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TITLE AN INVESTIGATION OF METHODS OF IMPROVING THE BONDING QUALITIES OF SOYBEAN GLUE

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AN INVESTIGATION OF METHODS OF IMPROVING THE BONDING QUALITIES OF SOYBEAN GLUE

by

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AN INVESTIGATION OF METHODS OF IMPROVING THE BONDING QUALITIES OF SOYBEAN GLUE

INTRODUCTION

Soybean glue, developed in the Pacific Coast Region of the United States about 1923, has a unique combination of moderate water resistance and low cost which makes it superior to all other types of adhesives for certain uses. In the United States, it has won a commanding place in the giant Douglas-fir plywood industry and has been used extensively in the manufacture of box shooks. It has also come into wide use in Japan (35).* Despite the increased availability and technical efficiency in the use of synthetic resin adhesives, which have largely replaced many of the other non-resinous glues, soybean glue is still consumed at an annual rate of 25-31 million pounds in the United States (38, 74). This glue is probably even more important in Oriental countries, where soybean is abundant and synthetic resins are unlikely to attain commercial importance in the near future. The present investigation was undertaken to develop methods of formulating soybean glue with improved dry and water-resistant bonding qualities and thereby to contribute to the promotion of the plywood industry in China as well as in other underdeveloped countries in the Far East.

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*Numbers in parentheses refer to Literature Cited at the end of the dissertation.

Only recently has the manufacture of plywood started in China. The demand for plywood for use in construction and for the fabrication of furniture and tea chests is constantly increasing. However, only animal glue, which is poor in water resistance, is locally available for these purposes. Consequently, the development of a better and cheaper adhesive is essential in boosting the production of plywood. A rather thick phenolic film glue was reported to have been developed in a laboratory, but its commercial production cannot be expected very soon. The high cost of imported synthetic resin adhesives precludes their wide application except for special items where their greater durability is essential. Casein does not have a bright prospect for large commercial production in China because of the shortage of milk. On the other hand, soybean has been the leading agricultural export of China for many years. As far as can be predicted, in the next decade or two, the most promising, reasonably good, cheap adhesive in China is very likely to be soybean glue. Any improvement in this glue would be a direct contribution to the plywood industry in China and thus to the betterment of the living conditions of her people.

The improvement of soybean glue can be approached, in general, along five different lines: 1) by improving the qualities of soybean meal through better processing methods; 2) by adding chemicals which would make the soybean protein insoluble or impart to it other desirable properties; 3) by

incorporating other adhesives which would impart their own water resistance to the combination; 4) by copolymerizing the soybean protein with low molecular weight resins to form a more insoluble mass; and 5) by adding preservatives to increase the mold resistance of otherwise unmodified soybean glue.

The present standard mixing formula for soybean glue developed by the Monsanto Chemical Co. (59) through both the first and second approaches is definitely better than the initial one used in the early days. Over the years, many other mixing formulas designed to improve the properties of this glue in various aspects have been proposed and patented. However, none has gained wide acceptance.

In this study, the possibilities of improving the bonding qualities of soybean glue by selection of better soybean meals and by fortification with other adhesives were investigated in detail. In addition, limited observations were made concerning incorporation of chemicals and mold resistance of a soybean glue mix. The fourth approach was not considered because copolymerization of soybean protein with the required special resin would be limited to the large manufacturers of plywood, who produce their own synthetic resins (56). Further, a substantial amount of resin is often required for copolymerization. This would obviously deviate from the main purpose, which is to develop a better soybean glue with soybean meal as the chief adhesive component.

Thus, the specific scope of this investigation included:

1. A comparison of the bonding qualities of different soybean meals.
2. A determination of the effect of hardener concentrations upon the bonding qualities of soybean glue.
3. An investigation of the fortification of soybean glue with casein and blood albumin.
4. An investigation of the possibilities of fortifying soybean glue with synthetic resins.
5. An evaluation of the mold resistance of soybean glue prepared with mixing formula developed in this study.

The approaches listed above evidently center on exploring the possibilities of improving soybean glue mixes to be used mainly as cold-press glues. Formulation of soybean glue suitable for hot-press application is not considered.

In the fortification of soybean glue with synthetic resins, the work has been extended to include the fortification of starch glue, which is also a cheap, cold-press adhesive of vegetable origin. Limited observations indicate that improvement of starch glue by fortification offers outstanding promise. Therefore, the experimental results of this work are included in this paper as a supplementary report to the improvement of soybean glue with synthetic resins, for comparison with soybean glue formulations.

The presentation of the main experimental work is divided into the five parts listed above. In each part, formulation of soybean glue is described, and test results and discussions are presented.

Although this investigation is largely confined to one selected soybean meal, the methods used for improving the soybean glue should be helpful in developing better glue formulations with other soybean meals. Also the information concerning characteristic behaviors of soybean protein disclosed by the study should enhance the existing knowledge of soybean glue and stimulate interest in further research.

REVIEW OF LITERATURE

Soybean, serving as an important source of food in the Far East, has been known for a long time to be rich in protein. However, it was only in the twenties of this century that scientists were able to turn it into a potential source of low cost protein for industrial uses. With the advance of protein chemistry, the use of soybean protein has extended at an ever-accelerating pace into many diversified fields, among which plastics, paper sizing, varnish, food, and adhesives are the major ones. During the past two decades voluminous information about soybean protein has been accumulated. Some of the more important aspects of soybean glue, such as chemical composition of the soybean and its protein, and the processing of soybean meal for adhesive use, are dealt with in this review of the literature on the subject.

Chemical Composition of Soybeans and Soybean Protein

The chemical composition of soybean seed is very complex. Not only are its chemical constituents numerous, but their relative proportions often vary markedly as a result of differences in variety, state of maturity, soil, fertilizer, cultivation, and climatic conditions. In general, soybean seed consists principally of protein, oil, carbohydrates, and mineral constituents. The average composition of the soybean seed of Manchuria is close to the figures presented by L. H. Bailey et.al. (56) in the following table:

Table 1. Chemical Composition of Soybean

Constituents	Minimum	Maximum	Average
Moisture	5.02%	9.42%	8.0%
Ash	3.30	6.35	4.6
Fat	13.50	24.20	18.0
Fiber	2.84	6.27	3.5
Protein	29.60	50.30	40.0
Pentosans	3.77	5.45	4.4
Sugars	5.65	9.46	7.0
Starch-like substances	4.65	8.97	5.6

Besides these major constituents, soybean seed contains many minor constituents such as pigments, vitamins, antioxidant bodies, etc. Still other substances are believed to be present, but only a guess may be hazarded as to their identity (55).

The soybean protein, as well as other proteins, is an extremely complex and sensitive substance. Despite considerable study, its chemical structure is still not yet fully known, and its molecular weight (minimum value - 8800) has not been established with certainty (29,.54, 55).

The chemical composition of soybean protein according to Osborne and Campbell (64) is as follows:

1. The chief portion is a globulin, that is, a simple protein insoluble in water, but soluble in dilute solutions of salts. This globulin is named glycinin and

is composed of:

Carbon	52.12%
Hydrogen	6.93
Nitrogen	17.53
Sulfur	0.75
Oxygen	22.63

2. A very small amount of a more soluble globulin resembling phaseolin.
3. An albumin-like protein, legumin (0.5%).
4. A small quantity of proteose.

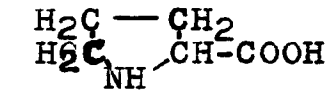
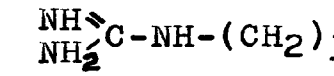
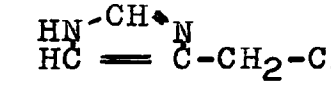
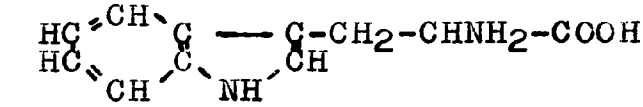
Hydrolysis of soybean protein by acids, alkalies or enzymes gives a mixture of amino acids. The results of investigations by various authors differ greatly. Table 2 shows the yields resulting from the hydrolysis of glycinin by Osborne (65) and the hydrolysis of whole protein by Heinrich (56.)

These results indicate that the proportion of amino acids in soybean protein is not very different from that of casein (71,78). Thus, it is not surprising that soybean glue is prepared in a manner quite similar to that of casein.

Processing of Soybean Meal for Adhesives

The quality of soybean meal is affected by the processing method employed. In general, there are three methods commonly in use for processing soybean for oil and meal, namely, hydraulic pressing, continuous pressing (expellers and

Table 2. Percentage Composition of the Amino Acids of Soybean Protein

Amino Acids	Osborne	Heinrich	Structure
Glycine	0.97	0.53	CH_2NH_2— COOH
Alanine	--	1.7	CH_3—$CHNH_2$—COOH
Valine	0.63	1.6	$(CH_3)_2$-CH-$CHNH_2$-COOH
Leucine	8.45	9.0	$(CH_3)_2$-CH-CH_2—$CHNH_2$-COOH
Proline	3.78	4.8	
Phenylalanine	3.86	3.8	C_6H_5-CH_2-$CHNH_2$-COOH
Aspartic Acid	3.89	3.7	COOH-CH_2-$CHNH_2$-COOH
Glutamic Acid	19.46	19.1	COOH-CH_2-CH_2-$CHNH_2$-COOH
Serine	--	--	CH_2OH-$CHNH_2$-COOH
Tyrosine	1.86	5.6	C_6H_4OH-CH_2-$CHNH_2$-COOH
Argnine	5.12	11.8	
Histidine	1.39	3.8	
Lysine	2.71	4.4	CH_2NH_2-$(CH_2)_3$-$CHNH_2$-COOH
Ammonia	2.56	2.4	NH_3
Tryptophane	present	--	

screw presses), and solvent extraction (55). In the Orient, soybeans are crushed largely by hydraulic presses or similar equipment, while in the United States, the screw press process and solvent extraction are employed. The advantages of solvent extraction are the high recovery of oil and the less degradation of the protein. Soybean meal from this process contains usually less than 1.0% of oil as against 4.0-5.0% of oil from other processes. The processing of soybean meal for adhesive use is done almost exclusively by continuous solvent extraction in the United States. In Japan and in the port cities of Korea and Manchuria, solvent extraction also comes into use.

Recently, further isolation of soybean protein from the solvent-extracted meal for adhesive use has been proposed recently by some researchers and claimed to give better adhesive strength. In the following paragraphs, the processes involved both in solvent extraction and in isolation of soybean protein will be summarized.

Solvent Extraction

Solvent extraction (39,46,55,56) can be executed either by batch type or by continuous process. The latter process is generally employed for processing soybean glue meals in the United States. The solvents may be hexane, ether, alcohol, acetone, etc., or a mixture of chemicals. In the port cities of Manchuria and Korea, alcohol is generally chosen for this purpose.

Alcohol is not as efficient in extracting oil as are other solvents. It is generally used in the Far East where hydrocarbon solvents are not economically available. Recent research indicates that introduction of hydrochloric acid of a normality of one-fifth in 60% methyl alcohol effects a considerable improvement. The soybean residue, after extraction by this method, contains 53% protein. An even more effective method of extraction is to use azeotropic mixtures of hydrocarbons such as petrol or benzene, and lower alcohols. A 60% protein can be obtained by a 50/50 mixture of methyl alcohol and petrol (68). However, the kind of solvents used greatly complicates the extracting system. It requires courage, capital, and special design of equipment in order to put such a new method into practice.

The solvent-extraction process may be considered as consisting of four parts.

Preparation of beans---The beans are first cleaned, dried (if above 13% moisture), and blended by transfer from one bin to another to temper them to like conditions. Then they are brought into the mill by conveyors, collected in storage bins, measured through automatic scales, passed over a magnetic belt to remove stray metal, and fed through a surge hopper into the cracking rolls. Each cracking roll unit consists of three pairs of corrugated rolls in vertical series turning toward each other at different speeds with crest to crest contact of the corrugations. This gives cutting and cracking, rather than mashing of the beans.

The cracked beans are passed over a 1/4-inch perforated dehulling shaker screen, where bean flakes drop out and hulls rise to the top to be removed by fan aspiration.

The dehulled cracked beans are then carried to a rotary stem-tube dryer conditioning to 9.5-10.0% moisture and fed to flaking machines. Each machine contains two sets of smooth-surface rolls in parallel position regulated to produce flakes about 0.008 inch thick in one pass. The desired thickness, size, strength, etc., vary over a wide range depending upon the type of extractor used. They can be regulated by proper adjustment of precracking moisture content, temperature, roll spacing, etc.

Extraction of oil---The bean flakes after passing through the flaking machine are conveyed to an extractor. There are a number of extracting systems such as Hilderbrandt, Bollman, Allis-Chalmers, and others. Although the equipment and method of carrying out the necessary steps of the process vary considerably among different systems, the principle of employing various solvents to remove the oil is somewhat similar. Prosoy-T soybean meal of the Glidden's Co., included in this study, is manufactured by the use of the Hilderbrandt System.

The Hilderbrandt extractor is a U-shaped cylinder into which bean flakes enter at one end and are discharged at the other end, while the solvent is pumped through the cylin-

der in countercurrent flow entering at the end where bean flakes are discharged. The bean flakes through the whole course are propelled by perforated screw conveyors which rotate at different speeds to produce considerable compacting in the bottom section of the U-shaped cylinder. The solvent from a storage tank is pumped through a preheater where it is heated by steam to about 120°F. and from there it flows to the extractor. After extracting oil from the flakes, the resulting miscella (oil-solvent mixture) is passed through a strainer and discharged.

The wet extracted flakes are discharged into meal dryers wherein residual solvent is driven off to be condensed in the surface condenser and returned to the system.

Reclamation of solvent---The miscella after discharge is filtered through specially constructed filter presses and carried to a steam tube evaporator which removes about 10% of the solvent. The rest of the solvent is removed in a distillation tower which consists of a series of evaporator sections. The oil leaves the solvent distillation equipment at a temperature of about 200°F. in the form of fluid emulsion with water and is clarified by a continuous separating centrifuge.

Flakes and meal---The extracted flakes on the meal dryers contain 0.5% oil. After drying they are subjected to toasting and other processes if they are intended for

food use, but for adhesive purposes they are conveyed to an attrition mill for grinding and screening to achieve uniform granulation. The size of the meal for glue use generally passes through 100 mesh in the screening operation. The final soybean meal usually contains from 44 to 53% protein depending upon the solvents and extracting systems used.

Isolation of Soybean Protein

The isolation process aims at obtaining relatively pure soybean protein, usually around 90% for paper sizing, plastics, paints, and various other industrial uses. Because of the inherent sensitivity of soybean protein to heat, acids, bases, organic solvents, and the concentration of their solution, the chemical nature of isolated soybean protein varies with the processing methods employed. The most extensive early work in the isolation, properties, and industrial utilization (mainly on molding products) of soybean protein is that of Satow, whose two voluminous Technology Reports (79,80) published in 1921-23 in Japan continue to serve today as a valuable source of information on these subjects. In the United States, a more recent monograph, "Soybean and Soybean Products" edited by K. Markley (56), gives a very comprehensive treatment in this field as well as in many other subjects about soybean. Soybean meals included in this study that have undergone the isolation process are Brier's Soybean Protein and Glidden's Alpha-Protein. The procedures of processing

these two meals are described briefly below.

Brier's Soybean Protein is essentially mechanically isolated (10). The procedure starts with washing the oil-free soybean flakes with an aqueous acid solution at pH 4.0 to 6.0 preferably around pH 5.0 to remove water soluble carbohydrates, hemicellulose, proteose, and other acid-soluble matter. Various acids may be used, although sulfuric acid or hydrochloric acid is preferred. This operation is carried out by either countercurrent leaching or repeated decanting.

The residue after leaching contains a mixture of insoluble protein, galactan, and fibers. The separation of the protein from other materials is effected by wet burring followed by wet screening. The wet burring strings out the fiber and galactans in long fibrils, whereas the protein agglomerates, being more or less spherical, are released and further separated from the fibrous materials by wet screening. The protein is allowed to settle, after which it is filtered and dried.

In both washing and wet burring the acidity of the aqueous mass of meal is maintained at the pH 4.0-6.0 so as to keep the protein in a non-sticky state. The final protein product thus processed is relatively pure, containing around 90% protein and less than 1% fibrous material, and is substantially undenatured.

Glidden's Alpha-protein undergoes an entirely chemical isolation process. It generally involves (a) dissolving the

protein from the oil-free soybean meals with alkali or salt solution, (b) separating the protein solution from the insoluble matter by filtration or centrifugation, and (c) precipitating out the protein with acids.

Cone and Brown (10,56) employed an alkaline salt solution, such as sodium sulfite, to dissolve the protein of the oil-free soybean flakes, thus separating the undissolved matter. Lime is added to the protein solution, precipitating more lime insoluble matter, which is similarly removed. The alkaline protein solution is then held at a suitable termperature for a length of time to effect sufficient denaturation.* After precipitating with acid at a pH of about 4.4, the resulting protein is dried and ground for use.

Optional alternative methods include an initial digestion of protein with a strong solution of caustic soda, followed by the addition of lime to remove lime insoluble matter, as well as a digestion with lime water to effect a separation of the protein fraction that is insoluble therein. Another patent (56) advocates the use of hot acid for treating soybean

*Denaturation is a term rather loosely applied to any process which results in alterations in the molecular configuration of protein (often uncoiling of the original protein molecule) and leads to a change of its physical properties, such as solubility, viscosity, etc., and of biological and chemical activities of certain groups. Terms such as digestion, hydrolysis, or modification are sometimes used interchangeably and loosely in the literature describing this process. The more common denaturing agents include heat, surface forces, ultraviolet light, hydrogen and hydroxyl ions, organic solvents, etc. The coagulation of egg white upon heating is a common phenomenon of denaturation (28,56,58).

flakes prior to extraction of the protein. In any case, the protein product going through these steps is greatly denatured.

Development of Soybean Glue

The introduction of soybean glue to the plywood industry on the Northwest region of the United States is largely due to the pioneering effort of I. F. Laucks. Conducting a commercial testing laboratory in Seattle in about 1920, he found that soybean meal has a high content of protein rather similar to casein. This led to the development of the soybean glue. His contributions have continued so that his company (now incorporated into Monsanto Chemical Co.) has become a leading producer of soybean glue in the United States.

While Laucks and Davidson first patented the process of making glue from soybean in 1923 in the United States (48), Omura and Okada in Japan and Johnson in Britain about the same time used soybean protein as a raw material for adhesives also (32,41,63). Johnson, following the technology of casein, employed sodium fluoride and lime in the preparation of the glue. The lime, which contributes to the formation of an irreversible gel, is one of the important ingredients in the soybean glue.

The literature pertaining to the immediate objective of the present study is found mainly in patent files. John Delmonte is perhaps the first to give a brief and comprehens-

ive treatment of the past work on soybean glue up to 1946 in his book, "The Technology of Adhesives" (24). A greater part of the early work deals with the addition of various chemicals to the soybean glue. Following is a brief resume of literature relevant to the present problem. It may be noted that improvement in water resistance of a soybean glue bond is extremely difficult to achieve beyond a maximum value which, however, is lower than can be considered adequate for severe exposure.

Incorporating Chemicals in Soybean Glue

Laucks and Davidson patented a number of mixing formulas in the early period. They recommended the use of caustic soda as a dispersing agent (48), and the employment of aluminum and chromium salts, tannine (50), quebracho (48), etc., to improve the water resistance of the soybean glue. Individually or jointly these two authors and Brown, Banks, Cone, and Eibertsen also proposed various other chemicals such as sodium sulfite (12), sodium dichromate (51), zinc chloride (49), potassium permanganate, boric acid, etc. (6,18,19) to obtain certain desirable qualities. Potassium permanganate and boric acid or some other weak acids such as phenols and cresols were claimed to stabilize the gel, thus preventing the breakdown of the glue under application of pressure. Rosin imparts stickiness and zinc chloride improves adhesive strength of the glue; while chromate salts prevent metal corrosion of the glue container and spreader. But the significant improvement

was their introduction of sulfur compounds such as carbon disulphide or polysulphides into the glue mixture. Their late patent (52) in 1939 included the following ingredients: 100 parts soybean flour, 3 parts lime, 8 parts caustic soda, 2 parts of a mixture of carbon disulphide and carbon tetrachloride in equal parts, and 10 parts of sodium silicate. The same ingredients were also indicated in an Italian patent but their proportions were different (9). The carbon disulphide makes the protein insoluble. This was an important step, as the present Monsanto mixing formulas for soybean glue were in fact, originated from this 1939 patent.

As the Douglas-fir plywood industry, the main consumer of soybean glue, expanded more and more, many investigators directed their attention to the study of this vegetable protein glue. Cement and paraffin (9) were suggested to improve the bonding and water-resisting qualities. White advocated the use of sulfonated oil with copper sulfate (94), and Wood, the use of Intramine (96) to increase the wet strength. Intramine is a sulphated product of the condensation reaction of fatty acids containing a substantial quantity of C_{12} and C_{14} acids with monoethanolamine. It was claimed to give an average wet strength of 232 psi when used in the proportion of 0.05-2.0% by weight of soybean meal.

Another composition comprising an aqueous solution of stearate chromic chloride at 1.0-5.0% by weight of the glue, having paraffin wax emulsified therein was also claimed to be

effective in making the protein insoluble (97). A German patent included 2,4-dioxooxazolidine as an ingredient to improve the water resistance of this glue (60). Soda lime and urea were employed in a Japanese patent (62). There were some procedures to make the soybean glue as smooth and homogeneous as casein. Davidson in his recent patent (20) dissolved rosin in an equal amount of fatty acid, then incorporated mahogany soap mixed with soybean flour, and added water, lime, and caustic soda in succession. Such a composition was said to have an excellent consistency.

The use of aldehydes as a jellying agent for soybean glue has been investigated for some time. Osgood employed aldehyde bisulphite at 0.5-5.0% by weight of soybean flour to increase the water resistance of this glue (66). Cone and Galber patented a procedure of mixing soybean flour and blood albumin with caustic soda in aqueous solution and adding formaldehyde or formaldehyde and copper sulfate (15). Furfural was also tried with soybean glue (45). Davidson et al. introduced both aldehydes and carbon disulphide into the soybean glue (19). Issac and Satow advocated formaldehyde in the preparation of soybean glue (40,81). The latter in a patent in 1935 chose ammonia or compounds of amide with active methylene groups to retard the coagulation action of formaldehyde. This glue mixture comprises 100 parts soybean flour, 10 parts sodium phosphate, 5 parts sodium fluoride, 7-10 parts reaction product of dilute formaldehyde and ammonia. Such a mixing formula was claimed to give a wet strength of 200-250 psi. The notable

point in this procedure is the technique of adding formaldehyde to the straight soybean glue.

