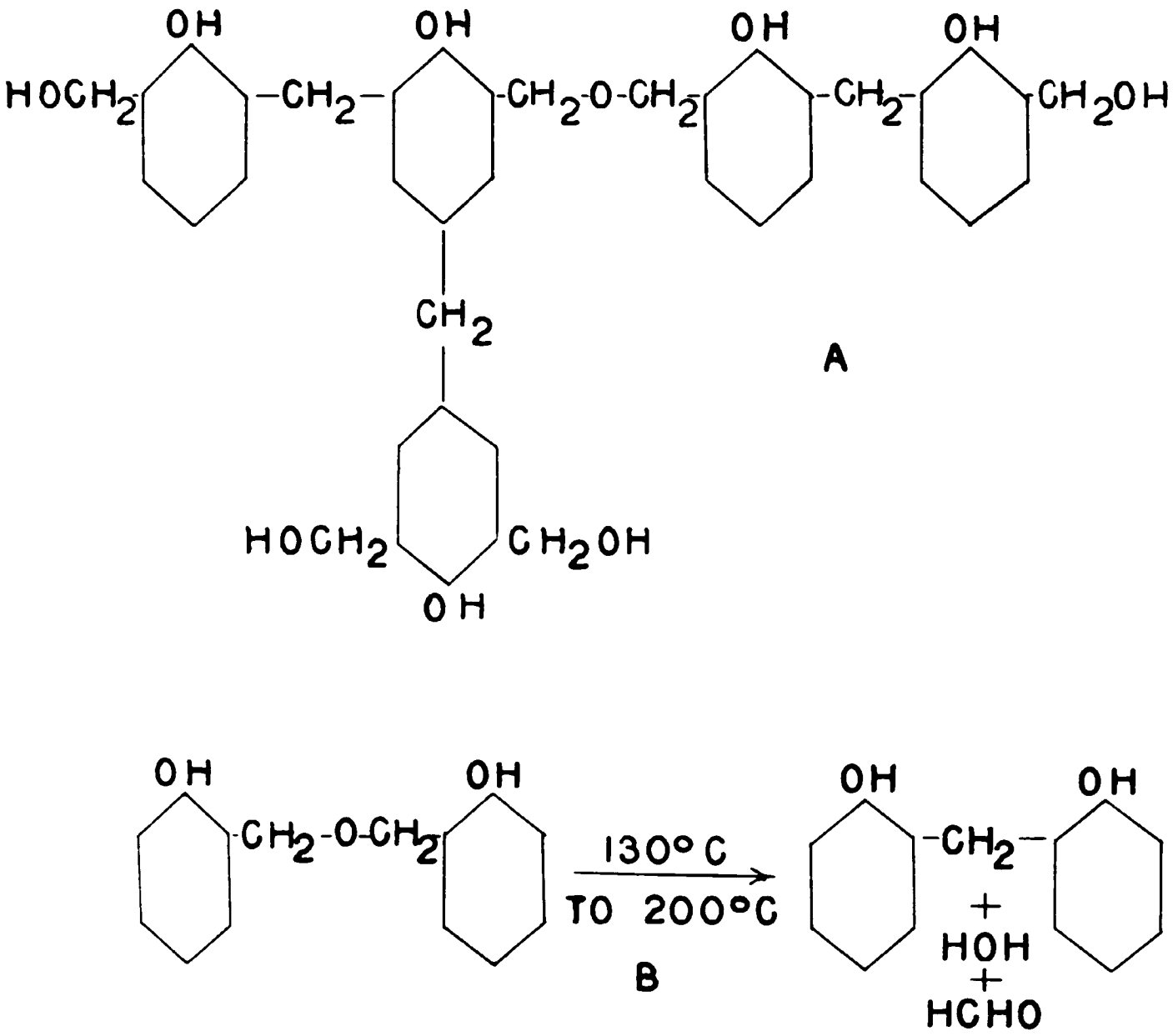
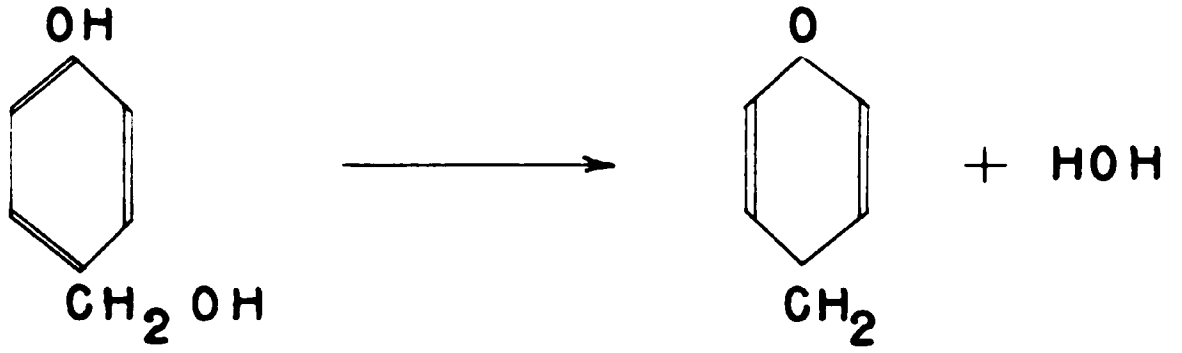
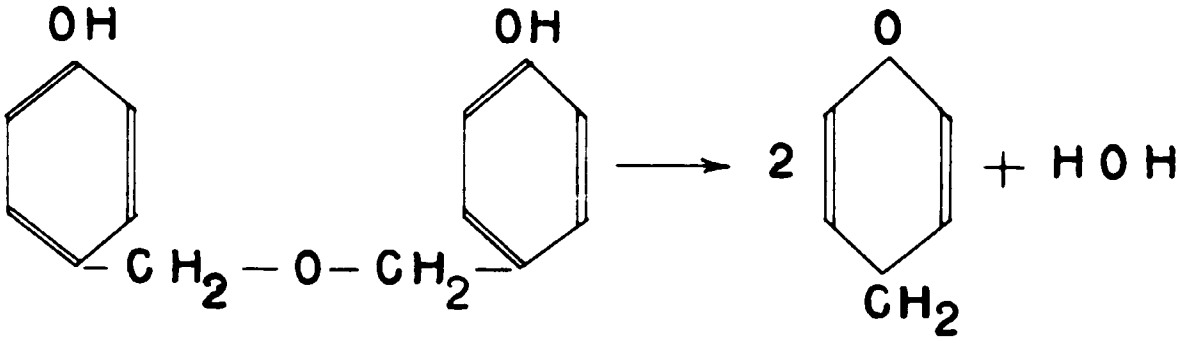


Figure 2. A. Representation of a branched chain molecule formed in the phenol-formaldehyde reaction in an alkaline medium.

B. Transformation of a methylene ether bridge into a methylene bridge at high temperature.



A



B

Figure 3. A. Possible transformation of a phenol alcohol into the quinone methide structure.

B. Possible transformation of dihydroxydibenzyl ether into the quinone methide structure.

tion reaction takes place in initial stages and at lower temperatures. The quinone methide reaction is of interest in explaining how ortho and para cresol resins produce insoluble and infusible resins, since the quinone methide structure introduces a new functional group into the resin reaction. This could account for the hardening of these cresol resins.

It should be mentioned that the phenol-formaldehyde reaction is not fully understood at the present time and any discussion of the reaction must take this into account.

The discussion of the theory of the phenol-formaldehyde reaction has mainly dealt with the reaction of phenol and formaldehyde. Other phenolic compounds such as m-cresol, 3,5-dimethylphenol, and m-ethylphenol could be substituted for phenol in the discussion.

In concluding this section, it is desirable to consider resinification time which has been considered by Holmes and Megson (24) as a measure of the reactivity of phenol or phenolic mixtures in the phenol-formaldehyde reaction. Megson (41) defined this resinification time as the time taken from initial heating of the clear solutions to the appearance of permanent turbidity. Before the turbidity point is reached the components of the reaction mixture are free to move about, which is desirable. This permits frequent contact between molecules, allowing for addition reactions to take place. At the turbidity point less soluble products are thrown out of solution and are contained in colloidal particles. After this point has been reached addition reactions are much more difficult. Using this idea of permanent turbidity, Holmes and

Megson (24) found that 3,5-dimethylphenol-formaldehyde resin resinifies faster than m-cresol-formaldehyde resin which in turn reacts faster than phenol-formaldehyde resin. The same order of activity has been shown by Sprung (53) using paraformaldehyde and the principle of formaldehyde disappearance.

The hardening time for the phenolic resins mentioned has been taken as the time between turbidity and stage C of the resin reaction. Robitschek and Lewin (47) report that the order of hardening for phenolic resins is exactly the reverse of resinification. Phenol-formaldehyde resin hardens faster than m-cresol-formaldehyde resin which in turn reacts faster than 3,5-dimethylphenol-formaldehyde resin.

The Douglas Fir Plywood Industry up to the Introduction of Synthetic Resin Adhesives

The manufacture and use of veneer in the Pacific northwest, according to Perry (42)(43), originated about 1890. The woods used in manufacturing this veneer included Douglas fir along with cottonwood and alder, the veneer first being produced at Tacoma, Washington, where the first veneer lathe had been set up. The veneer manufactured between 1890 and 1905 was made either on rotary lathes or on shaving machines which cut flat slices from dimensional bolts. Most of the veneer of this period was used for making fruit and vegetable containers. Some small Douglas fir plywood panels were made for door manufacture.

The first Douglas fir plywood panels of structural size were specially constructed in 1905 for exhibition at the Lewis and Clark Centennial Exposition in Portland, Oregon. These panels had been made by hand, using animal glue which had been brush-spread. Manually operated cold presses were used to press the veneers together to form the plywood panels (42).

Perry (43) states that the mechanical production of Douglas fir plywood in the United States began about 1916. However, this plywood was produced by door manufacturers for use in the production of their product.

Casein adhesives became commercially important during the years between 1916 and 1918 and were used in bonding Douglas fir plywood. These adhesives gave a definite boost to the industry as suggested by the fact

that the fir plywood industry came into being as a separate industry about 1919. In this year large size structural panels were made available. This new product was used extensively in the United States and was also exported to Europe where it was known as Oregon pine plywood.

Casein adhesives were relatively expensive and, although they helped the fir plywood industry, it was not until the introduction of relatively cheap soybean glues in 1923 that the industry began to be one of the more important industries of the United States. However, the real expansion of the industry started in 1926 when soybeans began to be grown in the United States.

Laucks (32) stated that in 1926 a competitive demonstration of all water resistant adhesives known up to that time was conducted. Soybean glue was shown in such a favorable light as a result of these tests that this type glue was adopted almost immediately by the Douglas fir plywood industry. From that time to the present day soybean glue has been an extremely important factor in the growth and extension of the Douglas fir plywood industry. Soybean glue was used almost exclusively by 1931 and up to about 1937, when synthetic resin adhesives became available in a form which could be used by the industry.

Up to the time of the first use of phenolic type resin adhesives in 1937, all glues used in the manufacture of Douglas fir plywood were water resistant, which meant that the plywood product could be used under conditions of occasional wetting but not under conditions of long exposure to water or weather. This product was called interior type Douglas fir plywood. Prior to the use of phenol-formaldehyde adhesive, all Douglas fir plywood was of the interior type. With the introduc-

tion of the phenol-formaldehyde resin adhesives into the fir plywood industry, a second type of plywood, so-called exterior plywood became available. This type plywood was bonded with phenol-formaldehyde resin adhesive which gave it a waterproof glue line and one immune to attack by molds and fungi.

Aspects of the Bonding of Wood

The art of gluing wood has been known for hundreds of years. However, through most of that time pieces of wood were bonded on a strictly empirical basis. The reasons why it was possible to glue wood were not known, and even today a complete understanding of the underlying principles involved in wood bonding is lacking. This situation is due primarily to the fact that wood is an extremely complex substance, the chemical nature of which is not entirely understood. The complicated nature of most wood adhesives is another factor making the problem difficult. This combination of complexities presents a thorny pathway for the investigator. However, some experimental work has been done on the problem of adhesion between wood and glue, leading to the theories discussed in the following paragraphs.

Theories of adhesion between wood and glue. The theories of adhesion between wood and glue stem from the work of McBain and co-workers in England, and of Browne and Truax in the United States. McBain and Lee (38) made a distinction between specific adhesion caused by molecular forces of attraction between smooth surfaces such as polished metal, and mechanical adhesion attributed to the mechanical gripping of the dried or cured adhesive in the pores and openings in such materials as wood or cloth. Mechanical adhesion was considered by these workers to be the more important of the two types of adhesion when related to wood. They defined it as adhesion due to tendrils of adhesive extend-

ing into the macroscopic, microscopic, and sub-microscopic openings in the wood surface. The strength of the wood-glue bond was thought to be due to the resistance which these tendrils of adhesive offered to a shearing force applied to the joint. The conclusion that mechanical adhesion was the more important gave the idea of artificially roughening wood surfaces before gluing.

Browne and Truax (13) and Brown and Brouse (11) recognized the two types of adhesion as defined by McBain and associates. However, their investigations indicated that adhesion between glue and wood is primarily due to specific adhesion, whereas mechanical adhesion plays a minor role. This conclusion was based on the results of shear tests on glued sugar maple (Acer saccharum Marsh) test-blocks which had been impregnated with paraffin or collodion to a depth that permitted sanding. When these blocks were glued and tested in shear they gave a high shear value even though penetration had been reduced considerably. These results appeared to indicate that mechanical adhesion was not of major importance but that specific adhesion played a very significant role in the gluing of wood. The major role of specific adhesion was further substantiated by microscopic examination of the glue lines. It was predicted that if mechanical adhesion were of greater importance, then microscopic examination of the glue line should show that the adhesive tended to draw away from the wood in the glue line and arch over the wood substance between openings in the wood surface. Also, tendrils of adhesive in the wood cavities should remain as solid adhesive fingers. However, it was found that the adhesive did not draw away from the

woody material but seemed to have an affinity for the wood, and furthermore the tendrils of adhesive did not remain as solid fingers but tended to become hollow cylinders with the adhesive attaching itself to the woody surfaces. These observations indicated that specific adhesion was the more important. Today, the importance of specific adhesion is well recognized but mechanical adhesion is also thought to be essential for good bonding results. These two theories of adhesion do not necessarily constitute the final concepts of adhesion in the bonding of wood. Since the earlier work of McBain and associates, and Browne and Truax, the subject of adhesion in wood has been studied by Rinker and Kline (46), Maxwell (37), and Kitazawa (27).

Present concepts of wood bonding. In considering the glued wood joint, Marra (35)(36) has represented the glue joint as having five links, each of which must be sound if a good joint is to be obtained, and each of which is influenced by particular factors. This convenient representation has segregated the glue bond into five distinct layers, each of which should be given consideration if satisfactory glue joints are to be obtained. In Figure 4 the central portion of the glue bond, the adhesive, is represented by link one. The interfacial or contact area, which is the area between wood and glue on one side of the central glue line and the same area on the other side of the central glue line, is represented by links two and three. The characteristics of the wood and its surface is denoted by links four and five. This classification of the glue bond can be used as a basis for a discussion of the various factors affecting the bonding of wood.

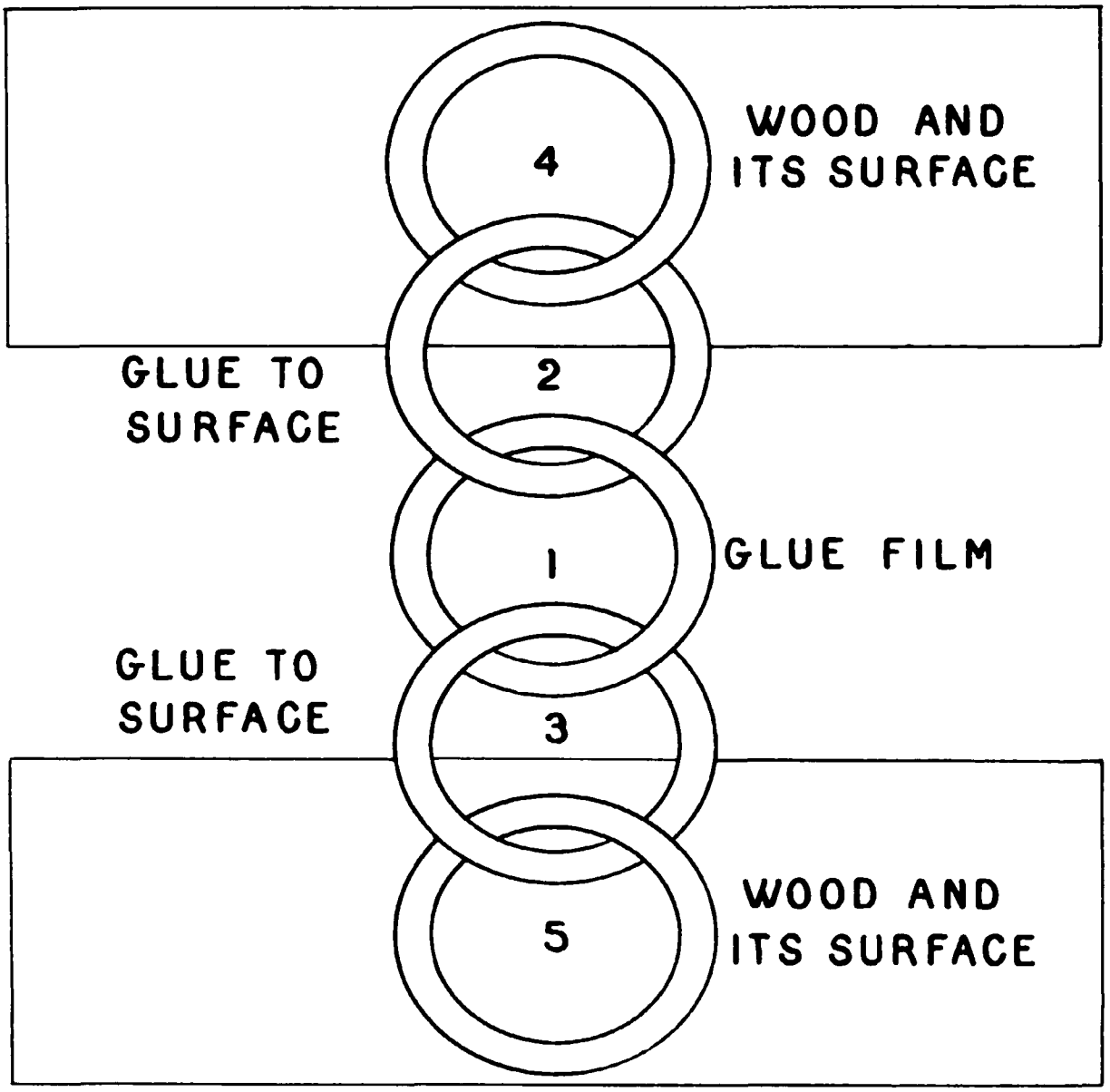


Figure 4. The five links of the wood-glue joint.

Factors involved in holding together a homogeneous material, such as a phenolic resin adhesive might be considered to be, have been divided into chemical bonding and residual forces of attraction. A chemical bond may be formed by an electron transfer from one atom to another to form an electrostatic or electrochemical bond. A chemical bond may also be formed by a sharing of electrons between atoms, the nucleus of each atom having the same magnitude of attraction for the electrons, to form a covalent bond. While the two mentioned types of chemical bonds are the most common, a third type of bond, in which one atom supplies all the electrons between two atoms, is referred to as a coordinate covalent bond. In the case of phenol-formaldehyde resin adhesives, the large molecules are built up by atoms and molecules joined together by means of covalent bonds. These, of course, are primary valence bonds that are considered to be the strongest of chemical bonds. The residual forces, referred to as Van der Waals forces, are attributed to residual charges left over when a chemical bond is formed, it being recognized that positive and negative charges are not completely neutralized when such a bond is produced. It has been pointed out by Brown, Panshin and Forsaith (11) that Van der Waals forces are believed to play an important part in cohesion between the molecules of cellulose in wood and further, that these forces play a significant role in adhesion between wood and glue. Forces of cohesion are very important since they are the factors that give strength to the set or cured resin adhesive.

In considering the adhesive several other directly related factors

should be mentioned. Among these influences on the glue line are the thickness of the glue line, the effect of solvents in the adhesive, the acidity or alkalinity of the glue line, and the molecular weight of synthetic type adhesives. These factors are directly related to the adhesive link in the glue bond.

It was reported in 1927 by McBain and Lee (36) that when polished metal surfaces were joined together by means of gums, resins, or waxes, thinner adhesive layers resulted in higher strength for the joint.

These results have been substantiated in recent years by industrial (44) and college (37) investigators and by work at the United States Forest Products Laboratory (15). At the laboratory, using casein, urea-formaldehyde, phenol, and resorcinol-formaldehyde resin adhesives, it was found for all adhesives that a thinner glue line gave greater strength values. It should be pointed out that the glue line must not be so thin as to disrupt the continuity of the adhesive seam. In gluing relatively rough wood surfaces, which might be the case for some veneers, the glue line will vary in thickness, if its continuity is not broken. It follows that in such a glue line there will be weak spots in the adhesive film.

Several reasons have been proposed to explain why thinner glue lines produce stronger glue joints. It has been suggested that a thermosetting resin is cured in the joint by means of heat used in conjunction with pressure (46). The adhesive reaches an equilibrium state under an abnormal set of conditions. When the heat and pressure are later removed, there is a tendency for the adhesive to reach a new

equilibrium condition at the lower pressure and temperature but it is restrained by the two surfaces to which it is bonded. Such a state of affairs results in stresses being set up in the glue line. The thinner the glue line then, the less stress will be developed in the glue film. It has also been suggested that thinner glue lines give stronger joint strength because there would be fewer flaws in thinner glue layers. In the case of a rigid adhesive, forces working parallel to the glue joint would be more noticeable in a thick glue line than in a thin one. These forces are caused by shrinking or swelling of the adhesive, or expansional differences between the adhesive and the material being bonded. The phenolic type resin adhesives can be considered to be of the rigid type.

Delmonte (18) has considered the effect of solvents in an adhesive. Solvents are considered beneficial in allowing for efficient spread of the adhesive and in permitting molecular orientation and polar adjustments. However, Delmonte suggested that after the adhesive is spread and has accomplished its purpose, the faster the solvent is removed the better will be the results of bonding. In porous materials such as wood the removal of the solvent is thought to take place in part by diffusion of the solvent into the material by means of capillary action, and in part by evaporation into the air. The removal of solvent may be speeded up by using an open assembly period.

Other references have indicated what deleterious effects may be caused by the retention of solvent in the glue line. Hockstra and Fritzius (23) have pointed out that when an adhesive is brought into

contact with a surface, that surface is wetted by the solvent. The solvent molecules thus take up the most favorable polar positions toward the surface, allowing only a limited number of the adhesive molecules such preferred positions. If the solvent is not removed the adhesive molecules which have not obtained these favorable positions will not orient themselves, that is, they will not turn their most active points toward the surface. Eventually, when the solvent is eliminated due to diffusion or evaporation the adhesive will become viscous, which will prevent orientation of the particles and a good glue bond cannot be obtained. In the case of the synthetic resins, the adhesive, when used in hot pressing, may be quite viscous when the wood assembly is placed in the hot presses, but loses some of its viscosity due to the heat. For a short period of time the adhesive may be able to orient its molecules while solvent is being forced out of the glue line by the pressure applied to the assembly. This period is relatively short. After that the adhesive becomes more viscous during the hardening phase and finally it solidifies. Under the conditions just mentioned, if pressure is not adequate during the bonding operation air bubbles may be trapped in the glue line, thus producing a weak bond (36).

Strong acids and alkalies are considered detrimental to the adhesive bond and this effect is known to be very marked if the material being bonded is affected by strong acids or alkalies. Delmonte (18) indicates that a pH value of an adhesive lower than 2.5 is considered detrimental to wood bonds. The effect of acids and alkalies on the strength of birch plywood has been investigated by Kline, Reinhart,

Rinker and Delollis (29). Results of these investigations have indicated that the glue bond is reduced in strength by the action of strong acids and bases. It was found that for phenolic resins a pH value of 3.5 or lower is detrimental to the strength of the glue bond and that strength begins to decrease at a pH value of about 8. Experiments conducted at the United States Forest Products Laboratory by Blomquist (10) on the effect of strong alkali on phenol-formaldehyde and resorcinol-formaldehyde resin adhesives have substantiated results obtained by the previously mentioned investigators.

The recorded molecular weight of a synthetic resin adhesive is not considered to apply to each molecule in the adhesive since molecules in a resin vary in molecular weight; but the given molecular weight is an average of the weights of large, medium and small molecules. There must be, therefore, a combination of molecular weights that give the best adhesive bonds. Delmonte (18) suggested that small molecules of resin are required to make contact with bonding surfaces and act as a bridge between these surfaces and the large molecules of the resin. Small molecules would be required for adhesion, and the large molecules would supply the required cohesion when the resin adhesive is cured.

Links two and three, as indicated in Figure 4, probably can be considered to be the most mysterious parts of the glue bond. However, certain factors are known to have an influence on the glue bond. For example, it has been stated that a satisfactory glue bond is directly related, in part, to the wetting characteristics that a liquid adhesive exhibits toward the surfaces which are to be bonded together (18).

This principle is agreed to by others who made it plain that for good adhesion, a liquid adhesive should wet the adherent surfaces (23). Both references agree that the wetting characteristics of the adhesive are dependent upon surface tension and viscosity.

In a liquid, such as a liquid adhesive, molecules in the interior are surrounded on all sides by other molecules, so that interior molecules are more or less equally attracted on all sides. Molecules at the surface of the liquid, however, are only attracted toward the interior of the liquid by interior molecules and there is no balancing attraction outside the liquid. This situation tends to cause surface molecules to be drawn into the liquid perpendicular to the surface of the liquid. This in turn tends to reduce the surface area of the liquid and the liquid tends to become spherical in shape. A tension force acting parallel to the surface of the liquid is considered to be equal to the free surface energy, which is mathematically the surface tension of the liquid. The greater the surface tension of a liquid, the greater is its cohesive forces and the greater is the tendency for the liquid to form spherical drops. It follows that in order for a liquid to wet a solid surface, the surface must provide attraction for the exterior molecules of the liquid adhesive equal to or greater than the cohesive forces at work in the liquid adhesive (13). The ability of a liquid to wet a surface usually is considered in relation to the angle of contact between the boundary of the liquid adhesive and the solid surface. If the angle of contact between a liquid and a solid is 180 degrees the liquid does not wet the solid surface (59). An example

of such a condition is a drop of mercury on a metal surface; the mercury does not adhere to the surface. The complete wetting of a solid by a liquid is represented by a contact angle of zero. Satisfactory wetting is indicated by complete spreading of the liquid over a surface without a tendency for droplets to be formed. A low surface tension for a liquid adhesive is a factor favorable for the spreading of the liquid over a surface; and it also aids in the wetting of the adherent surface (23). Viscosity influences the spreading of a liquid over a solid in that if viscosity is great it retards the movement of the liquid and in consequence the liquid will not spread freely.

In the case of the wetting of a solid surface by a liquid the polarity of the liquid and the solid should be considered. Basically, different substances can be broadly grouped into polar and non-polar substances, with some substances being included between these two extremes. Loveman (51) points out that a molecule may be completely non-polar, contain only active negative polarity, contain only positive polarity, or have both negative and positive active surfaces. Polar substances are those which have both negative and positive active surfaces. Polar molecules will attract one another.

In the bonding of wood with an adhesive, strong joints can never be made between polar surfaces with non-polar adhesives nor can the converse be true. Wood and derivatives of cellulose are polar materials and if a review is made of the outstanding adhesives used for bonding wood it will be found that they are characterized by strong polar groups such as hydroxyl groups (OH). The OH groups in phenolic type

resins make these resins polar and the same groups in wood and cellulose make these materials polar also. It is known that phenol-formaldehyde resin adhesive is definitely a satisfactory adhesive for bonding wood.

It has been suggested by Hinker and Kline (46) that the mechanism for the bond between wood and phenolic resins is probably hydrogen bridging accomplished through the hydroxyl groups of the resin adhesive and the wood surface. Reactivity of the hydroxyl groups in the phenolic resin adhesive is shown by the fact that a water-insoluble phenol-formaldehyde resin is dissolved readily in sodium hydroxide solutions of relatively mild concentration, and that even a cured resin is attacked by strong alkaline solutions.

Hudkin (40) has demonstrated that hydroxyl groups in wood play a part in adhesion between adhesive and wood. Working with urea-formaldehyde, it was found that if hydroxyl groups of wood were acetylated prior to gluing, a marked reduction in glue bond strength was observed. This work, although it did not indicate what kind of forces existed between wood and adhesive in glue joints, did show the importance of the hydroxyl groups in wood as related to wood bonding. In all probability the hydroxyl groups in wood and the amino and imino groups in urea resin adhesives contribute to the strength of the wood glue joint. Deactivation of hydroxyl groups in wood would undoubtedly reduce the glue bond strength if phenol-formaldehyde resins were used.

The final links in the wood glue bond, links four and five, as shown in Figure 4, represent the materials being bonded.

