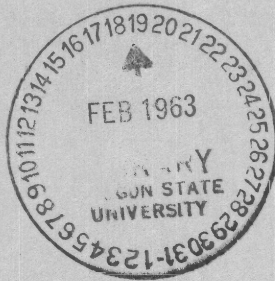


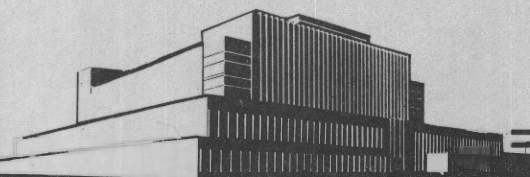
MODIFIED WOODS

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MODIFIED WOODS¹

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Abstract

Chemical and physical treatments of wood are described that modify the dimensional stability and mechanical properties of wood. The main emphasis, together with commercial applications, is given to the product made by phenolic-resin impregnation.

Introduction

Considerable research has been done to improve the utility of wood by modifying its properties by chemical, thermal, and compressive treatments. Some of these treatments involve permeating the wood with synthetic resin-forming chemicals; one consists of forming a cellulose derivative of the type used in plastics; another takes advantage of the plastic properties of lignin; and still others, although the materials they employ have no more plastic properties than the original wood, form cross linkages of the type sought in plastics. Because of these various methods of modifying wood, it appears desirable to consider each method and its product collectively.

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Dimensional Stabilization

Most of the efforts to modify wood have been directed toward increasing its dimensional stability under varying conditions of temperature and humidity that reduce the stability of the wood in service. The successful procedures for this purpose have involved one or more of the following methods:

(1) Coating the external or internal surfaces of the wood with water-insoluble materials to retard the rate of moisture loss or gain; (2) depositing bulking agents within the cell walls to block normal shrinkage; (3) chemically replacing the hygroscopic hydroxyl groups of cellulose and lignin with less hygroscopic groups; and (4) forming chemical cross bridges between the structural units.

It is possible to reduce both the final equilibrium swelling and shrinking and the rate of swelling and shrinking by the last three methods. Unfortunately, however, reductions in the final swelling and shrinking have not been attained by the coating method. All known coatings that adhere to wood allow the passage of some moisture. Internal coatings are in general less effective than external coatings, as it is impossible to coat completely all of the microscopically visible capillary structure (38).⁴ One thick, continuous surface film is more effective in blocking the passage of water than numerous imperfect internal films. On the other hand, while good surface coatings, such as synthetic resin varnishes and aluminum paints, do retard the rate of moisture absorption sufficiently to minimize the steepness of moisture gradients within the wood and subsequently to reduce the stresses that cause grain raising, warping, and checking (4, 11), they do not prevent the aggravating swelling, such as that of drawers and doors, that occurs during prolonged periods of high relative humidity.

Superficial internal coating of wood with so-called "water-repellants" has been advocated. The effectiveness of these materials in stabilizing the dimensions of wood is, however, less than that of the better surface coatings, so that their range of usefulness is limited (5).

The second method for stabilizing the dimensions of wood is to keep the wood in a partially or completely swollen state by the bulking action of chemicals deposited within the cell-wall structure. This can be accomplished by impregnating the wood with water-soluble chemicals such as water-soluble salts (33), sugars (2, 36), and polyethylene glycol (39), or with water-insoluble chemicals. Of the water-soluble chemicals used to stabilize wood,

⁴Underlined numbers in parentheses refer to Literature Cited at the end of this report.

only polyethylene glycol is used commercially. The treatment of wood with polyethylene glycol and its applications will be discussed later.

The treatment of wood with water-insoluble chemicals can be accomplished either by (1) replacing the water in the wood by a mutual solvent for the water and for the wax or resin with which the wood is to be treated, and then replacing the mutual solvent with the wax or resin; or (2) by insolubilizing a water-soluble material within the cell-wall structure. Procedure No. 1 has been successfully carried out on small specimens of wood by using ethylene glycol monoethyl ether as the mutual solvent, or intermediate replacing agent, and various waxes as the final bulking agent (35, 41). This procedure, although reasonably effective for reducing the swelling and shrinking, is, however, too involved for commercial use. Procedure No. 2 involves the formation of water-insoluble synthetic resins within the cell-wall structure of the wood. This is accomplished by impregnating the wood with a water-soluble resin solution and then heating the wood to insolubilize the resin (43). This latter procedure (resin treatment) has proved quite practical and is at present the most important commercial method of dimensionally stabilizing wood (32, 45, 46).

Resin Treatment

Many resin-forming systems have been tried, but none has been found so effective as a water-soluble phenol-formaldehyde resinoid. The molecules of the water-soluble resinoids have been formed from the phenol and formaldehyde molecules with such slight polymerization, or change in character of the molecules as they are formed in the new resinoid substance, that they remain small enough to penetrate the cell-wall structure readily; and because of the high polarity of the slightly polymerized phenol and formaldehyde molecules, the wood is swollen beyond its maximum swelling in water. Such swelling is indicative of selective adsorption of the phenol-formaldehyde resinoid within the intimate cell-wall structure (45, 46).

Some commercial phenol resinoids have been shown to be suitable for making uncompressed resin-treated wood (impreg) and compressed resin-treated wood (compreg). In addition to this, alcohol-soluble phenol-formaldehyde resinoids that have been slightly polymerized have also been successfully used (6, 9). Alcohol-soluble resins that are appreciably advanced, however, do not penetrate the cell-wall structure and are deposited only in the coarse, microscopically visible structure. Because of this lack of penetration, they do not bulk the fiber and can minimize swelling and shrinking only by retarding the rate of moisture absorption, as do coatings. Such resins have been used in Europe in making the equivalent of compreg, but they are not used in the United States.

Resorcinol resin can be substituted for phenol resin, but it is considerably more expensive. Its only advantages are that the resin can be set at lower temperatures and, since no acid or alkaline catalyst is needed, it offers the possibility of obtaining a product with somewhat better electrical resistance properties.

Cresols can be substituted for part of the phenol, but because of their lower solubility in water they are less suitable than straight phenol and are more expensive in the United States. Substituting furfural for formaldehyde also reduces the water solubility of the treating system. Furfural-aniline and furfural-alcohol systems have been tried and found to give fairly good dimensional stabilization, but they are difficult to cure completely within the wood. Melamine-formaldehyde resins have not been thoroughly studied as impregnating agents for wood, because their cost is higher than that of phenol resins and there is little likelihood that they would impart superior properties to the wood.

