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MICHIGAN
STATE HIGHWAY DEPARTMENT
Charles M. Ziegler
State Highway Commissioner

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HARDENING OF WOOD BY CHEMICAL PROCESSES

Research Project

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By: C. C. Rhodes

RESEARCH LABORATORY
TESTING AND RESEARCH DIVISION
December 9, 1944

HARDENING OF WOOD BY CHEMICAL PROCESSES

The usefulness of wood as an engineering material has been enormously enhanced and broadened by the development of a new method of treatment which profoundly alters the physical properties of the original wood. By means of this process, swelling, shrinking and warping can be almost entirely eliminated and the hardness and strength greatly improved. The process is largely chemical in nature, the essential principle being the introduction of resin-producing materials to form resins within the cell structure of the wood to produce in effect a filled or reinforced "plastic".

War restrictions of essential materials have compelled the substitution of wood for critical metals wherever possible. In highway work, one result of these conditions has been the replacement of metal in road signs by plywood. Plywood of good quality has given satisfactory service in the field, the chief disadvantages being manifested by separation, cracking and warping of the outer layers at the corners and edges after continued exposure.

A consideration of the new method of treatment suggested the possibility of developing a greatly superior durability in signs of this type by applying the process to plywood used in their construction. The Research Laboratory was requested to investigate the possibility of such an application, and it has been found that impregnation of the finished plywood is not advisable for reasons that will be explained in detail later on, although it can be done successfully during the process of fabrication. As a matter of record, however, and with a view to possible use in some other application, a description of principles and materials employed in the method and the application of those principles to the treatment of plywood are given in the report which follows.

Principles and Materials Employed

The hardening of wood by the above mentioned treatment is accomplished by first impregnating the cell structure with a water solution of resin forming compounds, which compounds react with the wood substance and themselves to form hard, water-insoluble, infusible resins throughout the mass. Formation of these end products called "curing" of the resin, may take place either with or without the application of heat and pressure, depending upon the type of resin to be produced and the properties desired in the finished material. There are two general classes of resins in use for this purpose at the present time, the phenol-formaldehyde and the urea-formaldehyde types. Curing of the former usually requires higher temperatures (280° to 300°F), while resins of the latter type may be formed at room temperature or by moderate heating (up to 140°F). Experience with both types of resins has shown superior durability of the phenolics when exposed to weather, moisture and heat (1, 2).

Impregnation of the wood with solution may be carried out by various means. For soft woods and thin sections of the hardwoods, the required resinification may be obtained by soaking in the solution for the required time before curing. The extent of penetration depends upon a number of factors, such as species of wood, moisture content of wood, whether heartwood or sapwood is being treated, duration of contact, and type of resin forming material used. Hardwoods are more difficult to penetrate than softwoods and sapwoods are impregnated more easily than heartwoods. Green and moist woods absorb the solution more readily than dry woods when soaked in an open tank. The steps in the process of impregnation by soaking may be summarised as follows:

1. Bring wood to maximum moisture content by steaming and subsequent soaking in water at 175°F (for hard woods such as maple).
2. Soak in impregnating solution until required penetration is obtained.
3. Allow time after removal from the tank for diffusion of solution in the wood before drying out.
4. Dry, to prevent blisters during heat cure.
5. Subject to simultaneous heat and pressure as required for the particular resin and properties desired.

Probably the most effective method of saturating the wood is by the vacuum-pressure or "full cell" process. The wood is first placed in a chamber and the air withdrawn. The treating solution is then introduced into the chamber, while still maintaining the reduced pressure, in amounts sufficient to completely submerge the wood after allowing for absorbed solution. Pressure is then restored to normal by opening to the air, or may be increased up to 200 pounds per square inch. When impregnation is complete the solution is drained off and the wood removed for drying. The particular cycle employed and the number of repetitions will depend upon the factors previously enumerated. For sapwood of both hardwoods and softwoods and the heartwoods of some hardwoods, an impregnation cycle of 20 to 50 minutes vacuum (26 to 28 inches of mercury) followed by a pressure of 100 pounds per square inch applied for 10 to 50 minutes at room temperature is usually sufficient. The equipment required for this process can be of the same type as that employed in the treating of lumber with wood preservatives such as creosote and flameproofing chemicals, although it may be on a smaller scale due to the shorter treating cycle.

The chemicals required for making up the solutions depend upon the particular type of resin to be produced and the qualities desired in the finished product. When working with the phenolic type of resin it is necessary to use a compound of relatively low degree of condensation and of lower molecular weight in order to effect complete penetration of the solution through the cell walls and into the cavities of the wood structure. This insures dimensional stability to the aggregate of impregnated wood cells, or to the entire piece of wood. Where dimensional stability is not a prime consideration, greater strengths may be obtained by the use of more condensed, higher molecular weight compounds, applied with heat and pressure.