The surface of wood can be modified to an appreciable extent to improve its adhesive properties. Wood surfaces should be machined smooth, even and flat for best results in gluing them together. Truax (55) referred to a planed surface as being the ideal surface for the bonding of wood. He indicated that numerous comparative strength tests conducted by the United States Forest Products Laboratory had definitely failed to show any advantage obtained by roughening wood surfaces prior to gluing. In recent years, it has been restated by Knauss and Selbo (30) that a smooth planed surface is considered ideal for wood glue joints.

A smooth planed surface obviously is out of the question with veneer which is to be made into plywood. Kaufert (26) has shown by an investigation carried out at the United States Forest Products Laboratory that the glue bond between veneers can be improved by light sanding to restore surface attraction.

IV. DEVELOPMENT OF PHENOLIC TYPE RESIN ADHESIVES AND THEIR USE FOR BONDING DOUGLAS FIR PLYWOOD

Development of Phenolic Resin Adhesives

There has been a substantial amount of research into the uses of phenolic type resins, mainly of the phenol-formaldehyde type, for the bonding of wood. Undoubtedly there has been considerable research into the specific problem of bonding Douglas fir veneers with phenolic type resins; however, the literature is not rich in the details of such research.

In respect to the phenolic resin adhesives available, commercial competition compels resin adhesive manufacturers to guard their products by not allowing free circulation of information on manufacturing processes. It is true that phenol-formaldehyde resins are described in patents but there is no way of linking the information in the patent with the manufactured product. Consequently the following discussion cannot present an exhaustive account of research in this field.

The first attempt to use phenolic resins as adhesives in the production of plywood is recorded in a British patent issued in 1901 to Societè Derepas Frères (50). In 1910 a French patent (22) was issued which covered the use of phenolic resins as adhesives for the production of plywood. In 1912 the use of phenolic resins as adhesives for the waterproof bonding of plywood was suggested in a patent issued to Baekeland (3). Three years later, in 1915, another patent was issued

to Aylesworth (2) in which he proposed the use of phenolic resins as adhesives for the bonding of veneer into plywood. Sontag and Norton (51) explained that these early phenolic adhesives were phenol-formaldehyde resin solids dissolved in alcohol to form a resin solution. This solution was applied in the same way as more common adhesives known at that time. The alcohol was allowed to evaporate before the spread veneer was pressed. The solutions were apparently quite thin since much of the resin soaked deep into the wood and was lost so far as its bonding effectiveness was concerned.

In 1913 a patent was issued to J. H. McClain (39). McClain outlined the production and use of a phenol-formaldehyde resin film which was dry and would have eliminated the inefficient method of using resins in alcohol solution. However, there is no evidence to indicate that this film was ever widely used.

Sorenson and Klein (52) indicated that the development of phenol-formaldehyde resins as wood adhesives during the period between 1911 through the first World War did not take place for three reasons. The first reason for this lack of development was the high cost of the resins. The second was a scarcity of sufficient data on the use of the phenolic resins as wood adhesives. Their use required that research be undertaken upon specific problems of wood bonding. It was thought that since the resins had performed satisfactorily as binders for laminated paper and for binding canvas, they should be satisfactory for gluing wood. However, all bonding surfaces are not alike and it is necessary to find adhesives suited for the particular surface which is to be bonded.

An adhesive suitable for one surface may not be suitable for another surface. The third reason was a lack of expensive hot presses required for bonding wood with phenol-formaldehyde resins.

Klein (28) states that activity in the phenolic resin adhesive field did not appear until the late 1920's when some development work was started in this direction. Once again, phenol-formaldehyde resin solids dispersed in alcohol became available for the bonding of wood. One company manufactured and sold phenolic resin solids in water solution. However, the resins could not be used with satisfaction mainly because the control of the spread was difficult and it was almost impossible to adjust the moisture content of the wood at the time of gluing. Sorenson and Klein (52) indicated that a very important problem encountered at this time was the lack of control of the flow of the resin adhesive during the pressing operation. Due to the failure of the resin solutions in volatile solvents, some manufacturers produced resins in powder form and also resins in water solution called colloidal resins. Klein (28) said the powders were used by sprinkling them on the wood to be bonded. The powder was then moistened with water and the wood assembly pressed. Neither of these attempts to use phenol-formaldehyde resin as an adhesive for wood was successful.

In the year 1927 the first resin glues for wood were produced in Europe. Wegner (58), as a consulting engineer for the European firm introducing the resins, worked on the problem of the best form for the resin adhesive for wood. The result of the work at that plant was the introduction of resin adhesives for wood in the form of a dry film.

Klein (28) indicated that in 1932 phenolic dry film for bonding wood was introduced into the United States. Production of phenolic resin film for wood bonding was started in the United States in 1934. The wide acceptance of this film was hampered at first by the fact that in the United States there were less than a dozen hot presses for wood bonding. However, by 1941 there were some 150 hot presses in operation.

Between the years 1934 and 1937, the resin film was probably the only satisfactory type of phenolic resin adhesives available. In the latter years, improved phenolic resin solutions and phenolic resin adhesives in powder form were in the experimental stage, although some of these adhesives were already used to a limited extent for bonding wood, including Douglas fir veneer (31). In 1940 improved phenolic resin adhesive solutions and the powder adhesives were accepted for wood bonding (28).

Since the introduction of resins in 1940, the trend has been to improve phenolic type resin adhesives and modify them for particular purposes.

Phenolic Type Resins Used With Douglas Fir Veneer

Phenol-formaldehyde resin bonded Douglas fir plywood, or exterior type plywood, did not become commercially important until the years 1939-1940. The advent of exterior type Douglas fir plywood paralleled closely the introduction of an accepted improved liquid resin adhesive and sprayed dried phenol-formaldehyde resin adhesive in powder form. The resin film which had been introduced in 1934 was of little use to the Douglas fir plywood industry for three reasons: 1) the phenolic film was much too expensive for use in producing the relatively cheap plywood product, 2) the film could not be adapted to the mass production industry, which the Douglas fir plywood industry had become in 1934, and 3) the resin film was not suited for the bonding of the rough veneers used in the Douglas fir plywood industry or for bonding wood having as wide a variability in density as Douglas fir veneer. It is true, as pointed out by Sawyer, Hodkins and Zeller (43), that some phenol-formaldehyde resin bonded Douglas fir plywood was produced between 1934 and 1939. However, this plywood was bonded using the old unimproved resin adhesive solutions of phenol-formaldehyde resin solids dissolved in alcohol (1).

The introduction of improved phenolic resins marked the real beginning of the production of exterior Douglas fir plywood (1). Although not used today, at least up to 1943 two excellent resins were used by the Douglas fir plywood industry. One adhesive was used in

aqueous form without extenders to give plywood of the highest exterior durability. The press temperatures used were between 280° F. and 300° F. A second phenol-formaldehyde resin was used with a soluble dried blood extender. With the latter, good boil-proof glue bonds were obtained at pressing temperatures of from 240° F. to 260° F. The use of blood extenders undoubtedly resulted in very economical glue line costs. It was indicated by Sawyer, Hodkins and Zeller (49) that blood extended phenol-formaldehyde resins were not used extensively in the Douglas fir plywood industry.

Wood and Linn (60) described "an excellent" adhesive for bonding Douglas fir plywood, which probably was tried at the time the Douglas fir plywood industry was beginning the production of exterior type plywood. The adhesive was prepared by the reaction of meta cresylic acid and formaldehyde in the presence of sodium hydroxide. The adhesive was soluble in water and was used under press temperatures of 320° F. to 340° F. and a pressure of 175 pounds per square inch. The high temperature requirements for this adhesive indicated that the resin had slow curing characteristics.

Beaty (7) studied the production of Douglas fir plywood relative to the factors that affected its quality. He based his results on plywood shear test strength data. In all cases, shear specimens were boiled in water for four hours, given a 20-hour drying period at 145° F., and then given a second four-hour boil treatment. The tests were conducted immediately after the second four-hour boil period. In all cases phenol-formaldehyde resin adhesives were the type used and test

specimens were obtained by sampling plywood panels that were bonded in the course of regular plywood production.

Pre-cure of the adhesive, which term refers to curing an adhesive on a wood assembly before pressure is applied, was considered by Beaty. This is an important factor in any gluing operation and it must be controlled rigidly in production processes. Beaty reaffirmed that a phenolic resin adhesive will pre-cure if brought in contact with the heated press and allowed to become heated before pressure is applied.

The effect of variations in texture and grain of the veneer used in the production of Douglas fir plywood was also examined by Beaty. Important factors were slope of grain or grain orientation in the core plies of plywood, number of growth rings per inch measured in a radial direction, smoothness of veneer, and veneer density. In considering these factors, Beaty pointed out that the variation found in Douglas fir veneer usually was attributed to two factors. The first concerned the large diameters of the peeler logs used in veneer production. The characteristics of the wood at the center of these logs were observed to be very much different than the wood at the outside of the log. Secondly, the trees grow in many and various sites from low swampy areas to higher rocky bluffs, the various sites having effect on the character of the wood.

As a part of his investigation, Beaty classified plywood shear specimens into three groups related to the orientation of growth rings in the core plies. Figure 5 shows plywood shear specimen diagrams in which the three types of growth ring orientation in the core are indi-

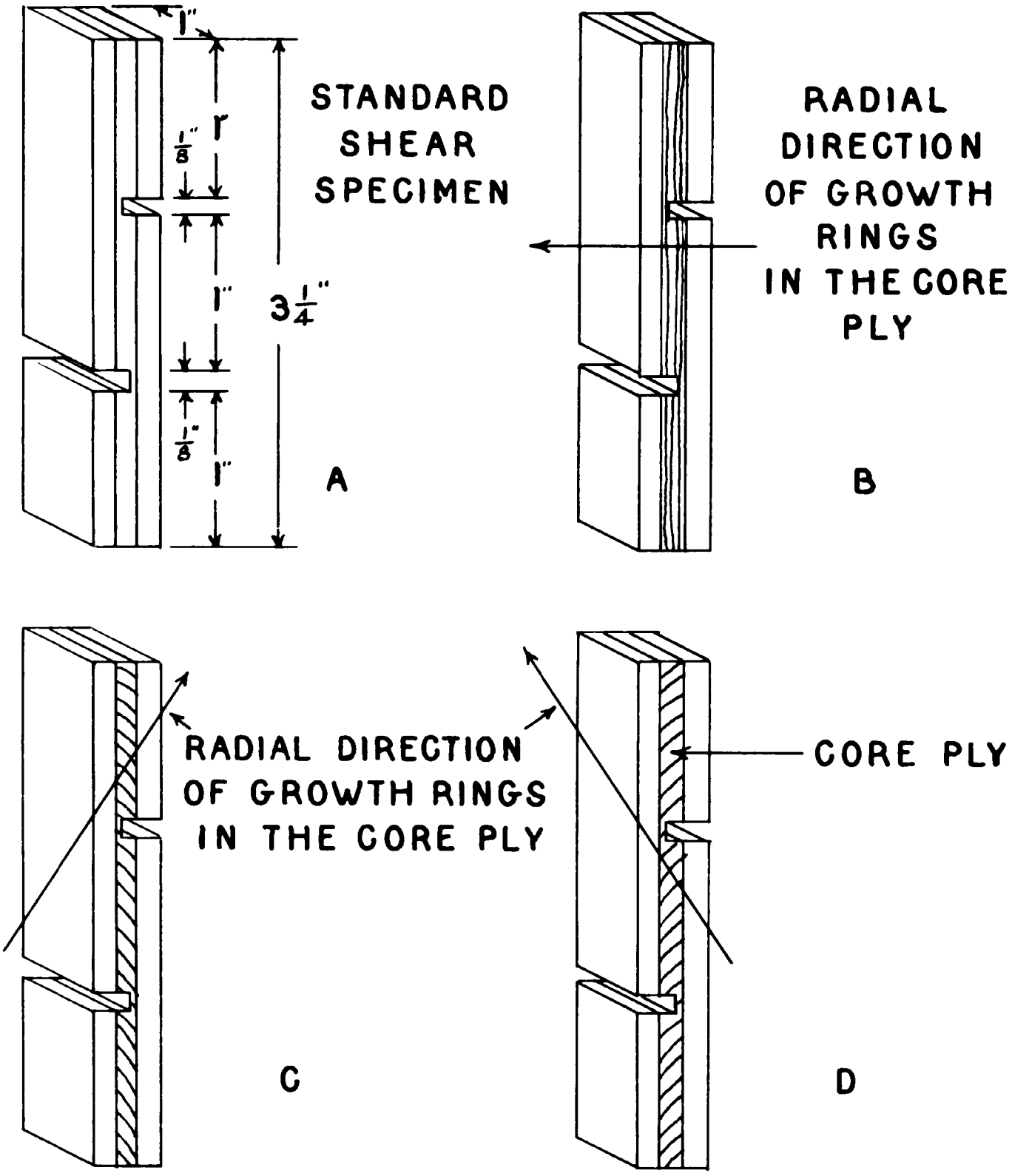


Figure 5. A. Dimensions of the standard plywood shear specimen.

B, C and D indicate the variation in the orientation of growth rings in the core ply of Douglas fir plywood shear specimens as described by Beaty (7).

orted: the plywood specimens are identical except for the position of the growth rings in the core plies. The dimensions of the standard plywood test specimen are shown by A in Figure 1. It is noted that the plywood specimens are oriented for testing: the one-eighth inch notches in the specimens are in the same position for all samples. Diagram I of Figure 5 shows the growth rings of the core ply parallel to the face plies. Diagrams G and H in the figure have core ply growth-ring orientation at some angle between rings parallel to the face plies and rings perpendicular to the face plies. With respect to the one-eighth inch notches, the growth ring orientation of diagrams G and H is approximately opposite. Diagrams E, F and I represent the three plywood specimen groups. The results of testing a large number of plywood shear specimens indicated that the orientation of growth rings or grain direction had no bearing on the strength of plywood.

The number of growth rings per inch, which in this environment varied from about 10 in the Douglas fir, was considered as a possible cause of plywood strength differences. However, it was found that rings per inch did not seem to affect the bond strength of Douglas fir plywood as measured by the tensile shear test method.

The smoothness or roughness of Douglas fir veneer surfaces had no effect on plywood strength.

In considering density, Seely suggested that the relative proportion of springwood to summerwood as well as the hardness of the veneer are closely associated with density, and that density directly reflects the effect of these two factors. On the basis of his tests, Seely

reports that variation in density did have an effect on the strength of the plywood, in that light veneers tended to be weaker than heavier veneers and showed greater wood failure percent than the plywood made of the heavier veneers.

V. APPARATUS AND METHODOLOGY

Statistical Design of the Experiment

In any experimental endeavor that involves a statistical analysis, it is important to develop a design for the experiment so that the data obtained may be easily analyzed. An experimental design was developed for the problem described in this thesis before actual investigation was started.

This experiment was designed for statistical analysis of variance procedures. Four variable factors were involved. An outline of the balanced design is shown in Figure 6. The symbols in Figure 6 are defined in Table II.

As shown in Figure 6 four adhesive resins were used to bond Douglas fir veneer into plywood panels. The total number of three-ply plywood panels was 768, so that 192 panels were produced using each individual resin. The veneer used for each resin was divided into four specific gravity groups and plywood panels were fabricated with veneer of each specific gravity group. For each resin 48 plywood panels represented each specific gravity group.

The number of plywood panels for each specific gravity group within each resin was divided by four to give 12 panels that represented each of four walnut shell flour groupings for each specific gravity group.

The four time factors completed the balanced design. For the

		Specific Gravity (groups)			
		1	2	3	4
		Walnut Shell Flour			
Resins	Time (days)	0 10 20 30	0 10 20 30	0 10 20 30	0 10 20 30
I	5				
	9				
	12				
	16				
II	5				
	9				
	12				
	16				
III	5				
	9				
	12				
	16				
IV	5				
	9				
	12				
	16				

Figure 6. Outline of the experimental design for the investigation.

TABLE II. DESIGNATION OF SYMBOLS FOR FIGURE 6

Design Factor	Designation
I	phenol-formaldehyde
II	m-cresol-formaldehyde
III	3,5-dimethylphenol-formaldehyde
IV	m-ethylphenol-formaldehyde
1	Specific gravity group (0.39 - 0.46)
2	Specific gravity group (0.47 - 0.54)
3	Specific gravity group (0.55 - 0.62)
4	Specific gravity group (0.63 - 0.70)
0	Walnut shell flour - 0% *
10	Walnut shell flour - 10% *
20	Walnut shell flour - 20% *
30	Walnut shell flour - 30% *
5	3 days plus 48 hours soak after pressing
9	7 days plus 48 hours soak after pressing
12	10 days plus 48 hours soak after pressing
16	14 days plus 48 hours soak after pressing

* Based on resin solids content.

entire experiment, each time factor was represented by 192 plywood panels or 48 panels for each individual resin.

It is noted that for each individual condition of the experiment, for example, for Resin I, Specific Gravity 1, and a Time of five days, there were three plywood panels. Furthermore, four plywood shear test specimens were obtained from each plywood panel.

The balanced statistical design was used as the basis for the entire thesis experiment.

Preparation of Douglas Fir Veneer for the Experiment

The veneer used in this experiment was one-eighth inch Douglas fir [Pseudotsuga taxifolia (Poir.) Britt.] veneer. Douglas fir veneer was selected because of the investigator's particular interest in Douglas fir veneer and plywood. Furthermore, Douglas fir plywood is considered to be an extremely important product for which many uses are known. Douglas fir plywood is used for roofing, sheathing, sub-flooring and paneling in the construction of houses, schools, churches and commercial buildings. It is used for concrete forms with the advantage of smooth concrete surfaces. Phenol-formaldehyde resin bonded Douglas fir plywood, or exterior type plywood, is used as exterior paneling for buildings including prefabricated constructions, aircraft hangars and low cost houses.

The actual veneer used was obtained from two Pacific northwest manufacturers of Douglas fir veneer. The shipment consisted of two packages; one package contained approximately 800 square feet of material in the form of two by eight foot sheets, and the second package contained about the same total number of square feet but in the form of seven by 36 inch pieces. The veneer was not specifically selected for the problem but it was believed that this offered no particular hardship in finding the desired pieces of veneer. However, the large

sheets of veneer were heavier, tighter cut*, and had smoother surfaces than the smaller pieces which were less tightly cut, were of low specific gravity, and had rougher surfaces. The entire amount of veneer showed all manner of growth ring orientation and growth ring widths as viewed on the end grain of the sheets. This situation was expected and represented the actual type of veneer used by the industry to bond into Douglas fir plywood.

The initial step in processing the veneer consisted in conditioning it to a seven percent moisture content, the percentage referring to the percentage of moisture in a piece of wood based on the moisture free weight of the wood. Seven percent moisture content was selected because it was considered to be an intermediate value for the gluing of wood and was a figure which could be maintained easily during the course of the study. The actual conditioning was accomplished in a Standard Dry Kiln designed for the particular purpose of drying or conditioning wood to a desired moisture content. The veneer was stacked in the dry kiln using stickers to separate the sheets so that air circulated through the pile of veneer during the conditioning period. The control mechanism of the kiln was set to attain equilibrium moisture content of seven percent in the veneer. Since the veneer did not constitute a full kiln load it was necessary to adjust the kiln control

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* In the cutting of veneer by the rotary method, checks or cracks are developed on the under or concave surface. The depth of the cracks depends on the adjustment of the pressure bar of the veneer lathe and on the sharpness of veneer knives. Tight cut veneer is indicated by shallow checks, and loose cut veneer is indicated by deep cracks.

mechanism during the conditioning; this adjustment was based on the moisture content of kiln samples.

When the veneer was placed in the kiln, small pieces of it were distributed throughout the pile. These small pieces were used as kiln samples. The average moisture content of these samples was taken as the average moisture content of the veneer at a particular time of testing. The moisture content of the veneer pile was followed from day to day until the samples indicated that the veneer was at the desired value, after which time two days were allowed to elapse in order to take care of any lag in moisture content change in the veneer sheets due to their large sizes.

It was decided to use four by five inch pieces of veneer to produce four by five inch plywood panels. This decision was based upon three factors: 1) the hot press to be used in the bonding of the panels had six by six inch plates, 2) from each panel it was desired to obtain four plywood test specimens, and 3) only a limited amount of resin adhesive could be prepared, which required that the smallest usable plywood panels be produced in order not to waste adhesive. Consequently the next operation consisted in sawing the veneer into four by five inch sheets. These were then returned to the dry kiln where they were placed into specially built racks that kept the individual pieces separated to allow circulation of kiln air. When a substantial number of sheets of veneer were sawed, a two-day period was allowed to elapse to stabilize the pieces. The specific gravity of each sheet was then determined.

Approximately 4,000 of these small sheets of veneer were cut. One-third of the sheets were core plies in which the grain direction of the sheet was oriented parallel to the longer five inch dimension, and two-thirds of the pieces were face plies in which the grain direction was oriented parallel to the shorter four inch dimension.

It is noted that a core ply inserted between two face plies forms a three-ply plywood panel.

Several points should be mentioned in regard to the determination of the specific gravity of the veneer sheets. It is well known that wood is subject to shrinkage and swelling when it dries or takes on moisture due to its hygroscopic character. In determining the specific gravity of wood a particular moisture content must be selected. Usually the specific gravity of wood is evaluated on the basis of oven dry weight or moisture free wood, and on volume in a green condition or at the point of fiber saturation. The fiber saturation point refers to the point when wood has taken up the maximum amount of moisture but the cell cavities of the wood are not filled with water. This is a theoretical point at which the wood is swollen as much as it possibly can be, and any additional moisture will not cause a change in its dimensions. If a piece of wood is accurately sawed when at the fiber saturation point the dimensions of the piece of wood will not change so long as this condition is maintained. It follows that if a particular moisture content for wood below the fiber saturation point is selected and that wood is sawed accurately to specific dimensions, these dimensions can be maintained as long as the particular moisture content remains

constant. Obviously the weight of the piece will remain the same at a particular moisture content.

In this investigation a moisture content of seven percent was selected as a basis for determining constant weight and constant dimensions for the Douglas fir veneer.

A common method for determining the specific gravity of wood is the volumetric method in which the wood must be sealed with paraffin so that it may be dipped into water to find the weight of water equal to the volume of the wood. It is obvious that if wood is to be glued later it would not be advantageous to cover it with paraffin. The dimensional method for specific gravity determination was used in this investigation. In this method, the piece of wood is measured accurately in length, width and thickness. The weight of an equal volume of water is calculated. The specific gravity can, then, be found by dividing the weight of oven dry wood by the weight of water corresponding to the volume of wood at a particular moisture content.

In order to determine the specific gravity of such a large number of veneer sheets, a sample of 300 sheets was selected at random. The dimensions of these sheets were accurately measured and then the sheets were weighed at seven percent moisture content. For all 300 sheets, the oven dry weight of each sheet was calculated, using the following relationship:

$$\text{oven dry weight} = \frac{\text{weight at seven percent moisture content}}{0.07 + 1.00}$$

Using the measured volume of the veneer sheet, the weight of an equal

volume of water was calculated. Specific gravity was determined by dividing the oven dry weight of the veneer sheet by the weight of a volume of water corresponding to the volume of the veneer sheet at a moisture content of seven percent. The specific gravities calculated were used in conjunction with the weight of veneer sheets at seven percent moisture content to construct a graph of specific gravity over weight of four-inch by five-inch pieces of veneer at that moisture content. In this graph the ordinate represents specific gravity and the abscissa represents weight of the four-inch by five-inch sheets of veneer. This graph is reproduced in Figure 7. Three hundred and eighty points were plotted and by the method of least squares a straight line was fitted to the plotted points. Thus for the lot of veneer under consideration, if the weight of a four by five veneer sheet were known, the specific gravity of the sheet could be determined from the graph. It should be stressed again that during the weighing operation the veneer sheets were maintained at the seven percent moisture content by removing sheets from the dry kiln, weighing them, and immediately returning the sheets to the kiln.

After determining the specific gravities of the veneer sheets, four specific gravity groups were selected. The specific gravity groups chosen were A) 0.39 to 0.46, B) 0.47 to 0.54, C) 0.55 to 0.62, and D) 0.63 to 0.70. There were sufficient pieces of veneer in each of these groups to carry out the investigation.

The veneer sheets were sorted to conform to the experimental design of the problem into lots of 48 veneer sheets, 16 core sheets

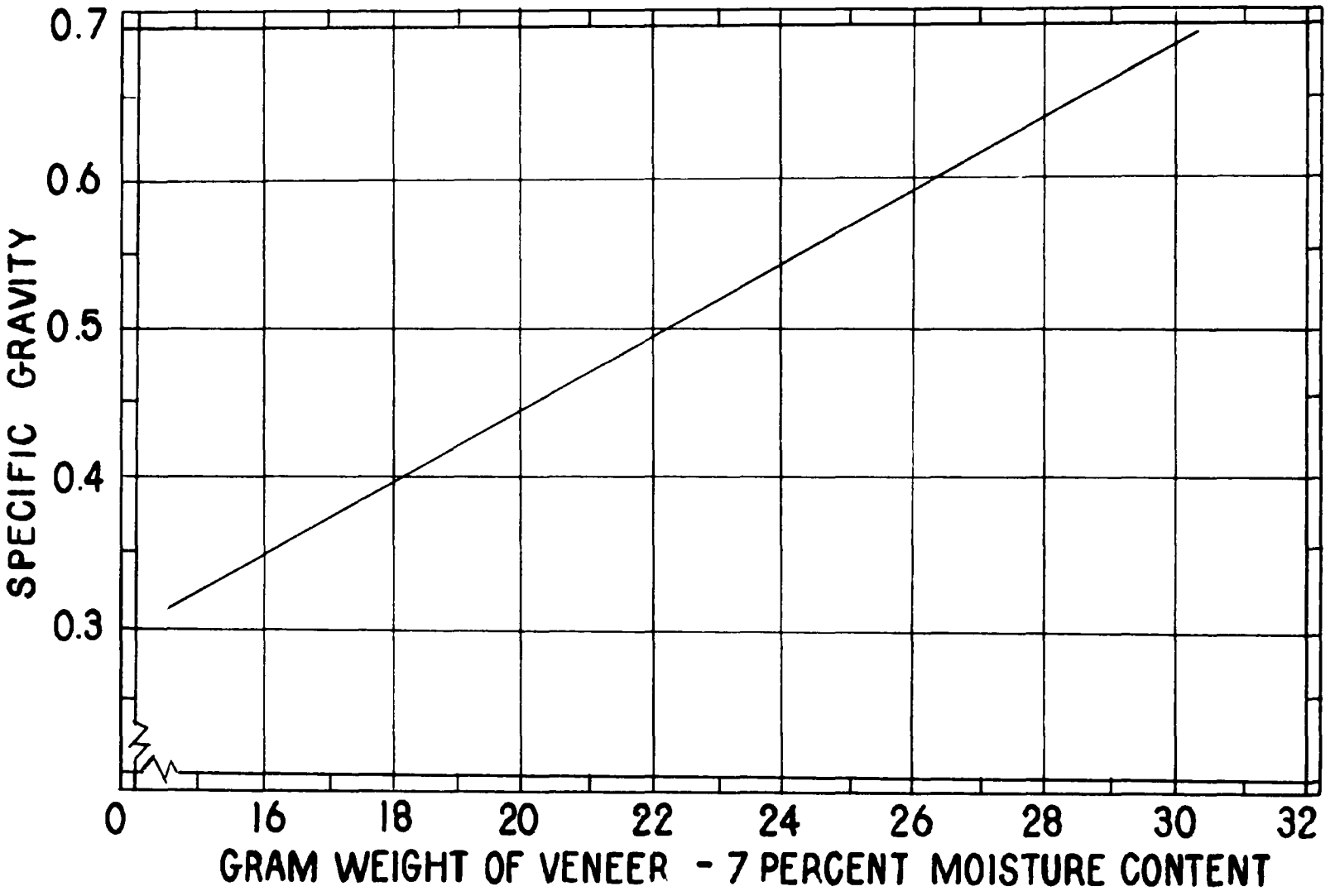


Figure 7. Relationship between specific gravity of veneer and veneer weight at seven percent moisture content.

and 32 face sheets. Each lot was made up of sheets from one specific gravity group. There were 16 such packs for each of four adhesives.

Each group of veneer was wrapped in wax paper, and the wrapped package sealed with paraffin. Two such lots were placed in moisture-proof polyethylene food bags which were then sealed. The veneer sheets wrapped in this manner were stored for later use.

Preparation of Phenolic Type Resin Adhesives

The determination of formaldehyde. The alkaline peroxide method as described by Walker (57) was used to determine the percentage of formaldehyde in a formalin solution.

The alkaline peroxide method for the determination of formaldehyde is based on the oxidation of formaldehyde by hydrogen peroxide in the presence of a measured excess of alkali. The aldehyde is converted to formic acid which is neutralized immediately by the sodium hydroxide. The amount of sodium hydroxide that reacts with the formic acid is determined by titrating the unreacted sodium hydroxide with hydrochloric acid.