Fortifying Soybean Glue

Dike developed a number of procedures for soybean glue for both cold pressing and hot pressing (26). Various additives have been suggested. Hot pressing was usually recommended for compositions containing blood albumin. Dike and Dunham employed an essential portion of blood albumin and comminuted cellulose together with some protein seed meal and casein in alkaline solution as a suitable mixture. Blood albumin was used with soybean glue to prevent starved joint by Cooper (15,16). A cementing composition comprising blood albumin, formaldehyde, ammonia and cobalt oxide was proposed by Cohen (14). While Hadert reviewed a number of casein-blood albumin blends (34), Wittka pointed out the possibility of improving adhesive strength of soybean glue by addition of casein. (95)

Extending Synthetic Resin Adhesives with Soybean Meal

During recent years, investigations have shown that soybean meal may be used to extend some synthetic resin adhesives without appreciable reduction of the durability of glue joints. Babcock and Smith described a method of combining a low molecular weight phenolic resin with soybean meal or corn gluten having a minimum of water-soluble constituents. Two examples were (a) phenol and formaldehyde in molar ratio of 1:1.5 with six grains of sodium hydroxide per

mol of phenol as catalyst and (b) phenol and formaldehyde in molar ratio of 1:2.5 with nine grams of sodium hydroxide per mol of phenol as catalyst. These were mixed together and heated. To this reaction product were added soybean meal or corn gluten, carbon bisulfide, alcohol, and water with continual stirring. The glue was then allowed to stand for 10-12 hours to reach suitable spreading consistency. (3).

Babcock and Smith have also investigated the extension of resorcinol resin adhesives with soybean meal and corn gluten. The latter was found more adaptable for this purpose. When the resin was prepared in the ratio of 1.0 mol resorcinol to 0.6 mol formaldehyde and adjusted to a pH of 7.5, addition of corn gluten up to even 80% of the dry weight of the resin appeared to have no marked effect on the initial dry strength and water resistance of joints in birch plywood (11).

Smith and Cowan employed a resin of low molecular weight and isolated soybean protein with carbon-black nickel as a catalyst to produce an adhesive (86).

Davis et al. in a British patent indicated that soybean meal could be successfully employed to lengthen the pot-life of phenolic resin adhesives (22).

Ford Motor Company developed an adhesive by heating a water-soluble phenol formaldehyde blended with soybean meal to an insoluble state. The mass was then finely divided and

reacted with a partial condensation product of water—soluble urea formaldehyde resin with $NH_4H_2PO_4$ as a catalyst. Such a catalyst would cause the adhesive to set at room temperature (21).

A water-proof, protein-resin adhesive useful for bonding plywood and metal was made by stirring an aqueous solution of a phenolic resin containing 1-3% free formaldehyde with a soybean meal in an amount of 10-40% by weight of dry adhesive to effect reaction between the resin and protein. The resultant gel was dried, milled with alkali, and ground to powder form. This process was patented in 1948 by Hieronymus (37).

Using soybean flour in place of wheat or rye flours as an extender for hot-press urea-formaldehyde resin has recently been claimed by Burnett and Eichenberger (56) to give a better glued joint. To overcome the high buffering action of soybean flour which prevented the development of a sufficiently low pH in the glue line on hot pressing, a special catalyst containing sodium bisulphite and a small amount of sodium fluoride was required. The former was to lower the viscosity of the glue mixture, and the latter, to prevent the evolution of ammonia from free urea by the action of the urease present in the flour. The high quality of such glued joint obtained in plant-scale tests with urea-formaldehyde resin extended with soybean flour is attributed to the high protein content of this flour.

No-Clamp Process

Finally, the recent development of the No-Clamp Process in the application of soybean glue should be mentioned (59). In this process the load is cold-pressed for 15 minutes at 175 psi without clamps and their attachments. It is then removed from the press and allowed to remain undisturbed for 30 minutes or four hours, depending upon whether the plywood is box-wood grade or structural grade. The load may then be disassembled and the panels redried. The success of this operation is due to the rapid development of adequate gel strength to hold the veneers in position through the use of a glue formula with lower ratio of water and higher proportion of sodium silicate than the regular one plus the constant pressure upon the load during the entire pressing period.

This process does not, however, improve the qualities of the soybean glue, but saves much labor in the pressing operation, as it eliminates all the handlings of clamps and beams required in the conventional cold-pressing method.

The above review indicates that there are a number of approaches to the improvement of soybean glue. However, much of the past work had been done with meals having rather high percentage of carbohydrates and other impurities. Since protein is generally regarded as the chief component responsible for adhesive strength in soybean glue, it appears logical to examine the possibilities of improving the bonding qualities of soybean glue with meals of high protein content through certain approaches as considered in this investigation.

TESTING PROCEDURE

The experimental work in this investigation consisted of five parts. They are presented separately following this section on testing procedure.

Since the approach and experimental procedure concerning glue gormulations are different for each of the five parts, they are described separately under each part to facilitate interpretation of the data and comprehension of the results.

This section covers the preparation of test specimens and methods of testing which are, in general, common to the entire experimental work. In addition, a brief description of the general design of the experiments, and the method of statistical treatment used in the analysis of data, are also included.

General Design Of Experiments

Part I of the experimental work was designed to compare the adhesive strength of four soybean meals having different protein content, so that a better soybean meal could be selected for further improvement. These four soybean meals were tested under similar conditions with two mixing formulas. This provides not only a comparison of the adhesive strength of the four soybean meals, but also brings out

the performance of each mixing formula and the reaction of different soybean meals to each mixing formula.

Part II was undertaken to determine whether the water resistance and other properties of the soybean glue prepared with the selected meal and mixing formula from the preceding experiment can be further improved by increasing the amount of lime and tetrasulphide mixture, which serve to harden the soybean protein in the glue mix. Three concentrations of each of the two chemicals in various combinations were employed in the preparation of soybean glue mixes for testing.

From here on, the investigation concentrated on the fortification of soybean glue with other adhesives of known high water resistance or durability. In Part III, the fortifying adhesives used were casein and blood albumin, while in Part IV only synthetic resins were used. In both cases, the fortifying adhesives were separately incorporated into soybean glue mixes in different amounts. These glue mixes were then tested in the same manner as previously. Experiments conducted in these two parts were to ascertain how much improvement in the bonding qualities of soybean glue can be achieved through fortification and which adhesives are best fitted for this purpose.

Finally, the soybean glue mix developed from this study was subjected to a mold resistance test, side by side with a soybean glue prepared with a commercial mixing formula

for comparison. In the meantime, the optimum amount of an effective preservative required for the protection of the developed glue mix from mold attack was also determined.

The bonding qualities of all the soybean glue mixes in this investigation were tested with one species of wood, yellow birch, and measured by one or a combination of three types of test (plywood shear test, delamination test, and block tension test) according to the objective of each experiment. Thus, the results of all experiments conducted in this investigation can be compared with one another according to the type of tests.

With the exception of Part IV, Fortification of Soybean Glue With Synthetic Resins, which is largely exploratory in nature, the experiments and replications of test specimens were so set up that the data obtained are capable of statistical treatment.

Preparation Of Test Specimens

Materials

Species --- In order to obtain a better measure of glue joint strength, yellow birch instead of Douglas-fir was chosen for this study, although both were considered suitable for matching the species potentially available in China for manufacture of plywood. Commercial grade of 1/16-inch, thick

rotary-cut veneer of birch was obtained in one single lot and properly stored in the conditioning room after its arrival. The average specific gravity of this veneer determined from five 11 by 11-inch sheets (73) was 0.64. The 1-inch thick birch lumber used was of a select grade. It was cut into suitable size and stored in the same conditioning room.

Soybean meals --- Four soybean meals, Monsanto's Lauxein 10-B, Glidden's Proxoy-T, Glidden's chemically isolated Alpha-protein and Brier & Mulder's mechanically isolated soybean protein (abbreviated as Brier's Soybean Protein) were employed in the initial investigation. In subsequent tests Brier's Soybean Protein was mainly used. Alpha-protein, sent by the Glidden Company at the end of this investigation, was tested for additional comparison only.

The protein content and manufacturing processes of these four soybean meals were as follows:

	Approx. protein content	Manufacturing process	Degree of fineness
Monsanto's Lauxein 10-B	50.0%	ether extracted	100 mesh
Glidden's Prosoy-T	53.3%	hexane extracted	100 "
Brier's Soybean Protein	90.0%	mechanically isolated	100 "
Glidden's Alpha-protein	96.9%	chemically isolated	50 "

Chemicals --- All the chemicals used in this investigation were obtained through the Chemistry Store of the Chemistry Department of the University of Michigan, and were of C. P. quality.

Four basic chemicals used in the preparation of soybean glue are as follows:

Flake caustic soda - 76% Na_2O

Silicate of soda (water glass) 41° Baumé and 8.9% sodium oxide, 29% silica of Philadelphia Quartz N-Brand.

Hydrated lime of at least 98% calcium hydrate, all to pass 200-mesh screen.

Tetrasulphide mixture -60% carbon disulphite and 40% carbon tetrachloride.

Other chemicals used mostly in the fortification of soybean glue with synthetic resins are: ammonia hydroxide (NH_3 minimum 28%), benzaldehyde, butyraldehyde, borax, boric acid, calcium chloride, formaldehyde (37%-neutral), furfuraldehyde, hexamethylene tetramine, oxalic acid, oleic acid, paraformaldehyde, phosphoric acid, sodium acetate, sodium bisulphide, sodium fluoride, sodium thiocyanide, and trisodium phosphate.

Fortifying adhesives --- Fortifying adhesives used include:

Casein Glue	Perkins Perfection
Blood albumin	Armours & Co.
Resorcinol-formaldehyde	Koppers Penacolite G-1131
Urea-formaldehyde	Plaskon 2502
Modified alkyd	General Electric Glyptol 2504
Phenated alkyd	Reichold 1030
Cumar-indene resin	Barret Div. Cumar P 10
Rubber-base adhesive	U.S. Stoneware Tygobond 30
Polystyrene emulsion	Reichold BKS-92

Glue Formulas

A number of soybean glue mixing formulas were used in the various phases of this investigation. Only the one upon which many other mixes were based is given here. Other glue formulas used are included under each of the main topics considered in experiments described in Part I through Part V.

Chemicals	Extra water resistance mix		
Soybean meal	100	gms.	
Water	380	"	(varies with different meals)
Lime	4	"	
Caustic soda	8	"	
Silicate of Soda	20	"	
Tetrasulphide mixture	4.8	"	

This formula was developed by Monsanto Chemical Company for its soybean meal, Lauxein 10-B. For Brier's soybean meal 240 more grams of water was required in order to produce an adequate consistency.

The pH value of different soybean glue mixes was determined with "PHydrin" paper (from Micro Essential Laboratory), which covers the range from 1 to 14 in units of 0.5.

Gluing of Test Panels

Rotary-cut birch veneers of 1/16-inch clear stock were cut into 8"x15" size and glued into 3-ply panel with the grain of the core at right angles to the faces. Straightness of grain was emphasized in the selection of veneer, particularly for faces. Moisture content of the veneer at the time of gluing was 10-12%, conditioned beforehand for at least one week at relative humidity 65% at 80°F. (E.M.C. = 11.6).

Mixing of soybean glue --- in accordance with Monsanto's Lauxein 10-B direction (59) as follows:

Place 200 grams of water (70°F.) in mixer.

Add 100 grams soybean meal.

Mix for 3 to 5 minutes until lump-free.

Add 150 grams of water (70°F.) and mix. (390 grams of water for Brier's soybean meal).

Add 3 grams of lime in 10 c.c. of water. (4 grams for extra mix).

Add 7 grams of caustic soda in 20 c.c. of water and mix. (8 grams of caustic soda for extra mix)

Add 15 grams of silicate of soda and mix. (20 grams of silicate of soda for extra mix)

Add 2.4 grams of tetrasulphide mixture (4.8 grams of this mixture for extra mix).

Mix for 5 minutes - Glue is ready for use.

Spread --- at the rate of 70 lbs. per 1000 sq.ft. of single glue line unless otherwise noted. All spreading was done by means of hand by means of hand brushing.

Assembly time --- closed assembly 10 to 15 minutes.

Pressing --- 200 lbs per square inch applied by the Universal Riehle Testing Machine and held under pressure overnight.

In the gluing of mold resistance test panels, the technique involved was the same as in the other test panels, except that in this case only sapwood veneer was used in order to reduce possible variations in results, which might occur due to presence of natural preservatives in the heartwood. The veneer selected was also glued into 3-ply panels. In the treated panels, 3%, 5%, and 7% of sodium trichlorophenate were separately incorporated into the glue as indicated in Part V, Mold Resistance.

Gluing of Test Blocks

The block tension test was used instead of the block shear test, as the former is believed to be more sensitive to adhesive variables. Clear stock of 1-inch thick, straight-grained birch was cut into 1 3/4-inch wide strips and conditioned in the 10-12% conditioning room (in the same room as the veneer) for two weeks. Immediately before gluing, these strips were jointed on one side and then planed on both sides down to 3/4" thick and cut to 2 1/2" length. A hole was then drilled in the center. When two pieces were glued together crosswise, the glued area was just three square inches. The gluing conditions were the same as those used in preparing the test panels, but the pressing jig was specially built (see Figure 2).

Methods of Testing

Three methods of testing were used in measuring the joint strength of soybean glue in this investigation. They are the plywood shear test, delamination test, and block tension test. Greater emphasis is placed on the plywood shear test in this study, as more specimens are employed in this test. Also it is the most widely used method in measuring both dry and wet joint strength of a glue. While the delamination test, together with wet joint strength from the plywood shear test, indicates mainly the water resistance of

the glue, the block tension test is employed here to measure the dry joint strength along with the plywood dry shear test.

Besides the joint strength tests, a mold resistance test was also conducted for the soybean glue prepared with mixing formula developed in this study.

Plywood Shear Test

All the panels were conditioned for at least one week before testing was done. Out of each panel, 12 shear specimens of 3 1/4" x 1" size were cut. Three panels for each treatment gave a total of 36 shear specimens: 18 for dry shear test and 18 for wet shear test. The allotment of dry and wet shear specimens from each panel was made as follows:

D_1	W_2	D_3	W_4	D_5	W_6	delamination test panel 6" x 6"
W_7	D_8	W_9	D_{10}	W_{11}	D_{12}	

D = dry shear test specimen

W = wet shear test specimen

These shear test specimens were then prepared according to the standard specifications (1), one half (W_7 - D_{12}) of the 12 shear specimens from each panel were slotted in the reverse manner so as to balance out the discrepancy in joint strength resulting from lathe check orientation (8).

Dry-Shear test --- The final test specimens were mounted in the jaws of the clamp fixture on a Riehle ply-

wood testing machine. Load was applied at a rate of 800 lbs. per minute until the specimens broke. The breaking load and percentage of wood failure were recorded (see figure 1).

Wet shear test --- Test specimens for the wet test were immersed in water at room temperature for 48 hours and tested while wet in the same way as in dry shear test.

Block Tension Test

The cross-wise glued blocks were conditioned for one week and then tested in the Dillon testing machine with a set-up developed at the Wood Technology Laboratory (67), School of Natural Resources, University of Michigan (see figure 2). For each treatment ten test blocks were used.

Delamination Test

The testing panels, after cutting the shear test specimens, were trimmed to 6" x 6" square for delamination study according to standard specifications for hardwood plywood CS 35-49 Par. 5.5 (36). For each treatment there were three such squares. They were submerged in water for four hours at room temperature, followed by drying in the conditioning room at 75°F. and 24% relative humidity for 20 hours. This cycle was repeated 15 times instead of the required 10 times in commercial inspection so as to bring out enough effect of this treatment for evaluation of the glue joint.

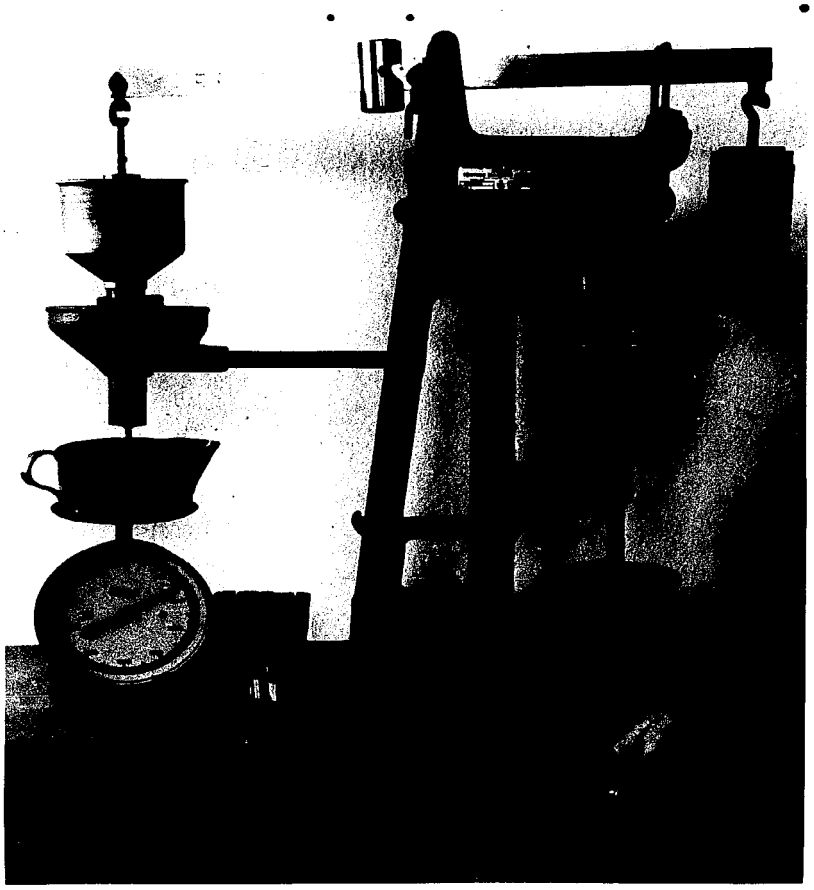
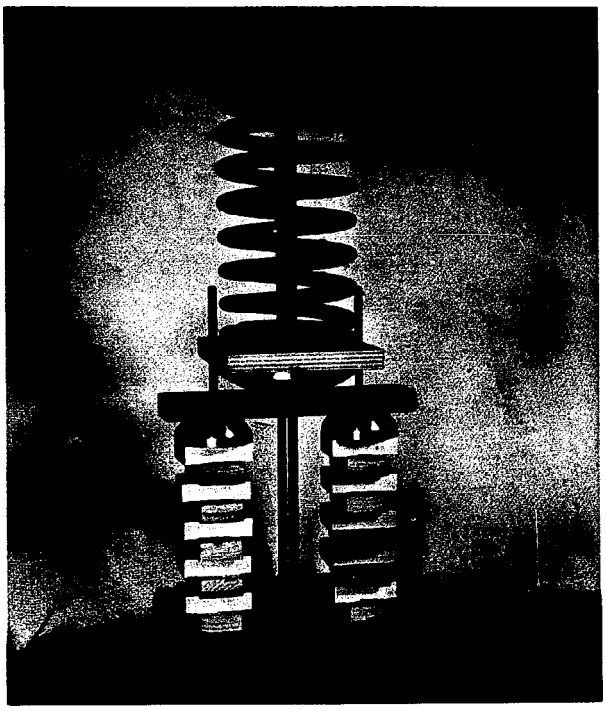
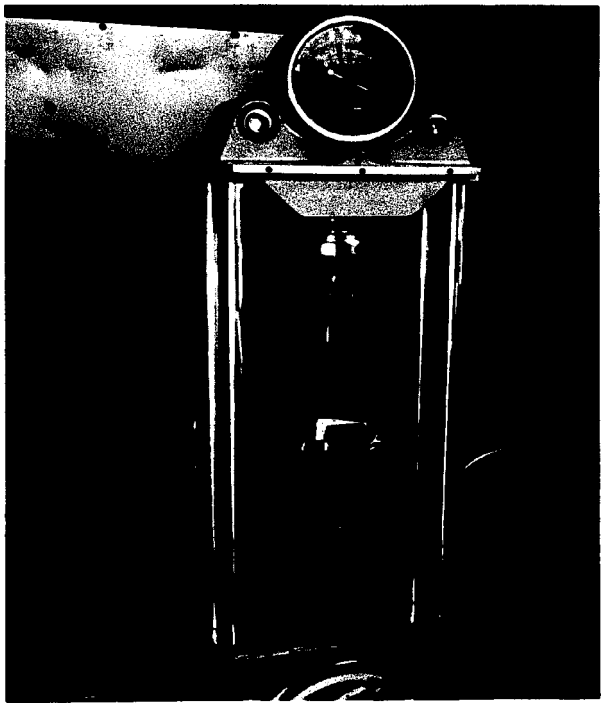


Fig. 1. Equipment used for plywood shear test.



A. Pressing jig with load of test specimens ready to press.



B. Block tension test machine with a test specimen in the angle grips for testing.

Fig. 2. Equipment used for block tension test.

The degree of delamination was inspected and measured at each cycle according to visible delaminated lines regardless of their depth.