Urea-formaldehyde is the only resin-forming system other than the phenol-formaldehyde system that has received serious consideration for the bulking treatment of wood. When dimethylolurea and urea are dissolved in formalin and buffered at a pH of about 8 and cured within the wood, they stabilize its dimensions about half as much as a water-soluble phenol-formaldehyde resinoid in the same concentration (19). A 13-percent phenol-resin content of the wood gives it the same dimensional stabilization as a 30-percent urea-resin content. This greater stabilizing effect of phenol resin offsets any price advantage that the urea resin may have. Urea-resin-forming systems are further inferior to phenol systems in plasticizing the wood (before curing), in preventing springback in compressed wood (20), and in ease of distribution throughout the wood (21). Only a limited amount of urea-resin-treated wood has been made commercially.

Phenol-Resin-Treated Wood (Impreg)

The term "impreg" is applied only to phenol-resin-treated wood in which the resin has been cured within the cell-wall structure without the application of pressure to cause compression. Impreg has been made almost exclusively from veneer to avoid the difficulties encountered in treating large specimens of wood. Unlike the treatment of wood with preservatives and fire retardants, it is not enough merely to treat an outer zone of the wood when making impreg; the resin must be distributed uniformly throughout the entire cell-wall structure to be fully effective. Furthermore, partial treatment would set up stresses between the treated and the untreated zones, because of the permanent bulking effect caused by the resin-forming chemicals. These

stresses would result in checking or honeycombing of the wood at the junction between treated and untreated wood.

For these reasons, the treatment of lumber or the treatment of freshly felled logs has not met with the success that some investigators have claimed. It has been found that veneer of almost any species and solid wood of species less resistant to penetration by resinoid solutions, in lengths up to 1 or 2 feet, can be treated adequately (46). With the exception of the sapwood of a few species, wood cannot be adequately treated in lumber sizes (21). Even if lumber could be treated adequately, the increase in cost would make the material prohibitively expensive.

Methods of Treatment

Three different methods of treating wood to form impreg have been used. These methods are: (1) Soaking in an aqueous phenol-formaldehyde resin-forming system; (2) immersing under pressure in a resinoid solution in a cylinder; and (3) applying water-soluble phenol resins with a glue spreader. All methods can be used for treating veneer, but only (1) and (2) can be used for solid wood.

Method No. 1. --The simplest method of treating wood with resin is to soak it in an aqueous phenol-formaldehyde system that is resin-forming. Green wood is used rather than dry, because the resin-forming chemicals diffuse best into the green, swollen wood structure (45, 46). When thin veneer is to be treated, it is not so important that the wood be green, because sufficient solution is taken up by capillarity to swell the structure completely. Unfortunately, this method is very slow, except in the case of very thin veneer, because the rate of take-up of chemicals varies inversely as the square of the thickness. For example, the heartwood of green sweetgum veneer 1/32 inch thick absorbed about 35 percent of its oven-dry weight of resin-forming chemicals from a solution containing 30 percent solids after the veneer soaked for 1 hour at 100° F. If the veneer had been 1/8 inch thick, it would have taken approximately a 16-hour soaking.

Method No. 2. --A more rapid means of treating, especially for thicker veneer, is the cylinder impregnation method, which involves either pulling a vacuum or applying a pressure, or both (38, 46). It has been shown that very little, if any, improved treatment is obtained by pulling a vacuum before applying pressure when treating veneer. Because the vacuum step causes a loss of volatile formaldehyde from the inappreciably condensed resin solutions generally used, it has been avoided. The most satisfactory procedure is to immerse the veneer in the resinoid solution in a container slightly larger than the sheets of veneer, and to make sure that both faces

of each ply are wetted as they are placed in the container so that no spacers between plies will be necessary to ensure contact of the surfaces with the solution. The plies should be weighted down and the liquid level above the veneer adjusted so that the veneer will still be immersed after it has taken up the desired amount of resinoid solution.

The container is then placed in a treating cylinder, in which an air pressure of 25 to 100 pounds per square inch is applied for 15 minutes to 5 hours, or even overnight. Cottonwood and basswood 1/16 inch thick can be treated in 15 minutes at 25 pounds per square inch, while birch and the sapwood of maple in the same thickness require about 5 hours at 75 to 100 pounds per square inch. Other suitable species can be treated adequately under intermediate conditions.

It has been found desirable to have the veneer take up a weight of resinoid solution equal to the air-dry weight of the wood. In the case of birch and maple, this is practically equivalent to filling the void capillary structure completely (treating to refusal), while in the case of spruce and cottonwood only 1/3 to 1/2 of the void capillary structure need be filled. This take-up of solution will require the use of a slightly greater resinoid concentration in the solution than the final resin content desired in the wood. A final resin content of 30 percent of the air-dry weight of the wood can be obtained by using a solution of about 35 percent resinoid concentration. A solution with this concentration remains sufficiently fluid to permit thorough treatment of the wood. It might seem advisable to treat the veneer with smaller amounts of more concentrated resinoid solutions so as to have less solvent to remove from the wood. The treatment, however, is never so complete and uniform as when a relatively dilute solution is used.

Method No. 3. --Veneer has also been treated successfully with water-soluble phenol resins, when low resin contents are sought and the optimum of resin distribution is not required, by applying the slightly diluted resinoid to the veneer with a glue spreader. The amount taken up can be increased by repeating the process several times of putting the veneer through the spreader, and then allowing it to diffuse and dry.

Drying

When a product with maximum dimensional stability is desired, veneer treated by any of the foregoing methods should be stacked under nondrying conditions for a period long enough to insure uniform diffusion of the resinoid throughout the structure. The diffusion time, before drying, will depend upon how uniformly the resinoid is distributed during the treating process. Veneer treated by the simple soaking method will require practically no

diffusion time, whereas veneer with a coarse capillary structure only half filled or less than half filled by cylinder treatment, will require a dead-piling period of about 1 day under nondrying conditions. The treated veneer can then be dried in a commercial veneer roller dryer or in a kiln that has circulating air.

If dried in a veneer dryer, the treated veneer should first be dried at 175° to 200° F. for approximately 30 minutes, which will result in a moisture content of about 10 percent. An initial low temperature (below the boiling point of water) is used to prevent the solution and the dissolved resin from being forced to the surface of the wood by the steam pressure developed in the wood at high temperatures. The resin in the dried, treated veneer is then cured by heating at a high temperature. This is a time-temperature reaction; at 310° F. the curing time is approximately 30 minutes. When kiln dried, the treated veneer should be stickered to allow adequate circulation between the plies. The time required to dry and cure the resin depends on the maximum temperature that can be maintained in the kiln and may vary from a few days to a week or more.