The first step of formaldehyde determination consisted in placing into a flask 50 m.l. of normal sodium hydroxide and 25 m.l. of six or seven percent hydrogen peroxide. The hydrogen peroxide solution was prepared by diluting 30 percent hydrogen peroxide with distilled water. A carefully weighed sample of formalin to be analyzed was added to the flask. This mixture was agitated for about a minute and then the flask was placed in a water bath at a temperature of 60° C. and allowed to remain for five minutes. The flask was allowed to remain in the bath without heating for another five minutes; after that the mixture was allowed to cool to room temperature and titrated with normal hydrochloric acid. Six drops of bromothymol blue solution were used as the indicator. The end point was taken when the color of the solution

changed from blue to green.

A blank titration was made with 50 mm. of the normal alkali and 25 mm. of the dilute peroxide.

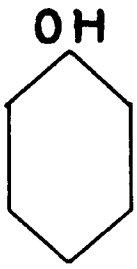
The percentage of formaldehyde in the formalin was calculated by the following equation:

$$\% \text{ formaldehyde} = \frac{(\text{blank titration} - \text{sample titration}) \times \text{normality of acid} \times 3.002}{\text{weight of formalin sample}}$$

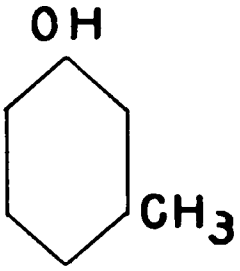
This procedure was carried out each time a new solution of formalin was used.

Initial preliminary investigations. Preliminary investigations were conducted to determine acceptable constant factors for the resins that were used in the principle part of the experiment. This research involved the preparation of resin in less than 100 gram batches which were used to examine the factors. The phenolic compounds used in the investigation included phenol, m-cresol, 3,5-dimethylphenol and m-ethylphenol. The formulas for these compounds are shown in figure 8.

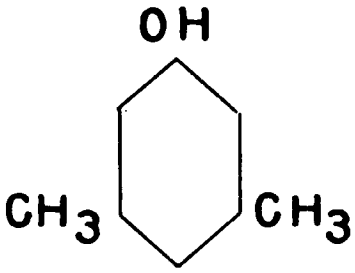
As a start in these investigations, small batches of phenol-formaldehyde resin were prepared. The phenol to formaldehyde ratio was one mole of phenol to 1.1 moles of formaldehyde and the final adjusted solids content was 50 percent. The catalyst was concentrated ammonium hydroxide used in the amount of nine percent of the weight of the phenol. This amount of catalyst produced a slow reaction between phenol and formaldehyde and was considered suitable for the resin reaction.



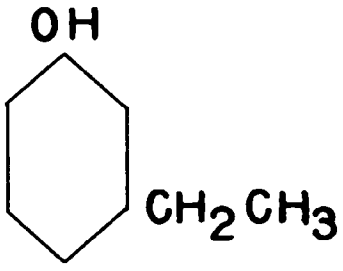
phenol
hydroxybenzene
Molecular Weight 94.111



m-cresol
1 hydroxy 3 methylbenzene
3 methylphenol
Molecular Weight 108.13



3,5-dimethylphenol
3,5-xylenol
1 hydroxy 3,5-dimethylbenzene
Molecular Weight 122.16



m-ethylphenol
1 hydroxy 3 ethylbenzene
Molecular Weight 122.16

Figure 8. Phenolic compounds used in the production of phenolic type resin adhesives for bonding Douglas fir veneer.

Six batches of phenol-formaldehyde resin with 50 percent resin solids were prepared. Reaction times for the resins were 40, 50, 60, 70, 80, and 90 minutes. For each resin the relative viscosity was determined.

Each of the six resin solutions was used to bond Douglas fir veneer into three-ply plywood panels that were tested for strength. The plywood panels were prepared and tested in the manner that will be described later. The relative viscosities and the results of the plywood strength tests are presented in the following table:

Reaction Time	Plywood Strength*	Relative Viscosity
40 minutes	204 p.s.i.	1.00
50 minutes	302 p.s.i.	1.49
60 minutes	310 p.s.i.	1.53
70 minutes	279 p.s.i.	1.59
80 minutes	263 p.s.i.	1.79
90 minutes	270 p.s.i.	1.94

* Average of eight plywood test specimens.

An examination of the work up to this point indicated that this was not the proper scheme to follow for two reasons. First, the plywood strength data obtained were considered too low. This suggested that a resin with better adhesive characteristics would have to be produced. The resin of 50 percent solids content was not of sufficient viscosity to prevent excessive penetration into the wood during the bonding operation. A considerable amount of resin was squeezed out of the glue line of the plywood panel because of the pressure applied in bonding, and also due to a temporary reduction in resin vis-

cosity caused by the heat applied to cure the resin. Second, the glycerol bath used in the preparation of the resins was not heated to a starting temperature of 115° C. before the reaction flask that contained phenol, formaldehyde, and ammonium hydroxide was immersed into it. Such a procedure contributed a large amount of variation in resin preparations created by unequal heating rates and unequal reaction times. The description of the procedures for resin reactions and dehydrations finally used in the experiment will clarify the procedure used for preparation of the phenol-formaldehyde resins of 50 percent resin solids content.

Procedure for resin preparations. For additional preliminary investigations and for final resin preparations, the procedures used for resin reactions, resin dehydrations, and viscosity determinations on the resins were the same.

The preparation of the resin consisted of two operations. The first operation was conducted using the apparatus shown in Figure 9. In this operation the required weight in grams of the phenolic compound and the formaldehyde was placed into the resin flask. The resin flask consisted of two parts as shown in Figure 10. The two parts were joined by means of ground glass flanges. The flask with the reactants was placed into the opening of the adjustable platform of the glycerol bath which had been heated previously to a temperature of 115° C.*. A stirring motor with a stirring rod, a water-cooled condenser and a

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* In the initial preliminary investigations the glycerol bath was not heated before the resin flask was immersed into the bath.

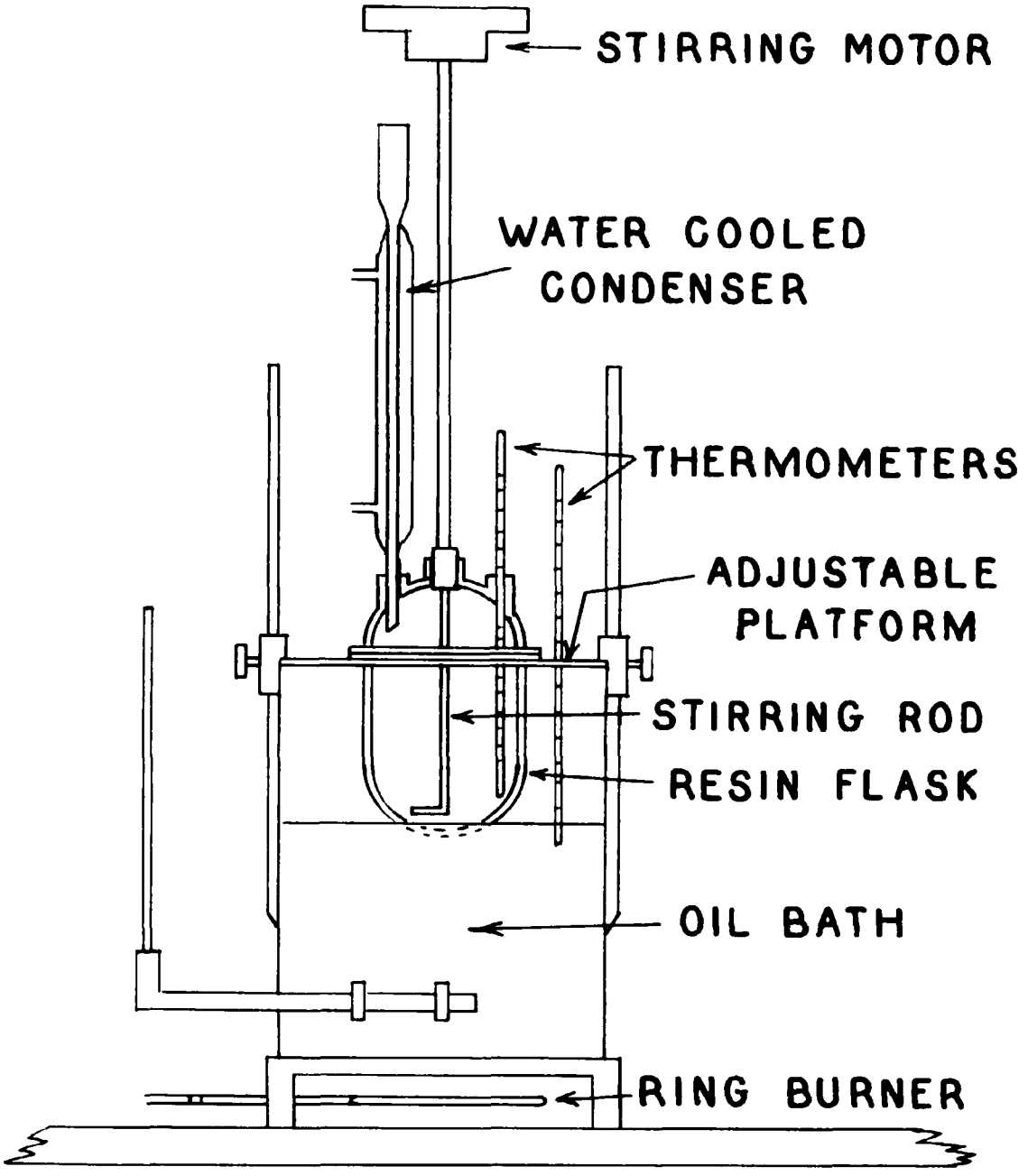


Figure 9. Diagram of the apparatus used for the resin reaction.

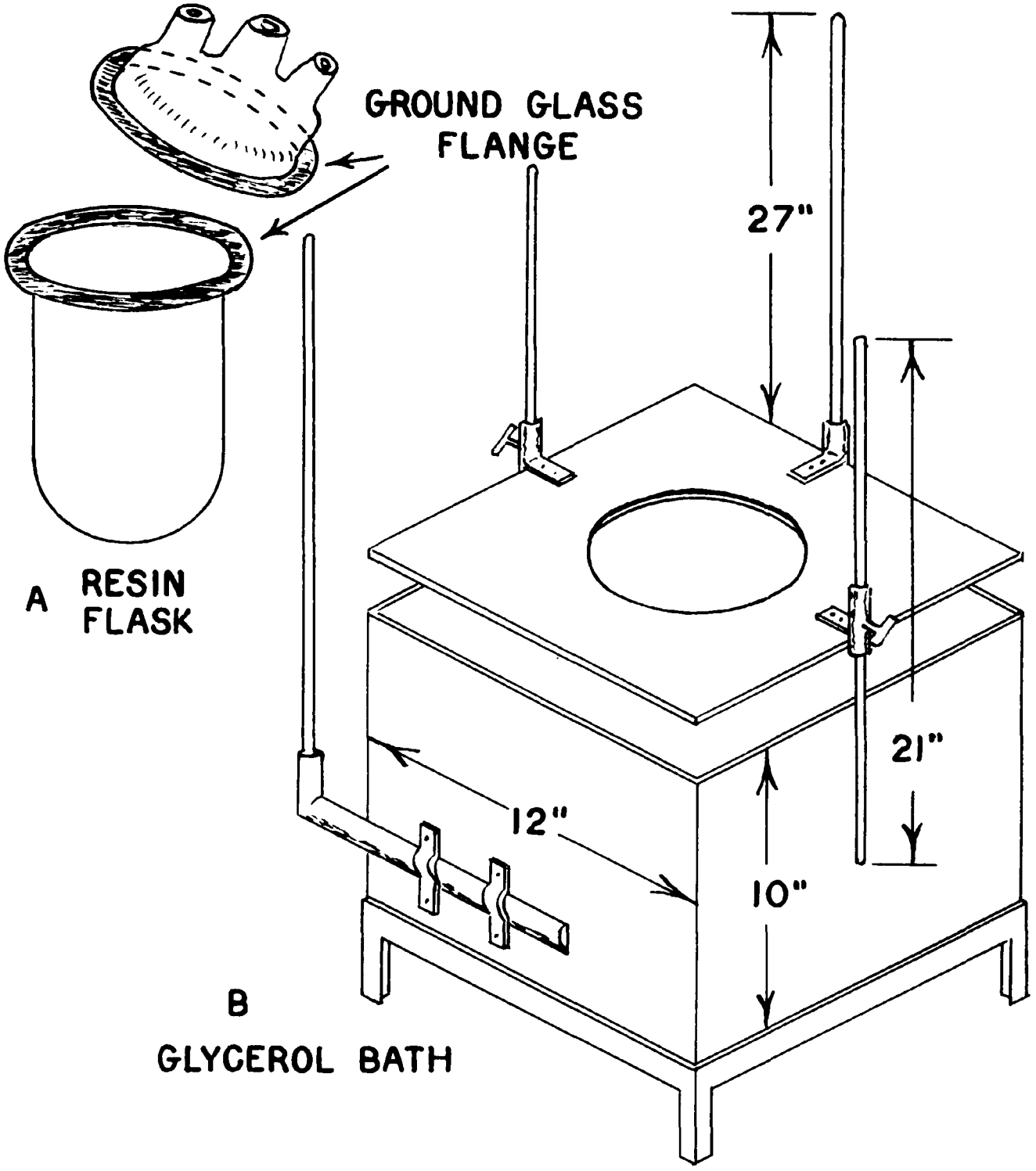


Figure 10. Details of the glycerol bath and the resin flask used in the resin reaction.

thermometer, was adjusted to the resin flask. The ammonium hydroxide catalyst in the amount of nine percent of the weight of phenol was poured into the flask. The resin flask, with stirring motor operating, was then immersed into the glycerol bath. At this point the starting time of the reaction was noted. The reaction was carried out for the desired length of time. It was also noted that the 115° C. temperature of the glycerol bath caused the temperature inside the flask to rise to 95° C. in about 15 minutes and this temperature was maintained during the resin reaction. At the end of the designated reaction time the flask was removed from the bath of glycerol and placed in a cold water bath to stop the reaction. The flask was permitted to remain in the cold water bath until it had cooled to room temperature. The ground glass flanges of the resin flask were greased to give the flask an airtight seal for the next operation, which was the dehydration process. The apparatus shown in Figure 11 was used in the dehydration operation.

The resin flask was placed in the glycerol bath once again and set up for the dehydration process. The arrangement of apparatus for dehydration is shown in Figure 11. The flask was immersed in the glycerol bath at 115° C., and the vacuum was applied until the resin in the flask had reached a temperature of 65° C. Vacuum was furnished by a water aspirator which was able to supply a vacuum of about 30 mm. of mercury. When dehydration was completed, the top of the flask was removed while the resin flask was still in the bath. About 150 ml. of a 50-50 ethyl alcohol-toluene solvent solution was poured into the

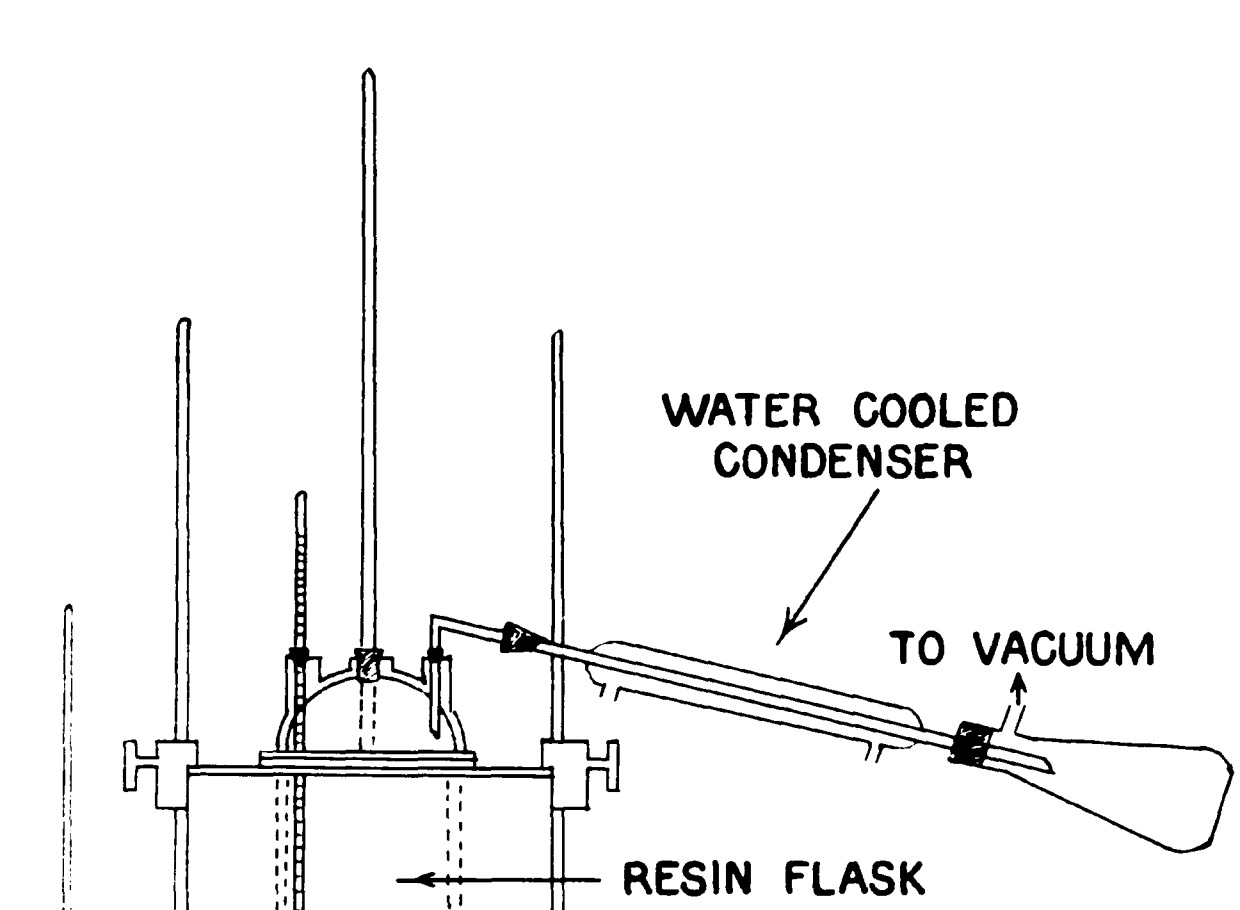


Figure 11. Diagram of the apparatus used for dehydration of the phenolic resins.

flask and stirred into the resin. Also at this time, an amount of stearic acid that corresponded to 0.65 percent of the weight of the phenol was added to neutralize the alkaline catalyst and to form ammonium stearate to act as a mold lubricant. The flask was then removed from the bath and the resin was poured into a beaker. The solids content of the resin was determined and enough of the previously mentioned solvent solution was added to bring the solids content to the desired percentage.

In making the determination of resin solids content, a weighed amount of resin was placed on a glass plate of known weight. The plate and the resin were then placed in an oven heated to 100° C. for a period of four hours. After the curing period, the cured resin and glass plate were weighed. The weight of the cured resin was divided by that of the uncured resin to obtain the percent of resin solids. The weight of solvent required to bring the solids content of the resin to the desired percent was calculated by dividing the weight of the resin solution by the solids content percentage reduced to decimals. The difference between the weight of the unadjusted resin solution and the calculated weight of the resin solution at the desired percent solids gave the weight of solvent to be added. Three determinations of resin solids content were made on each resin. The resin was then considered ready to be used as a wood adhesive.

In every case the relative viscosities of the resins were determined by means of an Ostwald viscometer. The efflux time of a 10 percent solution of a resin was found by placing 5 ml. of the resin into

the viscometer that was in a water bath regulated to a temperature of 20° C. The resin solution was allowed to stand in the viscometer until its temperature had reached the temperature of the water bath. Then the solution was pulled by vacuum through the upper bulb past the upper mark of the viscometer. The vacuum was then removed and the solution was allowed to flow by means of gravity back down through the upper bulb, from the upper mark to the lower mark on the viscometer. The time in seconds necessary for the meniscus of the solution to flow between the two marks was recorded. An average of six readings was taken as the efflux time for a resin. The efflux time was used in conjunction with the density of the resin to determine the relative viscosity of the resin.

The density of the resin was determined by using a 10 ml. specific gravity bottle, exact volume of which was calibrated by using water. The weight of the volume of a resin occupying the bottle was noted. Since the volume of the bottle was known, the density of the resin was calculated by dividing its weight by its volume.

The viscosity of the resin with respect to water was found by the relationship

$$A / B = d_1 t_1 / d_2 t_2$$

in which A represented the viscosity of the resin while d_1 and t_1 represented its density and efflux time respectively. B represented the viscosity of water while d_2 and t_2 represented the density and efflux time for water. The viscosity of the 90-10 ethyl alcohol-toluene solvent solution was determined as described for the resin. A

final viscosity figure for each resin, as compared to the solvent, was obtained by the relationship

$$\text{relative viscosity} = \frac{\text{viscosity of resin}}{\text{viscosity of solvent.}}$$

Additional preliminary investigations. Small batches of phenol-formaldehyde resin and m-cresol-formaldehyde resin were prepared for further preliminary study. A phenol-formaldehyde ratio of one mole of phenol or m-cresol to 1.5 moles of formaldehyde was used. The adjusted solids content was 65 percent. These resins were used to bond plywood panels. The viscosity was determined for all phenol-formaldehyde resins and m-cresol-formaldehyde resins. The results of the tests are shown in Table IV. The 90 minute phenol-formaldehyde resin and the 40 minute m-cresol-formaldehyde resin appear to give the best results.

In preparing the cresol resins, somewhat larger quantities were prepared in order to investigate several factors.

Portions of the 15, 20, 25 and 30 minute m-cresol-formaldehyde resins were adjusted to various solids content and then used to bond plywood panels. The panels were tested for plywood strength. The results shown in the following table were obtained:

Reaction Time	Solids Content			
	50%	55%	60%	65%
15	315*	313*	285*	320*
20	300*	304*	271*	332*
25	310*	297*	330*	334*
30	319*	303*	316*	338*

* Average of seven plywood test specimens in p.s.i.

From these results, it appeared that a 65 percent solids content should be used in the experiment. The results for the resin of 65 per-

cent solids content seemed to be generally somewhat higher than data for the other solids contents.

It was decided to use an adhesive spread of 40 pounds per 1,000 square feet in bonding plywood. In order to see if this spread could be reduced, plywood was bonded with various resin spreads. A 30 minute m-cresol-formaldehyde resin was used for this investigation. Two panels were bonded and tested for each different spread. Information shown in Table III was obtained.

These results suggested that a spread of 40 pounds per 1,000 square feet was a satisfactory spread.

The relationship between the molecular weight of a phenolic compound and the number of phenolic rings in a resin spread was then investigated. A phenol-formaldehyde resin of 63 percent solids content, spread in the amount of 2.5 grams per 20 square inch glue line area, was considered to supply a certain number of phenolic rings. Due to a greater molecular weight of m-cresol, caused by a methyl group side chain, equal weights of phenol-formaldehyde resin and m-cresol-formaldehyde resin would have a different number of phenolic rings. It was theorized that the m-cresol-formaldehyde resin in this case had a fewer number of phenolic rings in the resin spread and therefore was unable to form as many crosslinks between molecules as was possible for the phenol-formaldehyde resin. It was further thought that if the number of phenolic rings in the m-cresol-formaldehyde resin was increased by using a greater solids content of resin, the m-cresol-formaldehyde resin would possibly produce plywood of greater strength than shown in Table IV. The following calculation was performed to determine the

TABLE III

DATA ON RESIN SPREAD FOR THIRTY MINUTE
m-CRESOL-FORMALDEHYDE RESIN ADHESIVE

Spread	Plywood Strength*
1.6 grams per glue line (25# / 1,000 sq. ft.)	320 p.s.i.
1.9 grams per glue line (30# / 1,000 sq. ft.)	329 p.s.i.
2.2 grams per glue line (35# / 1,000 sq. ft.)	329 p.s.i.
2.5 grams per glue line (40# / 1,000 sq. ft.)	339 p.s.i.

* Average of eight plywood test specimens.

TABLE IV

DATA ON SMALL BATCHES OF PHENOL- AND m-CRESOL-FORMALDEHYDE RESINS

Resin	Reaction Time	Plywood Strength*	Relative Viscosity
phenol-formaldehyde	50 minutes	337 p.s.i.	1.84
	60 minutes	327 p.s.i.	1.87
	70 minutes	345 p.s.i.	2.00
	80 minutes	355 p.s.i.	2.03
	90 minutes**	368 p.s.i.	2.21
	100 minutes	366 p.s.i.	2.38
m-cresol-formaldehyde	15 minutes	320 p.s.i.	2.26
	20 minutes	332 p.s.i.	2.27
	25 minutes	334 p.s.i.	2.28
	30 minutes	338 p.s.i.	2.30
	35 minutes	348 p.s.i.	2.32
	40 minutes**	351 p.s.i.	2.35

* Average of seven shear specimens.
** Apparent best resin to use.

TABLE V

DATA ON SMALL BATCHES OF 3,5-DIMETHYLPHENOL- AND m-ETHYLPHENOL-FORMALDEHYDE RESINS

Resin	Reaction Time	Plywood Strength*	Relative Viscosity
3,5-dimethylphenol-formaldehyde	40 minutes	297 p.s.i.	2.14
	45 minutes**	325 p.s.i.	2.18
	50 minutes	317 p.s.i.	2.21
	55 minutes	284 p.s.i.	2.26
m-ethylphenol-formaldehyde	50 minutes	296 p.s.i.	2.15
	55 minutes	293 p.s.i.	2.18
	60 minutes	307 p.s.i.	2.22
	70 minutes**	311 p.s.i.	2.30

* Average of seven test specimens.
** Apparent best resin.

required solids content for the m-cresol-formaldehyde resin:

$$94.11 / 108.13 = 0.65 / x$$

$$x = 0.747 \text{ or } 75\% \text{ solids}$$

Two plywood panels each were bonded with the 15 minute, 20 minute, 25 minute and the 40 minute m-cresol-formaldehyde resin. These panels were tested for plywood strength. The results of these strength tests indicated that there was no basis for strength differences due to the possibility of a greater number of phenolic rings in one resin spread as compared with another. Furthermore, the 75 percent resin solids solutions were extremely difficult to spread because of their high viscosities.

Small batches of 3,5-dimethylphenol-formaldehyde resin and m-ethylphenol-formaldehyde resin were prepared and these resins were used to bond plywood panels. The plywood panels were tested for strength. The results of these tests are shown in Table V.

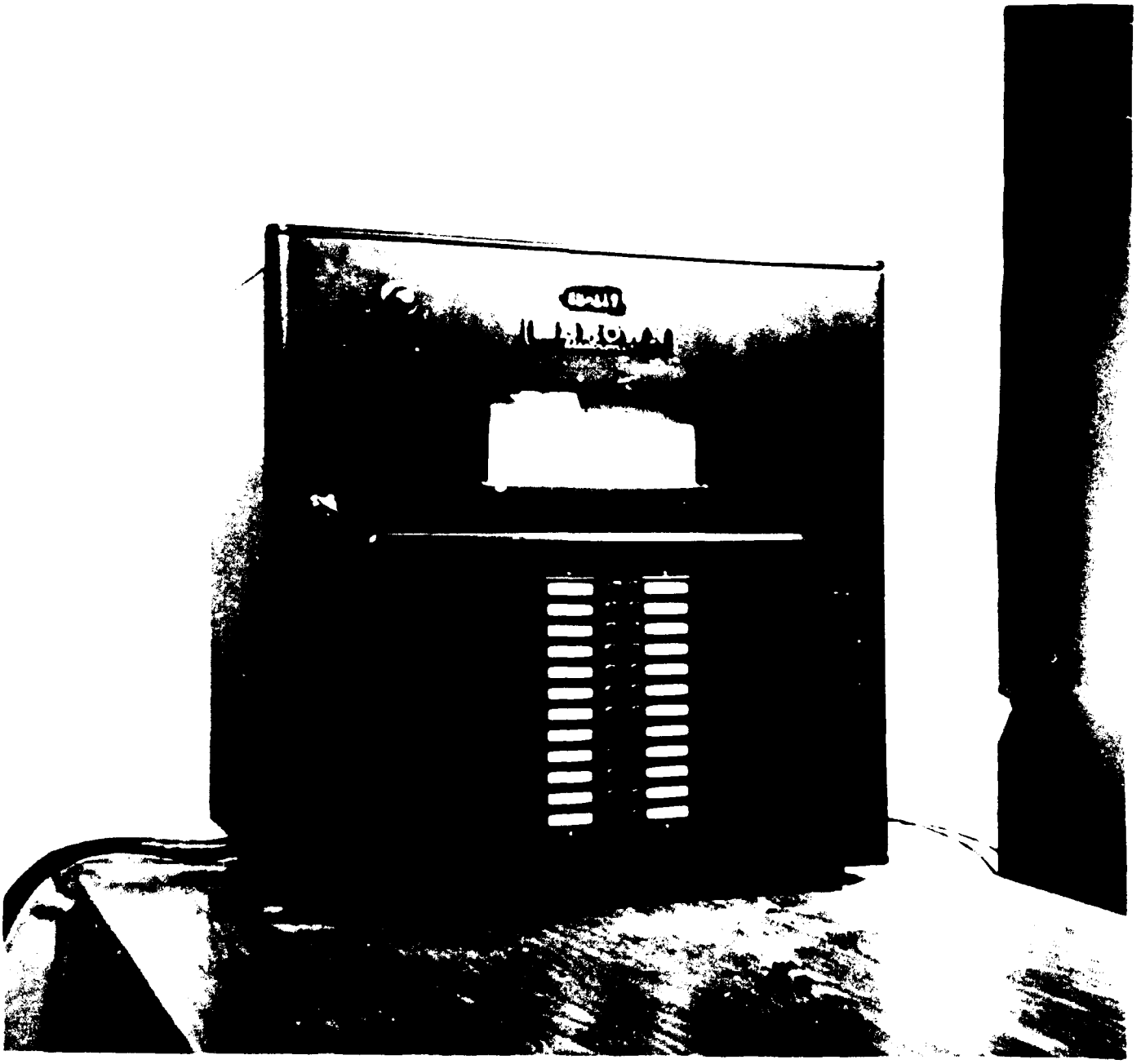
The small batches of all resins had been prepared and these resins had been used to bond plywood panels that had been tested for strength. It had been decided initially that the highest plywood strength value shown by any resin batch for any one of the resins would indicate which reaction times were most suitable to use in the experiment. However, it appeared that this particular procedure was sort of a try this, try that affair. Consequently, it was decided to find some other way for determining comparable reaction times for the resins.