Mold Resistance Test

The mold resistance test panels prepared from sapwood veneer with both the commercial glue formula and improved formula were cut into shear specimens for exposure to mold. There were six preservative treated panels and four control panels. Out of each panel 25 shear specimens were cut. Six treated and four control panels gave a total of 250 shear specimens for successive exposure tests at an interval of one week, two weeks, and four weeks. The size and allotment of shear specimens were as follows:

0	1	2	3	0	1	2	3	0	1
2	3	0	1	2	3	0	1	2	3

0 initial test
1 one week after exposure
2 two weeks " "
3 four weeks " "

These shear specimens were then soaked for one-half to one minute in a water suspension of mold spores which was prepared by mixing mold spores from sheets of molded casein-soaked veneer with tap water according to the Forest Products Laboratory proposed procedure (43). The moldy sheets of ve-

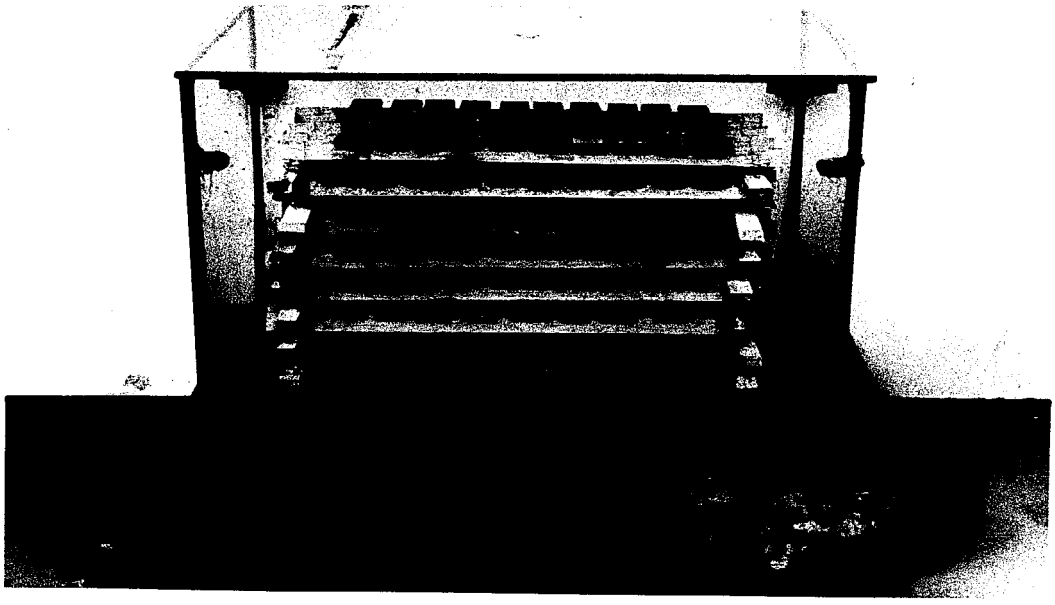


Fig. 3. Mold resistance set-up showing the placement of test specimens in the humidity chamber after soaking in the mold suspension solution.

neer were obtained from the Divisions of Forest Pathology of the U.S. Forest Products Laboratory, Madison, Wisconsin.

The shear specimens were then stacked on small wooden stickers in a glass humidity chamber with sufficient water present in the bottom of the chamber to insure a saturated atmosphere (see figure 3). The chamber was maintained at a temperature of 72-80°F. These specimens were left in the chamber for the period indicated above and tested upon removal. The decrease of joint strength at successive intervals is a measure of mold resistance of the glue.

Method of Statistical Analysis

The data obtained from the above tests were analyzed by means of a statistical method known as Analysis of Variance. For variability in results is typical of experimental data, and difficulty often arises in distinguishing with confidence between the variations due to pure chance and those due to treatment. Analysis of Variance provides a convenient tool by which the effect of two or more treatments can be properly estimated.

The execution of this statistical analysis followed the method described by O. L. Davis (23). In every case, when the F-ratio for treatment as determined from Analysis of Variance indicated significance at 5% level or above, the mean values for the treatment were further analyzed by

the t-test so as to detect which glue or mixing formula is significantly different from others in joint strength or delamination. In a few essential cases, the t-test was also made even when the group F-ratio fell between the 10% and 5% levels. This was done merely to find out the probability level of certain glues or formulas for more information, although Davis in his statistical book for Imperial Chemistry Industry use designated the probability range between 10% and 5% as "possibly significant" (some doubt is cast on the Null Hypothesis, but further evidence is required before it can be rejected). The tables of Analysis of Variance for various tests in this investigation are given in the Appendix.

PART I

BONDING QUALITIES OF DIFFERENT SOYBEAN MEALS

Soybean Meals and Mixing Formulas

It is generally recognized that the adhesive strength of a soybean meal depends upon the quality of its protein, which varies with the processing methods of its manufacture. In this investigation four soybean meals from different manufacturing sources were used, namely, Brier's Soybean Protein, Monsanto's Lauxein 10-B, Glidden's Prosoy-T, and Glidden's Alpha-protein. The first is essentially a mechanically isolated meal having a protein content of 90%, and the second is an ether-extracted meal having a protein content of about 50%, while the third is a hexane-extracted meal having a protein content of 53.3%. The fourth, having the highest protein content (96.9%), is chamically isolated. The bonding qualities of the first three soybean meals were determined by three types of tests with two mixing formulas. The fourth, received from the Glidden Company at the end of the investigation, was determined by similar tests with only one mixing formula.

The two mixing formulas are Monsanto's regular mix and extra-water-resistance mix. They are given below with the pH of each of the four soybean glue mixes indicated.

Soybean Meals and Chemicals	Regular Mix		Extra-Water-Resistance Mix		
	Lauxein 10-B & Prosoy-T	Brier's Soybean Protein	Lauxein 10-B & Prosoy-T	Brier's Soybean Protein	Glidden's Alpha-Protein
Soybean meal	100 gms.	100 gms.	100 gms.	100 gms.	100 gms.
Water	380 "	620 "	380 "	620 "	430 "
Lime	3 "	3 "	4 "	4 "	4 "
Caustic soda	7 "	7 "	8 "	8 "	8 "
Silicate of soda	15 "	15 "	20 "	20 "	20 "
Tetrasulphide mixture	2.4 "	2.4 "	4.8 "	4.8 "	4.8 "
pH of glue mix	11.5	11.5	12.0	12.0	12.0

It is evident that the only difference between the regular mix and the extra mix is in the amount of certain chemicals used. The extra mix contains more lime, caustic soda, and silicate of soda, and twice as much tetrasulphide mixture as the regular mix. Another point to be noted is that the amount of water required for Brier's soybean meal was much higher than for the other three soybean meals. This was because this soybean meal, after addition of caustic soda, dispersed to such an extent that an extra amount of water was needed to produce a spreadable mixture. In all cases, the amount of spread was, however, at the rate of 70 pounds per 1000 square feet of single glue line. The results of tests and number of specimens used for each test are presented in Table 3.

Results

The bonding qualities of the four soybean meals under investigation were evaluated on the basis of (a) the observed joint strength alone, and (b) the observed joint strength with respect to soybean meal concentration in the glue line. The necessity of taking the meal concentration into account in this case is due to the different amount of water involved in the preparation of the glue mixes. It is only on the latter basis that a comparative adhesive quality of the meals can be revealed, whereas analysis on the first basis gives only the bonding performance of the glue mixture prepared with the respective soybean meals without regard to the actual amount of meal in the glue mix.

Analysis on The Basis of Observed Joint Strength Alone

1. In the plywood shear test, the average dry shear strength among the four soybean meals was found to be about the same, all being close to 390 psi. In wet shear strength Brier's Soybean Protein and Glidden's Alpha-protein gave a higher value than Monsanto's Lauxein 10-B and Glidden's Prosoy-T, but the difference was not significant as is shown from the statistical analysis given in the Appendix. This means that the probability of the first two soybean meals being higher in wet strength than the other two is less than 95%.

Table 3. Results of Four Soybean Meals Tested with Two Mixing Formulas on Yellow Birch

Soybean Meals	Plywood Shear Test*						Delamination Test			Block Tension Test		
	Panels	No. of Specimens	Regular Mix		Extra Mix		No. of Panels	Regular Mix	Extra Mix	No. of Blocks	Extra Mix	
			Dry	Wet	Dry	Wet						
			Lbs. per sq. inch		Lbs. per sq. inch			delamination %	%		Lbs. per sq. inch	
Brier's Soybean Protein	(1)	6 each	397	220	424	239	1	6.8	7.1	10	342	292
	(2)	6 "	411	203	382	248	1	11.4	4.5		308	292
	(3)	6 "	363	185	366	191	1	9.0	8.1		283	283
											217	317
											317	367
	Avg.	18 each	390	203	391	226	3	9.1	6.6		302	
Monsanto's Lauxein 10-B	(1)	6 each	374	194	396	218	1	8.6	4.9	10	350	317
	(2)	6 "	358	186	400	214	1	12.9	9.9		370	275
	(3)	6 "	406	185	352	178	1	9.2	7.5		283	300
											233	342
											290	300
	Avg.	18 each	379	188	383	203	3	10.2	7.4		306	
Glidden's Prosoy-T	(1)	6 each	392	184	399	219	1	11.4	10.0	10	283	333
	(2)	6 "	401	199	428	201	1	7.8	6.3		242	308
	(3)	6 "	362	179	375	211	1	7.8	5.1		208	350
											225	367
											292	300
	Avg.	18 each	385	187	401	210	3	9.0	7.1		291	
Glidden's Alpha Protein	(1)	6 each			428	213	1		8.2		322	307
	(2)	6 "			417	239	1		5.2		35	268
	(3)	6 "			408	224	1		7.3		285	290
											332	360
	Avg.	18 each			418	225	3		6.8		309	301
											311	

*Wood failure was nil and therefore not included in the table

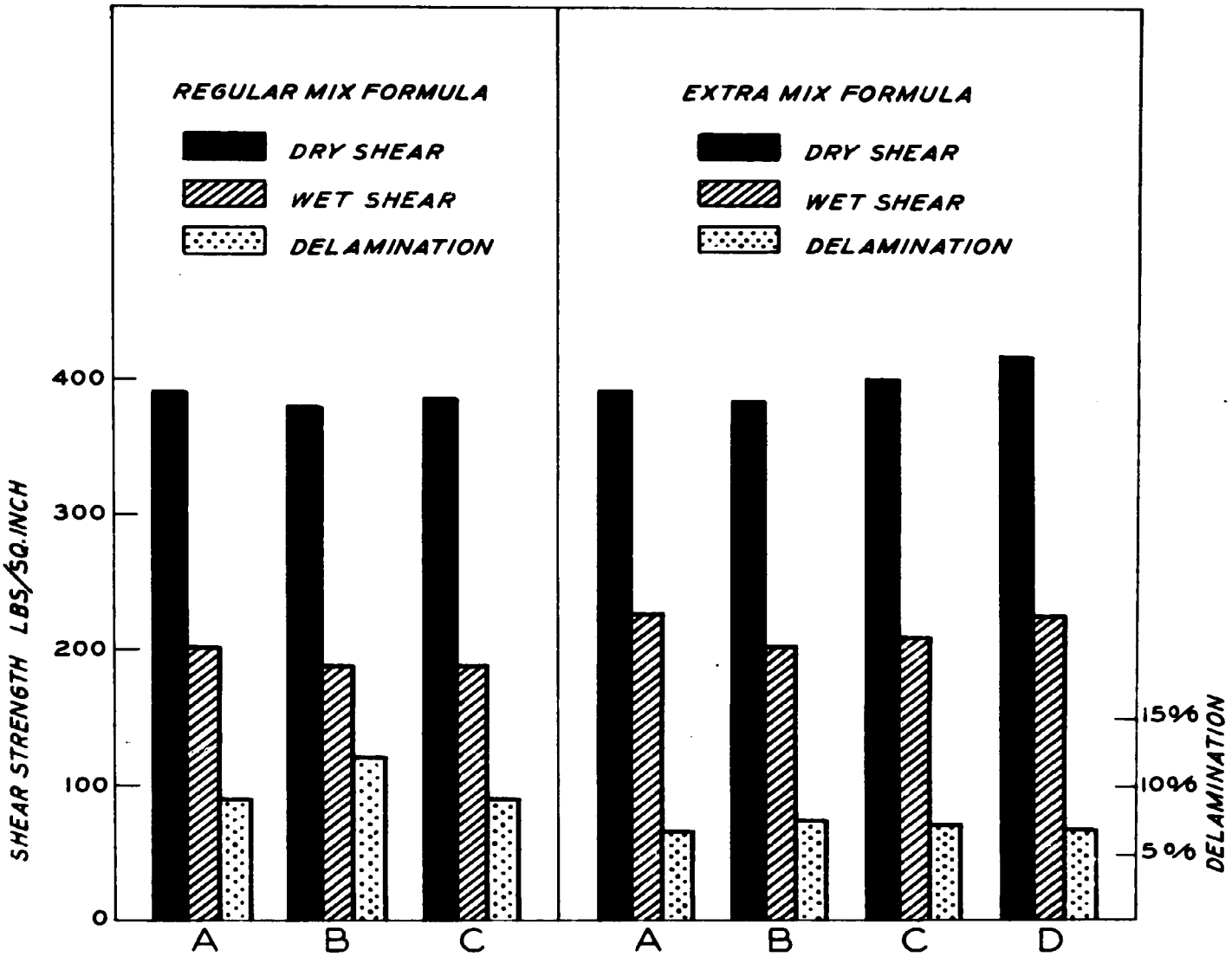


FIG.4a AVERAGE SHEAR STRENGTH AND DELAMINATION OF YELLOW BIRCH PLYWOOD BONDED WITH SOYBEAN GLUES PREPARED FROM DIFFERENT SOYBEAN MEALS:

A — BRIER'S SOYBEAN PROTEIN
B — MONSANTO'S LAUXEIN
C — GLIDDEN'S PROSOY-T
D — GLIDDEN'S ALPHA-PROTEIN

The results of delamination and block tension tests conformed with that of the plywood shear test. In both average tensile strength and percentage of delamination, the difference among the four soybean meals was not significant. This was particularly so with their average tensile strengths, which were approximately 300 psi. Some variation occurred with individual panels in the delamination test. However, the average percentage of delamination among the four meals, ranging from 6.6% to 10.2% does not indicate significant difference in water resistance.

2. Regarding the two mixing formulas employed in the plywood shear test, the extra mix appeared to be better than the regular mix in wet shear strength, but not in dry shear strength. The dry shear strength showed very little difference between the two formulas, whereas the wet shear strength with only one exception was consistently higher with the extra mix than with the regular mix for each soybean meal. The analysis of variances for the wet strength shows a 95% probability of the extra-mix formula being higher in this property than the regular mix.

The difference between the two mixing formulas was also demonstrated in the delamination test, in which the average percentage of delamination in the panels glued with extra mix formula was significantly lower than those glued with the regular mix.

3. As to the dry and wet shear strength in the plywood shear test, the difference between them was extremely significant. There seems little doubt that the dry shear strength would be always higher than the wet strength with the soybean glue, no matter which of the two formulas is used.

4. The insignificance of all interactions in the analysis of plywood shear test indicates that the four soybean meals reacted generally alike in respect to overall shear strength toward mixing formulas as well as dry versus wet tests.

Analysis on The Basis of Observed Joint Strength with Respect to The Soybean Meal Concentration

The observed joint strength with respect to the soybean meal concentration in the glue mix is expressed as a ratio of strength to meal-concentration. Such a ratio for each of the four soybean meals is presented in Table 4. It is quite obvious that on the basis of strength to meal-concentration ratio, Brier's soybean meal ranks highest among the four meals, being 35% higher than the Glidden's Alpha-protein, and approximately 50% higher than both the Glidden's Prosoy-T and Monsanto's Lauxein 10-B. Such differences, as shown in statistical analysis, are highly significant. This means that weight for weight, Brier's soybean meal is significantly higher in adhesive strength than the other three meals.

Table 4. Ratio of Shear Strength to Meal Concentration of Four Soybean Meals

Soybean Meals	Brier's Soybean Protein	Monsanto's Lauxein 10-B	Glidden's Prosoy-T	Glidden's Alpha Protein
Glue mix	gms.	gms.	gms.	gms.
Soybean meal (Protein content)	100 (90%)	100 (50%)	100 (53.5%)	100 (96.9%)
Water	620	380	380	430
Chemicals*	36.8	36.8	36.8	36.8
Total glue mix	756.8	516.8	516.8	566.8
Concentration of meal in glue mix	% 13.21	% 19.35	% 19.35	% 17.64
	Lbs. per sq. inch	Lbs. per sq. inch	Lbs. per sq. inch	Lbs. per sq. inch
Avg. dry shear strength	391	383	401	418
Avg. wet shear strength	226	203	210	225
Dry shear/meal-conc. ratio	29.60	19.79	20.72	23.70
Wet shear/meal-conc. ratio	17.11	10.49	10.85	12.76
Index of strength/meal-conc. with Monsanto's value as a base				
For dry shear	1.50	1.00	1.05	1.20
For wet shear	1.63	1.00	1.03	1.22
Avg.	1.56	1.00	1.04	1.21

*Chemicals used in the preparation of glue were in accordance with Monsanto's extra-mix formula.

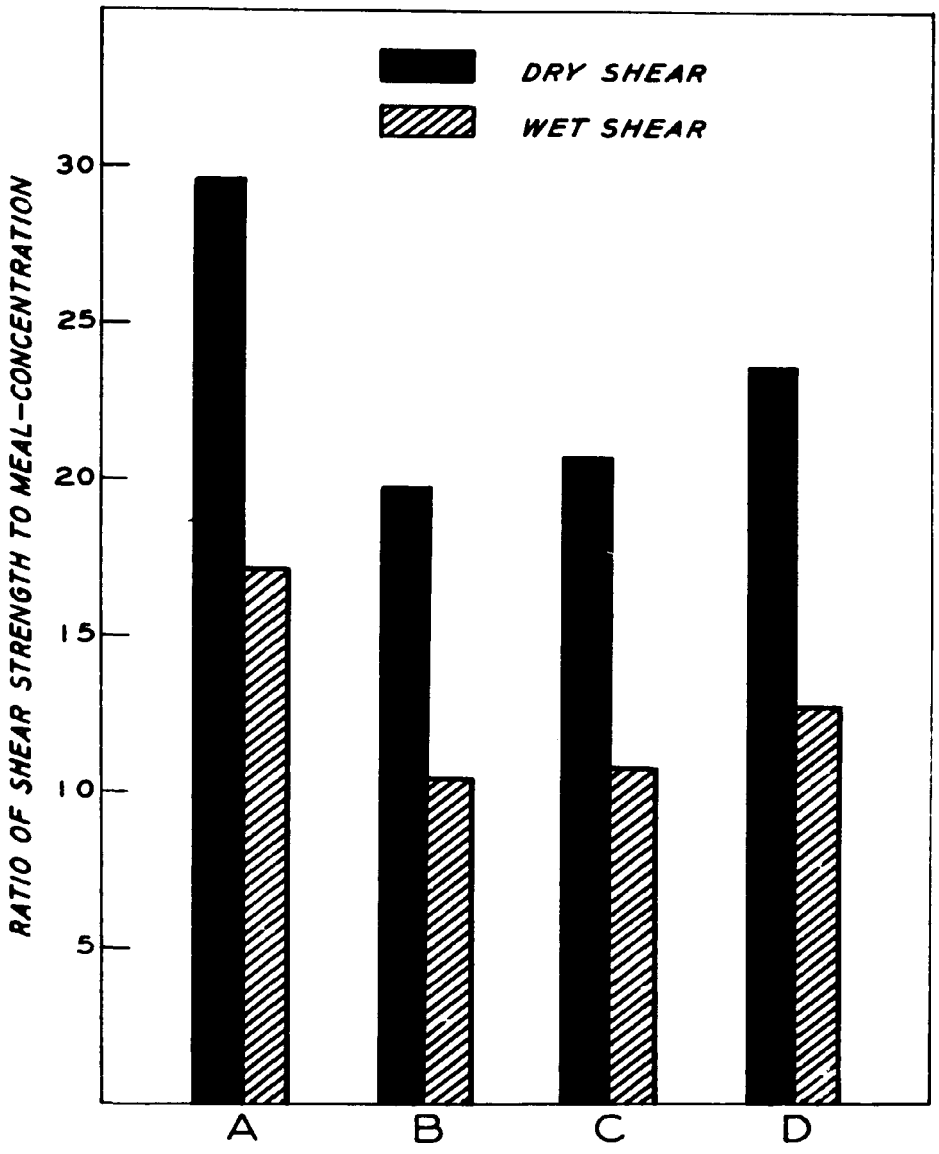


FIG. 4b RATIO OF SHEAR STRENGTH TO MEAL—CONCENTRATION OF FOUR SOYBEAN MEALS:

A — BRIER'S SOYBEAN PROTEIN
B — MONSANTO'S LAUXEIN 10-B
C — GLIDDEN'S PROSOY-T
D — GLIDDEN'S ALPHA-PROTEIN

In summing up the above analyses made on both bases, an important fact is that Brier's soybean glue produces at least as good a bond as other soybean glue mixes with much less meal solids on the glue line. This quality naturally makes Brier's soybean meal more economical for adhesive use than other soybean meals, particularly the Glidden's chemically isolated protein, if the cost of its processing is about the same as others and no other implications are involved in its application.

Discussion

The effect of processing methods upon the quality of protein lies in the fact that some methods degrade the soybean protein or leave more undesirable impurities than others. That is why soybean meals from hydraulic or screw presses used in early days were inferior to the present solvent-extracted meals (39). Brier's soybean protein, being mechanically isolated, is substantially a native protein, the preference of which over the denatured soybean protein for adhesive use has been recognized (56). Thus, Brier's soybean meal on the strength to meal-concentration ratio is significantly higher than the chemically isolated Glidden's Alpha-protein (33), which has undergone a great deal of denaturation.* The soybean protein of solvent-extracted meals

*See footnote on page 16.

such as Monsanto's Lauxein 10-B and Glidden's Prosoy-T is also undenatured. Their low strength/meal-concentration ratio in comparison with that of Brier's soybean meal is primarily due to their low protein content in the meal.

The insignificance of the observed test values of joint strength among the four soybean meals must be explained by the different water requirement in the preparation of glue for different soybean meals. As noted before, in order to obtain a suitable consistency for gluing, 620 grams of water per 100 grams of meal were required for Brier's soybean meal, whereas only 380-430 grams of water per 100 grams of meal were required for three other soybean meals. In other words, Brier's soybean meal requires 190-240 parts more water for every 100 parts of meal than do the other meals in glue mixing. As a result of this, its superior adhesive quality was converted to quantity advantage. With an equal amount of soybean meal using Monsanto's mixing formula, Brier's soybean meal yielded 46% more glue than Monsanto's and Glidden's solvent-extracted meals, and 36% more glue than Glidden's chemically isolated Alpha-protein, and was of equal bonding performance. Therefore, Brier's soybean meal should be much cheaper for adhesive use than other meals, if its cost of processing is not high.

Caustic soda is the chief dispersing agent in the formula used in this experiment. If a chemical with a dispersing power as good as caustic soda and yet requiring much

less water in a glue mixing were employed, it appears reasonable to expect that the observed joint strength of Brier's soybean meal would be increased more than in the present tests. However, extensive work in the past indicated that for the undenatured soybean protein, caustic soda gives the best dispersing effect (79, 80, 85). It is true that water requirement can be varied by increasing the proportion of caustic soda or decreasing other ingredients in the mix as in casein (13), but there is a limit to this manipulation. The pH value of a regular soybean glue is often above 11.5. Too much alkali such as caustic soda would cause too rapid hydrolysis of soybean protein, thus shortening its working life. Experiments in increasing the chemicals one and one-half to twice the regular amount were tried for this soybean meal. The results appeared to have been adversely affected.