Properties of Impreg

Impreg has a number of improved properties compared to those of normal wood and ordinary plywood. When 30 to 35 percent of resin on the basis of the oven-dry weight of the untreated wood is formed within the structure, the hygroscopicity and equilibrium swelling and shrinking of the wood are reduced to 25 to 35 percent of normal. The reduction in swelling and shrinkage is accompanied by a marked reduction in grain raising and surface checking. Figure 1 shows what can be done in protecting the surface of Douglas-fir plywood by a suitable treatment of only the face plies.

The treatment also imparts to wood considerable resistance to decay, termite and marine-borer attacks. Figure 2 shows a Douglas-fir plywood specimen with resin-treated faces and an untreated core ply that was inserted in the ground for 1 year in a field in Mississippi where termite action is severe. The termites cleaned out the untreated cores completely up to the ground line and left the faces virtually untouched. Similar core material that had its edges protected with a preservative treatment withstood termite action and decay for about 3 years. Similar ground exposure panels with all their plies treated with 30 percent of phenol resin had an average life of 12.4 years as compared to that of 1.9 years for an untreated panel. Panels treated with 15 percent resin had an average life of 6.8 years. Impreg specimens with all their plies treated (30 percent resin) showed little or no attack by marine borers after 4 years' exposure to sea water in Pensacola Bay, Fla.

Decay-culture tests on phenol-resin-treated wood blocks show growth of fungus on the surface of the treated blocks as well as on the control blocks, even though the loss in weight of the treated blocks is negligible in contrast to that of the controls (38). This growth indicates that decay resistance is not due to the presence of a toxic agent, such as an excess of either phenol or formaldehyde. When an excess of either of these chemicals is present, fungi shun the block. The decay resistance of impreg presumably results from either the reduced hygroscopicity whereby insufficient water is permitted to enter the cell-wall structure to support decay, or from a chemical change occurring within the wood that makes it no longer susceptible to fungus attack, or from both. Experience to date has indicated that any treatment that appreciably reduces its hydroscopicity also imparts decay resistance to the wood.

The treatment of wood with phenol resin cuts down the passage of water vapor through the panels to a marked extent (44), and greatly increases its electrical resistance (57) and its resistance to most chemicals, with the exception of strong alkalis. Contrary to many publicity claims, resin treatment has a negligible effect in improving fire resistance. Fire-resistant salts, however, may be incorporated in the wood with the treating resin and be fixed by it in the wood structure to give good fire-retardant properties.

Only a few of the strength properties of wood are increased significantly by a resin treatment; moreover the toughness, Izod impact, and tensile strength parallel to the grain are decreased significantly (8), facts that are contrary to many of the publicity claims for resin-treated wood. The only properties that are increased appreciably more than the specific gravity are hardness, compressive strength and stiffness perpendicular to the grain. A sugar pine specimen, with a resin content of 47 percent on the basis of the oven-dry weight of the untreated wood, increased in hardness by 85 percent (31). To become as hard as sugar maple, the hardness of sugar pine would have to be increased 3.8 times. Thus it would hardly pay to treat such wood with resins if the primary objective were to increase its strength properties. When increases in strength are sought, the wood should be compressed as described later.

Applications

Impreg was manufactured during World War II only for military uses, one of which was for housings for electrical-control equipment, in which the improved electrical properties of impreg were utilized. Another use was for treating veneer faces that would be applied to a redwood core for laminated aircraft-carrier decking. In service tests for such purposes,

impreg showed its superiority to the normally used edge-grain Douglas-fir (14). The chief current application for impreg is for making pattern and die models. Impreg has practically replaced mahogany lumber for this use in the automobile industry (32).

Phenol-Resin-Treated Compressed Wood (Compreg)

Compreg is resin-treated wood that is compressed while the resin is being formed within its structure (47). Although a number of different resins have been tried in making this material, none has proved so successful as phenol-formaldehyde. There are two quite different types of compreg: (1) an old form, developed in Europe, that is composed of wood treated with a spirit-soluble phenol resin prepolymerized to a stage at which it does not penetrate the cell-wall structure and does not bond to the polar groups of the wood and, as a result, does not stabilize the dimensions of wood appreciably; and (2) a new form (developed by the U.S. Forest Products Laboratory) that is composed of wood treated with a water-soluble, phenol-formaldehyde resinoid, as in the case of impreg, so as to form the resin throughout the cell-wall structure of the wood and to bond it to the active polar groups of the wood. The new form of compreg is much more stable than the old, but tends to be more brittle. All of the compreg now being made in the United States is either of the new type or of an intermediate type.

The term "compreg" should be reserved only for woods that are truly treated and not be given to laminated compressed wood that may have been impregnated by only a very small amount of glue-line resin. Untreated compressed wood is preferably called "dense wood" (24, 27), when made from solid wood, or "superpressed plywood" (3, 26, 56), when made from veneer. "Dense wood" corresponds to the German material, Lignostone, and "superpressed plywood" is similar to the German product, Lignofol (13). English Jicwood and Jablo are of the superpressed-plywood type. The German equivalent of compreg is known as Kunstharzschichtholz (13).

Veneer for making compreg can be treated by any of the methods given under phenol-resin-treated wood (impreg). The amount of resin used and the uniformity of its distribution will depend upon whether maximum dimensional stability or maximum impact strength is sought. To obtain the maximum dimensional stability, about 30 percent of resin on the basis of the oven-dry weight of the untreated wood, distributed uniformly throughout the structure, is desired (47). To obtain the maximum impact strength, 10 to 20 percent of resin, with an appreciable proportion of it at the surface, is desired.

An important advantage of compreg is that it can be made from a great variety of woods, including such normally inferior species as cottonwood, to give a product with properties that approach the optimum values.

Assembly, Compression and Cure

The term "compreg" is commonly used to designate material compressed to a specific gravity of 1.3 to 1.4. Compreg can, however, be made with any specific gravity between that of impreg (about 18 percent higher than that of the original wood) and these high values. It is suggested that the term "semicompreg" be used to designate the material of intermediate specific gravity.