It had been noted during resin preparations that each of the resins became turbid at particular times; the phenol-formaldehyde resin

assumed turbidity in about 6) minutes, the m-cresol-formaldehyde resin indicated turbidity in about 12 minutes, the 3,5-dimethylphenol-formaldehyde resin became turbid in about seven minutes, while the m-ethylphenol-formaldehyde resin showed turbidity in about six minutes. With this information, supported by the account of the work of Megson as described in a previous chapter of the thesis, it was decided to use turbidity times as a basis for determining comparable reaction times for the resins. Turbidity time has been referred to as resinification time by Megson (31). Resinification time has been defined as the time taken from initial heating of clear resin solutions to the appearance of permanent turbidity.

In order to use turbidity time as a basis for finding comparable reaction times for the resins, an observable point after the point of turbidity had to be found. To find such a point, large test tube batches of phenol-formaldehyde resin were prepared. A phenol to formaldehyde ratio of 1 to 1.5 was used. The formalin solution was 40 percent formaldehyde. Ammonium hydroxide catalyst was added in the amount of nine percent of the weight of the phenol. During the reaction the test tube was stirred with a stirring motor and a stirring rod that was brought to the same depth into the test tube each time. The test tube was heated by means of an oil bath that was heat-controlled by what is an electronic temperature control which maintained a temperature of 95° C. inside the test tube during the reaction. The temperature inside the test tube was observed by means of a Brown electronik potentiometer as shown in Figure 11. The reactants and catalyst were

Figure 12. The potentiometer used in the experiment for the determination of temperatures.



weighed accurately for each resin batch. The test tube was immersed into the oil bath and the starting time was noted. During the reaction the resin was agitated by means of the stirring rod and the time it took for it to reach the point of turbidity was recorded. The reaction was carried into the B stage of hardening until the resin became viscous enough to wind up on the stirring rod. At this point the reaction was stopped and the time was recorded. This point was designated as point Y in the B stage of hardening and was considered to be a point at which the resins reached equal viscosities. The average of turbidity time for a phenol-formaldehyde resin to reach point Y, and the difference of these average times are shown in Table VI. As shown in Table VI, the same procedure was carried out on the other resins used in the experiment.

As a basis for the use of these data, the phenol-formaldehyde resin that had given the most satisfactory plywood strength results was selected. The reaction time for this resin was 90 minutes, as shown in Table IV. The difference between turbidity time of 69 minutes and the reaction time of 90 minutes was 21 minutes. The time for the phenol-formaldehyde resin reaction to reach point Y was recorded as 115.2 minutes, which gave a time of 46.2 minutes between the average turbidity time of 69 minutes and the Y time of 115.2 minutes. Then 21 divided by 46 represented a percentage of the reaction time from turbidity to point Y for phenol-formaldehyde resin. This percentage was then applied to the difference between turbidity time and Y time for the other resins. The difference between turbidity time for the m-cresol-formaldehyde resin

TABLE VI

RESINIFICATION AND HARDENING DATA

Resin	Average Turbidity Time (minutes)	Time to Reach Stage Y (minutes)	Time Difference (minutes)
phenol-formaldehyde	69.0	115.2	46.2
m-cresol-formaldehyde	12.3	64.1	51.8
3,5-dimethylphenol-formaldehyde	6.9	86.1	79.2
m-ethylphenol-formaldehyde	5.8	114.8	109.0

Calculations for Reaction Times

90 minutes = Reaction time for phenol-formaldehyde resin.

90-69 = 21.0 Minutes between time for turbidity and reaction time for phenol-formaldehyde resin.

51.8/46.2 = 1.12 Ratio difference of m-cresol-formaldehyde resin and phenol-formaldehyde resin.

1.12 x 21.0 = 23.5 Reaction time after turbidity for m-cresol-formaldehyde resin.

23.5 + 12.3 = 35.8 Reaction time for m-cresol-formaldehyde resin.

Calculations for 3,5-dimethylphenol-formaldehyde Resin and for m-ethylphenol-formaldehyde Resin

79.2/46.2 = 1.71; 1.71 x 21.0 = 35.7

35.7 + 6.9 = 42.6 or 43 Minutes reaction time for 3,5-dimethylphenol-formaldehyde resin.

109.0/46.2 = 2.36; 2.36 x 21.0 = 49.56

49.6 + 5.5 = 55.1 or 55 Minutes reaction time for m-ethylphenol-formaldehyde resin.

and point Y for this resin was 51.0 minutes. The fraction 21 divided by 46 times 51.0 gave a period of 23.5 minutes for the m-cresol-formaldehyde resin to be reacted after turbidity. Since the turbidity time for the m-cresol-formaldehyde resin was 12.3 minutes, the reaction time to produce a comparable resin was 23.5 plus 12.3 or 36 minutes. The m-cresol-formaldehyde resin for the final gluing problem was reacted for 36 minutes. The other resins were treated the same way to give a reaction time of 43 minutes for the 3,5-dimethylphenol-formaldehyde resin, and 56 minutes for the m-ethylphenol-formaldehyde resin. This procedure was based on the assumption that when the resins had reached point Y they had approximately the same viscosity.

Using the calculated reaction times as indicated above, the final resins were prepared.

Resin adhesives for the main part of the experiment. The resin adhesives for the main part of the experiment were prepared in the same manner as that used for the resins of 65 percent resin solids content in the preliminary investigations. This procedure has been described. Each final resin was prepared in four batch lots of about 450 grams of resin per lot. The same procedure was used to prepare each lot of a particular resin and the lots were mixed to produce a final resin quantity of about 1,800 grams of resin for each resin used in the experiment. By preparing four batches of each resin, an average solution resulted for each type used in the experiment. This particular procedure provided a resin in each case that could be reproduced satisfactorily. It also provided the means of producing 1,800 grams of

resin more easily than would have been the case if the entire quantity of resin had been produced at one time. The resin flasks available were not considered of sufficient size to produce 1,600 grams of resin satisfactorily.

The following conditions for resin manufacture, as determined in the preliminary investigations, were adhered to in the main part of the experiment. A phenol to formaldehyde ratio of one mole of phenol, or of an alkyl-substituted phenol, to 1.5 moles of formaldehyde was used. In all cases concentrated ammonium hydroxide catalyst was used in the amount of nine percent of the weight of phenol so that the quantity of catalyst used was the same for all resins produced. In all cases the weight of stearic acid added at the end of the dehydration period was the same. This amounted to 0.65 percent of the weight of phenol. The reaction time for the various resins was determined by the preliminary resinification and hardening investigation. The periods used were 90 minutes, 36 minutes, 45 minutes, and 55 minutes for the phenol-formaldehyde resin, m-cresol-formaldehyde resin, 3,5-dimethylphenol-formaldehyde resin, and m-ethylphenol-formaldehyde resin, respectively. All resins were adjusted to a final solids content of 65 percent.

Supplemental investigations. As supplemental investigations, two experiments were carried out.

The first supplemental investigation concerned the effect of using methyl alcohol instead of ethyl alcohol in the 90-10 alcohol-toluene solvent solution. It is known that methyl alcohol has a greater vapor pressure than ethyl alcohol. In theory, the greater vapor pressure of

methyl alcohol, when used in the solvent solution, could cause a more rapid evaporation and diffusion of solvent from resin spread on Douglas fir veneer during the open assembly period*. If the theory were valid the use of methyl alcohol instead of ethyl alcohol would reduce the time required for open assembly and optimum plywood strength could be obtained in this shorter period.

In order to test the validity of the theory, about 100 grams of dehydrated phenol-formaldehyde resin were removed from the resin flask when the first batch of this resin was prepared for the final experimental phases of the principle investigation. The 100 grams of resin were adjusted to 65 percent solids content using a 90-10 methyl alcohol-toluene solvent solution. The resin was then used to spread enough Douglas fir veneer to make eight plywood panels. The veneer for each panel was subjected to a different open assembly period. These periods ranged from four hours to 30 hours at intervals of four hours. As each time period elapsed the panel was bonded, then placed in an oven for 24 hours to assure complete cure of the resin. At the end of the required time period in the oven, each panel was sawed into shear specimens and the specimens were tested. The results of these tests were compared with results obtained by using a similar procedure but substituting ethyl alcohol as the alcohol component of the solvent solution. Approximately the same plywood strengths were observed in both cases,

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* The open assembly period refers to the time between spreading an adhesive on pieces of wood and bonding these pieces of wood, during which time the spread wood surfaces are allowed to remain spread surface up to the surrounding atmosphere.

indicating that methyl alcohol and ethyl alcohol could be interchanged but neither one nor the other made any appreciable difference in the open assembly period required for bonding plywood in this experiment.

The second supplemental investigation was carried out by preparing two batches of o-cresol-formaldehyde resin. One of the resin batches was reacted for a period of two hours and then dehydrated. The second batch was reacted for two and one-half hours and then dehydrated. In both cases the dehydrated resins had very low viscosities and gave off very strong formaldehyde fumes. The latter characteristic indicated that a large proportion of formaldehyde had not reacted. The resins could not be used to bond plywood. It was assumed that p-cresol-formaldehyde resin would act the same as the o-cresol-formaldehyde resin and p-cresol-formaldehyde resins were not prepared.

Fabrication of Douglas Fir Plywood

The resin adhesives were stored under refrigerated conditions until veneer had been processed for bonding. Resins were prepared one at a time and only the veneer required to glue the necessary number of plywood panels in relation to one resin was prepared for bonding. The time between preparing the resin and using it for bonding veneer was 96 hours for the individual resins, this amount of time being required to determine the open assembly time to use in bonding the plywood and to prepare the veneer.

The optimum open assembly period was determined for each resin used in the experiment. As an example of the method used for all resins the procedure followed in the case of phenol-formaldehyde resin will be presented. Five open assembly times were considered. These were two hours, four hours, eight hours, 16 hours and 24 hours. Two plywood panels, representing eight plywood test specimens, for each period were tested for strength. The average plywood strength results were found to be as follows:

2 hour period	292 p.s.i.
4 hour period	339 p.s.i.
8 hour period	333 p.s.i.
16 hour period	324 p.s.i.
24 hour period	359 p.s.i.

The results obtained in this investigation indicated that a 24

hour open assembly should be used for the phenol-formaldehyde resin. Similar results were obtained for the other resins. Consequently, a 24 hour open assembly was used for all resins.

The veneer to be glued was first removed from its protective wrappings. The veneer sheets were hand sanded lightly, using 3/0 open coat garnet finishing paper. The amount of sanding was controlled by using 10 sanding strokes on each sheet. The purpose of the sanding was to remove oily, waxy, or gummy substances from the sheets, to freshen the surface, and to reduce grain ridges on the sheet surfaces. Since sanding tended to occlude the openings in the wood surfaces, compressed air was used to remove loose wood-dust and wood particles. The sheets were then placed into three-ply assemblies in such a way that lathe checks in the core were oriented properly. Lathe checks are fine checks or cracks on the under surface of veneer, developed by the rotary lathe knife as it cuts the veneer.

Experimental evidence has shown that the strength of plywood is affected by the orientation of lathe checks in the core ply. It was found by Bethel and Huffman (9) that plywood shear specimens could be tested in two ways: 1) specimens could be pulled open, which would open lathe checks, or 2) specimens could be pulled closed which would tend to close lathe checks. Figure 13 shows how orientation of lathe checks in relation to plywood shear specimen notches will cause lathe checks either to be opened or to be closed during plywood shear tests.

When shear specimens are pulled open, the principle component of force, pulling the specimen apart, acts at right angles to the lathe

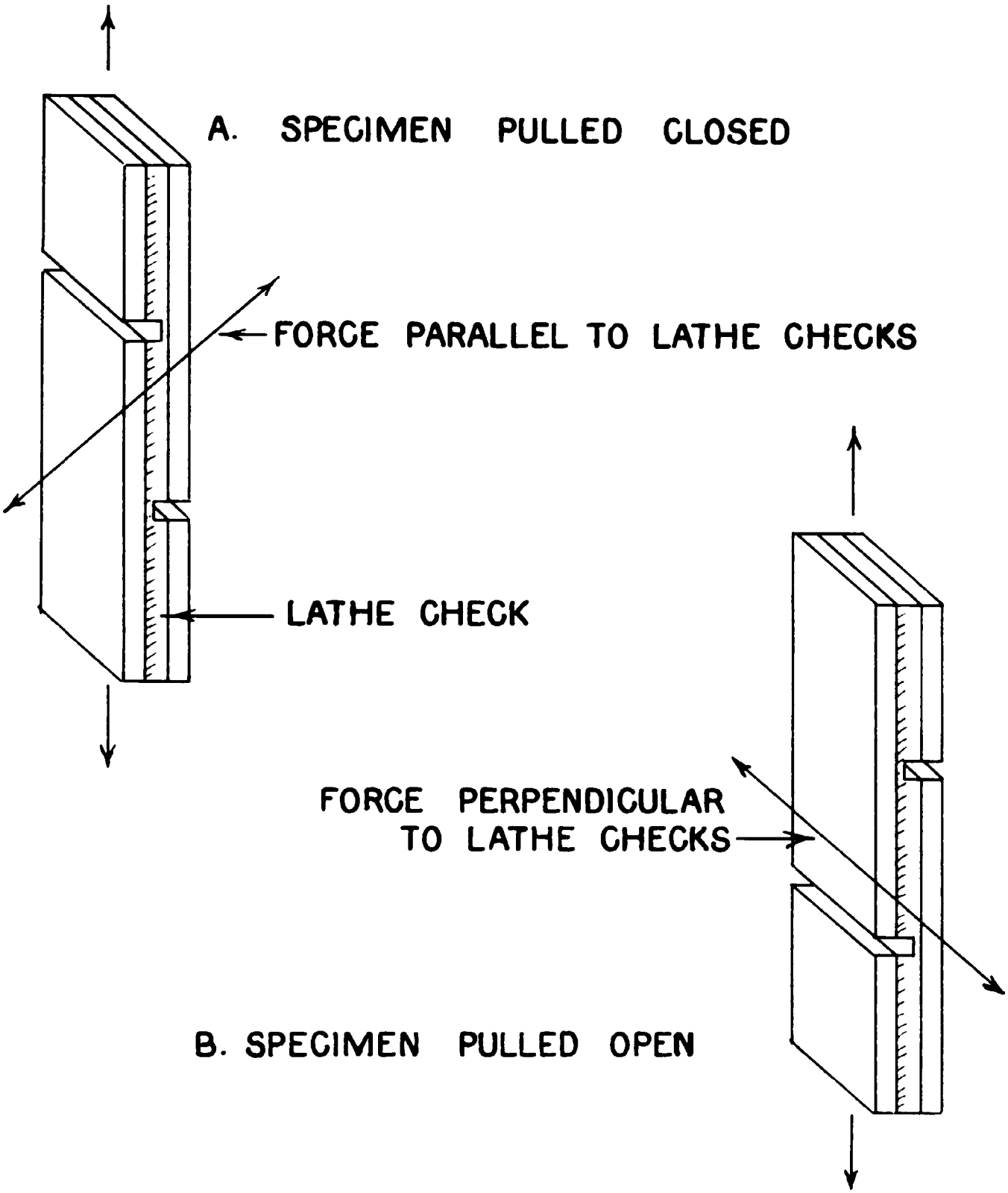


Figure 13. Types of pull in plywood shear test specimens as related to lathe check orientation.

A. Notches in the specimen oriented so that lathe checks remain closed during the shear test.

B. Notches in the specimen oriented so that lathe checks are pulled open during the shear test.

checks and the failure of the specimen results from opening up these checks. It appears that the beginning of failure is the result of a series of elevated stresses which cause the fibers of wood between lathe checks to roll out, producing the type of shear failure known as rolling shear. When shear specimens are pulled so that lathe checks are not opened during testing, the forces acting on the specimens are parallel to the lathe checks and the stresses set up are more nearly true shearing stresses. A significant increase in specimen strength was noted when specimens were tested with lathe checks oriented with the notches in the specimen so that the pulling forces did not tend to open the checks.

The three plies were placed with their open surfaces toward the core ply. The three-ply assemblies were numbered to identify the bonded Douglas-fir panels and to identify plywood test specimens which were to be tested later. After pressing, the sheets were placed in polyethylene bags to avoid moisture loss.

The hand application involved first the spreading of adhesive on the open surfaces of the face plies of the three-ply assemblies. A spread of 40 pounds per 1,000 square feet of gluing area was selected for the unmodified 33 percent resin solution. This spread was reduced to a figure that gave the number of grams of resin solution per veneer sheet by the following simple calculation:

40 pounds per 1,000 square feet

.040 pounds per square foot

.040 x 453.6 = 18.14 grams per square foot

Gluing area = 4 x 5 = 20 square inches and 20 / 144 = 0.139 square feet

Then 1 / 16.14 = 0.139 / X

X = 2.5 grams per gluing area.

For parts of the problem that did not require the addition of walnut shell flour, the spread per face veneer sheet was 2.5 grams of resin solution.

For the experimental phases of the problem that required the addition of walnut shell flour to the resin, the number of grams of resin solution per face veneer was calculated as follows:

For the addition of 10 percent walnut shell flour.

2.5 grams x 0.65 = 1.63 grams of resin solids in the unmodified resin spread

1.63 grams x 0.10 = 0.16 grams of walnut shell flour added for the spread on each face veneer

2.50 + 0.16 = 2.66 grams of resin solution with 10 percent walnut shell flour spread per face veneer.

For the addition of 20 percent walnut shell flour.

2.5 grams x 0.65 = 1.63 grams

1.63 grams x 0.20 = 0.33 grams

2.50 + 0.33 = 2.83 grams of resin solution with 20 percent walnut shell flour spread per face veneer.

For the addition of 30 percent walnut shell flour.

2.50 + 0.49 = 2.99 grams of resin solution spread per face veneer.

It is noted that the percentage of walnut shell flour added to the resin solution was based on the resin solids content of the solution. The increased spread for resins to which walnut shell flour had been

added had as its purpose the maintenance of constant resin solids and constant solvent proportions. This technic permitted only variation in the quantity of walnut shell flour, which was the desired effect.

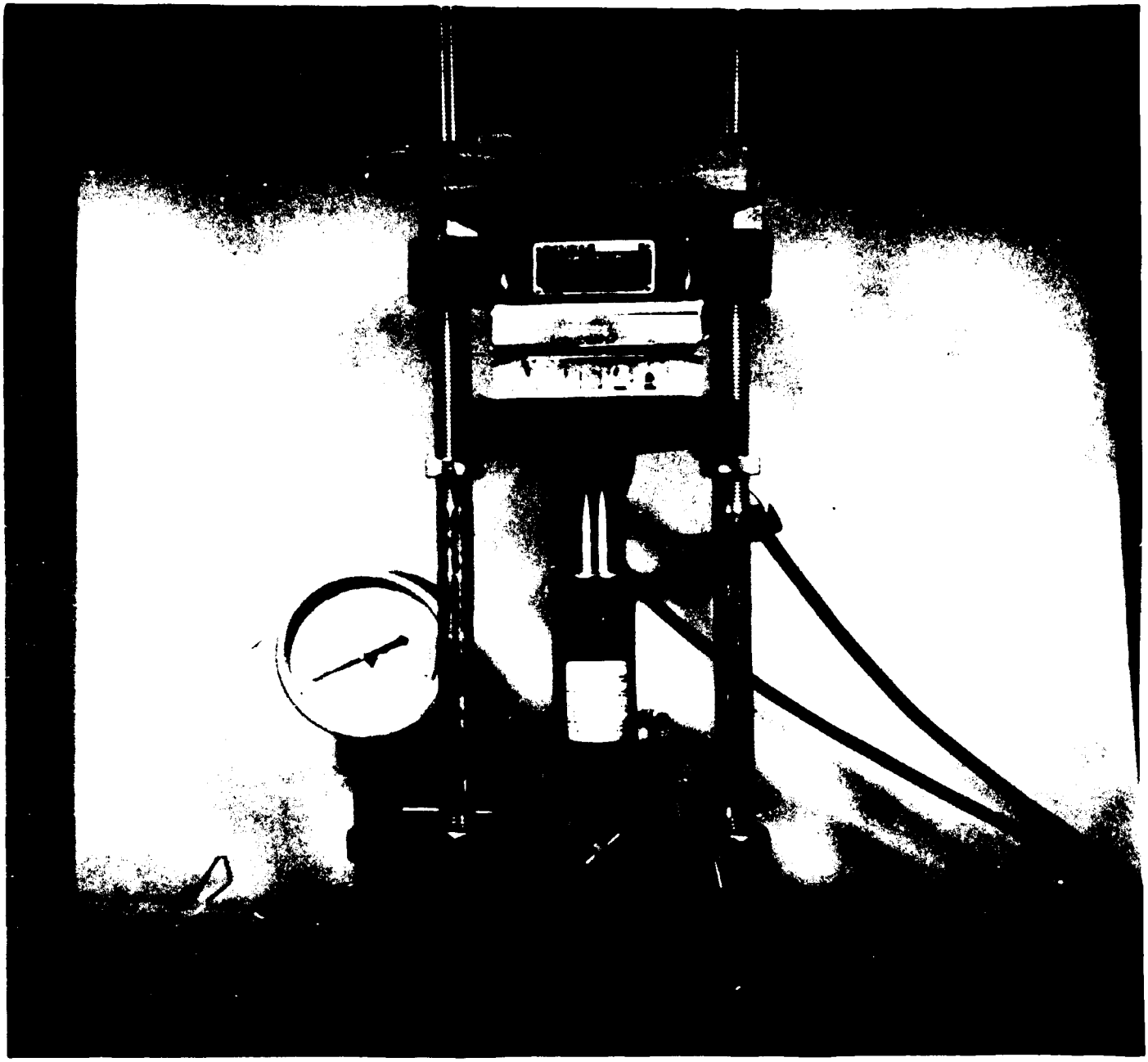
It was noted that the moisture content of the veneer dropped from seven percent to five percent during open assembly, which is considered to be a more desirable moisture content for bonding wood with phenolic type resin adhesives.

The actual bonding of the veneer was accomplished by using a Carver Laboratory Press with electrically heated hot plate platens. This press is shown in Figure 14. The temperature, which was 320° F., was controlled by thermostats inserted in the plates of the press. This temperature could be controlled to plus or minus five degrees, which was much closer control than would be found in a commercial plywood press. Temperature of the plates was monitored by the Brown electronik potentiometer shown in Figure 12.

The pressure used on bonding panels was 175 pounds per square inch. Pressing time was 15 minutes. After a panel had been removed from the press it was placed in an electric oven which had a controlled temperature of 75° C. in order to completely cure the resin adhesive.

Preliminary bonding tests of plywood indicated that 15 minutes in the press was not sufficient time to completely cure any of the resins. These tests involved an empirical procedure in which two plywood panels were bonded for each of six bonding times. Bonding times were 12, 15, 18, 21, 24 and 30 minutes. Plywood shear specimens from these panels were sawed, soaked in water for 48 hours, and tested. The tests showed

Figure 14. The hot press used in the experiment for bonding plywood panels.



that bonding times from 12 to 30 minutes caused an increase in plywood strength, the 30 minute bonding time giving the highest strength. The results of these tests are shown in the following table:

Curing Time* (minutes)	Plywood Shear Strength** (p.s.i.)
12	190
15	213
18	225
21	246
24	285
30	294

* Minutes in a hot press at 320° F.

** Average of eight plywood shear specimens.

In view of the large number of panels bonded in this investigation, a 30 or more minute bonding time was not convenient. Furthermore the test values obtained indicated that the resin was not completely cured.

Consequently additional tests were conducted to determine what length of time in an electric oven at 75° C. would be necessary, after a 15 minute press time, to completely cure the adhesive in the glue bond. The results of the tests indicated that the length of time the panels should remain in the oven varied with the resin used. As the basis for the determination of oven time, phenol-formaldehyde resin was used to bond plywood. The data obtained from shear specimens prepared from this plywood are shown in the following table:

Curing Time≠ (hours)	Plywood Shear Strength≠ (p.s.i.)
6	270
10	295
14	320
18	334
24	351
48	348

≠ Time period in an electric oven at 75° C. after 15 minutes pressing time in a hot press at 320° F.

≠ Average of eight plywood shear specimens.

The data for the phenol-formaldehyde resin bonded plywood indicated that 24 hours in the oven after a 15 minute press time was the apparent best time. In order to determine oven times for the other three resins, stroke cure tests* were conducted to determine cure time for the resins. Cure ratios were calculated for three resins, using the stroke cure time and best oven time for phenol-formaldehyde resin as a basis. The ratios were used to determine oven cure time. Oven time for m-cresol-formaldehyde resin was determined as follows:

Stroke cure time for phenol-formaldehyde resin, 105.0 seconds; stroke cure time for m-cresol-formaldehyde resin, 122.9 seconds.

Cure ratio = 122.9 / 105.0 = 1.17

Oven time = 1.17 x 24 = 28.08 or 28.1 hours

Stroke cure time, curing ratio, and oven time for all resins are shown in the following table:

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* The stroke cure test involves the curing of a small weighed quantity of resin on a hot plate at a particular temperature. The resin is stroked with a spatula in a two and one-half inch square area until cured. If constant conditions of weight of resin and temperature are maintained, stroke cure time of different resins can be compared.

Resin	Stroke Cure Time* (seconds)	Curing Ratio**	Required Time in Oven*** (hours)
phenol-formaldehyde	105.0	1.00	24.0
m-cresol-formaldehyde	122.9	1.17	28.1
3,5-dimethylphenol-formaldehyde	140.2	1.34	32.2
m-ethylphenol-formaldehyde	156.8	1.49	35.8

* Resins cured on a hot plate regulated to 320° F.

** Stroke cure time of phenol-formaldehyde resin divided into the stroke cure time for other resins.

*** Curing ratio of resins multiplied by 24 hours to give required curing time in the oven at 75° C.

As indicated in the above table, 24 hours were required to cure the glue bond in panels bonded with phenol-formaldehyde resin, 28 hours were used for the m-cresol-formaldehyde resin bonded panels, 32 hours was the time to cure the glue in panels bonded with 3,5-dimethylphenol-formaldehyde resin, and the panels bonded with m-ethylphenol-formaldehyde resin required a period of 36 hours.

It was necessary to be certain that all resins were completely cured for two reasons. First, the plywood test specimens were to be given a 48 hour soak in cold water before testing to reduce variability in plywood test results. Second, the objective of using the time factor was to try to determine whether or not the strength of the completely cured glue bond increased with time, since an increase might indicate that a conditioning period was required for glued plywood to allow additional adhesion between the glue and the wood.

After the curing period in the oven, the plywood panels were stacked without special means being used to control moisture content since each plywood test specimen would be soaked for the 48 hour period in water.

In order to examine some physical characteristics such as hardness, toughness, and crazing of the resins, resin films for each resin were cured on glass plates. Both unmodified and walnut shell flour filled resin films were examined. Characteristics observed for resin films will be referred to later in this thesis.

Preparation and Testing of Plywood Shear Specimens

The plywood panels were sawed with a special veneer and plywood saw into test specimens one inch wide and three and one-quarter inches long. Two notches were cut into the specimen, one on either side, so that a one square inch shear area remained in the center of the test specimen.

Figure 15 indicates the procedure used in bonding and sawing plywood panels into test specimens. At the top of the figure is shown three pieces of veneer with the grain direction of the face plies at right angles to the grain direction of the core-ply. These pieces of veneer are bonded together into a three-ply plywood panel. From this plywood panel four plywood test specimens are sawed. The test specimens show the position of the notches and the one square inch of shear area.