Similar considerations apply to the use of urea-formaldehyde resins. In this case dimethylolurea (DMU) and urea are mixed in a water solution in varying proportions, but for most purposes mixtures of 6 parts DMU and 1 to 2 parts urea by weight dissolved in 20 to 24 parts of water are employed. The proportions required will depend on the nature of the item being treated, and the results desired.

Wood which has been sufficiently treated in the resinification process is dimensionally stable and will not shrink, swell, or warp appreciably with humidity changes. It is considerably harder, stronger, and more durable. The surface is smooth and dense, does not require filling or polishing and the grain will not rise on wetting. Resin impregnated wood is easily machined and the tendency to shred or splinder during sawing, planing and turning is reduced. It is markedly resistant to flame, chemicals and infestation by fungi, rot and pests. The natural color of the wood is not altered, although any desired color may be obtained by the introduction of suitable dyes in the treating solution. So far there appears to be no adverse effect on the gluing and finishing characteristics of wood which has been so treated. Because of its high dimensional stability, resin-impregnated wood should present no serious difficulties in the application of paint coatings when desired. Several such organic coatings have already been formulated for this purpose.

Application of Principles to the Treatment of Plywood

The resinification process is particularly well adapted to the treatment of plywood and laminates, since the individual layers of veneer may be impregnated separately before bonding. For the past few years most plywoods have been constructed by bonding untreated veneers with resins of the phenol-formaldehyde type. In this method sheets of the resin in films were placed between the veneers and bonding accomplished by applying pressure to the assembly through heated platens. Resin bonded plywood is distinctly superior to the old casein bonded type in resistance to both water and bacterial and fungus growth (4).

Plywood is now being manufactured by a process in which impregnating resins of the same type, but lower molecular weight are used first to saturate the veneer, this being followed by the application of heavier adhesive resins for bonding. The method has been applied so far only to sheets of veneer up to 1/8 inch in thickness. Plywoods containing either urea-formaldehyde or phenol-formaldehyde impregnants show marked retardation of deterioration of edges and corners due to outside exposure. However, the phenolic type gives maximum durability although the use of the ureas might result in a lower cost (1).

It does not appear to be practicable to attempt the resinification of plywood after bonding has been completed. For more than 2 plies only the surfaces and edges can be penetrated by this process. Impregnated veneers are not moisture vapor impermeable, which means that on exposure the unimpregnated core will swell during periods of high humidity. Because the outside shell will be "case-hardened", the core will be compressed, followed by shrinkage from the new dimension during dry periods, resulting in splits. This has been proven in trials by the United States Plywood Corporation (1).

Although several companies are manufacturing resin treated plywoods and laminated products for war purposes, it is doubtful if these materials will be available in quantities for civilian use until the emergency eases, so we are faced with the same problem as in the use of metals for this purpose. There is a possibility, however, that treated plywoods may have advantages over metal which would justify their use after the war. Embossed characters can be produced on the wood during the process of manufacture (2), and the objectionable corrosion associated with the use of metals could be eliminated. No data are available at present on comparative costs.

<u>Conclusions</u>

On the basis of the facts presented, the following conclusions seem to be justified:

1. Treatment of finished plywood by resinification is not practicable from the standpoint of highway use.
2. The Department should employ only resin-impregnated plywood for wooden highway signs as soon as such material is available.
3. The possibility of using resin-impregnated plywood permanently in the place of metals should be considered.

REFERENCES

1. Communication from U. S. Plywood Corporation.
   Charles B. Hemming, Chief Chemist, July 6, 1944.

2. Communication from Resinous Products and Chemical Company.
   Thomas D. Perry, July 17, 1944.

3. Communication from E. I. duPont de Nemours & Company.
   Dr. J. F. T. Berliner. June 22, 1944.

4. Plywood for War.
   Thomas D. Perry; Chemical and Engineering News, May, 10, 1944.

5. Forest Products Laboratory Urea-Plasticized Wood (Uralloy) Mimeograph R1277.
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   Forest Products Laboratory Mimeograph No. 154.

7. Methylolurea Advances Resin Impregnation of Wood.
   J. F. T. Berliner; Chemical Industries, May, 1944.

8. Chemistry's New-Born Wood.
   J. F. T. Berliner; duPont Magazine, June, July, August 1944.

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July 6, 1944

Mr. E. A. Finney
State Highway Department
Lansing, Michigan

Dear Mr. Finney:

Please refer to your letter to us of June 19 concerning plywood for Highway signs in which you asked a number of questions.

As far as we know, no one is in subtantial production of flat resin impregnated plywood at the present time. We have made small lots from time to time for interested customers and are now seriously considering regular production. This type of plywood is made by impregnating the veneers with water soluble phenol formaldhyde resin in solution before bonding with the adhesive resin.

We have been studying carefully both the phenol formaldhyde and urea formaldhyde types. The resin chosen will depend on the problem on hand but at the present time, we believe it is safe to say the maximum durability is to be obtained with the phenol formaldhyde resin. The urea formaldhyde type will perhaps result in a lower cost.