When veneer is treated with at least 30 percent of a phenol-formaldehyde penetrating resinoid, it can be made up into high-density parallel-laminated compreg without the application of bonding resin between the plies, as sufficient resin is exuded from the plies under compression to give a good bond (6). When cross-banded compreg is made, the dried plies should be spread with a small amount of hot-press phenol bonding resin. When treating-resin contents lower than 30 percent are used and when the product is to be compressed only to the semicompreg stage, a thin glue spread of about 15 pounds per 1,000 square feet should be used. When water-soluble glues are spread on the plies, the veneer should again be dried to a moisture content of 2 to 4 percent before assembly.

The pressure required in pressing compreg depends upon the resin and its volatile contents, the degree of precure of the resin, and the distribution of the resin throughout the structure, as well as the species of wood. Compreg with a specific gravity of 1.3 to 1.4 can be made from veneer of most species containing 30 percent of a water-soluble phenol-formaldehyde resinoid on the basis of the weight of the dry untreated wood, by applying pressures of 1,000 to 1,200 pounds per square inch and a temperature of 300° F., when the volatile content of the resinoid is between 2 and 4 percent (45, 47).

The pressure required to make semicompreg varies with the nature of the treating resin, as in the case of full compreg, and to a greater extent with variations in the species. When most of the softwoods (coniferous woods) and the softer hardwoods (deciduous woods), such as cottonwood, basswood, and aspen, are treated with a stabilizing resinoid, they can be compressed to two-thirds to one-half of their original thickness under pressures as low as 250 pounds per square inch to give a product with a specific gravity of 0.7 to 1.0 (47). Under this pressure, the same woods in the dry untreated form or when treated and precured will compress only 5 to 15 percent. Because of this increased plasticization of the treated but uncured wood,

plywood with semicompreg faces and either an untreated or a treated and precured uncompressed dry core can be made in a single assembly and compression operation without significantly compressing the core (48).

Compreg should be made up from dry treated but uncured veneer with a residual volatile content between 2 and 4 percent. The drying of the treated veneer must be done at temperatures (175° F. or less) which will not set up or cure the resin in the veneer as is done in the final drying (30 minutes at 310° F.) of treated veneer for impreg. The curing of the resin in the treated veneer to be used for compreg is done during the heating and densification process. When thick panels are made, moisture content values near 2 percent should be approached to avoid subsequent checking of the product. Thinner material and semicompreg can be made up at a slightly higher moisture content without subsequent checking. Compreg compressed to specific gravities above 1.35 is more subject to checking than a lower specific gravity product. Hence, the highest specific gravities should be avoided. The center of the wood should be held at a temperature of 300° F. for 30 to 40 minutes to obtain complete cure of most of the resins. Thicker material should be cured at a lower temperature to avoid a building-up of the temperature at the center of the panel by the exothermic resin-curing reaction.

Properties of Compreg

The water absorption by compreg, determined according to Military Specification (55) (a 3- by 3/8-inch specimen by 1 inch in the fiber direction after a 24-hour immersion in water) will range, for products of high specific gravity, from less than 1 percent for the best stabilized compreg to 6 percent or more for the less stabilized compreg. In all cases, a decrease in specific gravity will result in increased water absorption.

Small blocks of the dimensionally stable form of compreg that is compressed to a specific gravity of 1.35 will swell only 4 to 7 percent in thickness upon prolonged immersion in water at room temperature (47). Blocks 4 inches square by 1/2 inch thick hardly came to swelling equilibrium when soaked in water at room temperature for a year. When dried to the original moisture content (about 2 percent) the stabilized material will practically regain its original compressed dimensions, an indication that the loss of compression is negligible.

The older form of compreg made with appreciably prepolymerized resin will not only swell about three times as much in thickness as the stable form, but will swell much more rapidly and also lose a large part of its compression (47). The more rapid swelling of the less stable form is presumably due to

the fact that water is sucked into the structure as it recovers from compression, with the result that water is distributed throughout the structure much more rapidly than by diffusion alone. The combined swelling and recovery from compression of the specimen of the older form of compreg 1 inch long in the fiber direction may be as much as 20 to 60 percent in several weeks. Thin cross sections will give these values in 1 day. One-half to two-thirds of this dimensional change may be due to recovery from compression.

Because compreg swells so slowly, the old 24-hour water-absorption test has little meaning. A new rapid equilibrium swelling and recovery test (developed by the Forest Products Laboratory) is included in a recent Military Specification (55). In this test, cross sections 1/8 inch wide by the thickness of the panel by 2 inches long are measured in the thickness direction of the original panel, then soaked in water at 70° F. for 24 hours, and again measured in the same direction. These thin sections come virtually to swelling plus recovery equilibrium in this period of time. Tests have shown that when the equilibrium swelling plus recovery does not exceed 12 percent increase in thickness, which is the newly specified maximum, the tendency for the particular compreg to washboard in service (exhibit uneven swelling plus recovery) without a surface finish is negligible. Most of the compreg now made in the United States will meet this specification, although the earlier material would not.

Like impreg, compreg is fairly resistant to decay, termites and marine borers (38,47). Its improved electrical resistance is similar to that of impreg (57). Its resistance to the passage of water vapor is appreciably greater than that of impreg because of the practical elimination of the capillary structure (47). The acid resistance is also improved to some extent beyond that of impreg, due to the fact that it is more difficult for acid to penetrate the structure (47). The resistance of compreg to flaming is somewhat greater than that of impreg because of its greater density, and it can be further improved to some extent by incorporating phosphate salts in the treating solution.

A high degree of polish can be imparted to any cut surface of stabilized compreg or semicompreg with a specific gravity of about 0.8 or higher by merely sanding the surface with fine sandpaper and then buffing it. This potential polish exists throughout the structure. All that is necessary to bring it out is to smooth the surface. This easy way of restoring the finish would be an advantageous property of compreg or compreg-faced furniture or flooring. The natural finish is highly resistant to such organic solvents as alcohol and acetone, which destroy most applied finishes.

Compreg has a higher coefficient of thermal expansion than normal wood, largely because of its high degree of compression. The increase is mostly in the direction of compression and is generally about 50 percent. The increase in the thermal-expansion values can be calculated from the resin content and degree of compression (58).

The strength properties of compreg, with the exception of the toughness and the Izod impact, are increased about in proportion to its increase in specific gravity. Table 1 gives strength data for parallel-laminated birch compreg and semicompreg made with three different commercial resins (9). The water-soluble resin B gives lower water absorption, swelling and recovery properties than alcohol-soluble, low-molecular-weight resin A, but also a lower Izod impact strength. The other strength properties do not vary significantly with the different resins.