There were 192 panels for each resin adhesive, from which 768 test specimens were obtained. The panels were numbered from one to 192. Each panel, and subsequently each test specimen, was also marked with the letter P, C, X or E to indicate that it was bonded with phenol-formaldehyde, m-cresol-formaldehyde, 3,5-dimethylphenol-formaldehyde or m-ethylphenol-formaldehyde resin, respectively.

After sawing and marking the test specimens they were placed in a wire basket, and the basket was suspended in cold water for 48 hours. After this, the specimens were tested with a Riehle Plywood Testing

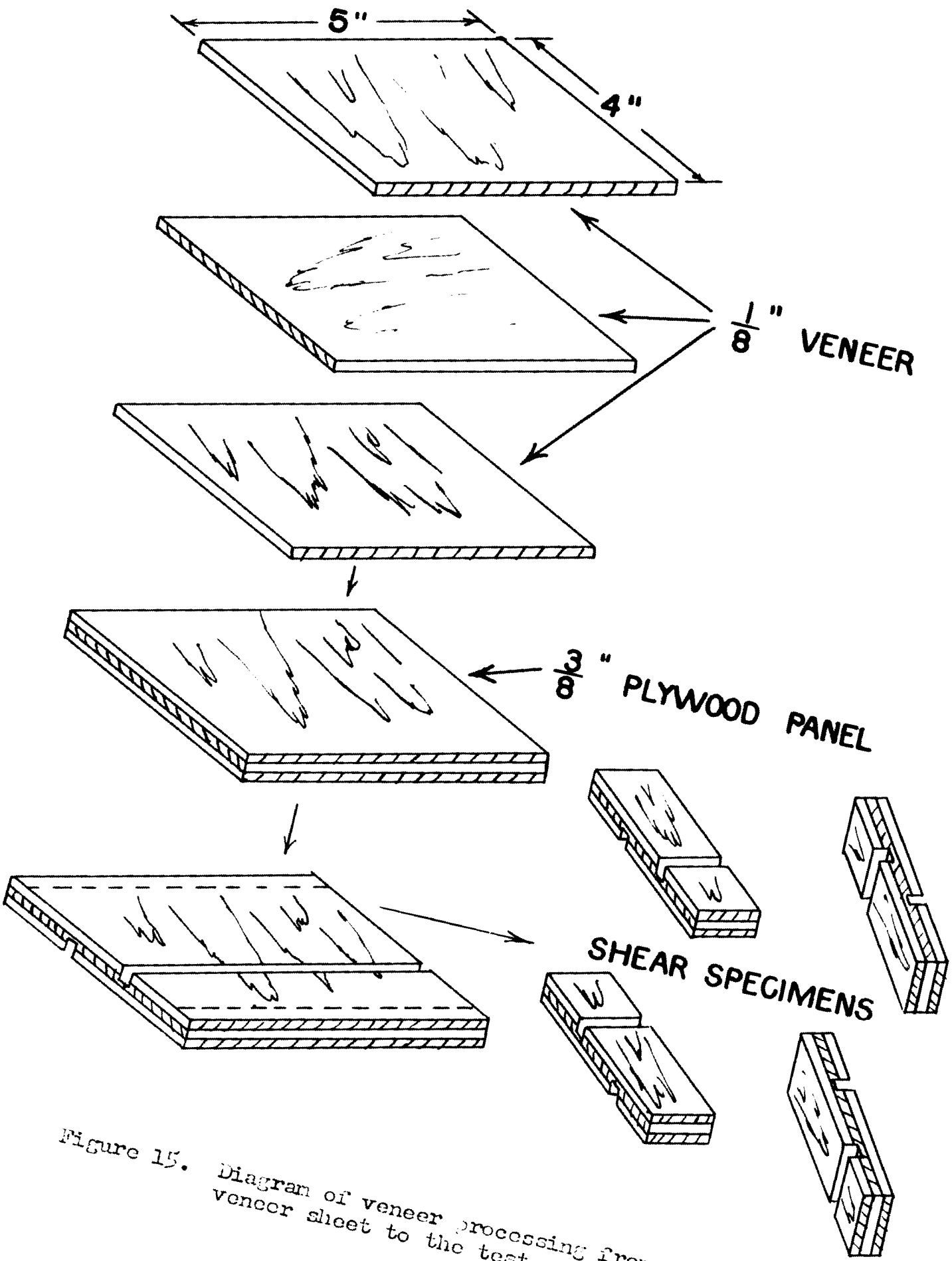


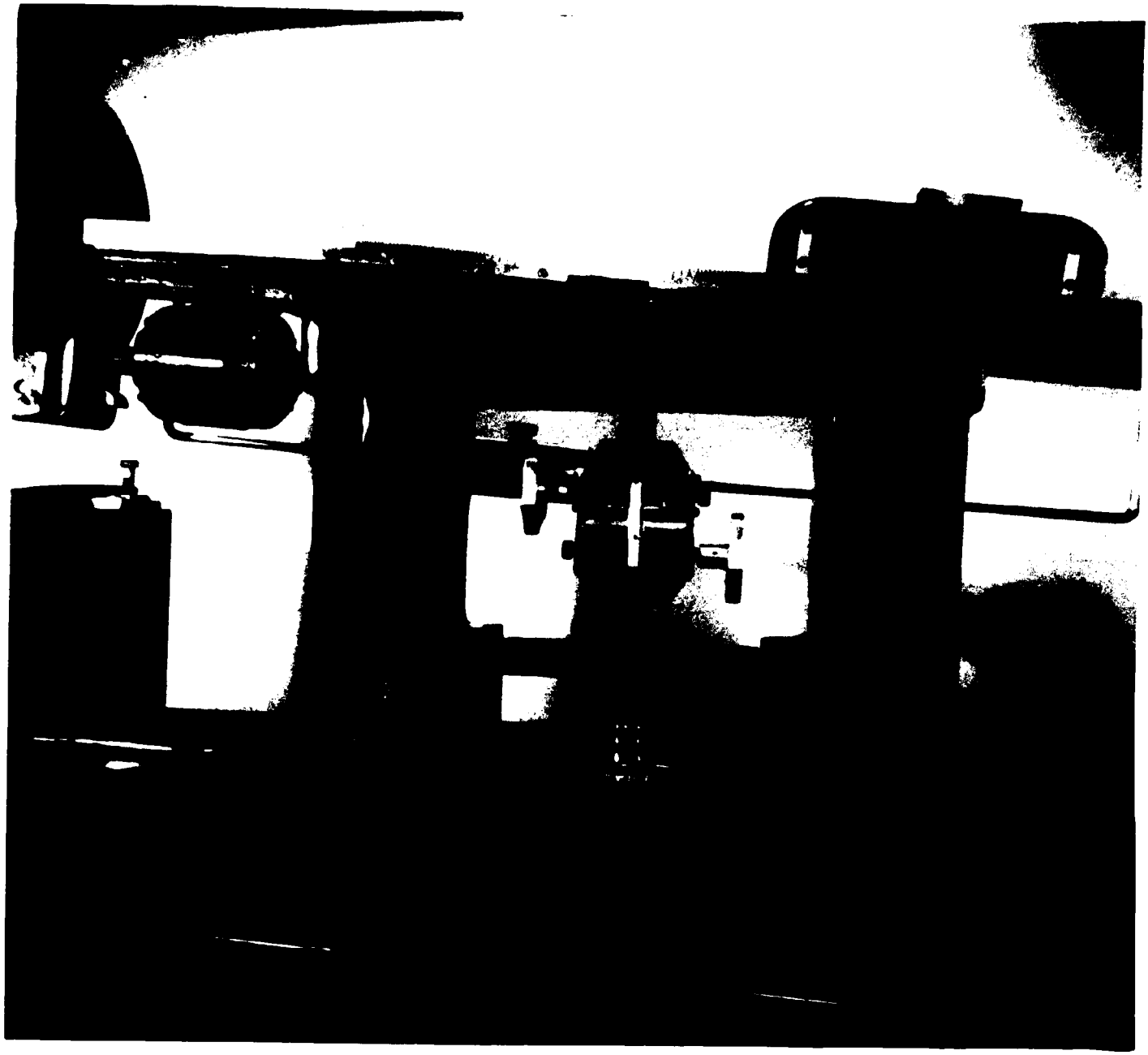
Figure 15. Diagram of veneer processing from the veneer sheet to the test specimen.

Machine, which is illustrated in Figure 16.

The plywood testing machine has a capacity of 1,000 pounds and loads a plywood test specimen at the rate of 600 pounds per minute by means of an electric motor which acts, through a screw, to advance a poise riding on the beam of the machine. The beam of the machine balances on knife edges which are located above the upper gripping head. A rod and balance weight are attached to the beam of the machine. The testing procedure includes the following operations: The test specimen is placed in the special wood gripping heads. The poise which rides on the beam is adjusted to the right side of the beam so that the indicator on the beam coincides with the zero mark on the scale on the beam. The beam is allowed to balance and, if out of balance, the balancing weight is moved until balance is obtained and then is tightened on the rod. The beam is then lowered on the right side. The gripping jaws are tightened on the test specimen which has been inserted into the heads. The lower grip adjusting handwheel at the bottom of the machine is turned until a very slight tension has been applied on the specimen. The lever on the poise is moved from the up to the down position which engages the poise and the loading screw. The beam is gradually unbalanced by the movement of the poise until the leverage created by the beam breaks the specimen. A clutch automatically stops the loading screw and the strength in total pounds is shown by the indicator on the poise, pointing to the scale on the beam. For plywood shear specimens having a one inch shear area, the total load is read in pounds per square inch.

In making plywood shear tests certain factors were considered in

Figure 16. Plywood shear testing machine used in the experiment.



order to reduce as much as possible the variability of test results. Experiments with 3/16 inch yellow birch plywood, conducted by Bensend and Ireton (.) at the United States Forest Products Laboratory, have been made to determine what factors tended to increase the variability of shear test results. Factors influencing the variability of tests were 1) increase of the span between machine jaws, 2) slope of grain in the face plies in relation to the cut of the shear specimen, 3) variation in the depth of the saw cuts when notching specimens, and 4) variations in moisture content of the specimens at the time of testing. Low shear strengths were reduced by increasing the span of the jaws and it was suggested that the full length of the jaws should be in contact with the specimen. The grain direction of the face plies should be at right angles to the saw cuts in the specimen. The plywood specimen received a more or less severe shear test depending on the grain direction in relation to the saw cuts. Differences in the depth of the saw cuts of the plywood specimens gave test results which definitely indicated that variation in the depth of the saw caused considerable variation in the value of the test results. Three depths of saw cuts were used in the tests: saw cut through the face ply, saw cut through the face ply one-third through the core, and saw cut through the face and through the core but not into the opposite face ply. The strength results increased in the order of the saw cut depths given. The moisture content of the specimens at the time of the shear test had a great influence on the shear results obtained. It was shown that strength values of the plywood specimens increased as the moisture content of

the specimen was increased up to a point where the specimens had a moisture content of about 12 percent. Beyond that point the strength results began to decrease.

VI. PRESENTATION AND ANALYSIS OF DATA

Presentation of Data

Values obtained for shear strength of Douglas fir plywood in pounds per square inch are shown in Tables VII, VIII, IX and X for phenol-formaldehyde resin bonded plywood, m-cresol-formaldehyde resin bonded plywood, 3,5-dimethylphenol-formaldehyde resin bonded plywood, and m-ethylphenol-formaldehyde resin bonded plywood, respectively. Supplemental data of wood failure, which is the percentage of a one square inch area showing failure in the wood rather than in the glue line, are shown below each shear strength value in these tables. Wood failure is not related to plywood shear strength values and is supplied only to show the adequacy or inadequacy of glue bond quality.

For each individual experimental condition, for example, for the conditions of resin I, specific gravity group 1, zero percent walnut shell flour, and a time of five days, 16 plywood shear tests were made. In each case only 12 shear test results were used for each condition in the final analysis. Four specimens for each condition were discarded because of defective qualities or by the statistical elimination which will be described.

Several conditions were sufficient for discarding plywood specimens. If lathe checks in the core ply were not oriented properly the specimen was eliminated. Specimens were removed if the growth rings of the core ply were oriented parallel to the long dimension of the speci-

TABLE VII

PLYWOOD STRENGTH AND WOOD FAILURE DATA
FOR PHENOL-FORMALDEHYDE RESIN

Time (days)	Specific Gravity (Groups) 1 — Walnut Shell Flour (Percent) 0	10	20	30	2 — 0	10	20	30	3 — 0	10	20	30	4 — 0	10	20	30
5	244	255	250	264	284	303	275	250	340	352	346	314	348	361	385	320
	100	99	100	100	100	97	100	100	72	97	100	76	89	97	87	93
	263	260	251	271	281	315	286	253	338	353	346	316	363	360	393	320
	100	100	100	100	100	98	100	100	77	97	95	93	91	100	93	82
	246	259	248	266	294	305	284	249	343	350	347	310	359	361	396	327
	100	100	100	100	100	97	100	100	73	100	100	97	91	100	93	80
	247	256	254	271	294	317	280	251	339	353	343	316	368	363	388	313
	100	100	100	100	100	100	100	100	85	82	90	97	86	93	90	82
9	247	296	248	246	287	268	321	287	350	344	351	335	353	360	412	376
	100	100	100	100	100	100	100	100	82	92	97	100	77	68	92	98
	239	291	237	248	286	275	318	295	340	340	351	340	352	362	403	378
	100	100	100	100	100	95	100	100	83	87	90	100	85	73	80	97
	243	301	245	241	279	278	318	274	342	345	355	338	358	370	406	377
	100	100	100	97	100	95	100	100	93	83	100	100	80	81	95	96
	248	298	240	242	280	271	314	294	345	340	362	343	357	369	408	370
	100	100	100	100	100	85	100	100	100	87	100	97	75	93	96	98
12	267	284	245	248	287	262	310	271	346	365	365	354	358	395	410	366
	97	100	100	100	98	100	100	100	83	95	100	100	90	97	100	97
	265	285	245	249	287	258	313	271	343	363	368	356	353	390	416	377
	100	100	100	100	100	100	100	100	72	98	100	100	75	98	100	96
	270	280	243	245	289	256	311	271	350	371	385	345	360	390	406	376
	100	100	100	100	100	100	100	100	80	95	100	100	75	97	100	93
	259	282	242	243	284	258	312	279	347	369	388	350	358	386	417	369
	100	100	100	100	99	100	100	100	82	95	100	100	73	97	98	99
16	243	288	244	257	288	256	289	272	370	358	395	365	368	378	415	384
	100	100	100	100	100	100	100	100	90	97	100	98	90	100	98	88
	239	277	246	248	280	253	308	278	360	376	388	358	363	380	421	394
	100	99	100	100	100	100	100	100	90	97	100	97	72	100	95	94
	243	269	240	253	269	255	308	276	372	356	383	369	362	385	415	396
	100	100	100	100	100	100	100	100	97	97	98	100	68	100	93	87
	235	279	241	249	288	262	296	270	361	360	395	364	361	380	415	398
	100	100	100	100	100	100	100	100	90	100	95	97	65	97	92	97

TABLE VIII

PLYWOOD STRENGTH AND WOOD FAILURE DATA
FOR m-CRESOL-FORMALDEHYDE RESIN

Time (days)	Specific Gravity (Groups) 1				2				3				4			
	Walnut Shell Flour (Percent) 0	10	20	30	0	10	20	30	0	10	20	30	0	10	20	30
5	252	254	265	254	274	309	300	268	346	343	351	373	367	412	367	389
	100	100	87	100	100	91	100	97	80	88	97	96	91	90	100	92
	265	248	254	248	288	303	292	280	326	334	335	372	357	405	380	393
	90	100	87	100	90	100	98	99	75	81	100	98	93	93	100	93
	266	255	268	246	280	301	296	282	343	337	334	387	356	410	375	393
	100	100	98	100	90	98	92	100	91	96	78	98	90	93	93	92
	257	257	258	246	282	314	297	282	330	344	352	374	342	404	370	402
	97	100	97	100	100	93	98	97	93	88	86	99	100	82	100	97
9	265	270	262	257	317	328	273	288	366	351	368	380	369	383	379	387
	100	100	100	100	98	93	100	100	91	97	98	82	82	92	96	80
	273	268	268	247	317	330	275	295	359	359	371	368	367	380	380	396
	100	100	100	100	99	94	100	100	98	77	94	85	91	77	90	63
	270	265	270	243	317	328	277	296	371	347	376	359	370	385	384	383
	100	100	100	100	97	98	100	100	90	94	93	68	95	85	96	63
	273	267	253	252	318	323	277	280	370	348	380	377	376	377	383	395
	99	100	100	100	97	93	100	100	86	100	96	73	90	88	83	75
12	271	255	263	266	290	310	260	307	357	372	383	397	361	387	393	412
	100	100	100	100	97	100	97	100	86	88	85	85	86	91	98	93
	267	257	260	262	292	315	260	295	367	362	377	397	353	385	382	407
	100	100	100	100	100	85	97	95	90	100	96	90	82	83	86	90
	276	256	252	269	312	325	272	303	367	350	387	406	357	381	382	406
	100	100	100	100	92	80	100	96	93	100	88	98	70	88	92	92
	268	250	257	266	317	322	264	296	344	358	387	397	357	388	387	407
	100	100	100	100	95	100	91	99	86	85	76	91	50	97	94	95
16	290	279	248	274	303	334	282	297	353	373	374	373	355	371	476	385
	100	97	100	100	78	100	100	100	71	91	88	86	70	100	93	85
	287	279	257	275	301	329	286	305	364	377	370	383	370	367	482	396
	95	100	100	100	86	98	100	100	80	96	85	81	71	97	93	90
	279	275	257	270	295	324	289	306	365	372	370	387	361	369	476	393
	80	100	100	100	93	100	100	97	82	98	90	78	67	97	92	82
	288	285	260	279	297	336	284	301	368	380	369	379	370	382	481	393
	100	100	100	100	100	93	100	100	80	90	65	81	70	93	90	88

TABLE IX

PLYWOOD STRENGTH AND WOOD FAILURE DATA FOR
3,5-DIMETHYLPHENOL-FORMALDEHYDE RESIN

Specific Gravity (Groups)

Time (days)	1				2				3				4			
	Walnut Shell Flour (Percent)															
	0	10	20	30	0	10	20	30	0	10	20	30	0	10	20	30
	171	190	242	243	179	207	198	213	207	270	340	387	247	357	325	294
	50	82	73	97	43	67	90	77	30	57	88	82	22	90	57	65
	164	183	243	242	172	199	196	211	213	267	335	388	243	352	320	303
	80	95	73	95	47	65	47	77	27	63	88	63	40	87	68	75
5	155	185	247	246	173	205	202	209	223	282	340	379	243	357	325	300
	100	83	80	97	43	70	75	60	27	50	92	73	23	82	70	77
	163	188	239	249	182	218	199	210	210	275	338	372	247	354	328	293
	80	78	53	95	33	70	65	57	33	67	87	60	43	65	67	82
	188	203	203	241	172	239	235	247	228	325	338	373	228	354	360	320
	57	100	87	80	27	87	80	85	43	87	87	80	50	63	77	67
	175	200	197	248	160	228	230	243	223	328	338	367	249	357	350	310
	40	100	100	60	30	73	60	87	65	68	90	93	33	73	70	53
9	178	203	197	241	169	222	234	239	225	330	336	370	235	352	351	331
	53	100	100	60	27	80	73	78	50	70	98	93	37	80	80	57
	180	199	195	237	166	231	233	243	235	324	343	376	245	346	365	329
	20	82	97	53	27	80	63	87	63	93	98	88	37	65	83	57
	210	213	230	238	217	244	233	236	227	325	363	341	228	341	382	330
	77	87	90	43	27	78	70	50	57	90	90	70	47	72	70	52
	216	204	228	237	207	245	228	237	227	333	380	333	237	343	386	327
	87	77	67	57	47	88	77	53	73	83	87	60	53	83	67	77
12	212	206	225	230	197	241	229	239	224	330	393	344	225	342	289	322
	100	82	87	57	50	67	67	67	53	92	97	60	53	73	77	70
	205	213	226	234	212	253	226	242	233	322	386	334	232	335	377	319
	67	100	70	57	37	73	40	63	47	65	93	37	43	83	77	52
	199	223	231	221	161	234	239	235	186	319	357	331	209	322	338	324
	69	74	77	70	20	63	30	43	20	50	63	65	15	53	40	57
	204	217	227	239	162	229	239	234	185	315	349	326	188	321	337	311
	90	80	60	53	8	40	23	67	17	50	78	77	13	50	70	80
16	194	217	231	233	167	237	236	234	187	317	359	330	184	322	334	320
	70	85	63	98	17	50	27	73	30	63	67	100	17	47	52	47
	199	217	229	227	163	225	240	227	184	315	356	321	186	320	345	314
	70	100	88	83	20	47	80	67	17	50	47	88	7	40	90	75

TABLE X

PLYWOOD STRENGTH AND WOOD FAILURE DATA FOR m-ETHYLPHENOL-FORMALDEHYDE RESIN

Time (days)	Specific Gravity (Groups) 1				2				3				4			
	Walnut Shell Flour (Percent)															
	0	10	20	30	0	10	20	30	0	10	20	30	0	10	20	30
5	212	267	223	260	276	265	269	247	332	290	349	355	388	341	393	362
	100	100	100	100	100	100	98	100	57	92	97	93	93	99	67	85
	207	270	228	257	271	267	270	250	336	287	355	352	387	347	385	363
	100	100	100	100	98	98	95	100	75	82	97	97	88	70	85	90
	211	275	225	260	261	260	271	251	328	283	352	353	391	340	387	363
	100	100	100	100	87	100	77	100	70	87	90	92	88	100	91	80
	210	265	229	250	267	274	269	247	336	295	354	356	385	351	383	366
	100	100	100	100	100	100	94	100	77	93	93	88	92	72	72	75
9	248	258	230	265	259	282	273	256	304	338	358	324	412	391	392	312
	97	100	100	100	100	92	94	100	93	100	87	90	78	72	80	84
	259	272	237	256	256	284	271	259	302	347	361	328	409	387	385	318
	97	100	100	100	93	100	94	100	93	67	80	92	77	77	82	88
	253	265	233	258	260	278	274	256	302	341	355	323	407	392	389	312
	100	98	100	100	100	100	94	100	93	90	87	93	63	72	82	92
	256	260	237	262	261	276	272	257	302	350	357	325	410	396	384	313
	100	99	100	100	100	100	98	100	97	73	83	97	78	80	80	95
12	241	258	240	271	264	279	277	288	292	363	360	353	345	363	385	373
	98	100	98	100	93	97	100	90	87	95	87	96	73	93	68	93
	241	270	242	265	279	268	278	286	292	358	364	355	346	367	384	365
	97	99	99	100	92	100	93	90	83	100	82	93	77	87	91	73
	243	269	238	265	275	267	277	289	294	365	367	352	337	369	390	365
	87	100	94	100	95	100	78	100	83	97	80	94	83	92	73	87
	244	266	240	262	270	261	278	284	292	375	367	352	341	361	393	363
	100	100	98	100	93	98	100	100	70	99	93	96	60	87	80	77
16	265	293	243	271	277	272	284	287	348	376	386	356	359	426	422	368
	95	98	100	100	100	100	60	90	76	97	67	87	75	60	60	97
	253	303	241	271	277	272	282	297	344	380	380	359	348	442	420	365
	100	100	97	100	99	100	70	100	90	87	73	88	83	77	77	83
	257	301	241	277	273	282	285	285	346	378	386	363	353	440	426	365
	100	100	95	100	97	100	83	100	87	100	73	90	82	72	82	85
	267	292	243	279	273	267	285	286	344	383	384	357	352	437	422	363
	90	100	100	100	100	100	87	95	80	90	80	91	87	80	67	90

men. Such orientation of the growth rings caused the specimen to break through the weak springwood of the core only, giving a low shear strength value. Specimens that gave a low shear strength value associated with a low wood failure were eliminated in the case of phenol-formaldehyde resin bonded plywood, m-cresol-formaldehyde resin bonded plywood, and p-ethylphenol-formaldehyde resin bonded plywood.

The majority of test specimens over 12 were discarded by means of the statistical drawing of chips from a jar. In making the statistical drawing of chips, each strength value in a group of test specimens was marked on individual chips. These chips were placed in a jar that contained approximately 60 unmarked chips. Chips were then drawn one at a time until 12 chips representing 12 strength values for a group had been drawn. In drawing chips, the first four chips were placed in a single row, the second four chips were placed in a row directly under the first, and the last four chips placed in the third row. This gave a pattern of chips three by four. To obtain the final data for each group of values for test specimens, the average shear strength and wood failure of three test specimens was taken so that for each group four values of each were obtained. These values were recorded for each experimental condition. The same procedure was carried out for the entire experiment.

Analysis and Discussion of Data

Procedure for analysis of variance. The analysis of variance carried out for this experiment required calculations for each resin; from these values the results for the entire investigation were obtained. This scheme made possible an examination of the effect of the different factors for each resin, as well as the effect of the various variables among the different resins.

The analysis of variance for the entire experiment appears in Table XXXVI. It is noted that all factors—resin, time, specific gravity and walnut shell flour—are highly significant. This indicates that all of these factors influence the strength of the Douglas fir plywood bonded with the resin adhesives used in this investigation.

In order to clarify the analysis of variance procedures used in this investigation, sample calculations will be presented. The computations for the shear strengths of phenol-formaldehyde resin bonded plywood will show how analysis of variance was carried out for each resin. The scheme for the entire investigation will indicate how the analyses for the individual resins were combined to give the final results. In presenting the statistical analysis no attempt will be made to give the mathematical reasons for the procedures.

Values for plywood shear strength in Table VII were squared and the sum of squares computed. A correction term for the mean was determined to adjust the total sum of squares for the shear strengths of

phenol-formaldehyde resin bonded plywood. These initial calculations were made as follows:

Sum of all shear strengths of Table VII = 81,253

Correction terms = $(81,253)^2 / 256 = 25,709,257.84$

Total sum of squares = $(244)^2 + (255)^2 + \ldots\ldots +$
$(415)^2 + (398)^2$ - correction

$= 26,506,921.00 - 25,709,257.84$

$= 717,663.16$

The total sum of squares, without the decimal, is entered in Table XII. The number of degrees of freedom for this analysis is always (n-1), where n represents the number of items in a sample or subsample. For example, the total number of items going into the total sum of squares for the shear strength values of Table VII is 256. The degrees of freedom for the total sum of squares in Table XII is 255.

The sum of squares shown in Table XII for time, specific gravity and walnut shell flour as well as sum of squares for the first order interactions* (time x specific gravity), (time x walnut shell flour), and (specific gravity x walnut shell flour) were determined from the two-way Tables XIII, XIV and XVI. The sum of squares for the interaction** (time x specific gravity x walnut shell flour) was obtained from

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* The term "interaction" is used in analysis of variance procedure to indicate the discrepancy between experimental treatments. A non-significant interaction reveals only experimental error. A significant interaction reflects that an increment of a certain treatment imposed on a second treatment will not produce the same effect every time, but will depend on the combined effect of the two treatments. A first order interaction involves two treatments.

** A second order interaction involves three treatments.

TABLE XI

ANALYSIS OF VARIANCE OF PLYWOOD STRENGTH DATA FOR PLYWOOD BONDED WITH PHENOL-FORMALDEHYDE RESIN ADHESIVE

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square
Total	255	717,663	
Main Effects			
Time	3	7,320	2,440*
Specific gravity	3	616,662	205,554**
Walnut shell flour	3	20,243	6,748**
Interactions			
Time x specific gravity	9	13,056	1,451
Time x walnut shell flour	9	6,585	732
Specific gravity x walnut shell flour	9	27,451	3,050*
Time x specific gravity x walnut shell flour***	27	21,614	801
Error	192	4,733	25

F to be significant	5%	1%
For 27 and 3 degrees of freedom	2.96	4.60
For 27 and 9 degrees of freedom	2.25	3.14

Calculated least significant difference = 10.25

* Signifies significance.
** Signifies high significance.
*** Proper error term to use.

the three-way Table XVIII.

The two-way Table XXII concerns the factors specific gravity and walnut shell flour. The time factor is ignored in this table. The large values in the table are the sums of the shear strength values in the columns of Table VII. The smaller figures are the averages of the larger figures. The following computations will make this clear.

For specific gravity group 1 and zero percent walnut shell flour.

$$244 + 263 + 246 + \ldots\ldots + 23[illegible] + 24[illegible] + 235 = 3,996$$

$$3,996 / 16 = 250$$

For specific gravity group 4 and 30 percent walnut shell flour.

$$320 + 3[illegible]0 + 327 + \ldots\ldots + 3[illegible]4 + 396 + 39[illegible] = 5,841$$

$$5,841 / 16 = 365$$

An analysis of variance was worked out for the data in Table XXII. The analysis is shown in Table XXIII. The calculations of the sums of squares are as follows:

$$\text{Total S.S.} = (3,996)^2 + \ldots\ldots + (5,841)^2 / 16 - \text{correction}$$

$$= 26,4[illegible],[illegible]13.31 - 25,7[illegible],[illegible]27.04 = 664,[illegible].47$$

$$\text{S.S. Flour} = (1[illegible],[illegible]90)^2 + \ldots\ldots + (1[illegible],6[illegible]3)^2 / 64 - \text{correction}$$

$$= 25,[illegible],[illegible].20 - 25,78[illegible],[illegible]27.04 = 20,243.26$$

$$\text{S.S. Sp. Gr.} = (16,4[illegible])^2 + \ldots\ldots + (2[illegible],[illegible]7[illegible])^2 / 64 - \text{correction}$$

$$= 26,4[illegible],929.3[illegible] - 25,78[illegible],[illegible]27.04 = 616,661.46$$

$$\text{S.S. (Flour x Sp. Gr.)} = 664,39[illegible].47 - (616,661.46 + 20,243.26)$$

$$= 27,490.73$$

These sums of squares without their fractional values are shown in Table XXIII.