The function of large amounts of carbohydrates (sugars and hemicellulose) present in a low protein content soybean glue is not well known. Some regard then as non-essential components or partly as fillers, whereas others believe they also play a role in the glue and call the total of these components, including the protein, the "colloidal complex" (56). In any case, the dispersed particles of the colloidal complex of the soybean glue with larger amount of carbohydrates appeared in this study much coarser than with higher protein content, as in Brier's soybean meal. The addition of caustic soda to the latter gave within 3-5 minutes a colloidal dispersion much closer to that of animal glue in appearance. This quality,

which would enhance the possibility of more effective reaction with other added components, together with its potential high strength, was the main reason for choosing it in the subsequent studies.

PART II

EFFECT OF HARDENER CONCENTRATION ON THE BONDING QUALITIES OF SOYBEAN GLUE

Glue Formulation

The most widely used commercial soybean glue formula consists of the following four chemicals in addition to water: sodium hydroxide, lime, silicate of soda, and tetrasulphide mixture (60% CS_2 and 40% CCl_4). While sodium hydroxide serves to disperse the protein portion of the meal into a fluid colloidal complex, making it suitable for use as an adhesive, silicate of soda reacts with both protein and lime to function chiefly in prolonging the working life and im improving the spreading and bonding properties of the glue. The main ingredients responsible for hardening or making the protein less water soluble are the lime and tetrasulphide mixture. To determine at what concentration these two hardening agents (hardeners) would give the soybean glue maximum water resistance without seriously shortening its working life or causing severe stain to the veneer, three variations of each of them were made in this study.

The three concentrations of lime and tetrasulphide mixture (all based on the weight of soybean meal) used in the preparation of the glue were: 4.0%, 7.0% and 10.0%, and 4.8%, 7.2%, and 9.6% respectively. In varying the concentra-

tions of these two hardening agents, the amount of the rest of the chemicals was kept constant to that indicated in the Monsanto's extra-mix formula. The bonding qualities of these glue mixes prepared with Brier's soybean meal were tested by the plywood shear and delamination tests according to the testing procedure. The results of this investigation are condensed on Tables 5 and 6.

Results

The data and the figures 5 and 6 clearly indicate that increase of either lime or tetrasulphide mixture from 4% up to 10% by weight of soybean meal was not accompanied by an increase of dry shear strength of the soybean glue joints. There was, indeed, little change in average dry shear strengths as a result of varying the concentrations of these two hardening agents. However, increasing the lime content affected the wet shear strength and delamination of the soybean glue joints significantly. The average wet shear strength increased slightly with an increase of lime to 7%, but significantly decreased with further increase of lime to 10%. On the other hand, average delamination slightly decreased or remained approximately constant with an increase in lime to 7%, but definitely increased with further increase of lime to 10%. Panels bonded with glue having 4% or 7% of lime were 10-13% higher in average wet shear strength and 30% or more (relative percentage) lower in average delamination than

Table 5. Results of Plywood Shear Test on Yellow Birch Panels Bonded with Brier's Soybean Glues of Various Concentration of Hardeners

Lime*	Replicates of Panels	No. of Test Specimens	Tetrasulphide Mixture* 4.8% Shear Strength** Lbs. per sq. inch dry	4.8% wet	7.2% Shear Strength** Lbs. per sq. inch dry	7.2% wet	9.6% Shear Strength Lbs. per sq. inch dry	9.6% wet
4%	(1)	6 each	424	239	397	233	378	234
	(2)	6 "	382	248	401	257	400	230
	(3)	6 "	366	191	368	223	374	197
	Avg.	18 each	391	226	389	238	384	220
7%	(1)	6 each	394	208	397	246	366	208
	(2)	6 "	374	241	410	241	395	232
	(3)	6 "	400	249	375	229	396	240
	Avg.	18 each	389	233	394	239	386	227
10%	(1)	6 each	405	244	397	230	377	192
	(2)	6 "	388	185	396	212	393	213
	(3)	6 "	386	203	371	189	390	189
	Avg.	18 each	393	211	388	210	387	198

*Amount of lime and tetrasulphide mixture was based on the weight of Brier's soybean meal. A defoaming agent, Monsanto's Defoamer #31 was added to the glue according to directions, when the proportions of lime reached 7% and 10%.

**Wood failure in all the shear test specimens was less than five percent and therefore not included in the table.

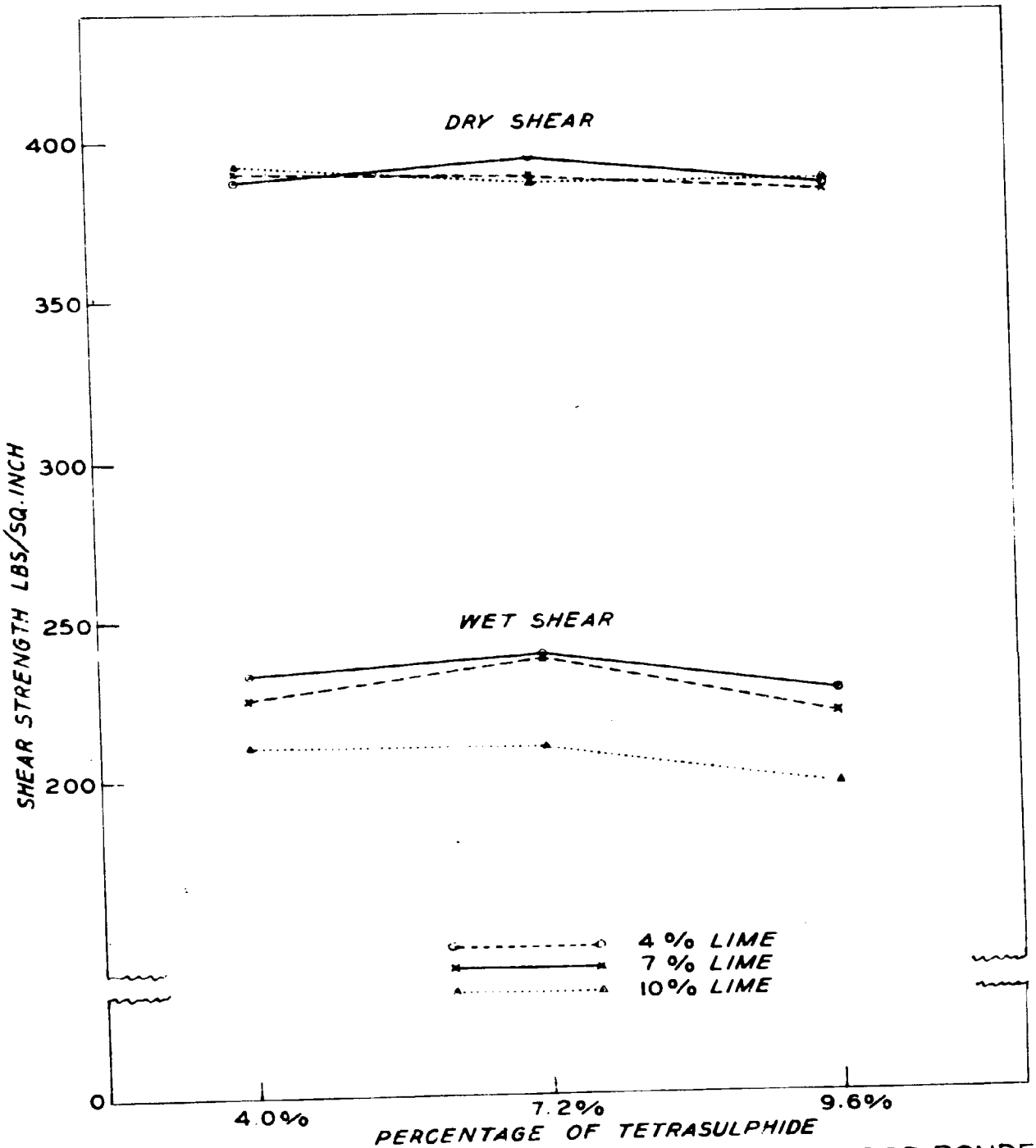


FIG. 5 SHEAR STRENGTH OF YELLOW BIRCH PLYWOOD BONDED WITH SOYBEAN GLUES OF VARIOUS CONCENTRATIONS OF LIME AND TETRASULPHIDE

Table 6. Results of Delamination Test on Yellow Birch Plywood Bonded with Brier's Soybean Glue of Various Concentration of Lime and Tetrasulphide

Lime*	Replicates of Panels	Tetrasulphide Mixture* 4.8% Percentage of delamination	7.2% Percentage of delamination	9.6% Percentage of delamination	Means for Lime Classes
4%	(1)	7.1	7.8	6.2	
	(2)	4.5	3.9	5.8	
	(3)	8.1	5.4	9.0	
	Avg.	6.57	5.70	7.00	6.42%
7%	(1)	8.0	4.0	5.7	
	(2)	5.4	6.7	5.6	
	(3)	5.0	7.3	9.0	
	Avg.	6.13	6.00	6.77	6.30%
10%	(1)	5.5	6.0	7.7	
	(2)	8.8	9.1	12.2	
	(3)	9.1	7.3	10.8	
	Avg.	7.80	7.47	10.23	8.50%
Means for Tetrasulphide Classes		6.83%	6.39%	8.00%	

*Amount of lime and tetrasulphide mixture was based on the weight of Brier's soybean meal. A defoaming agent, Monsanto's Defoamer #31, was added to the glue according to directions of manufacturer when the proportions of lime reached 7% and 10%.

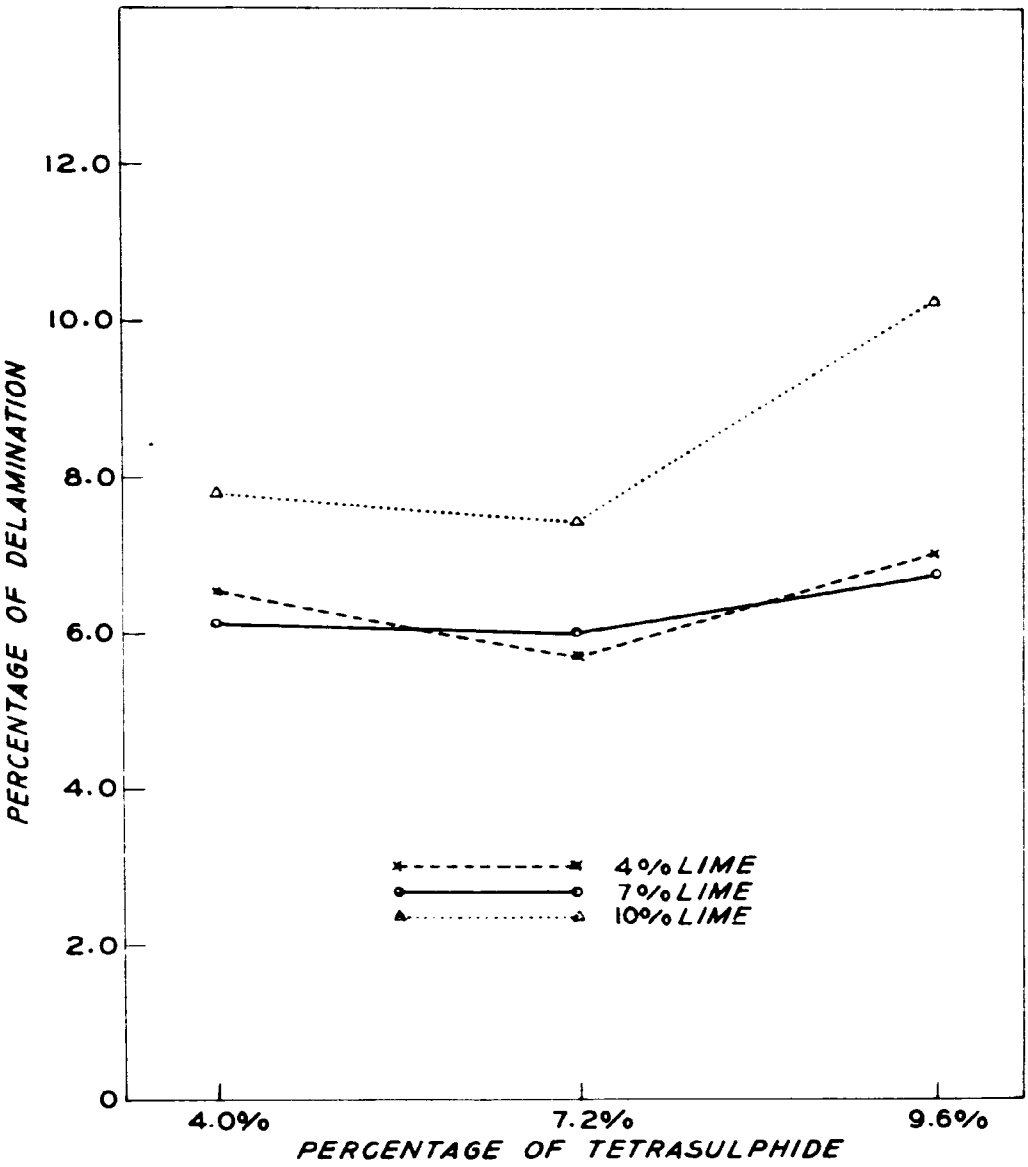


FIG. 6 DELAMINATION OF YELLOW BIRCH PLYWOOD BONDED WITH SOYBEAN GLUES OF VARIOUS CONCENTRATIONS OF LIME AND TETRASULPHIDE

those bonded with glue having 10% of lime. Since wet shear strength and delamination are a measure of water resistance of a glue joint, it appears that concentration of lime much above 7% would have a detrimental effect on the water resistance of Brier's soybean glue.

Increase of tetrasulphide mixture beyond 4.8% by weight of soybean meal, did not have as much effect on the water resistance of the glue as did lime. Superior results in wet shear strength and delamination occurred in the glue with 7.2% of tetrasulphide, but its difference from that with 4.8% or 9.6% of this agent was found statistically insignificant. The worst one appeared to be the glue with high proportions of both lime and tetrasulphide at the same time.

Previous experiments in the study of adhesive strength of different soybean meals under Part I showed that increase of lime and tetrasulphide mixture from 3% to 4% and from 2.4% to 4.8% respectively increased the wet shear strength and decreased the delamination of the soybean glue joint to a considerable extent. It appears that there was a sharp increase of water resistance of the glue in increasing these two hardening agents from 3.0 to 4.0% and from 2.4 to 4.8%, respectively. After that the increase in water resistance became very gradual and did not increase further when the amount of these two agents approached 7.0 - 7.2%. Thus, the data pointed out that for maximum water resistance, the amount of the two hardening agents should not exceed 7% of Brier's soybean protein when using Monsanto's extra-mix formula.

Discussion

Effect of Lime

The slight increase in water resistance of the soybean glue obtained by an increase of lime from 3% to 7% by weight of soybean meal in the mixing formula was attributable to the fact that lime reacts with silicate of soda and the soybean protein to form a complex calcium-silicate-proteinate, which is an irreversible gel (61). Increase of lime tends to make this reaction more complete and consequently to increase its water resistance. This is what one would expect.

The point contradictory to some of the past work is that further increase of lime up to 10% produced an adverse effect on the wet shear strength and delamination. Several suggested formulas in the literature included lime up to 10% (69). There is a popular assumption that the more lime added to the glue, the more water resistant it is, the amount of lime being limited mainly by its effect on the working life of the glue and staining of the veneer.

On account of this contradiction, part of this experiment was repeated. The results were still in line with those of previous tests. It is difficult to explain this point with certainty, because information on the lime-combining capacity of soybean protein is not available and different soybean meals and mixing formulas used in testing by different investigators are involved.

One of the possible explanations would be the adverse effect on the flow property of the soybean glue through the addition of large amounts of lime (4). This flow property has close connection with the pH value of the glue. Burnett et al. have established that the viscosity of an unmodified soybean protein is maximum at pH 11.5-12, beyond which it sharply drops (56). Studies of T. Komuro and M. Asakura on the solubility of soybean protein in acid and alkali also show such relationship (47). The pH value of the soybean glue prepared according to Monsanto's extra-mix formula with 4% lime is initially close to 12. Addition of more lime without varying the proportions of other chemicals could conceivably change the viscosity of the glue and consequently result in poor joint strength, since viscosity and adhesive strength are closely related properties. Under severe conditions, the poor joints are easily observed. This might be part of the reason that in increasing the lime over an optimum amount, the dry shear strength of the glue joint appeared to be least affected, while the wet shear strength and delamination were significantly affected.

Another factor to be considered is that the soybean meal used in this experiment was Brier's soybean protein which has much higher protein content than any commercial soybean meal for adhesive use at present. As protein is much more sensitive to chemical reaction than carbohydrate, excessive lime might easily alter the properties of the glue of this meal, whereas this alteration would not be revealed

in the case of commercial meals which contain approximately 50% carbohydrate.

Smith and Circle have shown quantitatively the influence of lime over pH 11 in reducing the dispersion of soybean protein (56). The use of lime in the preparation of soybean glue perhaps originated from the technology of casein adhesives which require a much higher proportion of lime in their formulation.

Effect of Tetrasulphide Mixture

Carbon disulphide is the functioning ingredient in this mixture, carbon tetrachloride serving simply to reduce the fire hazard of the former. The increase of water resistance through increase of this mixture from 2.4% to 7.2%, as shown in the study of bonding qualities of different soybean meals, was due to the formation of insoluble protein-sulphide compounds in the presence of caustic (61). The reaction of carbon disulphide is in part analogous to the reaction of this sulphide with cellulose in the viscose process for rayon (47).

Carbon disulphide also reacts with sodium hydroxide (47). If the latter is kept constant, excessive carbon disulphide tends to thicken the glue and this would adversely affect the glue joint. The slight drop in wet shear strength and increase of delamination which occurred with a high proportion of carbon disulphide might be explained on this basis. Generally speaking, the requirement for carbon disulphide in the

preparation of soybean glue is not high. Beyond the optimum amount there is no further advantage in adding it.

Evidence in many instances suggested that the reactivity and combining capacity of soybean protein with different chemicals vary with the degree of denaturation in its processing and with the amount of impurities in the meal. For example, Glidden's Alpha-protein tolerates formaldehyde in greater amounts than other soybean proteins of similar purity. In the study of bonding qualities for different soybean meals, Brier's soybean protein has been tried with chemicals one and a half to twice the amount of that used for a much lower protein content soybean meal; and the results appeared to have been adversely affected. Hence, it appears that for each differently processed soybean meal, appropriate amounts of chemical ingredients used in the preparation of the glue should be determined empirically.

PART III

FORTIFICATION OF SOYBEAN GLUE WITH CASEIN GLUE AND BLOOD ALBUMIN

The use of casein or blood albumin for improving the bonding qualities of soybean glue is not new. As indicated in the review of literature, a few patents have been granted on the addition of either one of them to the soybean glue. Unfortunately, in these patents a systematic study of the proportions of such additives is not given. Also very little published work, if any, has yet appeared on the fortifications of soybean glue with both casein and blood albumin.

Glue Formulation

In this investigation, soybean glue was used as a base and blended with different proportions of a ready-mix casein glue, Perkins Perfection, and a mixture of this casein glue and blood albumin. The soybean glue was prepared with Brier's Soybean Protein according to Monsanto's extra-mix formula. The percentages of casein and blood albumin added to the soybean glue were all based on the weight of soybean meal.

The percentages of casein glue chosen for this fortification were 20, 35, and 50%. These different amounts of casein glue were added to separate batches of soybean glue. The bonding properties of these casein-soybean mixtures as determined through three types of test are given in Table 7. For comparison, the results of tests made with straight soybean glue and casein glue are also included in this table.

From the above study, the best casein-soybean glue mixture was selected for further fortification with blood albumin to see if the albumin would give additional improvement. The 20%-casein-fortified soybean glue was selected for the reason given under "Results". To the samples of this glue, blood albumin in quantities of 10, 20, and 30% was separately added. The joint strength of these glue mixtures is presented in Table 8.

Since the addition of 10-20% blood albumin to the selected casein-fortified soybean glue mixture resulted in increase only in dry shear strength, a test was made to incorporate formalin (37% formaldehyde) into the soybean glue mixture having 10% blood albumin and 20% casein. This approach is based on the capacity of blood albumin to combine with formaldehyde for its water resistance (91) and the hardening effect of formaldehyde on protein materials.

The procedure of incorporating formalin with soybean

glue, developed by T. Satow (81), was slightly modified in this experiment. To four parts of 7.0% ammonia solution, one part of formalin was added slowly so that the temperature did not rise above 20°C. during the addition. This mixture was kept in a cold-water bath for 30 minutes before use.

Trial experiments showed that 3.0% of formalin based on the weight of soybean meal could be stirred into the 10%-blood albumin and 20%-casein-fortified soybean glue mixture without causing gelation for at least six and a half hours. The results of tests made with this fortified glue are indicated in Table 8.

Results

Fortification with Casein Glue

The addition of casein glue increased the adhesive strength and water resistance of soybean glue to an appreciable extent. However, the increase was not parallel in all three tests, i.e., the plywood shear test, delamination test, and block tension test; nor was it proportional to the amount of casein glue added. In fact, a decrease in joint strength was observed when the amount of casein glue reached 50% of the soybean meal in the glue mixture.

In the plywood shear test, soybean glue fortified with 20-35% casein glue resulted in practically no increase in dry shear strength, but an appreciable increase in wet

Table 7. Joint Strength and Delamination of Yellow Birch Panels and Blocks Bonded with Soybean Glues Fortified with Different Amounts of Casein Glue

	Soybean Glue with Casein	Plywood Shear Test: Replicates of Panels	No. of shear specimens	dry shear	wet shear	Delamination Test: No. of Panels	delamination %	Block Tension Test: No. of blocks	tensile strength
A	Straight soybean glue	(1)	6	424-0**	239-0**	1	7.1		
		(2)	6	382-0	248-0	1	4.5		
		(3)	6	366-0	191-0	1	8.1		
		Avg.	18	391-0	226-0	3	6.57	10	302-0**
B	(A) + 20% casein	(1)	6	373-0	240-0	1	5.8		
		(2)	6	434-0	258-0	1	4.5		
		(3)	6	373-0	250-0	1	4.9		
		Avg.	18	393-0	249-0	3	5.07	10	365-0
C	(A) + 35% casein	(1)	6	396-0	243-0	1	5.4		
		(2)	6	440-0	271-0	1	4.1		
		(3)	6	382-0	237-0	1	5.0		
		Avg.	18	406-0	250-0	3	4.83	10	372-0
D	(A) + 50% casein	(1)	6	360-0	188-0	1	7.7		
		(2)	6	417-0	203-0	1	6.6		
		(3)	6	370-0	186-0	1	8.7		
		Avg.	18	382-0	192-0	3	7.67	10	305-0
	Straight casein glue	(1)	6	521-7	205-0	1	3.3		
		(2)	6	564-14	197-0	1	3.1		
		(3)	6	519-11	204-0	1	4.0		
		Avg.	18	535-11	202-0	3	3.47	10	462-5

*Casein is ready-mixed "Perkins Perfection," and soybean meal, Brier's Soybean Protein.