Compreg made with higher resin contents has greater compressive-strength values but lower tensile and Izod impact values (8). Many of the strength properties of compreg, such as the modulus of rupture and the modulus of elasticity in static bending and shear, are but slightly affected by manufacturing variables and degree of cure, whereas the water-resistance properties continue to be improved with a more complete cure (31). The toughness and Izod impact values of compreg, however, vary considerably with variations in the manufacturing technique and curing time (18). For this reason, one of these two tests should be regularly made.

The regular American Society for Testing and Materials hardness tests for wood cannot be applied to compreg, as embedding the steel ball to the depth required splits the wood. The hardness can, however, be expressed in terms of the slope of the linear load-penetration curve. In this way it is possible to make correlative measurements on both normal and densified wood by the same method. The hardness has been shown to increase rapidly with an increase in the specific gravity of the wood.

The resin has a minor effect upon the hardness. The hardness of untreated compressed wood is about 20 percent less than the values for normal resin-treated wood of the same specific gravity. Compreg may be 10 to 20 times as hard as normal wood.

The abrasion resistance of compreg is significantly higher than that of normal wood, chiefly because of the compression of the wood.

Fabrication and Molding

Due to its increased hardness and the presence of the resin, compreg is more difficult to machine than normal wood. In appreciable thicknesses, it should be cut with special saws such as those used for cutting brass or plastics. Machine speeds should in general be lower than for cutting normal wood. Compreg machines nicely and can be turned on a lathe using metal-working tools with greater precision than normal wood.

Compreg is more brittle than normal wood and most metals, although it is considerably tougher than the ordinary molding plastics. Because of its brittleness, objects made from it should have rounded fillets rather than sharp edges. This is true of threads cut in compreg.

Compreg can be glued to itself or to normal wood with both hot-press and room-temperature-setting, nonacidic resin glues. The compreg surfaces to be glued should be lightly sanded to remove the surface gloss before gluing (45), and when the panels are thick these surfaces should be milled plane so as to ensure perfect contact. Glue spreads of 15 to 27 pounds per 1,000 square feet should be applied. Gluing pressures should be adequate to get good contact, generally 150 to 250 pounds per square inch.

A simple method of molding compreg was developed by the Forest Products Laboratory and used during World War II by manufacturers for short stubby "club" propellers used for testing motors on the ground, and for an airplane antenna mast, both of which were in large production. The method consists of assembling dry but uncured resin-treated veneer with a hot-press phenol glue under a pressure of 150 to 250 pounds per square inch at 200° to 250° F., which is inadequate to cure the treating resin and only partially adequate to cure the glue (47). Although the shear strength of such a block is not great, it is sufficiently strong to permit the block to be carved or turned in such a manner that each of its final dimensions is obtained in one direction. The thickness of the uncompressed block at right angles to this direction is, however, made from 1.5 to 3 times the final dimension, depending upon the original specific gravity of the wood. The block is then heated to about 250° F. by means of high frequency, placed in a split mold, and pressed, in the direction in which it was carved, to 1.5 to 3 times the final dimension with the mold heated to 270° to 300° F. A slight squeeze-out, or flash, that occurs at the parting line of the two halves of the mold must be removed. The remaining surface requires little or no further finishing. When a product with a uniform specific gravity is sought, the number of times the carved thickness should exceed the final thickness must be kept constant over the entire object. By varying this thickness multiple from one part of the object to another, variations in specific gravity between any desired parts of the object are obtainable.

A more generally applicable means of molding compreg after precompression without the use of a press has recently been developed (52). This method, known as expansion molding, consists of precompressing dry but uncured resin-treated wood at about 200° to 240° F. At this temperature the wood is plasticized by the resin-forming chemicals but the resin does not cure in the short period involved. If the pressure is released while the wood is hot, it springs back immediately. If cooled under pressure, however, the wood retains its compression for months when kept dry. This uncured material is cut to templates and laid up to fit and fill a mold. The mold is then locked in the closed position and heated. The tendency for the wood to expand and release the pent-up stresses exerts back pressure as high as 750 pounds per square inch against the mold.

The precompressed resin-treated veneer can be prepared by feeding single heated plies into a rapidly operated press, the platens of which are kept cold. When 1/10-inch thick veneer is used, it need be in the press only about 15 seconds to be pressed completely and cooled.

Metal inserts or surfaces can be molded to compreg by this expansion-molding method. The method can also be used for gap filling and for applying pressure in making various kinds of joints. In this case, the material into which the precompressed resin-treated wood is inserted acts as the mold.

Applications

Solid compreg was used chiefly during the war for trainer-plane adjustable-pitch propellers, motor-test propellers, antenna masts, spar and connector plates, refrigerator blocks for ships, and tooling jigs. The flight propellers were carved from glued-up blocks of compreg made up from compreg panels 1-1/4 inches thick. Compreg, because of its high compressive strength, was found to make excellent spar and connector plates. For this purpose, the cross-banded product is usually used. Its combined load-bearing and thermal-insulating properties were taken advantage of in using it for supporting blocks for refrigerators. Compreg was found extremely useful for aluminum drawing and forming dies, drilling jigs, and jigs for holding parts in place while welding, because of its excellent strength properties, dimensional stability, low thermal conductivity, and ease of fabrication.

Solid compreg shows promise for use in silent gears, pulleys, water-lubricated bearings, fan blades, shutters, bobbins and picker sticks for looms, instrument bases and cases, electrical insulators, tool handles, knife handles, and various novelties (59) (Fig. 3). Compreg has better strength properties than fabric-reinforced plastics, and it should be significantly cheaper because veneer is cheaper than fabric on a weight basis and

because half as much resin is used per unit weight of compreg as for fabric laminates. Compreg may thus replace fabric laminates in a number of uses.

Compreg and semicompreg show their best promise for future use as facing materials for ordinary plywood. These facing materials may find external use in house, trailer, and box-car panels and in boat siding, and internal use in panels, furniture and flooring. A test floor has been laid at the Forest Products Laboratory consisting of tongue-and-groove panels 10 inches square, composed of 3-ply semicompreg faces of yellowpoplar compressed from a 3/16-inch to a 1/8-inch thickness, a single back ply 1/16 inch thick of impreg to balance the construction from a swelling standpoint, and a 5-ply Douglas-fir core 1/2 inch thick, with all plies glued with phenol glues. The floor has a very attractive greenish-tan natural finish. It is in excellent shape after 10 years' service. Such a floor would be more expensive than the normal strip oak floor. It is, however, hoped that it will require less service to keep in good condition. The original finish can be restored by sanding with fine sandpaper, and then buffing.