TABLE XII

SUMS AND MEANS OF PLYWOOD STRENGTH DATA FOR SPECIFIC GRAVITY AND WALNUT SHELL FLOUR FOR DOUGLAS FIR PLYWOOD BONDED WITH PHENOL-FORMALDEHYDE RESIN ADHESIVE

Specific Gravity

		1	2	3	4	Total	Mean
Walnut shell flour (percent)	0	3,998 250	4,557 285	5,594 350	5,741 359	19,890	310.8
	10	4,460 279	4,392 275	5,607 355	5,990 374	20,529	320.8
	20	3,919 245	4,843 303	5,873 367	6,506 407	21,141	330.3
	30	4,041 253	4,338 271	5,473 342	5,841 365	19,693	307.7
	Total	16,418	18,130	22,627	24,078	81,253	
	Mean	256.5	283.3	333.5	376.2		317.4

TABLE XIII

ANALYSIS OF VARIANCE OF SUMS OF PLYWOOD SHEAR STRENGTH DATA FROM TABLE XII

Source	Degrees of Freedom	Sum of Squares
Total	15	664,355
Flour	3	20,243
Specific Gravity	3	616,661
Specific Gravity x Flour	9	27,450

The two-way Table XIV involves specific gravity and time; the walnut shell flour is ignored in this table. The large figures of the table are sums of plywood shear strength values. The small figures are shear strength averages.

For specific gravity group 1 and time of five days, the summation of the squares of shear strengths is as follows:

$$241 + 255 + 256 + \ldots\ldots + 256 + 258 + 171 = 4,109$$

For specific gravity group 4 and a time of 15 days the summation is

$$366 + 371 + 415 + \ldots\ldots + 366 + 413 + 396 = 6,215$$

The analysis of variance for the shear strength summation values of Table XIV is shown in Table XV. This calculation was made in a manner similar to that for the analysis in Table XIII.

Table XVI concerns walnut shell flour and time, with specific gravity ignored. The large figures are the sums of plywood shear strength values of Table VII, the small numbers are their averages. The summation of the squares of plywood shear strength values will be made clear by the following examples.

For zero walnut shell flour percentage and a time of five days.

$$244 + 260 + \ldots\ldots + 264 + \ldots\ldots + 340 + \ldots\ldots + 348 + 363 - 359 - 365 = 4,951$$

For 30 percent walnut shell flour and the time of 15 days.

$$297 + 336 + \ldots\ldots + 372 + \ldots\ldots + 368 + \ldots\ldots + 396 + 396 = 5,191$$

The analysis of variance for the values of Table XVI is shown in Table XVII. This analysis was calculated as were the analyses already

TABLE XIV

SUMS AND MEANS OF PLYWOOD STRENGTH DATA FOR SPECIFIC GRAVITY AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH PHENOL-FORMALDEHYDE RESIN ADHESIVE

		Specific Gravity					
		1	2	3	4	Total	Mean
Time (days)	5	4,105 257	4,527 283	5,406 338	5,725 358	19,763	308.8
	9	4,110 257	4,645 290	5,529 346	6,011 376	20,295	317.1
	12	4,152 260	4,510 282	5,765 360	6,127 383	20,554	321.2
	16	4,051 253	4,448 278	5,927 370	6,215 382	20,641	322.5
	Total	16,418	18,130	22,627	24,078	81,253	
	Mean	256.5	283.2	353.6	376.2		317.4

TABLE XV

ANALYSIS OF VARIANCE OF SUMS OF PLYWOOD SHEAR STRENGTH DATA FROM TABLE XIV

Source	Degrees of Freedom	Sum of Squares
Total	15	637,037
Time	3	7,320
Specific Gravity	3	616,661
Time x Specific Gravity	9	13,055

TABLE XVI

SUMS AND MEANS OF PLYWOOD STRENGTH DATA FOR WALNUT SHELL FLOUR AND TILE FOR DOUGLAS FIR PLYWOOD BONDED WITH PHENOL-FORMALDEHYDE RESIN ADHESIVE

		Walnut Shell Flour (percentage)					
		0	10	20	30	Total	Mean
Time (days)	5	4,951 309	5,123 320	5,072 317	4,617 289	19,763	308.8
	9	4,914 307	4,108 319	5,289 331	4,984 312	20,295	317.1
	12	5,023 314	5,194 325	5,376 336	4,961 310	20,554	321.2
	16	5,002 313	5,104 319	5,404 338	5,131 321	20,641	322.5
	Total	19,890	20,529	21,141	19,693	81,253	
	Mean	310.8	320.8	330.3	307.7		317.4

TABLE XVII

ANALYSIS OF VARIANCE OF SUMS OF SHEAR STRENGTH DATA FROM TABLE XVI

Source	Degrees of Freedom	Sum of Squares
Total	15	34,148
Time	3	7,320
Flour	3	20,243
(Time x Flour)	9	6,584

presented.

Up to this point in the explanation of analyses of variance procedures, all sums of squares in Table XI have been determined except for the second order interaction (time x specific gravity x walnut shell flour) and for the error term.

The sum of squares for the interaction (time x specific gravity x walnut shell flour) was determined from the data of Table XVIII and the analysis of variance of Table XIX. The summation values of Table XVIII were squared and their sum was computed to give the total sum of squares. The sums of squares for time, specific gravity, walnut shell flour and for the first order interactions (time x specific gravity), (time x walnut shell flour), and (specific gravity x walnut shell flour) were added and this value was subtracted from the total sum of squares to give the second order interaction sum of squares.

The sum of squares for error in Table XI was calculated by subtracting the sum of the sums of squares of the treatments and interactions from the total sum of squares.

The mean square values in Table XI were obtained by dividing the sum of square values by the number of degrees of freedom associated with the sum of squares*. The significance or non-significance of treatments and interactions was determined by dividing mean square values by the mean square value for the second order interaction (time

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* The number of degrees of freedom for an interaction is determined by multiplying the number of degrees of freedom of the individual treatments involved in the interaction.

TABLE XVIII

SUMS AND MEAN VALUES OF PLYWOOD STRENGTH DATA FOR WALNUT SHELL FLOUR, TIME AND SPECIFIC GRAVITY FOR DOUGLAS FIR PLYWOOD BONDED WITH PHENOL-FORMALDEHYDE RESIN ADHESIVE

Time (days)	Specific Gravity	Walnut Shell Flour (percentage) 0	10	20	30	Total	Mean
5	1	1,000	1,030	1,003	1,072	4,951	
		250	258	251	268		309.4
	2	1,153	1,240	1,125	1,009	5,123	
		288	310	381	252		320.2
	3	1,360	1,408	1,382	1,256	5,072	
		340	352	346	314		317.0
	4	1,438	1,445	1,562	1,280	4,617	
		360	361	391	320		288.6
9	1	977	1,186	970	977	4,914	
		244	297	243	244		307.1
	2	1,132	1,092	1,271	1,150	5,108	
		283	273	318	288		319.3
	3	1,385	1,369	1,419	1,356	5,289	
		346	342	355	339		330.6
	4	1,420	1,461	1,629	1,501	4,984	
		355	365	407	375		311.5
12	1	1,061	1,131	975	985	5,023	
		265	283	244	246		313.9
	2	1,147	1,034	1,246	1,083	5,194	
		287	259	312	271		324.6
	3	1,386	1,468	1,506	1,405	5,376	
		347	367	377	351		336.0
	4	1,429	1,561	1,649	1,488	4,961	
		357	390	412	372		310.1
16	1	960	1,113	971	1,007	5,002	
		240	278	243	252		312.6
	2	1,125	1,026	1,201	1,096	5,104	
		281	257	300	274		319.0
	3	1,463	1,442	1,566	1,456	5,404	
		366	361	392	364		337.8
	4	1,454	1,523	1,666	1,572	5,131	
		364	381	417	393		320.7

TABLE XIX

ANALYSIS OF VARIANCE OF THE SUMS OF PLYWOOD SHEAR STRENGTH DATA FROM TABLE XVIII

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares
Total	63	712,929
Main Effects		
Time	3	7,320
Specific gravity	3	20,243
Walnut shell flour	3	616,661
Interactions		
Time x specific gravity	9	6,584
Time x walnut shell flour	9	13,055
Specific gravity x walnut shell flour	9	27,450
Time x specific gravity x walnut shell flour	27	21,613

x specific gravity x walnut shell flour) which was used as the error term in the analysis. The quotients obtained were F values that were compared to a statistical table of F values. The F values for significance at the five and the one percent levels of significance are indicated in Table XI.

It is emphasized that the interaction (time x specific gravity x walnut shell flour) was used as the error term in the analysis. Using the actual error term produced high significance for all mean square values. The actual error term was considered to reflect only sampling error and the interaction term was considered to be the proper one to use as the error term. This situation is the same for all resins used in the experiment.

Since significance was indicated for treatments, it was necessary that the t test be used to determine the least significant mean difference*. This difference was calculated as follows:

$$\text{Standard deviation of the mean} = \frac{\sqrt{.001}}{\sqrt{64}}$$

$$\text{Standard error of the difference} = \sqrt{\frac{.001}{64} + \frac{.001}{64}} = \sqrt{\frac{.001}{32}} = \sqrt{.25} = .5$$

t (at 5% level) = 1.05 (taken from "t" table for 47 degrees of freedom)

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* When the difference between two means exceeds the value of the least significant mean difference, the two means are said to belong to different populations and are considered to be significantly different.

Difference to be significant:

$$m_1 - m_2 = t \times S$$

$$= 2.05 \times 5$$

$$= 10.25 \text{ (least significant mean difference)}$$

It is pointed out that the figure 501 is the mean square value for the second order interaction in Table XI. The number of items involved with this interaction is 5. These are recognized formulae for calculating the least significant difference between mean values, in this case, mean values of Tables XIII, XIV and XVI.

The procedures involves in the analysis of variance calculations for the shear strength of plywood bonded with phenol-formaldehyde resin show the procedure followed for each of the three other resins used in the investigation. The analyses of variance and the two-way tables for shear strength of plywood bonded with the remaining resins are found in Tables XI to XXII.

The analysis for the entire investigation is shown in Table XXII. The methods used for the calculation of values in this table are merely extensions of the methods used with the shear strength values of plywood bonded with phenol-formaldehyde resin. The two-way tables used in the calculation of the final analysis are presented to aid in the explanation of the effects of variable treatments.

Discussion of results for each resin. An examination of the statistical results for each resin reveals that the experimental treatments—time, specific gravity and walnut shell flour—had a definite effect on the shear strength of plywood bonded with each of the resins.

The analysis of variance for the shear strength of phenol-formaldehyde resin bonded plywood is presented in Table XII. It is noted that the treatments—specific gravity and walnut shell flour—are highly significant indicating that there is one chance in 100 that these factors exhibited such effects only in this case. Such a circumstance is highly unlikely and the influence of these factors can be accepted with confidence.

The effect of time is significant, revealing there is one chance in 20 that this factor is effective only in this particular situation. The influence of time can be accepted but with less confidence than the effects of specific gravity and walnut shell flour. Figure 17 shows the trends of the mean shear values for specific gravity, walnut shell flour and time. These trends are based on the mean shear strength values of Tables XII, XIV and XVI.

The interaction (specific gravity x walnut shell flour) is significant. A brief explanation of the meaning of the term interaction was given in a footnote on page 112. A further discussion of this term is in order at this point.

An ideal non-significant interaction is one that is completely additive. By this is meant that an increment of one treatment imposed on a second treatment produces exactly the same increment on the second treatment. As an example, if two factors—specific gravity and time—are considered, an increment of time on specific gravity would give the same effect each time an increment is added. Such a situation could be illustrated by a graph having both abscissa (specific gravity) and

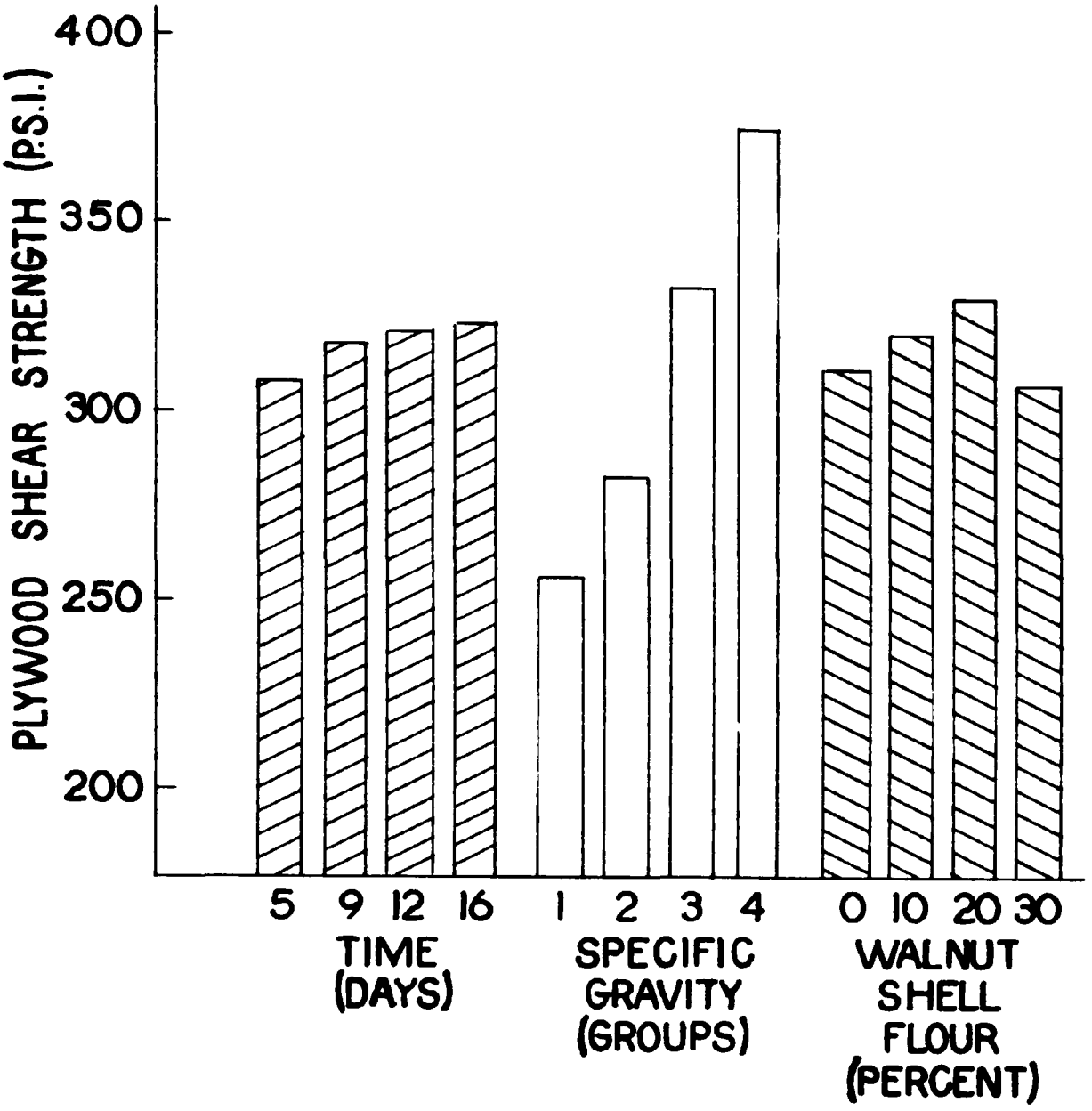
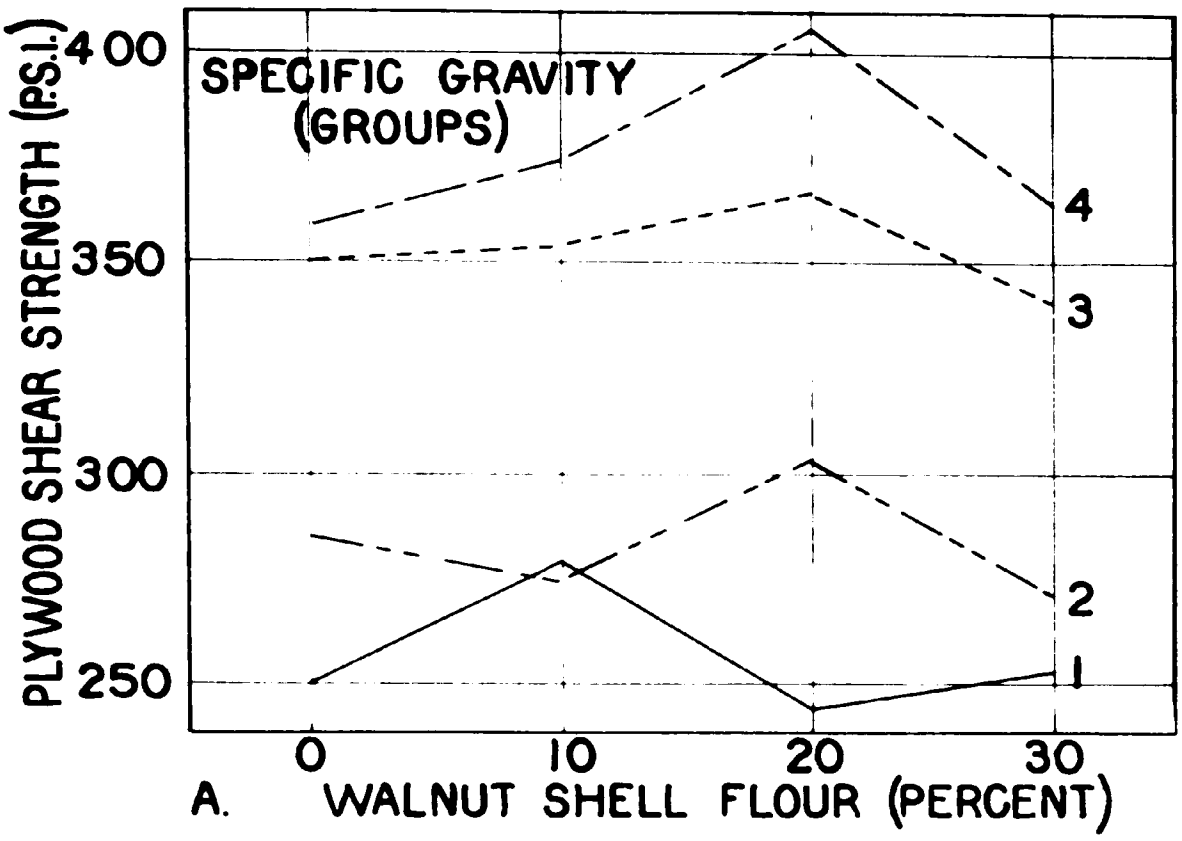


Figure 17. Trends of mean shear values of plywood bonded with phenol-formaldehyde resin for time (days), specific gravity groups and walnut shell flour percent.

ordinate (time) calibrated in the same size units with a straight line drawn having a slope of one. An increase of time would give an equal increase of specific gravity. It is rare in most experimental work to have an ideal additive effect between treatments. However, there can be some variation from the ideal non-significant situation before significant differential effects are evident. The evidence of significant differential effects may appear in an analysis of variance calculation as was the case in this investigation.

Figures 18, 19 and 20 show graphs of interaction trends. The basis for these graphs are the average shear strength values within Tables XII, XIV and XVI. Graphs of Figure 18 originated from Table XII, graphs in Figure 19 came from Table XIV, and graphs in Figure 20 were obtained from Table XVI. In Figure 18, graph A shows the effect of walnut shell flour increments on specific gravity groups, and graph B indicates the influence of increments of specific gravity on walnut shell flour percentages. These graphs were constructed by plotting the average shear values for the specific gravity groups against walnut shell flour percentages in graph A, and average shear values for the walnut shell flour percentages against specific gravity groups in graph B. A similar procedure was followed in plotting the graphs in Figures 19 and 20. In Figure 18, graph A, for the interaction (specific gravity x walnut shell flour), indicates that increments of one treatment did not produce similar effects in the other treatment, the variations being great enough to be significant. Graph B also shows significant variations. Graphs in Figures19 and 20 do not indicate variations



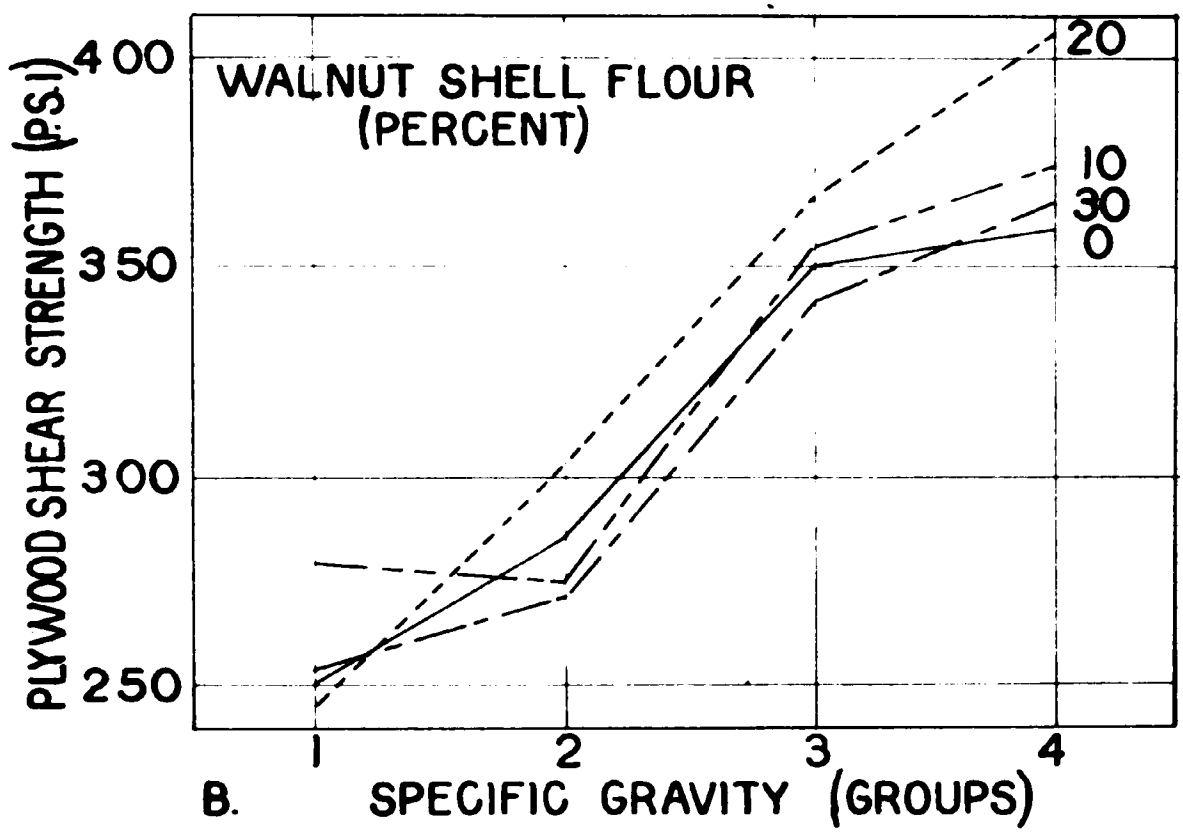
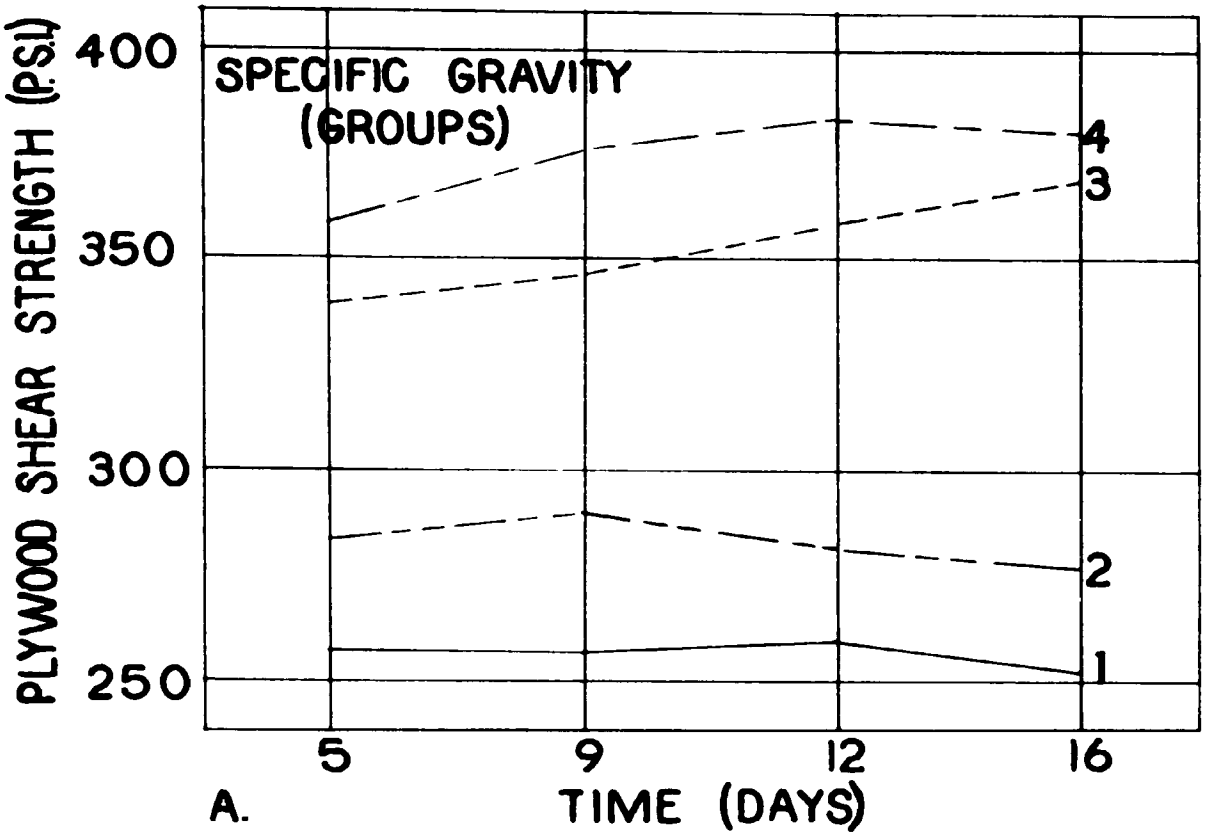


Figure 16. Graphs of interaction trends for plywood bonded with phenol-formaldehyde resin. A. The effect of increments of walnut shell flour percent on specific gravity groups. B. The effect of increments of specific gravity groups on walnut shell flour percent.