**The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent was recorded as zero.

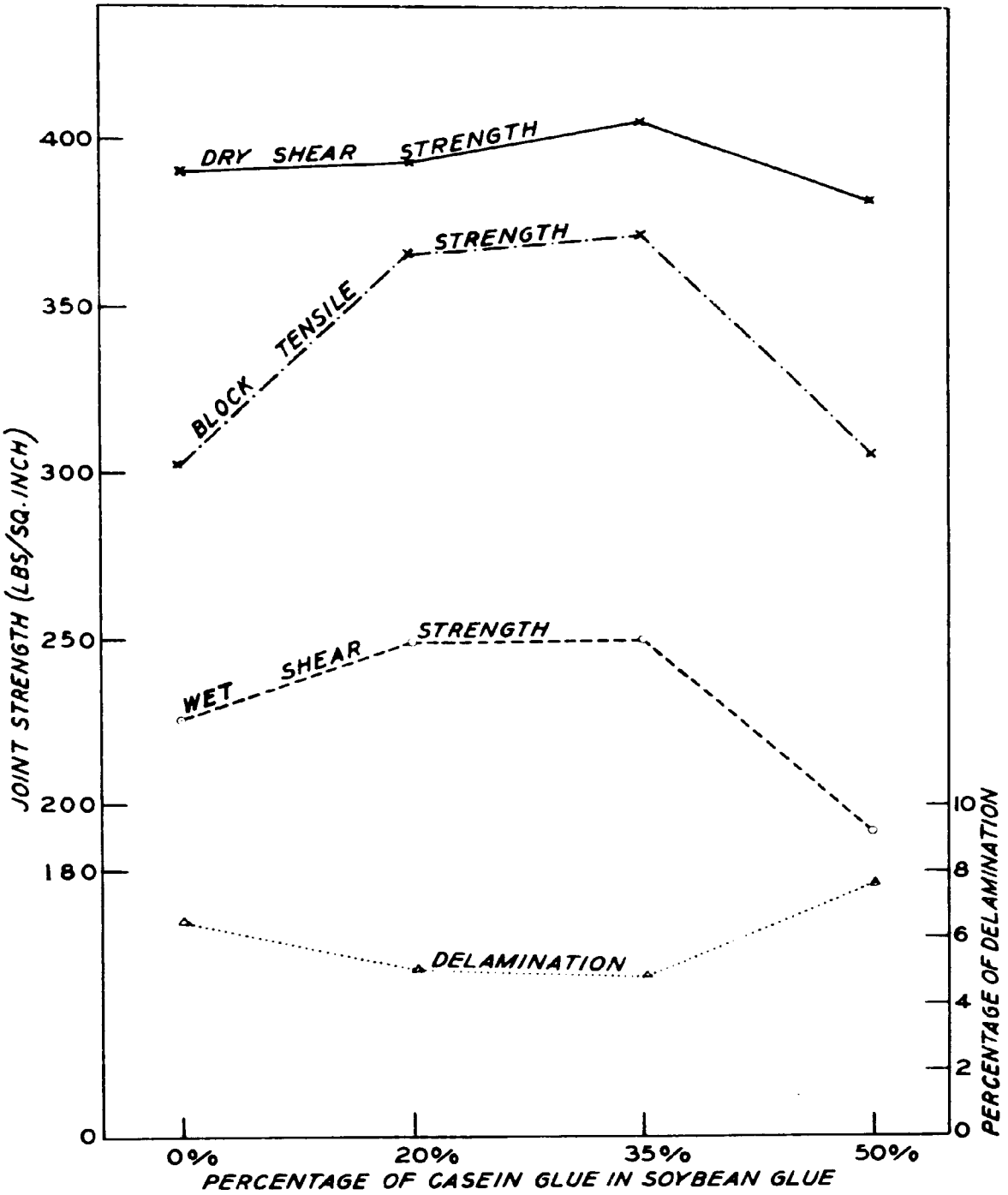


FIG. 7 JOINT STRENGTH AND DELAMINATION OF YELLOW BIRCH PANELS AND BLOCKS BONDED WITH SOYBEAN GLUES FORTIFIED WITH DIFFERENT AMOUNT OF CASEIN GLUE

Table 8. Joint Strength of Yellow Birch Panels Bonded with 20%-Casein and Fortified Soybean Glue Plus Various Amount of Blood Albumin

	Soybean Glue with 20% Casein & Various Amounts of Blood Albumin	Plywood Shear Tests		
		Replicates of Panels	Dry Shear	Wet Shear
E	Soybean glue with 20% Casein	(1)	373-0*	240-0*
		(2)	434-0	258-0
		(3)	373-0	250-0
			393-0	249-0
F	(E) + 30% blood albumin	(1)	380-0	206-0
		(2)	400-0	203-0
		(3)	389-0	203-0
			390-0	204-0
G	(E) + 20% blood albumin	(1)	427-0	259-0
		(2)	445-0	251-0
		(3)	429-0	243-0
			434-0	251-0
H	(E) + 10% blood albumin	(1)	440-0	238-0
		(2)	445-0	248-0
		(3)	404-0	259-0
			430-0	248-0
I	(E) + 10% blood albumin & 3% formalin**	(1)	452-0	255-0
		(2)	445-0	275-0
		(3)	458-0	277-0
			452-0	269-0

*The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure of which less than five percent was recorded as zero.

**Delamination and block tension tests were made only for this combination. The average delamination of three panels (4.42%, 5.27%, 5.00%) was 4.93%, and the average tensile strength of ten blocks was 366 psi.

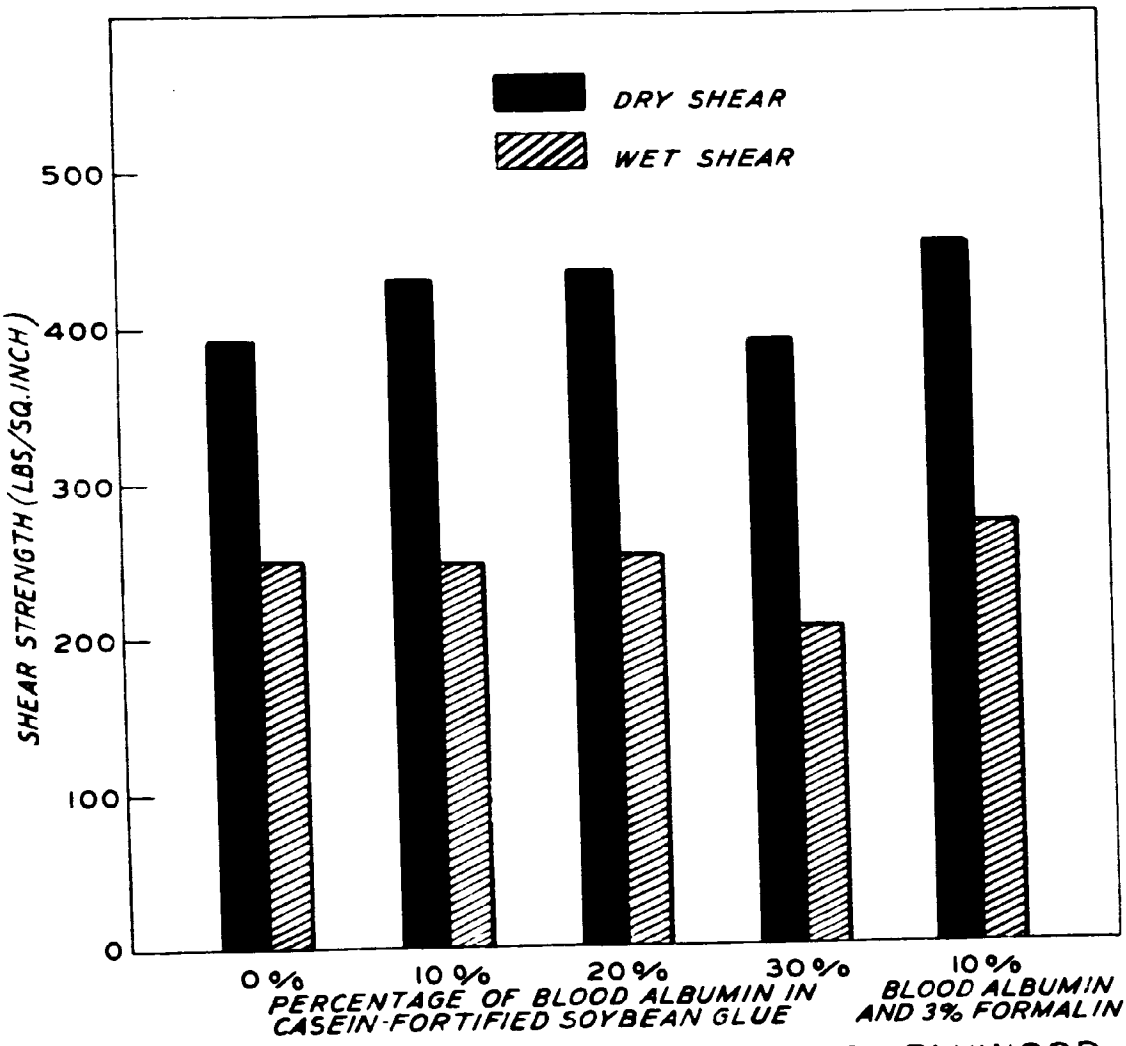


FIG. 8 SHEAR STRENGTH OF YELLOW BIRCH PLYWOOD BONDED WITH 20% CASEIN-FORTIFIED SOYBEAN GLUE PLUS VARIOUS AMOUNT OF BLOOD ALBUMIN

shear strength. Statistical analysis shows that in eighty out of one hundred chances, the wet shear strength of the 20-35% casein-fortified soybean glue would be higher than the straight soybean glue. Addition of casein glue up to 50% to the soybean glue resulted in considerable decrease in both dry and wet shear strength. The difference among the three casein-fortified soybean glues and the straight soybean glue was significant only when their wet shear strengths were considered alone. Between the soybean glues fortified with 20% casein and 35% casein, there was not much difference in the shear strength.

In the delamination test, the fortified soybean glue with 20-35% casein showed the least delamination and that with 50% casein the most. Such results were in agreement with those of the wet shear tests. However, the relative differences in the degree of delamination were less pronounced than the differences between the wet shear strengths among the four glues.

The block tension test brought out conspicuously the superior bonding quality of the fortified soybean glue with 20-35% casein. Study of Table 7 indicates that such fortified soybean glue was 21-23% higher in tensile joint strength than the straight soybean glue. When casein in the fortified glue reached 50% the tensile joint strength dropped down to the level of straight soybean glue, but was not significantly lower as was the case in shear and delamination tests.

In summary, the best bonding qualities were observed in the fortified soybean glue with 20-35% casein; and of the two casein-soybean mixtures the 20%-casein-fortified soybean glue was as good as the 35%-casein-fortified-ones.

Fortification with Casein Glue and Blood Albumin

Addition of 10-20% blood albumin significantly increased the dry shear strength of the 20%-casein-fortified soybean glue. Such increase, however, was not observed in the wet shear strength. With 30% blood albumin, a decrease in shear strength resulted in both wet and dry tests.

The glue with 10% blood albumin was as good as that with 20% blood albumin in shear strength. Addition of blood albumin in excess of 20% of the soybean meal did not improve the quality of the joint.

The overall data indicate that the advantage of adding blood albumin lay in its ability to give a uniform joint strength to the casein-fortified soybean glue. As easily seen from Table 8, the variation of shear strength among individual test specimens or panels in blood-albumin-fortified soybean glue generally did not exceed 10%, whereas in straight soybean glue and casein-fortified soybean glue, variation over 15 or 20% was not uncommon.

Incorporation of Formalin

Best glue joints were obtained with the glue mixture

having 20% casein and 10% blood albumin plus 3.0% formalin. The analysis in Appendix Tables L—M shows a 95% to 99% probability of this glue being higher in joint shear strength and water resistance than those soybean glue mixtures fortified either with casein alone or with casein and blood albumin in combination. Its wet shear strength was 32% higher than the commercial straight soybean glue, Lauxein 10-B, and 19% higher than the Brier soybean glue itself without such fortification. Compared with the best casein-fortified soybean glue, this casein and blood-albumin-fortified soybean glue with formalin was still 8% higher in wet shear strength. The tensile strength from block tension tests and the results from delamination tests also demonstrated its relatively high bonding qualities.

Discussion

Effect of Casein Glue

The increase in adhesive strength and water resistance of the soybean glue as a result of adding the proper amounts of ready-mix casein was attributable to the high bonding qualities of casein itself plus the chemical ingredients present in the casein and soybean glue mixture. In a ready-mix casein, the proportion of lime is much higher than that required in soybean glue (13, 27). This additional lime imparted by the casein would within certain limits improve the water resistance of the soybean glue. On the other

hand, the carbon disulphide in the soybean glue would in the meantime xanthogenate the casein portion in the blend, which also helps to insolubilize the casein (17,53,82). Because of the beneficial effect of these two chemical ingredients on the two components in the glue mixture, the casein adhesive could bolster the water resistance of the soybean glue, although the wet shear strength of this casein adhesive itself is not particularly high.

One of the outstanding qualities of casein adhesive in respect to water resistance is that its glue, while weakened by soaking in water, will regain much of its original strength when redried (61). Thus, it is not surprising to find that the casein adhesive showed only moderate strengths in wet shear test and yet much less delamination under repeated wet and dry conditions in comparison with soybean glue. The ability of casein adhesive to regain strength also helps explain why a properly fortified casein-soybean glue shows less delamination.

The reason for the significant decrease of shear strength observed in the casein-fortified soybean glue, when casein adhesive amounts to 50% of the soybean meal, is not due to casein itself, but rather to the adverse effect of too much lime introduced by such large quantities of the ready-mix casein adhesive. As demonstrated previously, the optimum amount of lime for Brier's soybean glue is 7%, beyond which a weak joint results. With 50% ready-mix casein, the

lime imparted to the soybean glue component is perhaps over this optimum point. The cause of the adverse effect of too much lime in the soybean glue has been dealt with in Part II.

Casein increases the adhesive strength in the tensile test more than it increases the strength in the plywood shear test. This may be explained in part by the particle size of the soybean glue. It is believed that the particle size of soybean glue is larger than other glues such as casein or animal glues, and consequently does not penetrate into wood as well as it does into rotary-cut veneer. (61) As a result, it does not bond well in lumber gluing. With an addition of casein, its drawback in this respect can be greatly improved.

Effect of Blood Albumin and Formalin

The increase in dry shear strength through addition of small amounts of blood albumin to the casein-fortified soybean glue is somewhat unusual, because the blood albumin itself is low in dry strength. A possible explanation appears to be its interaction with protein and the chemical ingredients present in the glue mixture. The uniformity of shear strength obtained in this test suggests that blood albumin might also function as a seal to prevent starved joints. This view was upheld by Cooper in his work on protein adhesives (16).

Since blood albumin alone is low in joint strength, it is conceivable that an increase beyond the optimum amount

would result in a decrease of shear strength. It may be seen from Table 8 that the optimum amount of blood albumin is 10-20%. When added in the proportion of 30%, it produces a weak joint.

It should be noted here that the fortification of soybean glue with casein and blood albumin, all the panels were cold-pressed. Blood albumin, although it can be cold-pressed, is preferably hot-pressed in order to develop its highest water resistance (27,91). The lack of improvement in water resistance by addition of blood albumin to the casein-fortified soybean glue is primarily due to this reason. Another point is that the casein-fortified soybean glue is already quite high in wet shear strength. Any slight improvement in water resistance to straight soybean glue obtained by the addition of blood albumin would be simply obscured in this case.

The significant improvement in both shear strength and water resistance obtained by the addition of 3.0% formalin to the casein-blood-albumin-fortified soybean glue was attributable to the fact that formaldehyde hardens the protein and decreases its water sensitivity. Although these effects have long been recognized in the preparation of blood albumin glue for plywood manufacture and paper sizing, the reaction of protein with formaldehyde is still not completely understood. Recent studies postulate that formalde-

hyde combines readily with $-NH_2$, =NH, -OH, -COOH, -SH, and other functional groups, and cross-linkages are formed through methylene bridges (28,83). This cross-linking is believed to add cohesive strength to the adhesive mass and increase its water resistance. For detailed chemical reactions which are beyond the scope of this study, the reader is referred to the more recent works of French et al. (30) and Traill (90), in which old errors on this subject have been corrected.

PART IV

FORTIFICATION OF SOYBEAN GLUE WITH SYNTHETIC RESIN ADHESIVES

Soybean meal has been employed to extend some synthetic resin adhesives, but very little literature has appeared covering the use of synthetic resin adhesives to fortify the soybean glue. This part of the investigation was to explore the possibilities of the latter approach to the improvement of the soybean glue.

Resorcinol-formaldehyde resin was chosen for this purpose, partly because it is a cold-press resin adhesive of high durability, and partly because it is neutral in chemical reaction which presumably would be compatible with the alkaline soybean glue. As the experiment progressed and difficulties in incorporating this resin in the soybean glue continuously arose, urea-formaldehyde and five non-formaldehyde resins of high water resistance were also included in the study.

The incompatibility of alkaline soybean glue with many synthetic resins led to the trial of fortifying starch glue, which is also of vegetable origin, with the resorcinol resin. Striking success was attained with starch glue, while the fortification of soybean glue was largely negative.

The results of such experiments with different synthetic resins are summarized in the following sections. It should be noted here that many of these tests are cursory in nature and cannot be regarded as conclusive. Only along those approaches which looked promising to the improvement of soybean glue were systematic tests made.

Fortification of Soybean Glue with Resorcinol-Formaldeyde Resin

Glue Formulation

The resorcinol-formaldehyde resin used was Koppers Penacolite G-1131. It consists of two parts: part A is the liquid resorcinol resin, already partially polymerized with a deficiency of formaldehyde; part B is a powder catalyst containing the required amount of paraformaldehyde and walnut shell flour. When ready for use, 20 parts of the catalyst is added to 100 parts of the liquid resin, and this promotes the polymerization of the resin at room temperature.

The soybean glue used here was prepared with Brier's soybean meal according to Monsanto's extra-mix formula. In the fortification of this soybean glue, different amounts of the resorcinol resin already mixed with its catalyst according to manufacturer's instruction were added to the soybean glue.

Results

When the resorcinol resin with its catalyst was added

to the soybean glue, the latter immediately coagulated. Even an amount of two parts of the prepared resin to 100 parts of the soybean glue by weight was enough to cause coagulation. If the resin was allowed to react with the catalyst for 30 minutes and then added to the soybean glue, the result was still the same except that it took a few minutes longer.

The coagulation of the soybean glue was due primarily to the reaction of the catalyst, paraformaldehyde, with the soybean protein; for if pure walnut shell flour or the resorcinol resin alone within 4.0% by weight of the soybean glue were added to the glue, no coagulation took place. On the other hand, pure paraformaldehyde in an amount as little as one gram would be enough to coagulate 100 grams of soybean glue. This pdymer releases formaldehyde very quickly in the soybean glue. It became evident, that soybean protein dispersed with NaOH and lime (Monsanto's mix formula) is very sensitive to formaldehyde. The reason that the resorcinol resin alone has to be kept within 4.0% is that in the resin itself there is a trace of formaldehyde. Beyond this limit the formaldehyde in the resin would be enough to gradually thicken the soybean glue.

These results clearly showed that in order to incorporate the resorcinol resin adhesive successfully in the soybean glue, either a suitable catalyst or some means to overcome quick reaction between the formaldehyde and the soybean protein must first be found. Several experiments along these

two approaches were conducted. These included the use of other aldehydes as catalysts, use of some formaldehyde compounds as catalysts, addition of retarding agents, and lowering the alkalinity of the soybean glue. Following are the results of these experiments.

Resorcinol with other aldehydes as catalysts --- Since the aldehyde group(CHO) of paraformaldehyde is the functional group for polymerizing the resorcinol resin, an attempt was made to use some other aldehydes with higher molecular weights instead of paraformaldehyde as catalysts. Of the several aldehydes tested, acetaldehyde, butyraldehyde, and benzaldehyde all coagulated the soybean glue in much the same manner as the paraformaldehyde except in speed. The aqueous formaldehyde (37% concentration) was the most reactive, causing coagulation of the glue instantly even in an amount as small as 2.0% by weight of the glue. With an equal amount of butyraldehyde or benzaldehyde it took 10-25 minutes longer for the glue to gel. The speed of gelation was in inverse proportion to the molecular weight of the aldehydes used to cure the resorcinol resin.

One exception was found to be furfural (furfuraldehyde), which would not readily convert the soybean glue into a gel. A mixture of four parts resorcinol resin and two parts of furfural with 100 parts of soybean glue was found to have a working life of 7-8 hours. However, panels cold-pressed with such glue mixture did not produce a good joint.

The average dry shear strength and wet shear strength for 24 such plywood specimens were much lower than for straight soybean glued joints, being only 260 psi and 174 psi respectively. It appeared that the resorcinol resin had not been cured by the furfural.

As furfural alone did not induce polymerization of the resorcinol resin, it was thought that slight addition of formaldehyde might cause the reaction to occur. A mixture of furfural and formaldehyde was therefore attempted. From a series of tests it was found that 3-4% of a mixture containing five parts of aqueous formaldehyde, 15 parts of furfural, and 100 parts of resin could be added to the soybean glue without causing its gelation. But the poor joint strength of the panels glued with this glue mixture indicated that slight addition of formaldehyde to the furfural as a catalyst was still not enough to thoroughly polymerize the resorcinol resin in the presence of soybean glue.

Resorcinol with formaldehyde compounds as catalysts--- A number of formaldehyde compounds, which would release formaldehyde in solution, have been reported to have the advantage of delaying the formaldehyde reaction with soybean protein (56). Among them, hexamethylene tetramine and sodium formaldehyde sulphite ($HOCH_2SO_3Na$) were tried as catalysts for resorcinol resin to be incorporated into soybean glue. The results, however, were not satisfactory since neither of them delayed the gelation of glue much over 20 minutes.