Staypak

Resin-treated wood in both the uncompressed (impreg) and compressed (compreg) forms is, unfortunately, more brittle than the original wood. To meet the demand for a tougher compressed product than compreg, a compressed wood containing no resin was developed by the Forest Products Laboratory (29,30). It will not lose its compression under swelling conditions as will ordinary compressed untreated wood. This material, named staypak, is made by modifying the compressing conditions to cause the lignin cementing material between the cellulose fibers to flow sufficiently to eliminate the internal stresses.

Staypak is not so water resistant as compreg, but it is twice as tough and has higher tensile and flexural properties. The natural finish of staypak is almost as good as that of compreg. Under weathering conditions, however, it is definitely inferior to compreg. For outdoor use staypak should have a good synthetic resin varnish or paint finish. The heat treatment used in making staypak is not sufficiently severe to give the wood a significant reduction in hygroscopicity. Staypak, consequently, is only slightly more resistant to decay, termites and marine borers than normal untreated wood of the same species.

Staypak can be used in the same way as compreg where extremely high water resistance is not needed. It shows promise for use in propellers, tool handles, forming dies, connector plates, and picker sticks and shuttles for

weaving where high impact strength is needed. It is not being manufactured commercially as yet. Similar material in a less dimensionally stable form has, however, been in production in England and Germany for some years.

Staybwood

Heating wood under drying conditions at higher temperatures (200° to 600° F.) than those normally used in kiln drying has been shown to reduce the hygroscopicity and subsequent swelling and shrinking of the wood appreciably. The stabilization, however, is always accompanied by loss of mechanical properties. Toughness and resistance to abrasion are most seriously affected.

Under conditions that cause a reduction of 40 percent in shrinking and swelling, the toughness is reduced to less than half that of the original wood. Extensive work was done to minimize this loss without success. Because of the reduction in strength properties from heating at such high temperatures, wood that is dimensionally stabilized in this manner is not used commercially (54, 37, 40, 42).

Acetylated Wood

Treating Method

The chief disadvantage of stabilizing the dimensions of wood by forming synthetic resins within its structure is that the resins embrittle the wood appreciably. For some uses, such as in aircraft, this is very serious. Efforts were therefore made to find some other bulking agent that would preferably react with the hydroxyl groups of wood without embrittling its fibers. Acetylation appeared to be a likely means of accomplishing this purpose, from the standpoints of both methods No. 2 and No. 3 given on page 2.

Acetylation, as it is normally practiced on cellulose with acetic anhydride, requires a swelling agent, such as acetic acid, to open up the structure, and a catalyst, such as sulfuric acid, to promote the esterifying reaction. Mineral acids such as sulfuric, however, promote hydrolysis and breakdown of the cellulose chains. This hydrolytic effect, if kept within bounds, is not harmful in plastic and rayon manufacture, but it would defeat one of the chief objectives of acetylating wood by breaking its structural bonds and embrittling its fiber.

It was found that pyridine acts as an excellent catalyst for the acetylation reaction without degrading the wood (49, 50, 53). It was also found that the acetylation can be carried out to advantage in the vapor phase (49, 50, 53). As with the treatment with resins, adequate treatment could only be made on veneer. The treatment is carried out in an acid-resistant air-tight chamber or kiln at atmospheric pressure. The spaced veneer is first dried in the chamber operated as a kiln. Air intakes are closed, and a mixture of liquid acetic anhydride and pyridine is introduced into a tray beneath the load. Air is circulated over the tray and through the load at a temperature of 80° to 120° C. until acetate groups equal to 18 to 25 percent of the weight of the wood are formed in the wood (50, 53). The tray is then drained. Heated air is circulated through the load and then through a condenser to remove the excess acetic anhydride, the pyridine, and the acetic acid formed in the reaction, and is then circulated back through the load until the wood is free from odor.

Properties

In the above way, the highest dimensional stabilization thus far attained by any treatment has been realized. The equilibrium swelling and shrinking have been reduced to as little as 20 to 30 percent of normal (53). The specific gravity of the wood is increased by only 6 to 12 percent. The wood is not darkened, as it is with resin treatments, and in the case of some species is bleached. High decay, termite and marine borer resistances are attained. Moisture transfusion through the wood is reduced to about one-fifth of normal. Most of the strength properties of wood are unaffected, but its toughness and Izod impact are frequently increased by 10 to 20 percent (53). This increase is an especially desirable feature of this treatment.

It has been shown that the dimensional stabilization achieved by this method results more from bulking the fibers than from reducing the hygroscopicity by replacing hydroxyl groups with acetate groups (50).

Experimental work (10) has been carried out to determine the suitability of this treatment for wood in lumber-size dimensions.

Polyethylene-Glycol-Treated Wood

The dimensional stabilization of wood with polyethylene glycol also stabilizes by bulking the fibers and thus keeps the wood in a partially swollen condition. This treatment, however, differs from most of those previously described in this report in that polyethylene glycol is used in the treatment of green or waterlogged wood in contrast to other methods in which air-dried wood is primarily used.

To obtain a high degree of dimensional stability, a penetration of the chemical throughout the wood is required, leading to a uniform uptake of 25 to 30 percent of chemical. The time necessary for this uptake depends on the thickness of the wood and may require weeks. This treatment has been effectively used in the treatment of walnut gunstocks (22).

Another application of this chemical is to reduce the checking of green wood during drying. For this application the polyethylene glycol is used as a seasoning agent and a high degree of penetration is not required. This method of treatment has been used to advantage to reduce checking during drying of small wood blanks or turnings (23).

More recently, it has been shown that the excessive cracking and distortion that old, waterlogged wood undergoes when it is dried can be substantially reduced by treating the wood with polyethylene glycol. The process was used to dry 200-year-old waterlogged wood boats raised from Lake George, N. Y. (28).