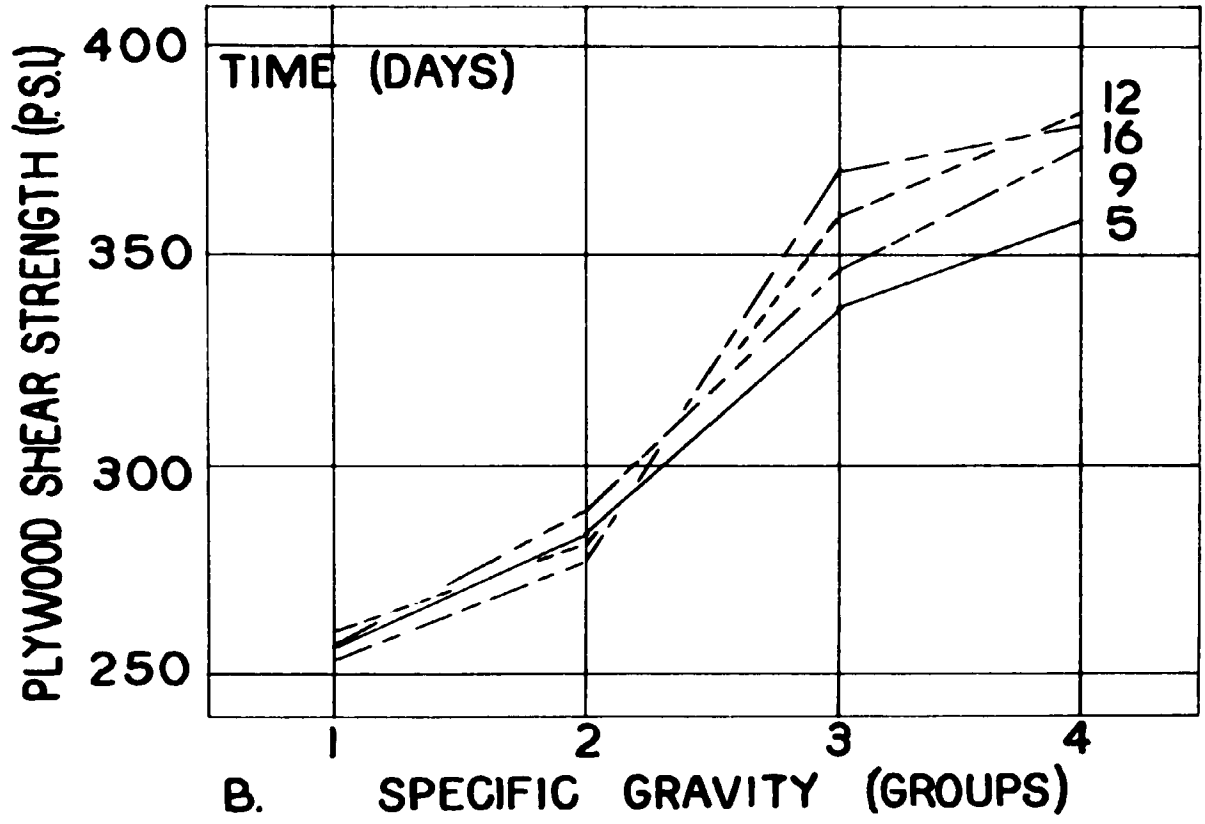
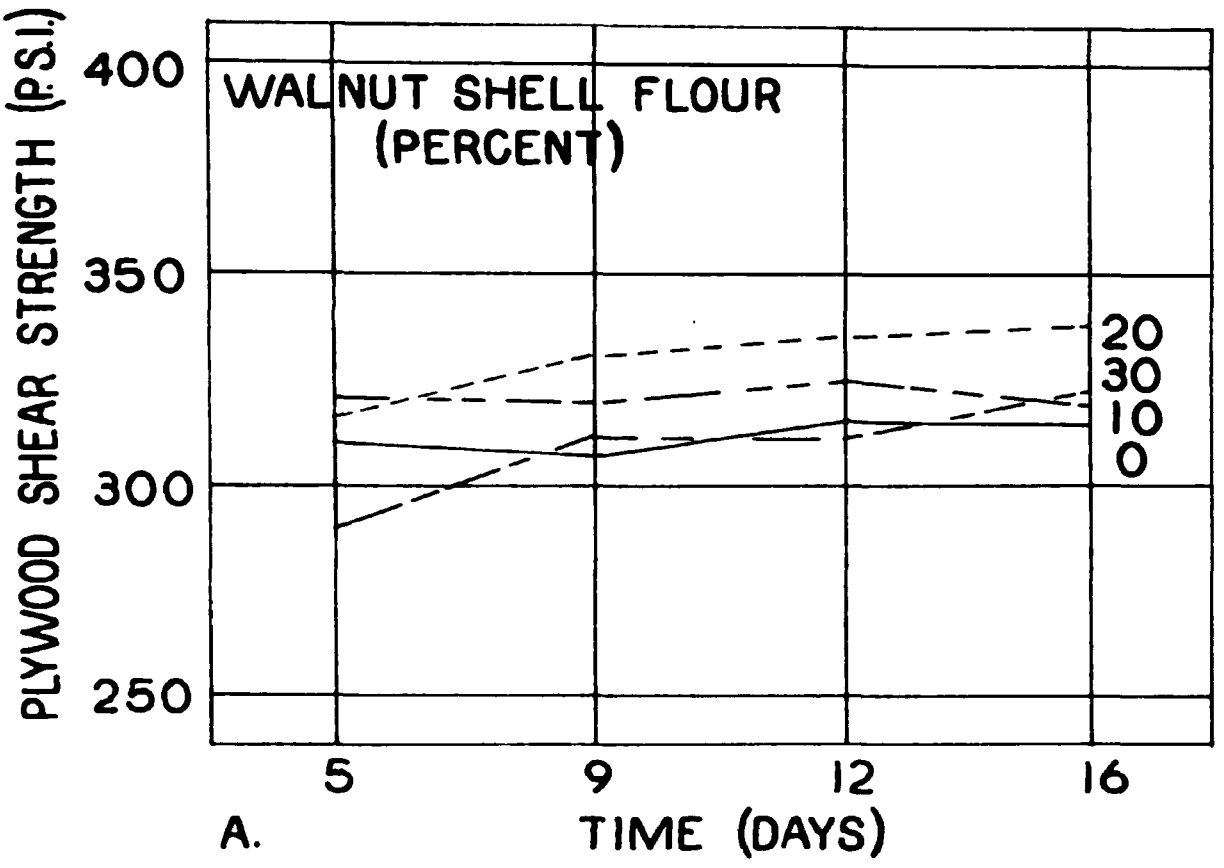


Figure 19. Graphs of interaction trends for plywood bonded with phenol-formaldehyde resin. A. The effect of increments of time (days) on specific gravity groups. B. The effect of increments of specific gravity groups on time (days).



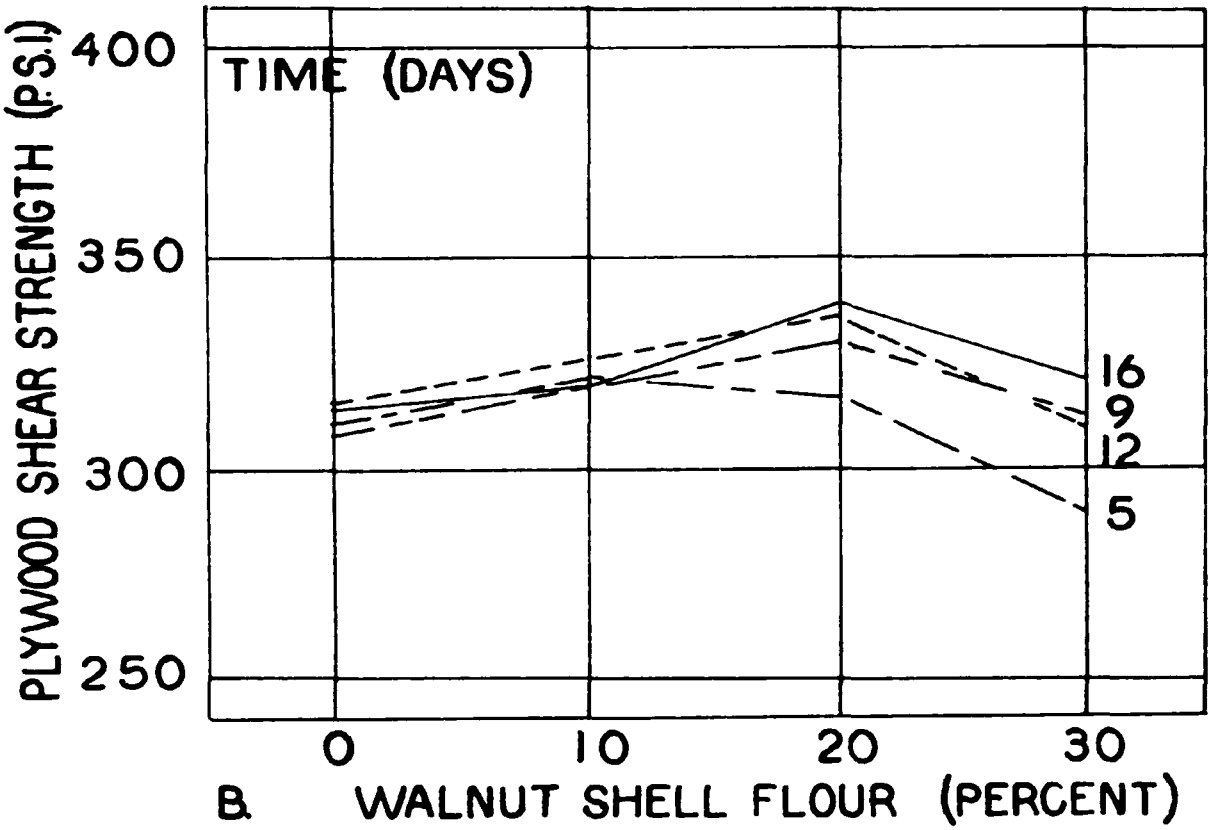


Figure 20. Graphs of interaction trends for plywood shear strengths for plywood bonded with phenol-formaldehyde resin. A. The effect of increments of time (days) on walnut shell flour percent. B. The effect of increments of walnut shell flour percent on time (days).

great enough to be significant. The significance of interactions does not detract from the main effects of the analysis of variance for the shear strength values of plywood bonded with phenol-formaldehyde resin.

The large mean square value for specific gravity in Table XI indicates that this factor has a considerable influence on the strength of phenol-formaldehyde bonded Douglas fir plywood. Tables XII and XIV show that the mean values for specific gravity increase from low to high specific gravity and differ from one another by a considerable amount. The difference exceeds the value of the last significant mean difference of 10.25*. It appears evident that for the conditions of this experiment, increasing specific gravity for well-bonded Douglas fir plywood results in higher strength. This coincides with the concept that the strength of wood, in general, is directly related to specific gravity.

The specific gravity of solid dry wood substance is about 1.5. Wood has a certain volume of cell cavity space and other open space so that the specific gravity of normal wood is much less than 1.5. A higher specific gravity for wood signifies more wood per unit volume which logically gives greater strength. The evidence in the case of phenol-formaldehyde resin bonded plywood appears to indicate that more wood per unit volume in Douglas fir veneer gives greater plywood strength if the glue bond is adequate. It is suggested that an adequate glue bond implies that the adhesive may be considered an integral part of the wood. The relatively high values of wood failure percent-

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* This value has been calculated previously on pages 122 and 123.

ages given in Table VII imply that an adequate bond was obtained in plywood bonded with the phenol-formaldehyde resin adhesive.

The means for walnut shell flour in Tables XII and XVI show that 20 percent walnut shell flour is significantly better than either zero percent or 30 percent. It appears that 20 percent walnut shell flour added to the phenol-formaldehyde resin gives a satisfactory plywood glue bond. Since 10 percent walnut shell flour is not significantly worse than 20 percent walnut shell flour, it can be concluded that slightly under 10 and somewhat more than 20 percent walnut shell flour filler is satisfactory for the phenol-formaldehyde resin.

It is known that walnut shell flour, when added to phenol-formaldehyde adhesives, retards the flow of the resin adhesive during that part of the curing period when the resin decreases in viscosity. At this point in curing, the resin tends to flow considerably, penetrating the wood excessively and flowing from between the veneer layers as squeeze-out. The flour tends to retain the adhesive in the glue line until the resin begins to solidify. At the same time, a certain amount of resin penetrates the wood to some extent, which is desirable.

Tables XIV and XVI show the mean values for time. Time periods of 12 days and 16 days belong to the same population since they are not significantly different. However, these two time periods are both significantly better than a time period of five days. A time period of nine days appears to be an intermediate mean that could belong to the same statistical population as the time period of five days or to the population that includes the time periods of 12 and 16 days. The nine

day time period cannot be safely included in the discussion of the conclusions for the time factors. This situation suggests that there is a significant increase in plywood strength between nine and 12 days after bonding Douglas fir veneer with phenol-formaldehyde resin adhesive under the conditions of the experiment. This suggests further that since the resin bonded plywood was treated to fully cure the resin before strength tests were conducted, both new bonds or stronger bonds between wood and adhesive must be formed over the nine to 12 day period.

The analysis of variance of shear values of m-cresol-formaldehyde resin bonded plywood appears in Table XX. The least significant mean difference, calculated in the same way as the least significant mean difference for the phenol-formaldehyde resin bonded plywood, is 12.7.

Tables XXI and XXII show the mean values for the specific gravity treatments. Each of these treatments is significantly different from other specific gravity treatments, with a definite increase in plywood strength associated with an increase in specific gravity. The suggested reason for increased strength related to increased specific gravity has been given in the discussion for the results of shear strength analysis for phenol-formaldehyde resin bonded plywood. This reason also applies for the m-cresol-formaldehyde resin bonded plywood.

Tables XXII and XXIII show that a time period of 16 days gives significantly greater plywood strength than a time period of five days. Time periods of nine days and 12 days are not significantly different than either a period of five days or a period of 16 days. This situation suggests that a marked increase in strength takes place in from 12

TABLE XX

ANALYSIS OF VARIANCE OF PLYWOOD STRENGTH DATA FOR PLYWOOD BONDED WITH m-CRESOL-FORMALDEHYDE RESIN ADHESIVE

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square
Total	255	738,857	
Main Effects			
Time	3	11,055	3,685*
Specific gravity	3	636,712	212,237**
Walnut shell flour	3	4,165	1,388
Interactions			
Time x specific gravity	9	4,711	523
Time x walnut shell flour	9	7,726	858
Specific gravity x walnut shell flour	9	34,589	3,843*
Time x specific gravity x walnut shell flour	27	33,450	1,239
Error	192	5,958	31

See Table XI for the significance of F.

Calculated least significant difference = 12.7

* Signifies significance.
** Signifies high significance.

TABLE XXI

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND WALNUT SHELL FLOUR FOR DOUGLAS FIR PLYWOOD BONDED WITH m-CRESOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Walnut shell flour (percent)	0	4,347	4,800	5,698	5,788	20,633	
		272	300	356	362		322.4
	10	4,220	5,127	5,707	6,186	21,240	
		264	320	357	387		331.9
	20	4,152	4,484	5,884	6,477	20.997	
		260	280	268	405		328.1
	30	4,156	4,681	6,109	6,337	21,283	
		260	293	382	396		332.5
	Total	16,875	19,092	23,398	24,788	84,153	
	Mean	263.7	298.3	365.6	387.3		328.7

TABLE XXII

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH m-CRESOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Time (days)	5	4,093	4,648	5,583	6,122	20,446	
		256	296	349	383		319.5
	9	4,203	4,839	5,850	6,094	20,986	
		263	302	366	381		327.9
	12	4,197	4,740	6,008	6,145	21,090	
		262	296	376	384		329.5
	16	4,382	4,865	5,957	6,427	21,631	
		274	304	372	402		337.9
	Total	16,875	19,092	23,398	24,788	84,153	
	Mean	263.7	298.3	365.6	387.3		328.7

TABLE XXIII

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR WALNUT SHELL FLOUR AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH m-CRESOL-FORMALDEHYDE RESIN

		Walnut Shell Flour (percentage)					
		0	10	20	30	Total	Mean
Time (days)	5	4,933 308	5,230 327	5,094 318	5,189 324	20,446	319.5
	9	5,298 331	5,309 332	5,176 324	5,203 325	20,986	327.9
	12	5,156 322	5,273 330	5,166 323	5,495 343	21,090	329.5
	16	5,246 328	5,428 339	5,561 348	5,396 337	21,631	337.9
	Total	20,633	21,240	20,997	21,283	84,153	
	Mean	322.4	331.9	328.1	332.5		328.7

to 16 days after bonding Douglas fir veneer with m-cresol-formaldehyde resin. This increase is evident even though the plywood was heat-treated to assure cure of the resin in the glue bond before plywood shear tests were made. The formation of new bonds or stronger bonds is suggested as the reason for this increase of plywood strength.

The mean values for the different walnut shell flour percentages belong to the same statistical population since none of the values differs from one another by as much as 12.7. This situation will be discussed later.

The trends of the effects of the treatments—specific gravity, walnut shell flour and time—are shown in Figure 21.

The significance of the first order interaction (specific gravity x walnut shell flour), indicated in Table XX, has the same meaning as the corresponding first order interaction that was considered in the discussion of the results for the shear strength values of phenol-formaldehyde resin bonded plywood.

Table XXIV, the analysis of variance of the average shear strengths of plywood bonded with 3,5-dimethylphenol-formaldehyde resin, shows specific gravity and walnut shell flour to be highly significant factors. Time is also significant. The least significant mean square was calculated to be 13.1.

Specific gravity influences the strength of the plywood bonded with the 3,5-dimethylphenol-formaldehyde resin. However, the erratic increase of plywood strength in relation to specific gravity suggests that some other factor is retarding the full effect of specific gravity.

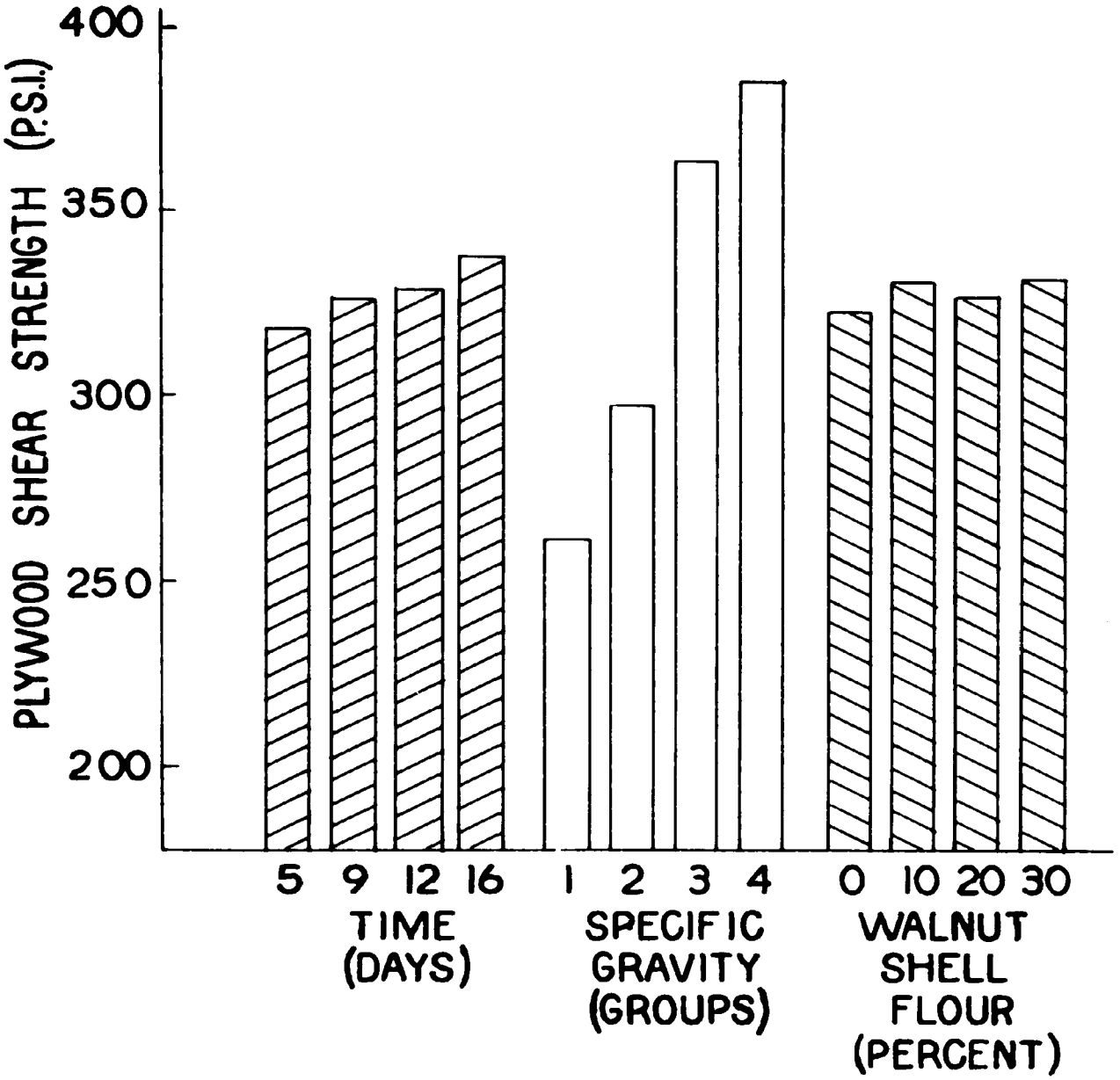

Figure 21. Trends of mean shear values of plywood bonded with m-cresol-formaldehyde resin for time (days), specific gravity groups, and walnut shell flour percent.

TABLE XXIV

ANALYSIS OF VARIANCE OF PLYWOOD STRENGTH DATA FOR PLYWOOD BONDED WITH 3,5-DIMETHYLPHENOL-FORMALDEHYDE RESIN

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square
Total	255	1,061,343	
Main Effects			
Time	3	14,507	4,836*
Specific gravity	3	565,385	188,462**
Walnut shell flour	3	315,583	105,194**
Interactions			
Time x specific gravity	9	10,271	1,141
Time x walnut shell flour	9	12,213	1,357
Specific gravity x walnut shell flour	9	103,112	11,457**
Time x specific gravity x walnut shell flour	27	35,634	1,320
Error	192	4,638	24

See Table XI for the significance of F.

Calculated least significant difference = 13.1

* Signifies significance.
** Signifies high significance.

This suggestion is substantiated by the relatively low values for wood failure shown in Table IX. The quality of the resin is evidently the cause. Subsequent discussion will clarify this situation.

Walnut shell flour influences the shear strength values of the plywood bonded with 3,5-dimethylphenol-formaldehyde resin in a manner similar to the two previously mentioned resin adhesives. However, the relatively higher mean square value, as shown in Table XIV, for walnut shell flour shows that its influence is somewhat greater. Tables XIV and XIVII show that the mean values for walnut shell flour from zero percent to 20 percent increase considerably, 10 percent being significantly better than zero percent and 20 percent being significantly better than 10 percent. This increase suggests that the quality of the unfilled resin is not high. The quality of the resin was definitely improved with a 20 percent addition of flour. A 30 percent addition of walnut shell flour does not seem to produce a significant decrease in plywood strength in relation to a 20 percent addition. This evidence suggests that while the walnut shell flour regulated resin flow during the bonding operation, it also improved the quality of the resin by acting as a binder between molecules of the resin. This binding effect evidently produces a stronger resin adhesive. Later discussion will amplify this point.

The means for time in Tables XIV and XIVI show that a significant increase in plywood strength is indicated after about 12 days. However, in about 16 days after bonding the strength of the plywood decreased significantly from the highest strength reached in 12 days.

TABLE XXV

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND WALNUT SHELL FLOUR FOR DOUGLAS FIR PLYWOOD BONDED WITH 3,5-DIMETHYLPHENOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Walnut shell flour (percent)	0	3,013	2,859	3,417	3,628	12,917	
		188	179	214	227		201.8
	10	3,261	3,657	4,977	5,475	17,370	
		204	229	311	342		271.4
	20	3,590	3,597	5,671	5,612	18,470	
		224	225	354	351		288.6
	30	3,797	3,699	5,672	5,047	18,215	
		237	231	354	315		284.6
	Total	13,661	13,812	19,737	19,762	66,972	
	Mean	213.5	215.8	308.4	308.8		261.6

TABLE XXVI

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH 3,5-DIMETHYLPHENOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Time (days)	5	3,350	3,173	4,826	4,888	16,237	
		209	198	302	306		253.7
	9	3,285	3,491	5,059	5,082	16,917	
		205	218	316	318		264.3
	12	3,527	3,686	5,115	5,115	17,443	
		220	230	320	320		272.5
	16	3,499	3,462	4,737	4,677	16,375	
		219	216	296	292		255.9
	Total	13,661	13,812	19,737	19,762	66,972	
	Mean	213.5	215.8	308.4	308.8		261.6

TABLE XXVII

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR WALNUT SHELL FLOUR AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH 3,5-DIMETHYLPHENOL-FORMALDEHYDE RESIN

		Walnut Shell Flour (percentage)					
		0	10	20	30	Total	Mean
Time (days)	5	3,192 200	4,089 256	4,417 276	4,539 284	16,237	253.7
	9	3,256 204	4,441 278	4,505 282	4,715 295	16,917	264.3
	12	3,509 219	4,490 281	4,901 306	4,543 284	17,443	272.5
	16	2,960 185	4,350 272	4,647 290	4,418 276	16,375	255.9
	Total	12,917	17,370	18,470	18,215	66,972	
	Mean	201.8	271.4	288.6	284.6		261.6

This suggests that the binding effect of the walnut shell flour is temporary and does not provide the necessary requirement for making the 3,5-dimethylphenol-formaldehyde resin an acceptable adhesive for bonding Douglas fir veneer into plywood. The possible reasons for this condition will be considered later in the discussion. The trends of the effects of the treatments—specific gravity, walnut shell flour and time—are shown in figure 11.

The significance of the first order interaction (specific gravity x walnut shell flour)* has the same meaning as it had for the phenol-formaldehyde and m-cresol-formaldehyde resins.

The analysis of variance for m-ethyl phenol-formaldehyde resin bonded plywood appears in Table XVIII. The least significant mean difference was calculated to be 13.9.

The high significance for specific gravity is the same as for all other resins and its meaning has been discussed.

The means for walnut shell flour in Tables XXIX and XXX suggest that between 10 and 20 percent walnut shell flour improves the flow characteristics of the resin for adhesive purposes. The flour filler increases the strength of Douglas fir plywood bonded with m-ethylphenol-formaldehyde resin when the filler is added in the percentage quantities suggested above.

Time is highly significant for shear values of plywood bonded with the m-ethylphenol-formaldehyde resin. Time influences this resin substantially. The means for time in Tables XXI and XXXI show a definite increase of plywood strength in 16 days. This evidence suggests that

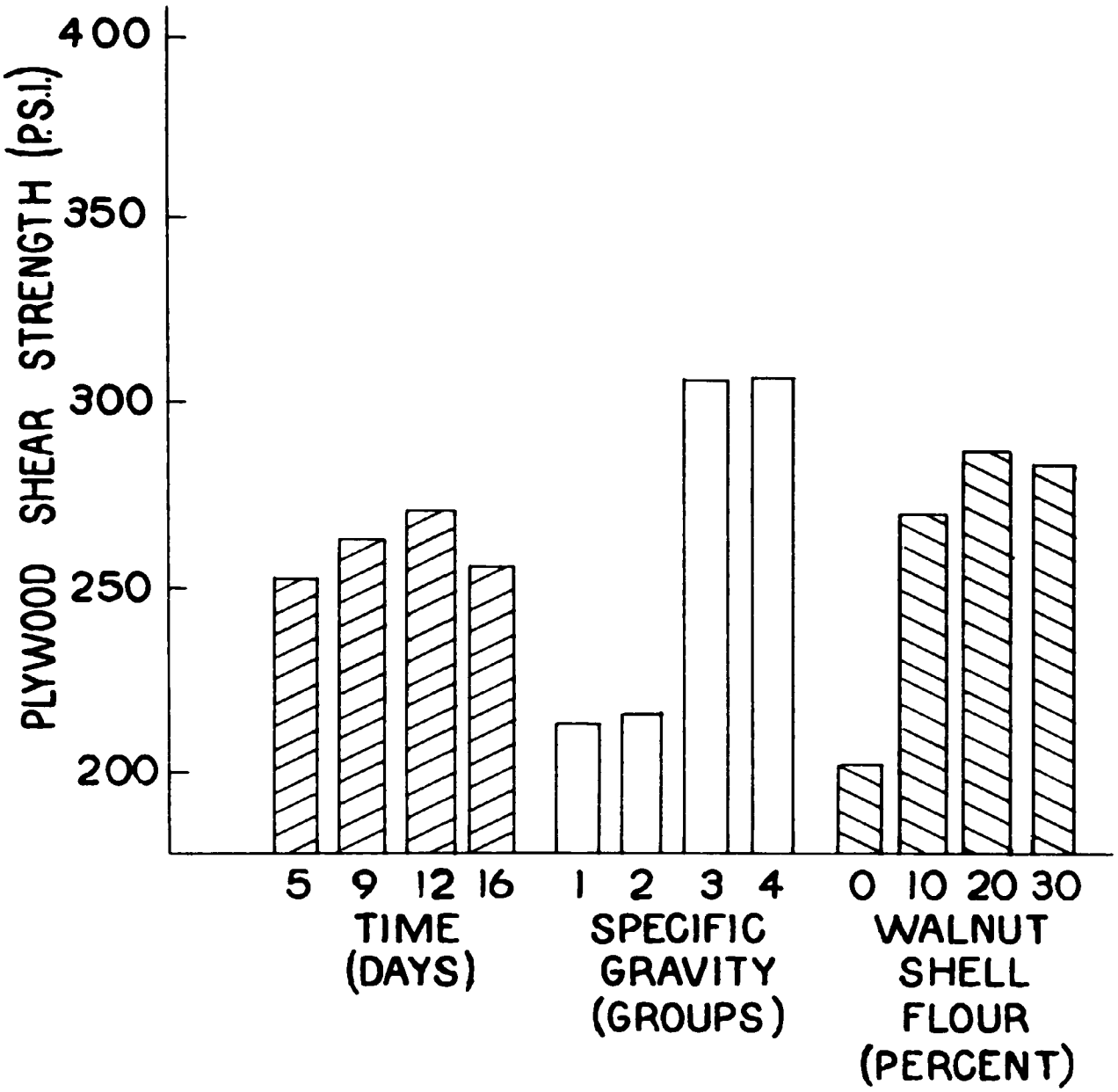

Figure 22. Trends of mean shear strength values of plywood bonded with 3,5-dimethylphenol-formaldehyde resin for time (days), specific gravity groups, and walnut shell flour percent.