Sodium formaldehyde sulphite appeared to release formaldehyde quickly in the highly alkaline soybean glue. Hexamethylene tetramine, although it showed only a slight degree of hydrolysis to formaldehyde and ammonia under room temperature in the absence of acid (92), was enough to cause gelation within half an hour.

Only dimethylol urea used as a catalyst in limited amount was able to maintain the working life of the soybean glue longer than the above two compounds; but the joint strength of such fortified glue was nevertheless low.

Addition of retarding agents --- In this experiment certain chemicals were used to retard the reaction of formaldehyde on soybean protein so that the soybean glue would not coagulate. These chemicals include sodium sulphite, sodium bisulfite, borax, trisodium phosphate, and ammonium hydroxide, which either react with formaldehyde and release it later or exhibit a buffer action over the formaldehyde. Sodium bisulfite reacts with formaldehyde forming bisulfite-formaldehyde compounds, which would release formaldehyde in alkaline solution as is indicated in the chemical equation below.

$$NaHSO_3 + CH_2O \rightleftharpoons HOCH_2SO_3Na$$

$$HOCH_2SO_3Na + NaOH \rightleftharpoons CH_2O + H_2O + Na_2SO_3$$

The reaction of sodium sulfite with formaldehyde proceeds in a similar manner. Unfortunately, this reversible

reaction in the highly alkaline soybean glue occurred so quickly that within 10-15 minutes the soybean glue coagulated.

Borax in an amount of 10% of soybean protein with addition of a little ammonium hydroxide was reported to be able to prevent protein gelation during introduction of formaldehyde for paper coating (84). Trisodium phosphate was said to be more effective than borax. When either of these two salts was added to soybean glue, they definitely delayed the reaction of formaldehyde with the protein. However, as soon as resorcinol was mixed into the glue, gelation still took place within a few minutes.

Comparatively, the most effective chemical for retarding formaldehyde reaction was found to be ammonium hydroxide. Not only does it react with formaldehyde, but it also has a stabilizing effect on the colloidal soybean glue. The procedure for adding this chemical was developed by T. Satow (81). To one part of 28% ammonium hydroxide is added three parts of water, and then one part of aqueous formaldehyde (37% concentration) is slowly added so that the temperature does not rise above 20°C. during the addition. This mixture is kept standing in a cold-water bath for 30 minutes before use. The methylene compounds formed during this period gradually generate free active formaldehyde after mixing into the soybean glue.

From a series of tests it was found that 3.0% of

aqueous formaldehyde based on the weight of soybean meal could be added to soybean glue in this manner without causing gelation for at least six hours. This technique was employed in Part III for adding formalin to the soybean glue mixture fortified with casein and blood albumin.

For incorporating resorcinol resin in the soybean glue, this formaldehyde-ammonia solution was first stirred into the soybean glue. Five to ten parts of the solution could be added to 100 parts of soybean glue and two parts of resorcinol resin. The working life of this glue mixture was around four hours. However, the joint strength of this fortified soybean glue was not encouraging, being even lower than the straight soybean glue. One reason for this may have been that since the amount of formaldehyde added was only enough to polymerize the resorcinol resin, it was prevented from doing so by two independent actions; first by the rather great dilution of the total mixture, and second by the side reactions with the protein. The incomplete polymerization of resorcinol resin in the glue mixture was therefore detrimental to the glue bond.

The results of this study indicated that means must be found for increasing the amount of formaldehyde in the glue mixture. One approach to this problem is pursued in the following section.

Lowering of alkalinity of soybean glue --- In view

of the fact that the reactivity of formaldehyde with both resorcinol and protein decreased with a decrease in pH (75, 84), an attempt was made to reduce the pH of the soybean glue so that more formaldehyde could be added. This would provide a longer working life of the fortified soybean glue and also improve the polymerization of the resorcinol. The pH of soybean glue prepared with Monsanto's extra mix is 12. By reducing the amount of lime to 3.0% of the dry meal and replacing half of the caustic soda with sodium fluoride, the pH of the soybean glue could be lowered to 10.5. It could be further lowered by addition of some acids, as boric, oleic, oxalic, and phosphoric or some acidic sodium salts, such as sodium acetate, sodium thiocyanide, etc.

Among the six chemicals mentioned, boric and oxalic acids were found to be the best for this purpose, being compatible with the soybean glue in greater amounts and able to retard the reaction of formaldehyde. Two parts of 10% boric acid to 80 parts of the soybean glue with pH of 10.5 was able to bring the glue mixture to a final pH of 8.0. Such low pH soybean glue could take considerably larger quantities of aqueous formaldehyde-ammonia solution and resorcinol. However, panels cold-pressed with such glue were poor in joint strength. The increased aqueous formaldehyde appeared to be still insufficient to completely polymerize the resorcinol resin component. Of perhaps equal importance to the adhesive properties of the glue mixture is that with decrease in pH there was also observed a decrease in viscosity

attributable to the poor dispersion of the soybean protein. It appears necessary to keep the soybean glue in a high alkaline condition in order to have its adhesive properties fully developed. Hence, the approach of lowering the pH of soybean glue was also not successful in solving the problem of fortification with resorcinol resin.

Discussion

From the foregoing experiments it can be easily seen that the great difficulty in fortifying soybean glue with resorcinol resin by simple addition lies in the necessary high alkalinity of the soybean glue and in the reactivity of its protein with formaldehyde under alkaline conditions. When the carboxyl group of the protein is neutralized by the base ingredients added to the glue, the formaldehyde reacts with amino, immino, and other groups in the protein resulting rapidly in a gel mass. (80) In addition, the protein consumes and otherwise prevents the formaldehyde from completely polymerizing the resorcinol component. That is why the joint strength of the glue mixture became poorer even when coagulation was delayed by the introduction of stabilizing agents.

Another adverse effect of the high alkalinity of the soybean glue in this case is that the speed of resorcinol resin polymerization is a function of both pH and the formaldehyde-resorcinol ratio (77, 84). At such high alkalinity of soybean glue (pH 12), the speed of polymerization

of resorcinol-formaldehyde is so great that even if the soybean protein could be completely prevented from consuming the formaldehyde, the working life of the resultant glue would inevitably be too short for practical application.

Reducing the alkalinity of the soybean glue was found effective in retarding the reaction of formaldehyde on the protein. Unfortunately, the optimum pH for dispersing soybean protein for adhesive use is consistently above 10. Reducing the pH decreases the adhesiveness of the glue, as previously mentioned. Such decrease of adhesive strength is not offset by the addition of resorcinol resin unless a prohibitive amount is used.

Since there appeared to be a conflict between optimum pH for adequate dispersion of the soybean protein and optimum pH for the maximum introduction of formaldehyde, this approach to the fortification of soybean glue with resorcinol resin was abandoned. However, note is made that increasing amounts of formaldehyde can be added to the soybean glue under low pH conditions. This gives rise to the possibility of using resins for fortification which polymerize with formaldehyde in acid solution. A series of investigations was therefore undertaken to determine the effect of formaldehyde on the soybean protein dispersed with acid chemicals and the adhesive properties of acid-dispersed soybean protein.

Fortification of Soybean Glue with Urea-formaldehyde Resin

An important point which is scarcely mentioned in the literature reviewed, is that soybean glue, in contact with formaldehyde will immediately coagulate under alkaline conditions, but will not do so under acid conditions. This behavior of soybean protein was substantiated in the preceding experiment, and the fortification of the soybean glue of a low pH with urea-formaldehyde resin or melamine-formaldehyde resin was considered to be a logical step. Urea resin was chosen for this study because of its low cost and its ability to cure at room temperature.

Glue Formulation

The soybean meal used was Brier's Soybean Protein as before. Instead of caustic soda and lime, which are two essential chemicals normally used for commercial soybean glue, the meal in this case was dispersed with 8% $CaCl_2$ and 8% NaF based on the weight of the soybean meal. A dispersion with pH about 5.5 was obtained with 250 parts of water. To this acid soybean glue were added various amounts of urea resin (Plaskon 250-2). An extra one percent of paraformaldehyde by weight of soybean glue was added to this glue mixture in order to insure the presence of sufficient formaldehyde for the polymerization of the urea resin. The joint strengths of yellow birch plywood panels bonded with such fortified acid soybean glue are given in Table 9.

Table 9. Shear Strength of Yellow Birch Plywood Bonded with Urea-fortified Soybean Glue of low pH

Soybean Glue with Urea Resin*	Panels	No. of Test Specimens	Dry Shear	Wet Shear
Straight soybean glue (S)	(1)	6 each	247-0**	78-0**
	(2)	6 "	285-0	100-0
	Avg.	12 "	266-0	89-0
(S) 5% urea resin	(1)	6 each	295-0	142-0
	(2)	6 "	365-0	178-0
	Avg.	12 "	330-0	160-0
(S) 10% urea resin	(1)	6 each	378-0	205-0
	(2)	6 "	345-0	155-0
	Avg.	12 "	362-0	180-0
(S) 20% urea resin	(1)	6 each	380-0	208-0
	(2)	6 "	412-0	250-0
	Avg.	12 "	396-0	229-0
(S) 30% urea resin	(1)	6 each	435-0	271-0
	(2)	6 "	404-0	243-0
	Avg.	12 "	420-0	257-0
(S) 40% urea resin	(1)	6 each	441-10	288-0
	(2)	6 "	415-0	236-0
	Avg.	12 "	428-5	262-0
(S) 50% urea resin	(1)	6 each	444-16	260-3
	(2)	6 "	426-5	286-5
	Avg.	12 "	435-11	273-4

*Soybean glue was prepared with $CaCl_2$ and NaF having a pH of approximately 5.5 in using Brier's soybean meal. The urea resin was "Plaskon 250-2." Amount of resin was based on soybean glue by weight.

**The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent in individual specimens was recorded as zero.

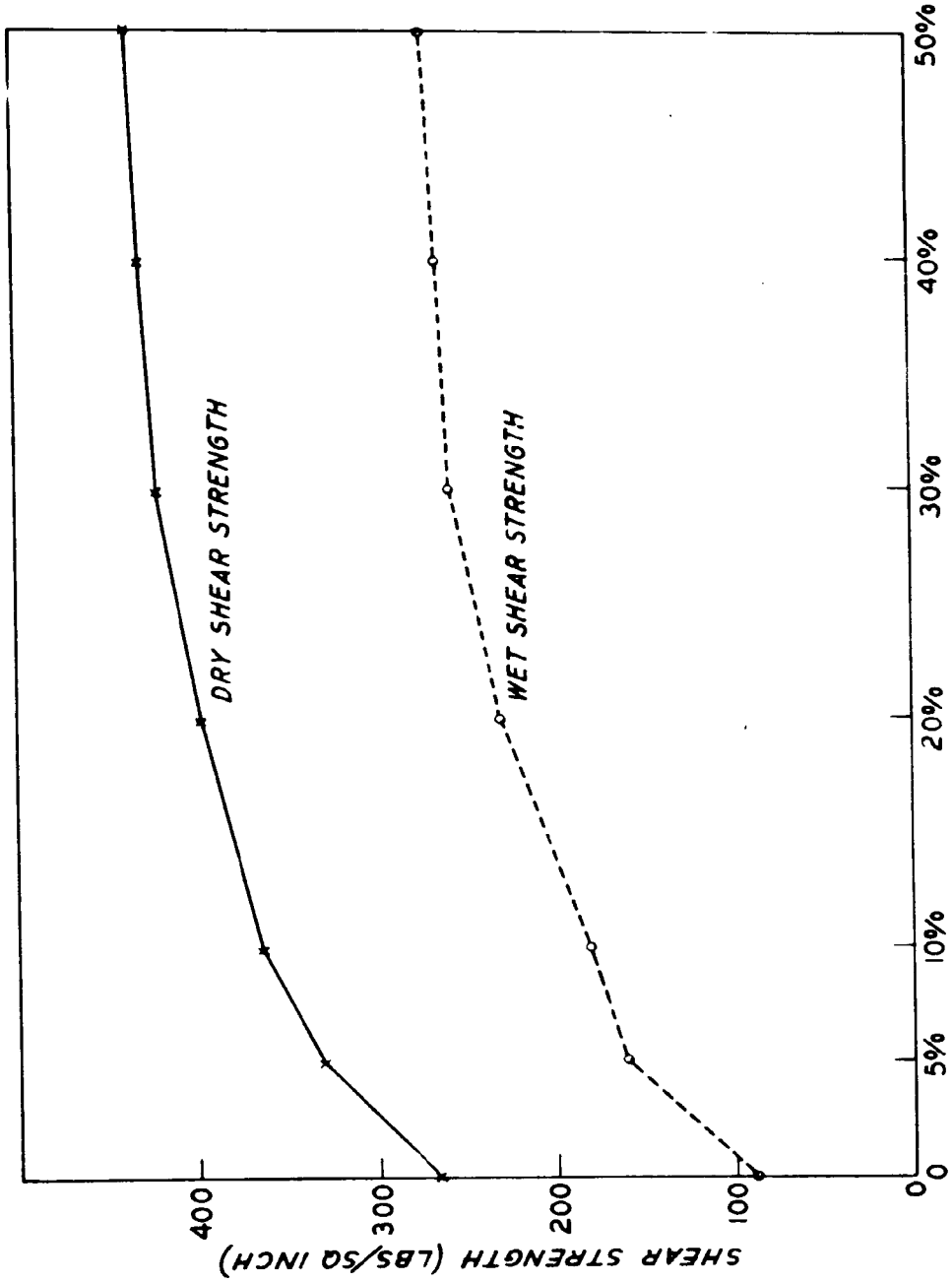


FIG.9 SHEAR STRENGTH OF YELLOW BIRCH PLYWOOD BONDED WITH UREA-FORTIFIED SOYBEAN GLUE OF LOW pH

Results

The experimental data clearly indicate that addition of urea resin to the acidic soybean glue resulted in an increase of both dry and wet shear strength of plywood bond. However, the rate of increase in shear strength was not proportional to the mount of resin incorporated. A sharp increase of shear strength occurred at the initial addition of 5% urea resin. From 5% to 30% urea resin, there was only a moderate increase of shear strength. Beyond 30% up to 50% resin, the increase still continued but became very gradual. The rate of increase in shear strength of this fortified soybean glue joint over the entire range of urea resin proportions is plotted in figure 9.

It is important to note from this figure that soybean glue dispersed with acid chemicals does not have the same adhesive strength as that dispersed under high alkaline conditions with a pH between 11.5 and 12.0. The shear strength of the straight acid soybean glue joint was 266 psi for dry shear and 89 psi for wet shear, while the straight alkaline soybean glue generally gave 390 psi for dry shear and 200 psi for wet shear. The reason for this difference is that with the soybean meal used in our study, the adhesive strength of the meal cannot be fully developed on the acid side. As a result, it took 20% urea resin to raise the wet shear strength of the acid soybean glue joint to the level of straight alkaline soybean glue joint. Not until urea resin

reached 30%, did the wet shear strength of the fortified acid soybean glue joint become significantly better than that of the straight alkaline soybean glue joint.

Discussion

It is apparent that although dispersion of soybean meal on the acid side opens a way for fortification of soybean glue with urea-formaldehyde resin or other acidic resins, it was actually done at the sacrifice of the full development of adhesive strength of soybean protein. Only when a substantial amount (30%) of urea resin was used, could a significant improvement in the water resistance of the soybean glue be achieved. The cost and improvement of wet shear strength by fortification with urea resin are not comparable with the alkaline soybean glue fortified with casein and blood albumin described in Part III.

To reduce the amount of fortifying agent, urea resin, means of improving the adhesive strength of the acid soybean glue base higher than the value obtained in this experiment must be made. Two immediate approaches along this line are suggested. One is an extensive search for better dispersing agents among the acids or acid salts. Another is the use of a moderately modified soybean protein in the preparation of soybean glue. The second approach looks promising according to the work of Burnett (56) on

the viscosity of modified and unmodified soybean proteins*. The latter possesses highest viscosity around pH 12, while the former generally gives higher viscosity at lower pH values. As mentioned in the previous section, viscosity and adhesive strength are directly related properties. It is very probable that greater adhesive strength would be developed under acid conditions, if a moderately modified soybean protein were employed.

Fortification of Soybean Glue with Non-formaldehyde Resins

Since all the four major synthetic resin adhesives for plywood manufacture contain formaldehyde which is incompatible with the highly alkaline soybean glue, some other resins without formaldehyde component were tried for fortifying the soybean glue. Included in this experiment are two modified alkyd resins, two rubber-base adhesives, and one cumar-indene resin.

The two modified alkyd resins are Glyptol 2504 and Reichold 1030. The former is a drying-oil-modified alkyd resin, while the latter is further modified with a small quantity of phenol resin. The films of both possess high water and weather resistance as well as hardness and flexi-

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*The modified soybean protein in this case was treated with alkali, resulting in change of its properties such as dispersion, viscosity, etc. The degree of modification depends upon the severeness of this alkali treatment. See also footnote on page 16.

bility (31,76). Of the two rubber-base adhesives one is a blend of synthetic rubber and resin (Tygobond 30), and the other, a polystyrene emulsion (BKS-92). The water resistance of Tygobond 30 was reported to be very high (87). The cumar-indene resin is a neutral thermoplastic resin with good water resistance, but rather poor heat resistance(5).

These five resins are all in liquid form. The soybean glue used here was prepared with Brier's soybean meal according to Monsanto's extra-mix formula. In this experiment only the compatibility of these resins with the soybean glue and the shear joint strength of the soybean glue fortified with resins at 5% level were determined. It should be noted that this experiment is cursory, but enough to indicate some of the merits and problems in the use of such resins for fortifying the soybean glue. The results are briefly presented here.

With the exception of the rubber-base adhesives, Tygobond 30, all these resins were found to be compatible with the soybean glue. The Tygobond 30 could be mixed into the soybean glue only in a limited amount. When its amount was increased to 10% by weight of the soybean glue, it became highly viscous and difficult to disperse with the protein glue. The joint strength of the soybean glue fortified with each of these resins at 5% level is given in Table 10.

This table and Figure 10 show that of the five resins tested in the fortification of soybean glue, only

Table 10. Shear Strength of Yellow Birch Plywood Bonded with Soybean Glue Fortified with Five Non-formaldehyde Resins

Soybean Glue with Non-formaldehyde Resins*	Panels	No. of Test Specimens	Dry Shear	Wet Shear
Straight soybean glue (S)	(1)	6 each	424-0**	239-0**
	(2)	6 "	382-0	248-0
	(3)	6 "	366-0	191-0
	Avg.	18 "	391-0	226-0
(S) 5% modified alkyd resin (Glyptol 2504)	(1)	6 each	386-0	256-0
	(2)	6 "	418-0	241-0
	Avg.	12 "	402-0	248-0
(S) 5% phenolated alkyd resin (Reichold 1030)	(1)	6 each	387-0	225-0
	(2)	6 "	401-0	260-0
	Avg.	12 "	394-0	243-0
(S) 5% rubber-base adhesive (Tygobond 30)	(1)	6 each	402-0	212-0
	(2)	6 "	381-0	180-0
	Avg.	12 "	392-0	196-0
(S) 5% polystyrene emulsion (BKS-92)	(1)	6 each	380-0	200-0
	(2)	6 "	355-0	184-0
	Avg.	12 "	368-0	192-0
(S) 5% cumar-indene resin (Cumar P 10)	(1)	6 each	420-0	205-0
	(2)	6 "	372-0	171-0
	Avg.	12 "	396-0	188-0

*Soybean glue was prepared with Brier's soybean meal according to Monsanto's extra mix formula. Percentage of resin was based on soybean glue by weight.

**The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent was recorded as zero.

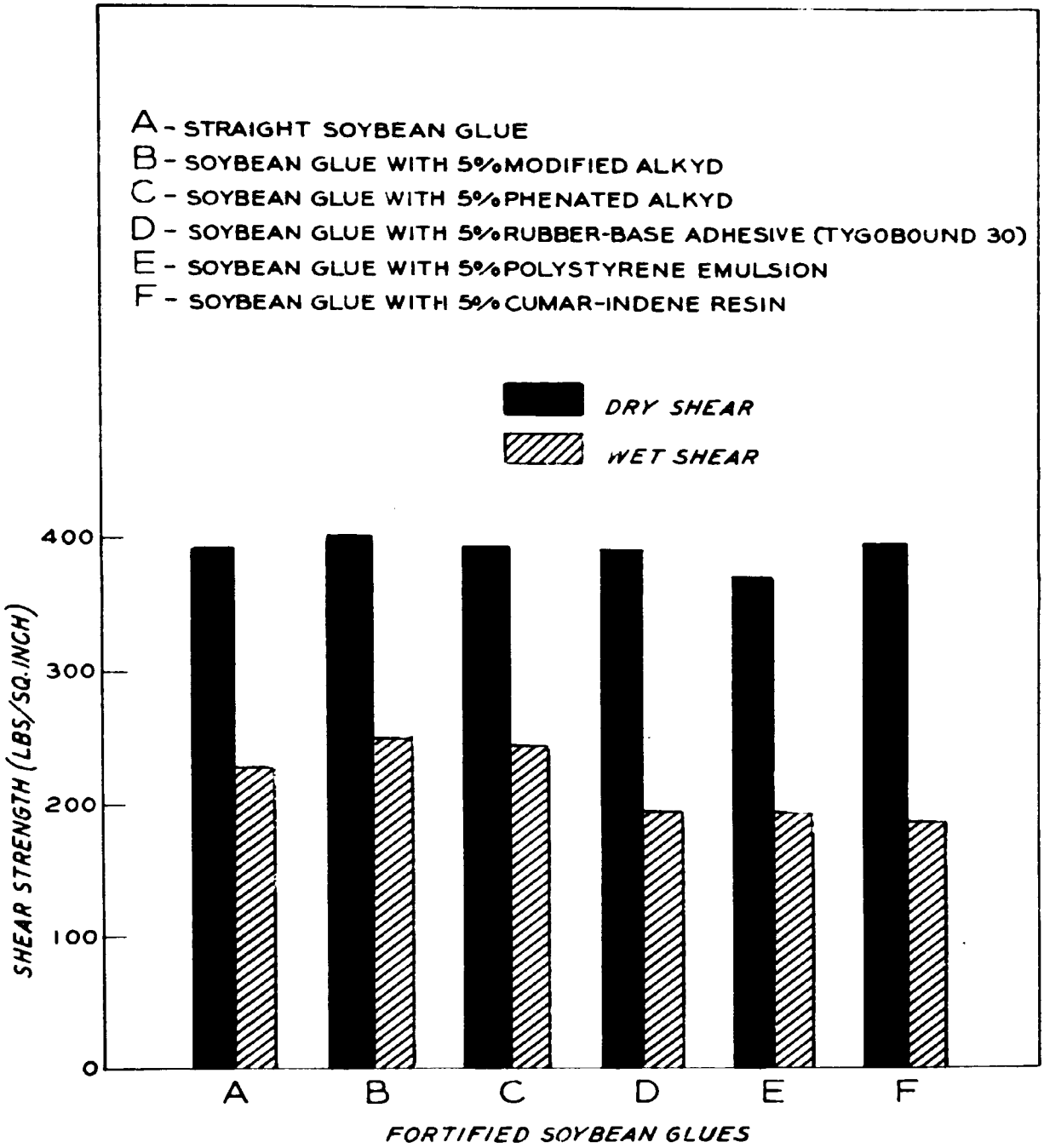

FIG. 10 SHEAR STRENGTH OF YELLOW BIRCH PLYWOOD BONDED WITH SOYBEAN GLUE FORTIFIED WITH FIVE NON-FORMALDEHYDE RESINS

two alkyd resins resulted in a slight increase of wet shear strength of the soybean glue. This increase was of the order of 10%. The other three incorporated into the soybean glue in the same amount (5%) as the two alkyd resins produced even poorer bonds than straight soybean glue. While these five resins all have very good water resistance in themselves, some of the causes of the observed results appear to be as follows:

1. Adverse effect of their solvent on the soybean protein dispersion, as in the case of the rubber-base adhesive, Tygobond 30, which contains acetone.