Formaldehyde-Treated Wood

All of the other methods thus far described for permanently stabilizing the dimensions of wood, with the exception of heating to high temperatures, involve either bulking the fibers, chemically making the product less hygroscopic, or both. Another general method for stabilizing wood is that of forming cross links between swelling units. It has been shown that heating dry wood in the presence of formaldehyde vapor and of a mineral-acid catalyst will appreciably stabilize the dimensions of wood, presumably as a result of the formation of acetal cross linkages in the wood (34, 51). High degrees of dimensional stabilization have been obtained with an increase in weight of as little as 3 to 6 percent. The dry vapor is generated by heating paraformaldehyde suspended in a mineral oil. The reaction can be carried out in the same type of chamber or kiln as used for acetylation. The chamber should be provided with a means of spraying small amounts of acid into the chamber to act as catalyst. Unfortunately, the acid catalyst tends to embrittle the wood and seriously detracts from the process.

Nuclear Irradiation of Wood

Numerous attempts have been made to modify the hygroscopic characteristics of wood by radiating with gamma rays and beta particles. Paton and Hearmon (25) exposed wood to 10^6 , 10^7 , and 10^8 roentgens of Cobalt-60

gamma rays. Small but measurable reductions in moisture regain were observed. However, this is always accompanied by moderate to severe losses in mechanical properties (15, 17). Attempts have also been made to polymerize monomers in impregnated wood with nuclear radiation. Kent (12) describes properties of wood treated with vinyl type monomers which were polymerized by gamma radiation. Substantial improvement in properties are reported. Some of these (swelling) are time dependent and suggest the improvements are due to the massive loadings of polymer. Russian workers (7) have reported similar results. Some of their data pertain to samples having 120 percent polystyrene.

Surface Densification

Besides methods that involve the impregnation or densification of the total wood, there are, however, methods which involve densification of only part of the wood, generally the outer surface. One patented process (16) involves the densification of the edge portion of desk legs and the edge portions of table and desk tops by the application of heat and pressure through forming dies. Local densification has the advantage that the major portion of the wood retains its normal characteristics and so is easier to work and is better adapted for connection with other untreated wood parts.

Another patented process (1) involves modification of surface properties by polishing at speeds which cause local heating of the wood surface. The aim of this process is to provide a better surface for surface finishes. Increased surface hardness can be obtained in flat panels by heating the surfaces to the desired depth and then applying sufficient pressure to compress the more readily compressible heated area. Cooling of the densified wood while still under pressure is necessary to avoid springback.

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Table 1.--Strength properties of parallel-laminated birch compreg made from 1/16-inch-thick veneer with three different commercial resins¹

Property	Resin A			Resin B			Resin C		
	Com-	Semi-	preg	Com-	Semi-	preg	Com-	Semi-	preg
Resin content, $\frac{2}{100}$ percent	28.5	28.0	31.5	32.0	28.0	28.5			
Molding pressure, p. s. i.	1,500	600	1,500	600	1,500	600			
Specific gravity	1.36	1.22	1.	1.24	1.37	1.24			
Modulus of elasticity in tension parallel to the grain, 10^6 p. s. i.	4.12	3.72	4.20	3.92	4.23	3.88			
Tensile strength parallel to grain, p. s. i.	53,700	43,600	54,600	43,500	51,300	47,900			
Modulus of elasticity in compression parallel to the grain, 10^6 p. s. i.	4.21	3.81	4.17	4.07	4.33	3.94			
Ultimate compressive strength parallel to the grain, p. s. i.	24,200	22,700	26,800	25,200	24,500	22,800			
Compression-yield strength at 0.2 percent offset parallel to the grain, p. s. i.	20,700	19,000	21,900	21,000	21,600	19,900			
Modulus of shear in torsion, 10^6 p. s. i.	.289	.248	.337	.298	.306	.251			
Modulus of rupture in torsion, p. s. i.	6,720	5,060	9,800	6,980	8,400	5,180			
Shearing-yield strength at 0.2 percent offset in torsion, p. s. i.	5,100	4,180	7,720	5,700	5,880	4,850			
Shear strength parallel to laminations, $\frac{3}{4}$ p. s. i.	4,840	3,640	4,450	4,230	4,340	3,620			
Izod impact, ft.-lb. per in. of notch	10.0	8.3	7.8	6.1	9.4	6.6			

(Sheet 1 of 2)

Table 1.--Strength properties of parallel-laminated birch compreg made from 1/16-inch-thick veneer with three different commercial resins¹ (continued)

Property	Resin A		Resin B		Resin C	
	Com-	Semi-	Com-	Semi-	Com-	Semi-
	preg	: compreg	preg	: compreg	preg	: compreg
Fatigue strength at 10 ⁷ cycles, p.s.i.	11,800	: 11,800	13,400	: 12,000	12,000	: 10,600
Water absorption, $\frac{1}{4}$ percent	3.0	: 7.0	1.7	: 5.0	2.0	: 6.7
Swelling, $\frac{5}{16}$ percent	14.2	: 13.9	9.7	: 9.9	11.5	: 12.2
Recovery, $\frac{1}{6}$ percent	2.90	: 2.97	1.87	: 2.22	2.28	: 2.00
	:	:	:	:	:	:

¹"Effect of Molding Pressure and Resin on Results of Short-Time Tests and Fatigue Tests of Compreg," by W. N. Findley, W. J. Worley and C. D. Kacalief, Trans. A.S.M.E. 68,317 (May 1946).

²On basis of oven-dry weight of untreated wood.

³Forest Products Laboratory block-shear test without offset in plane of plies.

⁴Eight cross sections, 1-inch in fiber direction by 3/8 by 3 inches immersed in water for 24 hours.

⁵Cross sections 1/8 inch in fiber direction measured in panel thickness direction before and after immersion in water for 48 hours.

⁶Increase in thickness of swelling specimens after air drying and oven drying over the original dry dimensions.