TABLE XXVIII

ANALYSIS OF VARIANCE OF PLYWOOD STRENGTH DATA FOR PLYWOOD BONDED WITH m-ETHYLPHENOL-FORMALDEHYDE RESIN

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square
Total	255	792,066	
Main Effects			
Time	3	23,495	7,832**
Specific gravity	3	647,956	215,985**
Walnut shell flour	3	14,404	4,801*
Interactions			
Time x specific gravity	9	5,730	637
Time x walnut shell flour	9	20,129	2,237
Specific gravity x walnut shell flour	9	37,105	4,123*
Time x specific gravity x walnut shell flour	27	40,423	1,497
Error	192	2,824	15

See Table XI for the significance of F.

Calculated least significant difference = 13.9

* Signifies significance.
** Signifies high significance.

TABLE XXIX

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND WALNUT SHELL FLOUR FOR DOUGLAS FIR PLYWOOD BONDED WITH m-ETHYLPHENOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Walnut shell flour (percent)	0	3,867	4,303	5,094	5,970	19,234	
		242	269	318	373		300.5
	10	4,392	4,354	5,509	6,152	20,407	
		275	272	344	385		318.9
	20	3,770	4,413	5,835	6,340	20,358	
		236	276	365	396		318.1
	30	4,247	4,319	5,563	5,636	19,765	
		265	270	348	352		308.8
	Total	16,276	17,389	22,001	24,098	79,764	
	Mean	254.3	271.7	343.8	376.5		311.6

TABLE XXX

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR SPECIFIC GRAVITY AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH m-ETHYLPHENOL-FORMALDEHYDE RESIN

Specific Gravity

		1	2	3	4	Total	Mean
Time (days)	5	3,857	4,215	5,313	5,932	19,317	
		241	263	332	371		301.8
	9	4,067	4,202	5,317	6,009	19,675	
		254	268	332	376		307.4
	12	4,055	4,414	5,501	5,847	19,817	
		253	276	344	365		309.6
	16	4,297	4,478	5,870	6,310	20,955	
		269	280	367	394		327.4
	Total	16,276	17,389	22,001	24,098	79,764	
	Mean	254.3	271.7	343.8	376.5		311.6

TABLE XXXI

SUMS AND MEANS OF PLYWOOD SHEAR TESTS FOR WALNUT SHELL FLOUR AND TIME FOR DOUGLAS FIR PLYWOOD BONDED WITH m-ETHYLPHENOL-FORMALDEHYDE RESIN

Walnut Shell Flour (percentage)

		0	10	20	30	Total	Mean
Time (days)	5	4,798 300	4,677 292	4,942 309	4,900 306	19,317	301.8
	9	4,908 307	5,125 320	5,008 313	4,634 290	19,675	307.4
	12	4,592 287	5,059 316	5,078 317	5,088 318	19,817	309.6
	16	4,936 309	5,546 347	5,330 333	5,143 321	20,955	327.4
	Total	19,234	20,407	20,358	19,765	79,764	
	Mean	300.5	318.9	318.1	308.8		311.6

Douglas fir veneer bonded with m-ethylphenol-formaldehyde resin requires a longer time for adhesion bonds to develop between glue and wood to give strong plywood.

The trends of the effect of the treatment—specific gravity, walnut shell flour and time—are shown in Figure 23.

Significance is indicated between a time of five days and a time of 12 days, and between the time of five days and a time of 16 days at both the five and one percent levels of probability. Sixteen days is significantly better than nine days at the one percent level. This indicates that the experimentally bonded Douglas fir plywood should not be used for at least nine days and that 16 days is a better waiting period for best strength. These results also seem to suggest that additional adhesive bonds are formed with the passage of time after bonding.

Specific gravity follows the familiar pattern of higher specific gravity giving greater strength. In Table XXXIII it can be seen that all means for specific gravity are significantly different from one another. The reason for this has been indicated previously.

The means for walnut shell flour for all resins indicate that between 10 and 20 percent of the flour gives the best bond strength. Table XXXIV shows that 10 percent walnut shell flour is not significantly different from 20 percent walnut shell flour. However, both 10 percent and 20 percent walnut shell flour are significantly better than zero percent and 30 percent walnut shell flour.

Discussion of results obtained with different resins. The method

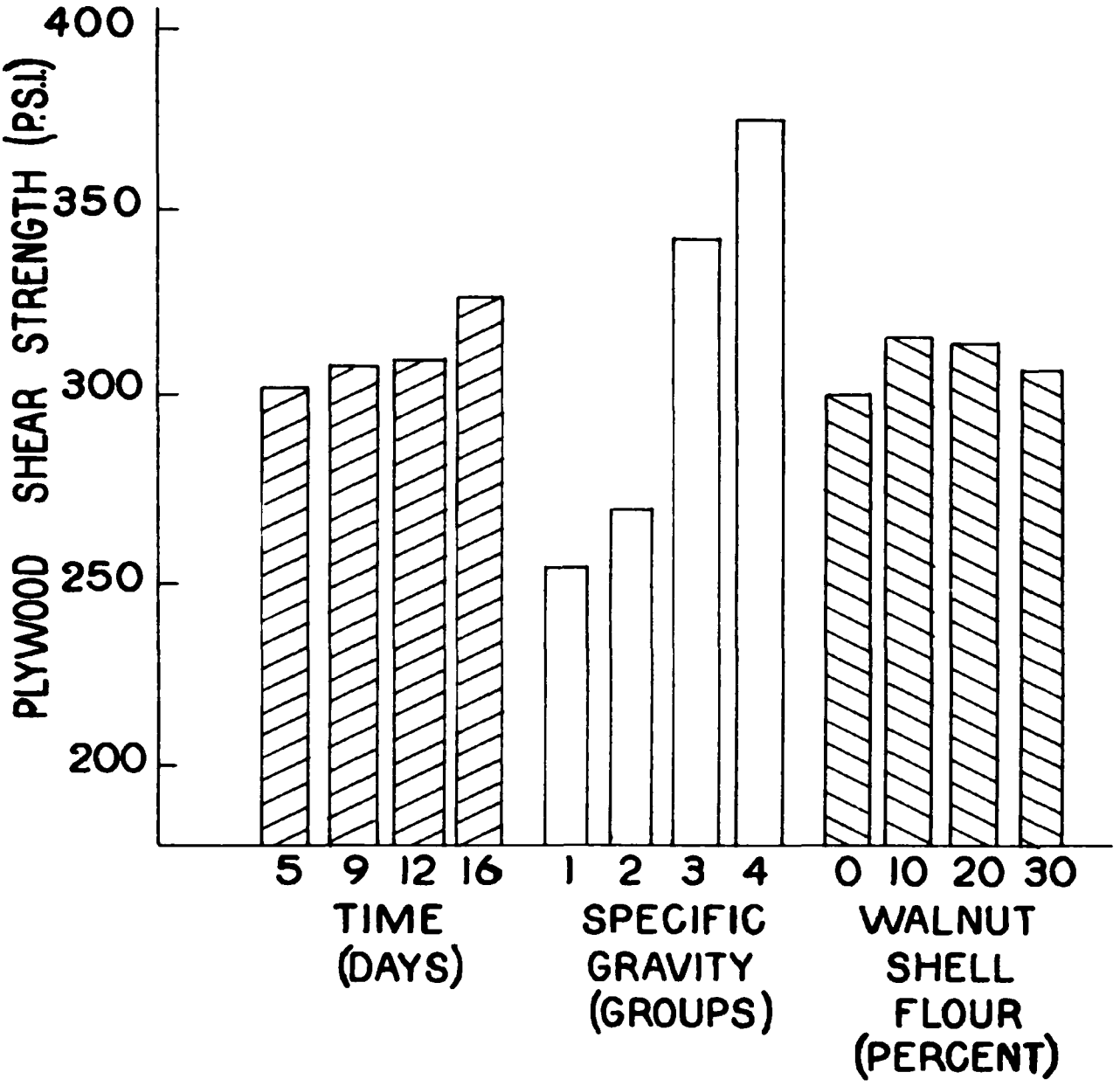

Figure 23. Trends of mean shear strength values of plywood bonded with m-ethylphenol-formaldehyde resin for time (days), specific gravity groups, and walnut shell flour percent.

TABLE XXXII

ANALYSIS OF VARIANCE OF DOUGLAS FIR PLYWOOD STRENGTH DATA FOR ALL RESIN ADHESIVES

Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square
Total	1,023	3,986,093	
Main Effects			
Resin	3	676,413	225,471**
Time	3	32,808	10,936**
Specific gravity	3	2,429,829	809,943**
Flour	3	152,041	50,680**
Interactions			
Resin x time	9	23,320	2,591*
Resin x specific gravity	9	36,636	4,071**
Resin x flour	9	202,107	22,456**
Specific gravity x time	9	5,335	593
Flour x time	9	15,878	1,764
Specific gravity x flour	9	104,250	11,583**
Resin x specific gravity x time	27	28,682	1,062
Resin x flour x time	27	31,023	1,149
Resin x specific gravity x flour	27	98,255	3,639**
Specific gravity x flour x time	27	38,051	1,409
Resin x time x specific gravity x flour	81	92,812	1,146
Error	768	18,653	24

F to be significant	5%	1%
81 and 3 degrees of freedom	2.72	4.04
81 and 9 degrees of freedom	1.99	2.64
81 and 27 degrees of freedom	1.62	1.98

* Signifies significance.
** Signifies high significance.

TABLE XXXIII

SUMS AND MEANS OF PLYWOOD STRENGTH DATA
SHOWING THE RELATIONSHIP OF
RESIN AND TIME

		Resin I	II	III	IV	Total	Mean
Time (days)	5	19,763	20,446	16,237	19,317	75,763	
		309	320	254	302		295.9
	9	20,295	20,986	16,917	19,675	77,873	
		317	328	264	307		304.2
	12	20,554	21,090	17,443	19,817	78,904	
		321	330	273	310		308.2
	16	20,641	21,631	16,375	20,955	79,602	
		323	338	256	327		310.9
	Total	81,253	84,153	66,972	79,764	312,142	
	Mean	317.4	328.7	261.6	311.6		304.8

TABLE XXXIV

SUMS AND MEANS OF PLYWOOD STRENGTH DATA
SHOWING THE RELATIONSHIP OF
RESIN AND SPECIFIC GRAVITY

		Resin I	II	III	IV	Total	Mean
Specific Gravity (Groups)	1	16,418	16,875	13,661	16,276	63,230	
		266	264	214	254		247.0
	2	18,130	19,092	13,812	17,389	68,423	
		283	298	216	272		267.3
	3	22,627	23,398	19,737	22,001	87,763	
		334	366	308	344		342.8
	4	24,078	24,788	19,762	24,098	92,726	
		376	387	309	377		362.2
	Total	81,253	84,153	66,972	79,764	312,142	
	Mean	317.4	328.7	261.6	311.6		304.8

TABLE XXXV

SUMS AND MEANS OF PLYWOOD STRENGTH DATA
SHOWING THE RELATIONSHIP OF RESIN
AND WALNUT SHELL FLOUR

		Resin I	II	III	IV	Total	Mean
Walnut shell flour (percent)	0	19,890	20,633	12,917	19,234	72,674	
		311	322	202	301		283.9
	10	20,529	21,240	17,370	20,407	79,546	
		321	332	271	319		310.7
	20	21,141	20,997	18,470	20,358	80,966	
		330	328	289	318		316.3
	30	19,693	21,283	18,215	19,765	78,956	
		308	333	285	309		308.4
	Total	81,253	84,153	66,972	79,764	312,142	
	Mean	317.4	328.7	261.6	311.6		304.8

TABLE XXXVI

SUMS AND MEANS OF PLYWOOD STRENGTH DATA
SHOWING THE RELATIONSHIP OF
SPECIFIC GRAVITY AND TIME

		Specific Gravity 1	2	3	4	Total	Mean
Time (days)	5	15,405	16,563	21,128	22,667	75,763	
		241	259	330	354		295.9
	9	15,663	17,257	21,755	23,196	77,873	
		245	270	340	362		304.2
	12	15,931	17,350	22,389	23,234	78,904	
		249	271	350	363		308.2
	16	16,229	17,253	22,491	23,629	79,602	
		254	270	351	369		310.9
	Total	63,230	68,423	87,763	92,726	312,142	
	Mean	247.0	267.3	342.8	362.2		304.8

TABLE XXXVII

SUMS AND MEANS OF PLYWOOD STRENGTH DATA SHOWING THE RELATIONSHIP OF WALNUT SHELL FLOUR AND TIME

Walnut Shell Flour (percentage)

		0	10	20	30	Total	Mean
Time (days)	5	17,874	19,119	19,525	19,245	75,763	
		279	299	305	301		259.9
	9	18,376	19,983	19,978	19,536	77,873	
		287	312	312	305		304.2
	12	18,280	20,016	20,521	20,087	78,904	
		286	313	321	314		308.2
	16	18,144	20,428	20,942	20,088	79,602	
		284	319	327	314		310.9
	Total	72,674	79,546	80,966	78,956	312,142	
	Mean	283.9	310.7	316.3	308.4		304.8

TABLE XXXVIII

SUMS AND MEANS OF PLYWOOD STRENGTH DATA SHOWING THE RELATIONSHIP OF SPECIFIC GRAVITY AND WALNUT SHELL FLOUR

Specific Gravity

		1	2	3	4	Total	Mean
Walnut shell flour (percent)	0	15,225	16,519	19,803	21,127	72,674	
		238	258	309	330		283.9
	10	16,333	17,530	21,880	23,803	79,546	
		255	274	342	372		310.7
	20	15,431	17,337	23,263	24,935	80,966	
		241	271	364	390		316.3
	30	16,241	17,037	22,817	22,861	78,956	
		254	266	357	357		308.4
	Total	63,230	68,423	87,763	92,726	312,142	
	Mean	247.0	267.3	342.8	362.2		304.8

used for calculating the analysis of variance for the entire experiment was simply an extension of the procedure used for computing the analysis of variance for shear strengths of phenol-formaldehyde resin bonded plywood. The sum of square values in Table XXXII for resin, time, specific gravity and walnut shell flour were determined from two-way Tables XXXIII, XXXIV, XXXV, XXXVI, XXXVII and XXXVIII. These same two-way tables were used to compute the sum of square values for the first order interactions (interactions involving two factors). Three-way tables supplied information for calculating the sum of square values for the second order interactions and a four-way table aided in the determination of the third order interaction. As before, the mean square values were obtained by dividing the sums of squares by the associated degrees of freedom. The value for F in every case was found by dividing the mean square by the mean square for the third order interaction. Thus any mean square value divided by 1,146 gave the F value for the factor or interaction involved. The value of F was used to determine the non-significance or significance of a factor or interaction.

In an analysis of variance in which the F test indicates significance, the t test is used to determine the least significant mean difference between the averages of the treatments used in the experiment. In this case the significant difference between the means of the resins, the times, the specific gravities, and the walnut shell flour treatments, as given in the two-way Tables XXXIII, XXXIV, XXXV, XXXVI, XXXVII and XXXVIII, was determined. The least significant mean difference at

the five percent level of probability is 5.9 and at the one percent level of probability is 7.9. For the analyses of individual resins only the five percent level was examined.

Resins I, II, III and IV represent shear strength values of plywood bonded with phenol-formaldehyde, m-cresol-formaldehyde, 3,5-dimethylphenol-formaldehyde and m-ethylphenol-formaldehyde resins, respectively. Tables XXXIII, XXXIV and XXXV give the means for the resin treatments. These means show resin II as significantly better than the other resins both at the five and one percent levels of significance. Resins I and IV do not show significant differences in plywood strength. Resin III is significantly worse than the other resins. An examination of cured resin films for all resins, and some chemical and physical aspects concerning the resins, may help to explain the differences in plywood strength among the resins.

In order to observe visually physical differences between the resins, equal weights of the different resin solutions were placed on glass plates, then cured into resin films. The films were cooled and inspected. Films for unfilled and filled resins were produced.

The unfilled m-cresol-formaldehyde resin film had all the characteristics of a tough resin. That is, the m-cresol-formaldehyde resin film could not be chipped easily with the fingernail. It could be handled without breaking. It showed no minute cracks or flaws due to crazing. The film did not craze over a period of two months but remained a solid film. Filled resin films exhibited similar characteristics.

The phenol-formaldehyde resin film showed characteristics similar to those observed for the m-cresol-formaldehyde resin film with the exception that this film could be chipped with the fingernail, suggesting a less tough resin film. The filled resin films were somewhat tougher than the unfilled film.

The m-ethylphenol-formaldehyde resin film was almost identical with the phenol-formaldehyde resin film but seemed to chip easier with the fingernail. The filled resin film seemed to be somewhat stronger than the unfilled film.

The cured unfilled film for 3,5-dimethylphenol-formaldehyde resin showed immediate crazing or showed what might be termed "delayed crazing" in that the minute cracks or flaws appeared after 24 or 36 hours. After crazing had occurred, the film crumpled and fell apart when handled. The filled 3,5-dimethylphenol-formaldehyde resin film appeared to be tougher than the unfilled film. However, there was some indication of flaws even in the filled resin film.

The apparent weakness of the 3,5-dimethylphenol-formaldehyde resin film is explainable if the phenomenon of steric hindrance is considered. Steric hindrance, as explained by Conant (16), refers to a theory that has been advanced to explain why some chemical reactions take place with difficulty. The explanation involves a consideration of the spatial interference to a chemical reaction by substituent chemical groups, as for example, groups on a benzene ring. Substituent groups may occur on a benzene ring in such a way as to hinder, by their configuration, a reaction on the ring by keeping a reacting substance away

from certain positions on the ring. The phenolic compound, 3,5-dimethylphenol, is made up of a benzene ring having an OH group in the number one position, and a methyl group in both meta positions, positions three and five. There are chemical groups in positions one, three and five, leaving the active positions, two, four and six, open. It can be understood that the methyl-groups could very well prevent other chemical groups from reacting with the ring by blocking reaction positions. In fact, Ellis (20) has stated that steric hindrance is the phenomenon which prevents 3,5-dimethylphenol from reacting fully with formaldehyde or from reacting with methylol groups on other rings in spite of the trifunctional nature of 3,5-dimethylphenol.

In view of what has been said, when 3,5-dimethylphenol is reacted with formaldehyde, the cured resin will not have as many crosslinks between molecules as the other resins used in this experiment. It should, therefore, be expected that lines of weakness will appear in the cured resin. Such flaws are verified by the craze effect found in the 3,5-dimethylphenol-formaldehyde resin film.

The means of the four resins given in Tables XXXIII, XXXIV and XXXV suggest that the ethyl group on the ring of m-ethylphenol-formaldehyde resin does not cause steric hindrance.

The above discussion offers an explanation for the effects of some factors within resins, which were not fully explained in the previous section. These effects should be clarified.

In Table XX of the previous section walnut shell flour was found not to be significant for the average shear strength values of plywood

bonded with m-cresol-formaldehyde resin. The analyses of all other resins show this factor to be significant. One possible explanation for this is that the more extensive polymerization of m-cresol-formaldehyde resin may produce a sufficient percentage of large molecules relatively early in the process of curing so that excessive penetration into the wood is prevented. In this case walnut shell flour is not necessary to retain the adhesive in the glue line.

The effect of specific gravity, walnut shell flour, and time in relation to the 3,5-dimethylphenol-formaldehyde resin bonded plywood should be explained. The effects of these factors appear in Tables XXV, XXVI and XXVII. While some effect is shown by specific gravity, the full effect of specific gravity could not be realized due to the extreme weakness of the resin film in the plywood. The addition of walnut shell flour gave a significant increase in plywood strength because it reduced the effect of crazing in this resin. However, the significant decrease in average plywood strength for a time of 16 days suggests that the walnut shell flour did not prevent crazing entirely. The strength of 3,5-dimethylphenol-formaldehyde resin bonded plywood decreased because of the crazing effect.

The results of average shear strength of plywood bonded with the different resins are shown in Tables XXXIII, XXXIV and XXXV. These data indicate that plywood strength decreased in the order m-cresol-formaldehyde resin bonded plywood, phenol-formaldehyde resin bonded plywood, m-ethylphenol-formaldehyde resin bonded plywood, and 3,5-dimethylphenol-formaldehyde resin bonded plywood. The reasons for this

order of strength have been given. It is noted that the order of strength invalidates the theory postulated in the Statement of the Problem. This theory suggested that the order of plywood strength as related to the phenolic resins would be phenol-formaldehyde resin bonded plywood, m-cresol-formaldehyde resin bonded plywood, 3,5-dimethylphenol-formaldehyde resin bonded plywood, and m-ethylphenol-formaldehyde resin bonded plywood. This theory was based on the possible effect of alkyl groups on the phenolic rings of the resins. However, the results of this investigation suggest that the strength of the resin adhesive itself determined the strength of the resin bonded plywood. The alkyl groups on the phenolic rings did not appear to affect the adhesion between wood and adhesive.

The effects of time, specific gravity, and walnut shell flour for the entire experiment are shown in Tables XXXIII, XXXIV, XXXV, XXXVI, XXXVII and XXXVIII. These effects can be observed quickly in Figure 24.

Table XXXIII shows that a significant increase in plywood strength is associated with a time of about nine days.

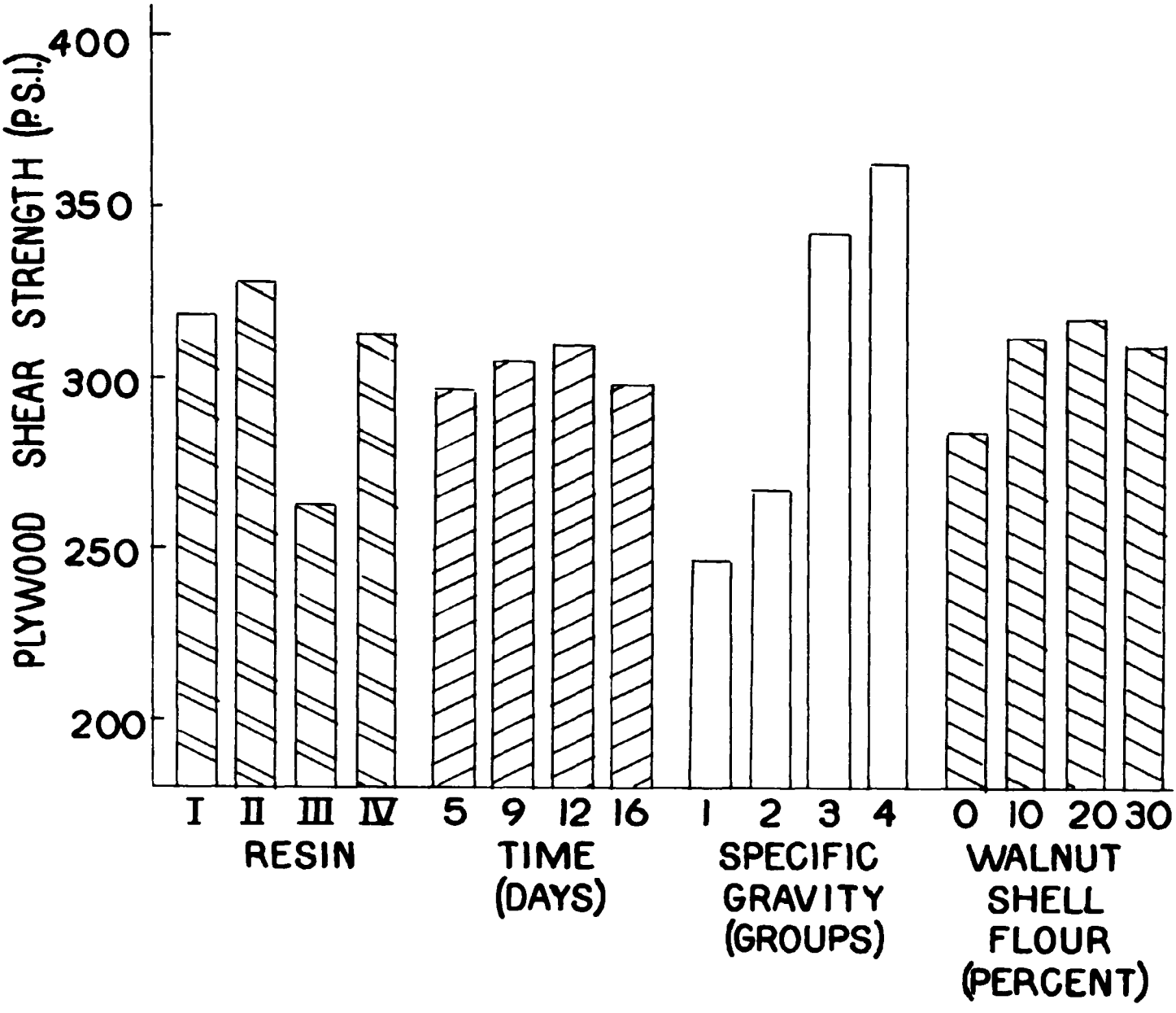

Figure 24. Trends of plywood shear strength means for the treatments, resin, time (days), specific gravity (groups), and walnut shell flour (percent) for all resins.

VII. SUMMARY AND CONCLUSIONS

Summary

The statistical analyses for the individual resins showed that specific gravity of the wood had a significant influence on the strength of Douglas fir plywood. Higher specific gravity of veneer gave higher plywood shear strength. When the glue bonds were adequate, as indicated by wood failure of about 75 percent or greater, specific gravity of the wood could be considered as exerting its full effect. In the case of the 3,5-dimethylphenol-formaldehyde resin body, steric hindrance prevented full polymerization of the resin. Due to a fewer number of crosslinks than functionally possible in the cured resin, the 3,5-dimethylphenol-formaldehyde resin showed a large amount of craze which reduced the full effect of specific gravity.

Walnut shell flour added to three of the resins increased the bonding strength of the resin when the flour was added in the amount of 10 to 20 percent of the resin solids. The shear strength of plywood bonded with m-cresol-formaldehyde resin showed no significant increase due to the addition of flour. It is suggested that this resin formed large molecules early in the curing stage which prevented excessive penetration of the resin into the wood.

The effect of time for individual resins was somewhat varied. When phenol-formaldehyde resin was used, a period of from nine to 12

days after bonding showed a significant increase in the strength of the plywood bonded with this resin. The m-cresol-formaldehyde resin bonded Douglas fir plywood gained significantly in strength after a period of from 12 to 16 days had elapsed between pressing and testing. The m-ethylphenol-formaldehyde resin bond gave increased plywood strength after 16 days. The 3,5-dimethylphenol-formaldehyde resin bond gave increased plywood strength in 12 days. However, a significant decrease in strength appeared in 16 days. This observation suggested the influence of lines of weakness in the resin which developed between 12 and 16 days after bonding Douglas fir plywood.

The m-cresol-formaldehyde resin adhesive gave the highest plywood strength because of its more complete polymerization. The 3,5-dimethylphenol-formaldehyde resin gave the lowest plywood strength values due to its characteristic low-polymerization because of steric hindrance. Phenol-formaldehyde and m-ethylphenol-formaldehyde resin bonds showed acceptable intermediate plywood strength since neither of these resins appeared to polymerize as extensively as m-cresol-formaldehyde resin, nor did they appear to be affected by steric hindrance.

The analysis of variance for the entire experiment showed that Douglas fir plywood of high specific gravity was stronger than that of low specific gravity. Walnut shell flour added to the resins in quantities of 10 to 20 percent of the resin solids gave increased plywood strength. The means of time treatments showed that plywood stored for a period of nine to 16 days after bonding increased in strength.

Conclusions

The strength of Douglas fir plywood varied with the phenolic type resins used in this investigation. The order of decreasing strength for plywood was as follows: 1) m-cresol-formaldehyde resin bonded plywood, 2) phenol-formaldehyde resin bonded plywood, 3) m-ethylphenol-formaldehyde resin bonded plywood, and 4) 3,5-dimethylphenol-formaldehyde resin bonded plywood.

All phenolic type resins used in the investigation appeared to give satisfactory adhesion between the resin and Douglas fir veneer. Even 3,5-dimethylphenol-formaldehyde resin appeared to adhere to the Douglas fir veneer.

The assumption that alkyl groups on the rings of the phenolic compounds would hinder adhesion between the phenolic resin adhesives and Douglas fir veneer does not hold. The alkyl groups appeared to have no influence in this respect.

Cohesive strength in the resin glue line of Douglas fir plywood appeared to be very important for plywood strength. It is suggested that this may be the important consideration when bonding Douglas fir with any alkyl-substituted phenolic type resin.

The strength of Douglas fir plywood bonded with phenol-formaldehyde, m-cresol-formaldehyde, or m-ethylphenol-formaldehyde resin will increase if stored for a period of nine to 16 days after bonding. Douglas fir plywood bonded with 3,5-dimethylphenol-formaldehyde resin

will gain strength if stored for 12 days but loses strength after this length of time.

The specific gravity of the Douglas fir veneer used to make the plywood has a definite effect on the strength of the plywood. Higher specific gravity gives greater plywood strength if the glue bond is adequate.

The addition of walnut shell flour in amounts of 10 to 20 percent of the resin solids, to the phenolic resin adhesives used in the investigation, with the exception of m-cresol-formaldehyde resin, increased the strength of Douglas fir plywood bonded with these resins.

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