2. Incomplete polymerization due to high alkalinity of the soybean glue, as in the case of cumar-indene resin (87), or due to the dilution effect of the total mixture and the presence of plasticizer, as in the case of polystyrene emulsion and the alkyds (57,93).

As limited tests with the five non-formaldehyde resins did not bring about significant improvement in the soybean glue, this experiment was not carried further. However, the development of these reins is increasing so rapidly that the prospect of using them for fortifying soybean glue is by no means ended. This experiment has demonstrated on the one hand the compatibility of some of these resins with the alkaline soybean glue, and on the other hand, the exacting nature of this vegetable protein glue for satisfactory fortification with synthetic resins.

Starch Glue Versus Soybean Glue Fortified with Resorcinol-formaldehyde Resin

Experience from the previous experiments in the fortification of soybean glue with synthetic resins led to the trial of fortifying starch glue with resorcinol-formaldehyde resin. Starch glue is undoubtedly very low in water resistance, but it has good adhesive strength under dry conditions, is cheap, and above all is far less sensitive chemically than the soybean glue. The last factor would possibly make it compatible with resorcinol-formaldehyde and other similar resins, which cause trouble in mixing with alkaline soybean glue.

Glue formulation

The starch glue employed in this experiment was Perkins Corox and the resorcinol-formaldehyde resin, Koppers Penacolite G-1131. The mixes of resin used in fortifying the starch glue were 5%, 10%, 20%, 30%, 40%, and 50% of the starch glue by weight. To insure the cure of the resin component in the starch-resin glue mixture, an extra 4% of paraformaldehyde was added to the blend. They mixed together very well and had a good working life. The joint strength of yellow birch plywood bonded with this resorcinol-fortified starch glue is given in Table 11.

Results and Discussion

The remarkable improvement in both dry and wet shear

Table 11. Shear Strength of Yellow Birch Plywood Bonded with Resorcinol-fortified Starch Glue

Starch Glue with Resorcinol*	Panels	No. of Test Specimens	Dry Shear	Wet Shear
straight starch glue (st)	(1)	6	411- 8**	0- 0**
	(2)	6	367- 0	0- 0
	Avg.	12	389- 4	0- 0
(St) + 5% resorcinol	(1)	6	517-15	239- 0
	(2)	6	543- 7	220- 0
	Avg.	12	530-11	230- 0
(St) + 10% resorcinol	(1)	6	553-12	325- 0
	(2)	6	535-33	293-10
	Avg.	12	544-23	309- 5
(St) + 20% resorcinol	(1)	6	558-40	275-13
	(2)	6	592-76	395-19
	Avg.	12	575-58	335-16
(St) + 30% resorcinol	(1)	6	607-47	433- 8
	(2)	6	569-42	369-12
	Avg.	12	588-45	401-10
(St) + 40% resorcinol	(1)	6	644-68	447-20
	(2)	6	545-50	403-27
	Avg.	12	595-59	425-24
(St) + 50% resorcinol	(1)	6	570-39	408-15
	(2)	6	626-85	454-43
	Avg.	12	598-62	432-29

*Starch glue was "Perkins Carox," and resorcinol resin, "Koppers Penacolite G-1131." Percentage of the resin was based on the liquid starch glue by weight.

**The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent was recorded as zero.

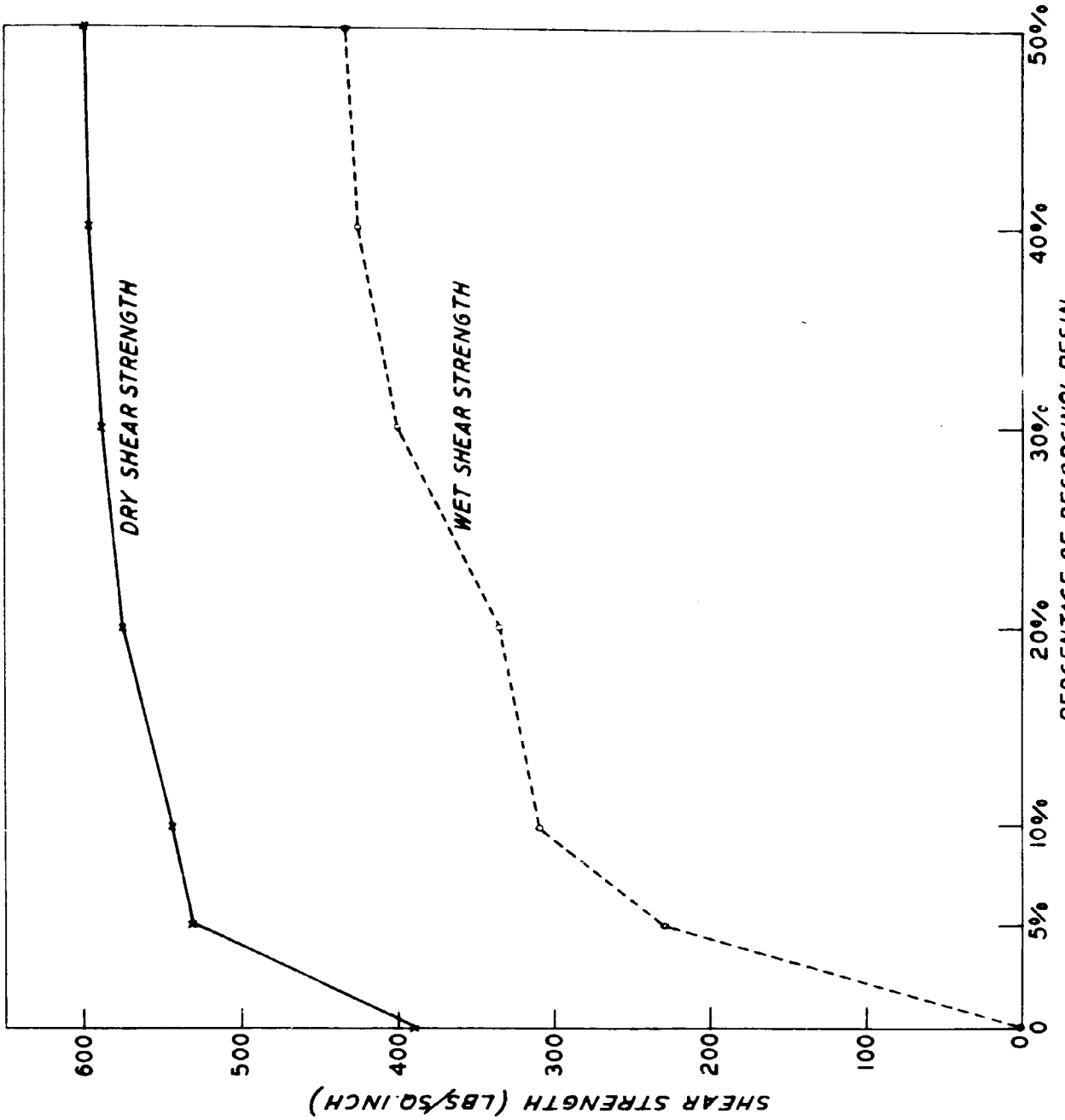

FIG.11 SHEAR STRENGTH OF YELLOW BIRCH PLYWOOD BONDED WITH RESORCINOL-FORTIFIED STARCH GLUE

strength of the starch glue resulting from the addition of resorcinol resin is clearly illustrated in Figure 11. Plywood specimens bonded with straight starch glue completely delaminated after 48 hours of soaking in water at room temperature, whereas those bonded with resorcinol-fortified starch glue having resin at 5% or above, all remained in good condition and gave an average wet shear strength of 200 psi to 432 psi according to the amount of resin used.

The rate of increase in both dry and wet shear strength was highest at the initial addition of 5% resorcinol resin. At the 10% level the increase in wet shear strength was still significant, but the increase in dry shear strength greatly slowed down. From the 10% level on, the increase in both wet and dry shear strength became more gradual, particularly the dry shear strength, which reached its peak at the range of 30-50% resin.

From the standpoint of cost and water resistance, it appears that 10% resorcinol resin is the most efficient amount for waterproofing the starch glue. On account of this, additional specimens were prepared for delamination and block tension tests and further plywood shear test. The results are as follows:

Table 12. Joint Strength and Delamination of Yellow Birch Plywood and Blocks Bonded with 10% Resorcinol-fortified Starch Glue

Panels	Plywood Shear Test				Delamination Test %	Block Tension Test
	No. of Specimens	dry	soaked (48hrs)	boiled (3hrs)		
(1)	6 each	553-12*	325-0*	144-0*	0.3	483-0* 625-5* 500-5 610-5
(2)	6 "	535-33	293-10	149-0	0.0	633-5 567-10 610-12 600-5
(3)	6 "	528-25	300-4	150-0	0.0	567-8 433-0
Avg.	18 "	539-25	306-5	148-0	0.1	563.6

*The first value represents the joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent was recorded as zero.

The above data demonstrate that the water resistance of starch glue can be drastically improved by fortification with 10% resorcinol resin. In comparison with commercial soybean glue (Lauxein 10-B), the average joint strength of such resin-fortified starch glue was about 40% higher in dry shear and 50% higher in wet shear. It even withstood the boiling test. After three hours of boiling, it still maintained an average shear strength of 148 psi. In this respect it is superior to casein glue and compare favorably even with straight urea resin (25, 70).

The unusual waterproofing action of the resorcinol resin on the starch glue involves not only the curing of the resin itself, but probably also a chemical interaction between the resin and starch. Should there be such an inter-

action, it may be that the methylene groups of the resorcinol resin react with the hydroxyl groups of the starch, which are principally responsible for its water sensitivity. This reaction is known to occur between urea resin and the starch solution in paper sizing (2,72,89).

The extra amount of paraformaldehyde added in might also play a role in insolubilizing the starch. Bauer and Hawley (7) in their patents claimed that formaldehyde could produce such effect on the starch.

Starch glue is of moderate alkalinity. A product of high joint strength has been developed recently. This fact, coupled with affinity with resorcinol resin produces a unique fortified starch glue. That work on the fortification of starch glue with resorcinol resin has not been done heretofore is perhaps mainly due to the high cost of the resin. However, such cost appears to be justified by the striking performance of the fortified glue, particularly in the underdeveloped countries, where starch glue is available and synthetic resins have to be imported from countries far away.

PART V

MOLD RESISTANCE OF A FORTIFIED SOYBEAN GLUE

Soybean glue as well as practically all other protein glues are very susceptible to attack by mold. The rapid breakdown of soybean glue under moist conditions is more often due to the activity of mold or other micro-organisms than to softening of the glue by water alone. Since extensive studies on preservatives for casein and soybean glues (42,44) have been made at the U. S. Forest Products Laboratory, this test was undertaken mainly to compare the mold resistance of a straight soybean glue with a fortified soybean glue having 20% casein glue, 10% blood albumin, and 3% formalin developed from this investigation. In addition, it was designed to determine the effective amount of a preservative required for this fortified soybean glue.

Glue Formulation

The preservative selected was sodium trichlorophenate-2,4,5. It was mixed into the fortified soybean glue in an amount of 3.0%, 5.0%, and 7.0% on the basis of soybean meal by weight. Panels bonded with Brier's straight soybean glue and the 20%-casein glue, 10%-blood albumin, and 3%-formalin-fortified soybean glue having different proportions of the preservative were cut into shear test specimens after condition

ing. These specimens were then exposed to mold attack and tested upon removal at one-week, two-week, and four-week intervals as described in the Testing Procedure section. The results are given in Table 13. The moisture content of the shear specimens after removal from the container for testing varied from 29% to 36.5%.

Results and Discussion

The test data indicate that the soybean glue joints without sodium trichlorophenate preservative possessed no measurable shear strength after two to four weeks exposure to mold. Comparatively the casein-blood-albumin-fortified soybean glue with 3.0% formalin as a hardening agent had slightly more mold resistance than the straight soybean glue without formalin, but the difference was not large. The latter completely delaminated at the end of two weeks, the former, at the end of four weeks. This slight difference could be attributed to the presence of formalin in the fortified soybean glue, since the incorporated casein and blood albumin were no more mold-resistant than the soybean itself.

Panels glued with fortified soybean glue with 3.0% sodium trichlorophenate on the basis of soybean meal exhibited some mold resistance. They possessed about 25% of the original dry shear strength at the end of four weeks under exposure conditions. However, great improvement was not obtained until the concentration of this preservative increased

Table 13. Results of Mold Resistance Tests on Yellow Birch Sapwood Plywood Panels Glued with Straight Soybean Glue and Fortified Soybean Glues With and Without Preservative.

Type of Glue	Concentration of Preservative**	Average Joint Strength & Wood Failure***				
		Original Dry	Wet After 48 Hours Soaking	After Exposure To Mold Test for 7-days	14-days	28-days
Straight soybean glue	none	382-0**	211-0**	81-0**	0-0**	0-0**
Fortified soybean glue***	none	447-0	260-0	124-0	39-0	0-0
Fortified soybean glue	3.0% sodium trichlorophenate	434-0	249-0	187-0	134-0	108-0
Fortified soybean glue	5.0% sodium trichlorophenate	445-0	253-0	234-0	218-0	225-12
Fortified soybean glue	7.0% sodium trichlorophenate	430-0	248-0	260-0	248-3	234-8

*Based on weight of soybean meal.

**The first value represents joint strength in pounds per square inch; the second value represents the percentage of wood failure, of which less than five percent was recorded as zero. Each value is an average of 10 plywood shear specimens.

***Soybean glue prepared with Brier's soybean meal according to Monsanto's extra-mix formula and fortified with 20%-casein glue, 10%-blood albumin, and 3% formalin based on weight of soybean meal.

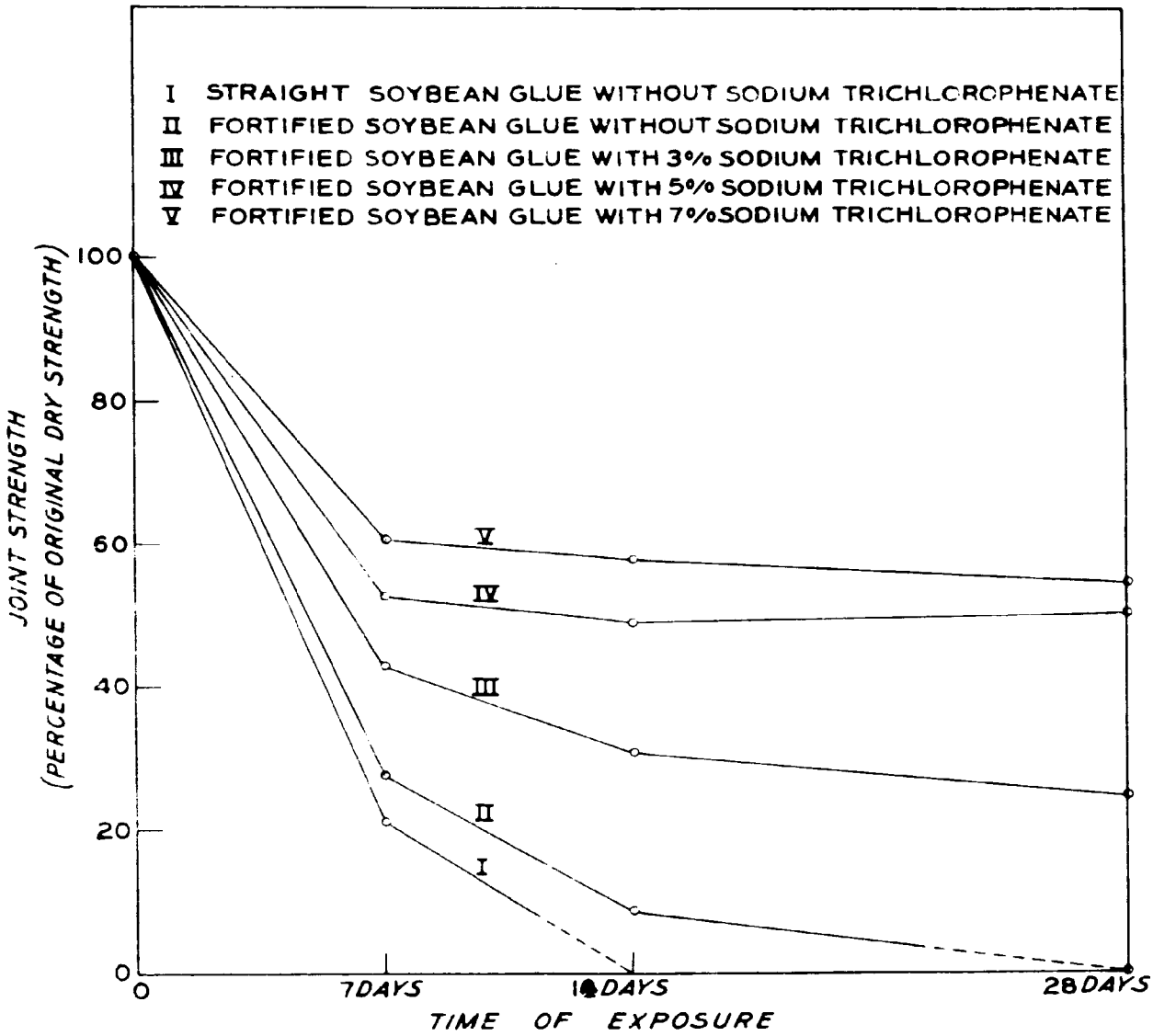

FIG.12 RATE OF DETERIORATION OF YELLOW BIRCH SAPWOOD PLYWOOD BONDED WITH STRAIGHT SOYBEAN GLUE & FORTIFIED SOYBEAN GLUES (FORTIFIED WITH 20% CASEIN, 10% BLOOD ALBUMIN AND 3% FORMALIN) WITH AND WITHOUT PRESERVATIVES AFTER EXPOSURE TO MOLD TESTS

up to 5.0% or 7.0%. The joint strength of panels with such concentrations of sodium trichlorophenate in the glue, after the initial drop in the first week, maintained or decreased very gradually throughout the rest of the exposure period. The 7.0% concentration appeared to be the most effective, as such preserved glue still possessed well over 50% of joint strength at the end of the four week's exposure. The degree of effectiveness of various concentration of sodium trichlorophenate is clearly shown in Figure 12.

A peculiar phenomenon occurred in the panels bonded with 5.0% concentrations of sodium trichlorophenate in the glue. In these panels, the joint strength at the end of the fourth week was even higher than that at the end of the third week under exposure to mold. This phenomenon was even more conspicuous with casein glue treated with preservatives as reported by Kaufert (42). He postulated that this might be partly due to drying of the shear specimens during the longer exposures. Perhaps also the change of flexibility of wood fibers through long period of exposure in the container might induce such variation.

The increase of wood failure with the increase of exposure period in the shear specimens with 5.0-7.0% of sodium trichlorophenate present in the glue was apparently due to the gradual weakening of wood through mold attack.

Regarding the growth of mold, the glue line of un-

preserved shear specimens was fully covered with mold at the end of first week, where as that of preserved ones with concentration of sodium trichlorophenate at 5.0-7.0% remained free from mold throughout the exposure period, although mold was abundant on the face of these shear specimens. This together with the joint strength proved that sodium trichlorophenate was very effective in increasing the durability of the soybean glue joint when employed up to a concentration of 5.0-7.0% on the basis of the meal. Indicated also is that the 3.0% formalin incorporated into the fortified soybean glue as a hardening agent lends little protection to the glue line from mold attack.

SUMMARY OF EXPERIMENTAL RESULTS

1. Among the four soybean glue mixes prepared with Brier's mechanically isolated soybean protein, Glidden's chemically isolated Alpha-Protein, and the solvent-extracted soybean meals such as Monsanto's Lauxein 10-B and Glidden's Prosoy-T, no significant difference was found on the basis of their observed joint strengths. However, on the basis of their strength/meal-concentration ratio, Brier's soybean meal ranked highest, because of its greater water requirement in the preparation of glue. The net result was that with the same amount of meal, Brier's soybean meal produced a glue mixture 36-46% greater than the other three soybean meals and was furthermore of equal bonding quality.

2. Brier's mechanically isolated soybean protein (90% protein) was found to require 240 more parts of water per 100 parts of meal than the solvent-extracted meals, Lauxein 10-B (50% protein) and Prosoy-T (53.3% protein). The extra amount of water was approximately proportional to its high protein content. On the other hand, Glidden's Alpha Protein with 96.9% protein but denatured was found to require only 50 more parts of water than the two solvent-extracted soybean meals.

3. Monsanto's extra-mix formula was higher in wet strength than the regular mix formula. With this extra-mix

formula, increase of either lime from 4.0% to 10.0% or tetrasulphide mixture from 4.8% to 9.6% had practically no effect on the dry joint strength of the soybean glue prepared with Brier's soybean meal. In wet strength an insignificant improvement was observed when both of these two hardening agents were around 7.0%. Further increase of lime to 10.0% without varying the amount of other chemicals in the glue mix resulted in decreased wet strength and increased delamination. In the case of tetrasulphide mixture, increase to 9.6% also showed an adverse effect on the wet strength, but not as significant as that of the lime.