Either type of impregnant shows marked retardation of deterioration of exposed edges and corners due to outside exposure. However, as noted above the phenol formaldehyde resin gives maximum durability.

Paint tests have not been extensive, but at least one company, E. I. du Pont de Nemours & Company, Finishes Division, Wilmington, Delaware, claims to be able to furnish a durable adherent finish. In our opinion the finishing problem should not be difficult, because of the high dimensional stability of the impregnated wood.

Considerable work has been done on impregnation of finished plywood. For more than 2-plies, only the surfaces and edges are impregnated. We are of the opinion that the technique is not advisable as it is likely to cause degrade of the core. Impregnated veneers are not moisture vapor impermeable. This means that on exposure the unimpregnated core will swell during periods of high humidity. Because the outside "shell" will be "case hardened", the core will compress, followed by shrinkage from the new dimension during dry periods resulting in splits. This has been proven in trials.

If you would like additional information or are interested in a specific quotation, we would certainly be happy to receive your inquires.

Yours very truly,

UNITED STATES PLYWOOD CORPORATION

Charles B. Hemming
Chief Chemist

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June 22, 1944

Mr. E. A. Finney
Assistant Testing and Research
Engineer in Charge of Research
Michigan State Highway Department
No. 3 Olds Hall
Michigan State College
East Lansing, Michigan

Dear Mr. Finney:

Your letter of June 19 is received and I will do my best to answer your questions, although it should be stated in advance that resin impregnated or high density plywoods are in their infancy and the exigencies of war have prevented their normal development for civilian purposes.

Taking your questions specifically:

1. Formica Insulation Company of Cincinnati, Ohio, Pluswood Company of Oshkosh, Wis., Rudolph Wurlitzer Company of DeKalb, Ill., the Haskelite Company of Grand Rapids, Mich. and the Camfield Manufacturing Company of Grand Haven, Mich. are all in production on various types of impregnated plywood and laminated products for war purposes.

2. Most of the work so far done has been with phenol formaldehyde resin adhesives that are described in notes we are enclosing herewith. Urea-formaldehyde is quite recent in the field and is being strongly sponsored by the duPont Company. Experience has shown superior durability of the phenolics both to weather exposure, moisture and heat. Hence we feel that it is the more encouraging line to progress and development.

3. This is largely covered by answer to question 2 above. The need of protecting the edges and corners will probably be directly proportional to the amount of resin impregnation. In other words, with a maximum pick-up of 25 or 30% we would imagine that edge protection would become relatively unimportant. With intermediate pick-up of 20% edge protection would be quite essential.

4. We have been informed that the painting of resin impregnated plywoods is quite similar to the painting of metals and we do not believe that any serious difficulty would be encountered here by those who are familiar with the requirements of formulating coating materials for special products.

5. We have no knowledge of any processes for the liquid impregnating of the edges of the plywood. It would probably be true that the impregnating of

the finished plywood, after the adhesive has been heat cured in the usual way, would be more difficult than the impregnating of the raw veneers. And we might raise some question as to the suitability of attempting to impregnate a phenol resin bonded plywood with a methyl urea.

There is another point that we think might be important in the considera- tion of high density plywood for road signs and that would be that letters and symbols can be impressed into this plywood when it is originally bonded, a process somewhat analogous to that of stamping raised metal in metal. For any standard signs this would give quantity production and justify the expense of the heated metal dies that would be required.

We ourselves are chemical manufacturers and do not enter into the plywood manufacturing field at all. However, we are sending a copy of your letter to our representative in Detroit, suggesting that he call on your some- time when in your vicinity and see whether we can be of any further service to you in your study.

If you would like samples of our impregnating resins Amberlite PR-23 and Amberlite PR-50, we will be glad to send them to you for your evaluation.

Thanking you for your inquiry, we remain

Very truly yours,

THE RESINOUS PRODUCTS AND CHEMICAL COMPANY

TDP:JO

Thomas D. Perry

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HARRY T. WARD
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January 16, 1945

#3 Olds Hall
Michigan State College
East Lansing, Michigan

Mr. W. W. McLaughlin
Testing and Research Engineer
Michigan State Highway Department
Lansing, Michigan

Dear Mr. McLaughlin:

In accordance with your request we have reviewed the subject of impregnated plywood prompted by an article appearing in the "Science News Letter" for April 29, 1944 and titled "Soft Woods Made Hard". A report is submitted herewith.

The study has disclosed two points worthy of consideration. First, in the light of present knowledge it would seem inadvisable for the Department to attempt the resinification of finished plywood for highway signs and second, the Department should consider the use of resin impregnated plywood for wooden highway signs when such materials are available after the war.

Very truly yours,

E. A. Finney

E. A. Finney
Assistant Testing and Research
Engineer in charge of Research

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