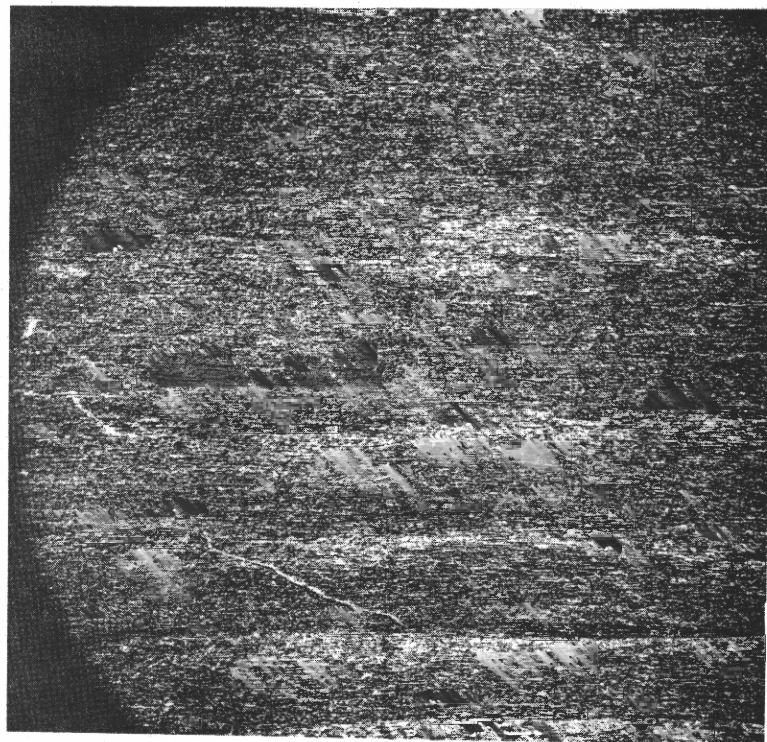
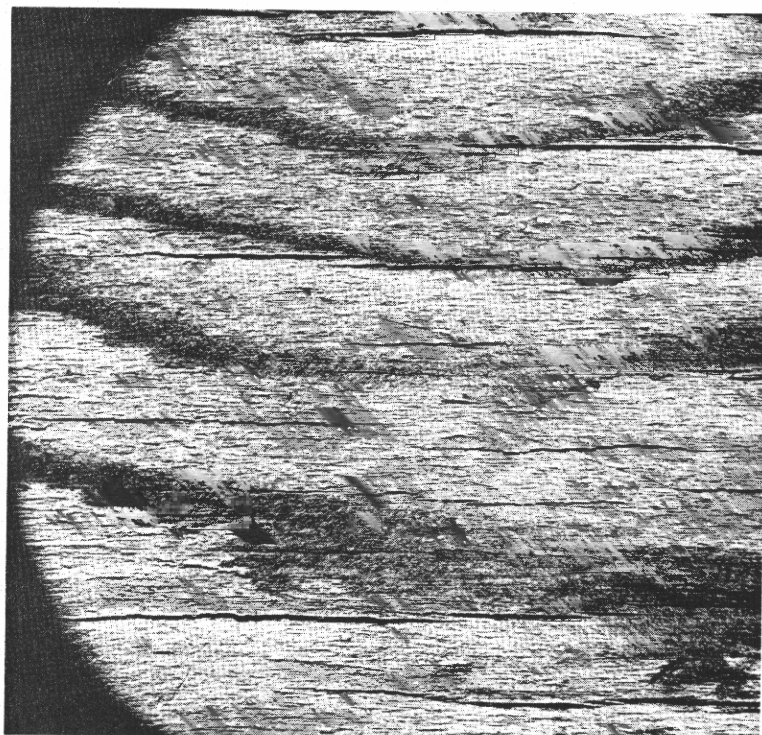


Figure 1. --Surface of Douglas-fir plywood after 6 months' weather exposure with no face treatment (left), and with resin-treated face (right).

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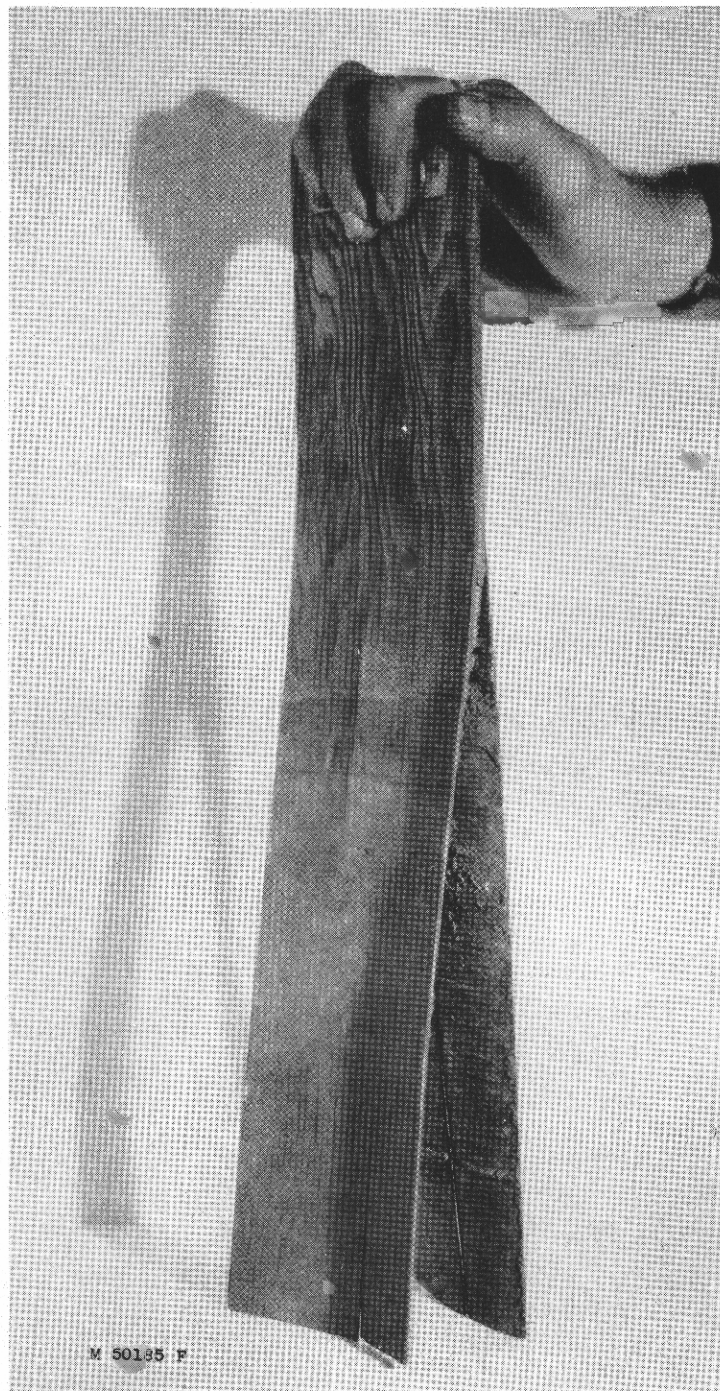


Figure 2. --Plywood specimen with resin-treated faces and untreated core ply, after exposure to termite action, shows core completely cleaned out and faces virtually untouched.

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Figure 3. --The use of compreg for knife handles is demonstrated in this display of cutlery.

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