4. Addition of a ready-mix casein glue, "Perkins Perfection", up to a range of 20-35% on the basis of soybean meal by weight resulted in a slight increase in water resistance and a significant increase of tensile joint strength of the glue prepared with Brier's soybean protein according to Monsanto's extra-mix formula. With further addition of the casein glue to 50%, a significant drop in both properties occurred. This drop is not due to the casein itself, but rather to the chemical ingredients, particularly the lime of the casein mix, which, added to the total glue mixture, upset the optimum amount required for the soybean glue.

5. Incorporation of 10-20% blood albumin in the 20%-casein-fortified (all additives based on the weight of soybean meal) soybean glue resulted in only a slight increase of dry shear strength. Increase of blood albumin to 30% pro-

duced a weak joint. Superior bond was obtained with the 20%-casein-fortified soybean glue by incorporation of 10% blood albumin and 3% formalin. Formalin functions to harden the protein, the addition of which requires the use of ammonium hydroxide according to a patented procedure. Panels bonded with the casein and blood-albumin-fortified glue having formalin in it were about 32% higher in wet shear strength than those bonded with straight commercial soybean glue, and were 19% higher in wet shear strength than those bonded with straight Brier's soybean glue. Its tensile joint strength and resistance to delamination were also appreciably increased(see Table 14).

6. A regular soybean glue, often with a pH of 11.5-12.0, was found incompatible with resorcinol-formaldehyde resin, because the catalyst of the resin, paraformaldehyde, invariably coagulated the glue. The results of several experiments to overcome this obstacle are as follows:

a. Use of aldehydes with higher molecular weight as catalysts --- Acetaldehyde, propionaldehyde, butyraldehyde, and benzaldehyde all coagulated the soybean glue in the same manner as paraformaldehyde except in speed. The higher the molecular weight of the aldehydes, the slower was the coagulation of the glue. One exception to this was furfural (furfuraldehyde), which did not readily convert the glue into a gel mass.

b. Use of formaldehyde compounds as catalysts --- Neither hexamethylene tetramine nor sodium formaldehyde sulfite succeeded in delaying the coagulation of the soybean glue much over 20 minutes.

c. Addition of retarding agents --- Borax, sodium sulphite, sodium bisulphite, and trisodium phosphate were ineffective in retarding the reaction between the protein and the formaldehyde long enough for practical purposes. The most effective retarding agent was found to be ammonium hydroxide. Aqueous formaldehyde in an amount of 3% by weight of soybean meal could be introduced into the soybean glue through mixture with this base without causing coagulation of the soybean glue for six hours.

d. Lowering alkalinity of soybean glue --- Reduction of lime and sodium hydroxide in the glue mix, accompanied by further addition of some acids compatible with the soybean glue such as boric or oxalic acides, was effective in lowering the alkalinity of the glue. It was observed that as the pH of the glue dropped, its sensitivity to formaldehyde correspondingly decreased, and so did its viscosity, which is directly related to the adhesive properties of the soybean glue.

Limited resorcinol resin could be added to the soybean glue through some of the above means, but the resultant glue mixtures all failed to produce a satisfactory bond. The critical factor was that as soon as formaldehyde was released into the glue mixture, it was consumed by the soybean protein, and thus prevented the resin from completely polymerizing.

7. As indicated above, soybean glue under alkaline conditions undergoes coagulation immediately when in direct contact with formaldehyde. However, it was found that this phenomenon will not occur if the soybean glue is dispersed with acid chemicals. The disclosure of this behavior made possible the fortification of soybean glue dispersed by calcium chloride and sodium fluoride with urea-formaldehyde resin. The drawback in this approach is that the adhesive strength of soybean protein developed by these two acid salts was much lower than that developed by the commonly used two base agents, lime and caustic soda. Not until the urea resin reached 30% (by weight of the soybean glue), did the water resistance of this fortified soybean glue become significantly higher than that of the straight soybean glue.

8. In the fortification of alkaline soybean glue with five non-formaldehyde resins, only two modified alkyd resins brought about a slight increase of the wet strength of the soybean joints. The two rubber-base adhesives and the cumar-indene resin when added to soybean glue produced even poorer joints than straight soybean glue. Some of the causes

appear to be the adverse effect of their solvent on the soybean protein, presence of plasticizer, and incomplete polymerization. However, these resins mixed well with the alkaline soybean glue except one of the rubber-base adhesives (Tygobond 30), which could be added only in a limited amount.

9. While efforts to fortify soybean glue with synthetic resins proved none too satisfactory, striking success was obtained in the fortification of starch glue (also a cheap glue of vegetable origin) with resorcinol-formaldehyde resin. Addition of 10% of resorcinol resin to the starch glue with extra paraformaldehyde produced an average joint strength 40% higher in dry shear strength and 50% higher in wet shear strength than the commercial soybean glue. It is superior to casein glue in water resistance, and even withstood a 3-hour boiling test, in which most straight urea resins would fail. Such an unusual waterproofing action of the resorcinol resin on the starch glue is attributed to (a) complete curing of the resorcinol resin itself, (b) chemical interaction between the resin and starch, and probably (c) the reaction of the extra paraformaldehyde added to the starch.

10. In mold resistance test panels bonded with ordinary soybean glue completely delaminated at the end of the first week when exposed to mold attack, but joints made with the 20%-casein and 10%-blood-albumin-fortified soybean glue having 3% formalin in it withstood the mold attack only

one week longer. In increasing the mold resistance of this fortified soybean glue, an amount of 5.0% to 7.0% of sodium trichlorophenate by weight of soybean meal was found to be very effective. Joints made with such preserved fortified soybean glue still possessed over 50% of their original dry joint strength and showed increasing wood failure in plywood shear test at the end of four-weeks' exposure.

Table 14. Summary Table of Average Joint Strength and Delamination of Selected Glue Mixes

Glue Mixes	Avg. Shear Strength Dry	Avg. Shear Strength Wet	Avg. Delamination %	Avg. Block Tensile Strength	Parts of Experiment
Commercial soybean glue (Regular mix - Monsanto's meal)	379-0*	188-0*	10.2	---	
Commercial soybean glue (Extra-mix - Monsanto's meal)	383-0	203-0	7.4	306-0*	I
**Brier's soybean glue (Extra mix)	391-0	226-0	6.6	302-0	
Brier's soybean glue (Extra mix with 3% more lime & 2.4% more tetrasulphide)	394-0	239-0	6.0	300-0	II
Casein-fortified soybean glue (20% casein glue)	393-0	249-0	5.1	365-0	III
***Casein & albumin-fortified soybean glue with 3% formalin	450-0	269-0	4.9	366-0	
Resorcinol-fortified soybean glue	unsuccessful				
Urea-fortified soybean glue (30% urea resin)	420-0	257-0	---	---	
Alkyd-fortified soybean glue (5% alkyd resin)	418-0	241-0	---	---	IV
****Resorcinol-fortified starch glue (10% resorcinol resin)	539-25	306-5	0.1	563-6	
Casein & albumin-fortified soybean glue with 3% formalin plus 7% sodium trichlorophenate	234-8	after exposure to mold for 4 weeks in a humidity chamber			V

*Wood failure less than five percent was recorded as zero.

**Brier's soybean glue contains much less meal solids than commercial soybean glue or others tested.

***This glue mix was fortified with 20% casein glue, 10% blood albumin, and 3% formalin.

****Its average joint strength after 3-hours' boiling test was 148 psi.

CONCLUSIONS

Conclusions from the foregoing study must necessarily be limited to the specific materials used under the conditions of investigation. However, the information as to the behavior of soybean glue in response to certain treatments as displayed in this investigation can be considered as basic, and adds materially to existing knowledge of the subject. In addition, the relative merits of the different approaches used here should be helpful in further research on methods of improving the bonding qualities of soybean glue.

1. Brier's mechanically isolated soybean protein with much less meal solids in the glue mixture, produces at least as good a bond as either chemically isolated soybean protein or solvent-extracted soybean meals, and therefore should be more economical than other soybean meals if its cost of processing is about the same.

2. The amount of water required in the preparation of glue with different soybean meals is approximately in direct proportion to the protein content of the meal and in inverse proportion to the degree of denaturation of the meal. This behavior has an important bearing on the strength efficiency of different soybean meals for adhesive use.

3. Monsanto's extra-mix formula, which includes

more lime and tetrasulphide mixture together with other chemicals, gives a definitely higher wet strength than the regular-mix formula. With this extra-mix formula, further increase of lime from 4% to 10% and of tetrasulphide mixture from 4.8% to 9.6% at different levels brought about no significant improvement in water resistance or other properties of the soybean glue prepared with Brier's soybean meal. The common assumption that water resistance of soybean glue increases with increase of lime appears to be valid only within certain limits.

5. The water resistance and tensile joint strength of soybean glue increase appreciably with addition of casein glue. This holds true provided the amount of lime in the casein mix when added to the total glue mixture does not upset the optimum amount of chemicals for the soybean glue.

6. Incorporation of blood albumin in the 20%-casein-fortified soybean glue should not be much over 20% by weight of the soybean meal in cold-press operation.

7. Significant improvement in both joint strength and water resistance of Brier's soybean glue can be obtained by fortification with 20% casein glue, 10% blood albumin, and 3% formalin (all based on the weight of soybean meal), the latter hardening the protein and decreasing its water sensitivity. This is the best mixing formula for soybean glue developed in this investigation.

8. Resorcinol-formaldehyde resin is unsatisfactory for fortifying the regular soybean glue, which is highly alkaline. The chief causes are the coagulation of soybean glue by the formaldehyde and the consumption of the formaldehyde by the soybean protein, which prevents the resin from completely polymerizing. The reaction of the soybean protein with the formaldehyde under alkaline conditions is so quick that it can be further concluded that any resin which requires active formaldehyde for polymerization will be difficult to use in the fortification of the regular soybean glue.

9. Some behaviors of the regular soybean glue in response to treatments with aldehydes of higher molecular weights, formaldehyde compounds, formaldehyde-retarding agents, and lowering of alkalinity are:

a. With the exception of furfural, aldehydes up to six carbon atoms all cause coagulation of the soybean glue. The speed of coagulation is, in general, inversely proportional to the molecular weight of the aldehyde.

b. Hexamethylene tetramine and sodium formaldehyde sulfite are not effective in delaying the coagulation of the soybean glue.

c. Among the five retarding agents used, ammonium hydroxide, added according to a patented procedure, is most effective in retarding the reaction of formaldehyde in the soybean glue mixture.

d. The viscosity of the soybean glue and its sensitivity to formaldehyde generally decrease with lowering of its alkalinity. Once on the acid side, soybean glue will not coagulate even if a large amount of formaldehyde is directly added to it.

10. Soybean glue dispersed with acid chemicals can be fortified with urea-formaldehyde resin, but a substantial

amount of the resin is likely to be required in order to achieve significant improvement in its bonding qualities.

11. Some of the non-formaldehyde resins are compatible with the alkaline soybean glue. However, there are some problems to be solved, such as the suitability of their solvents with the soybean protein, presence of plasticizer, etc., before satisfactory fortification with them can be obtained.

12. Synthetic resin adhesives most suitable for fortification of the regular soybean glue should have at least the following characteristics.

a. High water resistance

b. Freedom from active formaldehyde

c. Ability to polymerize under high alkaline condition at an appropriate speed.

d. Solvent without adverse effect on the adhesive strength of the soybean glue.

e. Ability to reduce the hygroscopicity of the soybean protein.

13. Because of the unusual waterproofing action of resorcinol-formaldehyde resin on the starch glue, fortification of this vegetable glue with resorcinol resin is far more promising and much simpler than that of soybean glue with similar resins.

14. The mold resistance of the casein-blood-albumin fortified soybean glue with 3% formalin is not much higher than the straight soybean glue. For adequate durability

5-7% of effective preservative such as sodium trichlorophenate is required.

APPENDIX

TABLES OF ANALYSIS OF VARIANCES

I. Analysis for Bonding Qualities of Soybean Glue.

Table A. Analysis of Variances for Dry and Wet Shear Strength of Three Soybean Meals Tested with Two Mixing Formulas

Source	D.F.	S.S.	M.S.	F.
Total	35	323,258.89		
Meals	2	1,174.06	587.03	1.44
Formulas	1	1,626.78	1,626.78	3.99
Dry-Wet	1	308,395.11	308,395.11	756.39**
M x F	2	170.05	85.02	<1
M x D-W	2	480.38	240.19	<1
F x D-W	1	441.00	441.00	1.08
M x F x D-W	2	1,186.27	593.14	1.45
Residue	24	9,785.24	407.72	

*Indicates significant difference at .05 level.

**Indicates significant difference at .01 level.

Table B. Analysis of Variances for Wet Shear Strength and Delamination of Three Soybean Meals Tested with Two Mixing Formulas

Source	D.F.	For Wet Shear			For Delamination		
		S.S.	M.S.	F.	S.S.	M.S.	F.
Total	17	7,020.00			92.25		
Meals	2	1,183.00	591.50	1.82	3.21	1.60	<1
Formulas	1	1,680.88	1,880.88	5.80*	25.21	25.21	4.79*
M X F	2	66.79	33.40	<1	0.66	0.33	<1
Residue	12	3,889.33	324.11		63.17	5.26	

Table C. Analysis of Variances for Wet Shear Strength and Delamination of Four Soybean Meals Tested with Extra-mix Formula

Source	D.F.	For Wet Shear			For Delamination		
		S.S.	M.S.	F.	S.S.	M.S.	F.
Total	11	4,490.25			37.97		
Meals	3	1,138.25	379.42	<1	1.20	0.40	<1
Residue	8	3,352.00	419.00		36.77	4.60	

Table D. Analysis of Variances for Block Tensile Strength of Four Soybean Meals Tested with Extra-mix Formula

Source	D.F.	S.S.	M.S.	F.
Total	39	62,981.38		
Meals	3	2,201.10	733.76	<1
Residue	36	60,780.10	1,688.38	

Table E. Analysis of Variances for Ratio of Shear Strength to Meal-concentration of Four Soybean Meals

Source	D.F.	S.S.	M.S.	
Total	23	957.1254		
Meals	3	249.8301	83.2767	41.08**
Dry-Wet	1	665.9174	665.9174	328.48**
M x D-W	3	8.94-5	2.9802	1.47
Residue	16	32.4374	2.0273	

Just significant difference test for the ratio of shear strength to meal-concentration of four soybean glues:

$$\text{J.s.d.} = \text{just significant difference} = t\sqrt{\text{error variance} \times \frac{2}{N}}$$

$$\text{J.s.d. at .01} = 2.910\sqrt{2.027 \times \frac{2}{6}} = 2.4014$$

$$\text{J.s.d. at .05} = 2.120\sqrt{2.027 \times \frac{2}{6}} = 1.7428$$

Soybean Meals		Mean (strength/meal-conc. ratio)
B	Brier's Soybean Protein	= 23.3417
M	Monsanto's Lauxein 10-B	= 15.1417
G_1	Glidden's Prosoy-T	= 15.7883
G_2	Glidden's Alpha-Protein	= 18.3917

Difference between the Means:

B & M =	8.2000**	M & G_1 =	0.6466
B & G_1 =	7.5534**	M & G_2 =	3.2500**
B & G_2 =	4.9500**	G_1 & G_2 =	2.6034**

II. Analysis for Effect of Hardener Concentration on the Bonding Qualities of Soybean Glue

Table F. Analysis of Variances for Effect of Lime and Tetrasulphide Concentration on the Dry Shear Strength of Soybean Glue

Source	D.F.	S.S.	M.S.	F.
Total	26	5,468.67		
Lime	2	17.55	8.78	< 1
Tetrasulphide	2	162.89	81.44	< 1
L x T	4	78.89	19.72	< 1
Residue	18	5,209.34	289.41	

Table G. Analysis of Variances for Effect of Lime and Tetrasulphide Concentration on the Wet Shear Strength of Soybean Glue

Source	D.F.	S.S.	M.S.	F.
Total	26	12,532.00		
Lime	2	3,554.00	1,777.00	4.01*
Tetrasulphide	2	876.22	438.11	< 1
L x T	4	121.11	30.28	< 1
Residue	18	7,980.67	443.37	

Just significant difference test for effect of lime on the wet shear strength:

$$\text{J.s.d. at .01} = 2.878\sqrt{443.37 \times \frac{2}{9}} = 28.57$$

$$\text{J.s.d. at .05} = 2.101\sqrt{443.37 \times \frac{2}{9}} = 20.85$$

Lime	Mean (wet shear-psi)	Difference (between Means)
A - 4%	228.00	A & B = 4.67
B - 7%	232.67	A & C = 21.67*
C -10%	206.33	B & C = 26.34*

Table H. Analysis of Variances for Effect of Lime and Tetrasulphide Concentration on Delamination of Soybean Glue

Source	D.F.	S.S.	M.S.	F.
Total	26	107.97		
Lime	2	27.51	13.76	3.92*
Tetrasulphide	2	12.46	6.23	1.78
L x T	4	4.87	1.22	< 1
Residue	18	63.13	3.51	

Just significant difference test for effect of lime on delamination:

$$\text{J.s.d. at .01} = 2.878\sqrt{3.51 \times \frac{2}{9}} = 2.54$$

$$\text{J.s.d. at .05} = 2.101\sqrt{3.51 \times \frac{2}{9}} = 1.86$$

Lime	Mean (delamination-%)	Difference (between Means)
A - 4%	6.42	A & B = 0.12
B - 7%	6.30	A & C = 2.08*
C -10%	8.50	B & C = 2.20*

III. Analysis for Casein-fortified Soybean Glues

Table I. Analysis of Variances for Shear Strength of Casein-fortified Soybean Glues.

Source	D.F.	S.S.	M.S.	F.
Total	23	178,916.96		
Glues	3	5,810.12	1,936.71	2.86
Dry-Wet	1	160,557.04	160,557.04	237.16**
G x D-W	3	1,717.80	572.60	< 1
Residue	16	10,832.00	677.00	

Table J. Analysis of Variances for Wet Shear Strength of Casein-fortified Soybean Glues.

Source	D.F.	S.S.	M.S.	F.
Total	11	9,535.00		
Glues	3	6,663.00	2,221.00	6.19*
Residue	8	2,872.00	359.00	

Just significant difference test for glues:

$$\text{J.s.d. at .01} = 2.355\sqrt{359 \times \tfrac{2}{3}} = 36.43$$

$$\text{J.s.d. at .05} = 2.306\sqrt{359 \times \tfrac{2}{3}} = 35.67$$

$$\text{J.s.d. at .10} = 1.860\sqrt{359 \times \tfrac{2}{3}} = 28.77$$

$$\text{J.s.d. at .20} = 1.397\sqrt{359 \times \tfrac{2}{3}} = 21.61$$

	Glues	Mean wet shear-psi	Mean delamination-%
A	Straight soybean glue	226.00	6.57
B	A + 20% casein	249.33	5.07
C	A + 30% casein	250.33	4.83
D	A + 50% casein	192.33	7.67

Difference between the Means Shear Strength

A & B = 23.33	sig. at .20 level	B & C = 1.00
A & C = 24.33	sig. at .20 level	B & D = 57.00**
A & D = 33.67	sig. at .10 level	C & D = 58.00**

Table K. Analysis of Variances for Delamination of Casein-fortified Soybean Glues.

Source	D.F.	S.S.	M.S.	F.
Total	11	26.87		
Glues	3	15.98	5.33	3.92
Residue	8	10.89	1.36	

Since the F-ratio for glues in the above table is close to the significant value, 4.07 at .05 level, the following just significant tests are proceeded in the usual manner.

$$\text{J.s.d. at .01} = 3.355\sqrt{1.36 \times \frac{2}{3}} = 3.194$$

$$\text{J.s.d. at .05} = 2.306\sqrt{1.36 \times \frac{2}{3}} = 2.195$$

$$\text{J.s.d. at .10} = 1.860\sqrt{1.36 \times \frac{2}{3}} = 1.771$$

$$\text{J.s.d. at .20} = 1.397\sqrt{1.36 \times \frac{2}{3}} = 1.330$$

Difference between the Means of Delamination

A & B = 1.50 ----- sig. at .20 level B & C = 0.24

A & C = 1.70 ----- sig. at .20 level B & D = 2.60*

A & D = 1.10 C & D = 2.84*

IV. Analysis for Casein and Blood-albumin-fortified Soybean Glues

Table L. Analysis of Variances for Dry and Wet Shear Strength of Casein and Blood-albumin-fortified Soybean Glues.

Source	D.F.	S.S.	M.S.	F.
Total	29	250,864.97		
Glues	4	13,854.13	3,463.53	14.51**
Dry-Wet	1	230,387.37	230,387.37	965.05**
G x D-W	4	1,848.80	462.20	1.94
Residue	20	4,774.67	238.73	

Just significant test for difference in shear strengths (dry and wet combined) among the five glues:

$$\text{J.s.d. at .01} = 2.845\sqrt{238.73 \times \frac{2}{6}} = 25.38$$

$$\text{J.s.d. at .05} = 2.086\sqrt{238.73 \times \frac{2}{6}} = 18.61$$

	Glues	Mean (dry & wet shear strengths combined) psi	Mean (wet shear strength alone) psi
E	soybean glue with 20% casein	321.33	249.33
F	E + 30% blood albumin	296.83	204.00
G	E + 20% blood albumin	342.33	251.00
H	E + 10% blood albumin	339.00	248.33
I	E + 10% blood albumin and 3% formalin	360.33	269.00

Difference between the Means of dry and wet shear strengths combined:

E & F = 25.00*
E & G = 21.00*
E & H = 17.67
E & I = 39.00**
F & G = 46.50**
F & H = 42.17**
F & I = 63.50**
G & H = 3.33
G & I = 18.00
H & I = 21.33*

Table M. Analysis of Variances for Wet Shear Strength of Casein and Blood-albumin-fortified Soybean Glues.

Source	D.F.	S.S.	M.S.	F.
Total	24	7,775.33		
Glues	4	6,962.00	1,740.50	21.40**
Residue	10	813.33	81.33	

Just significant difference test for glues:

$$\text{J.s.d. at .01} = 3.169\sqrt{81.33 \times \frac{2}{3}} = 23.33$$

$$\text{J.s.d. at .05} = 2.228\sqrt{81.33 \times \frac{2}{3}} = 16.41$$

Difference between the Means of wet shear strength alone:

E & F = 45.33**	F & H = 44.33**
E & G = 1.67	F & I = 65.00**
E & H = 1.00	G & H = 2.67
E & I = 19.33*	G & I = 18.00*
F & G = 47.00**	H & I = 20.67*

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