

Dimensional Stabilization of Wood with Carbowaxes¹

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The dimensions of small cross sections of wood were stabilized with Carbowaxes to virtually eliminate shrinkage. The stabilization was due to bulking of the fibers—cutting down shrinkage by deposition of materials within the cell walls. Carbowaxes can be readily leached from the wood but can, however, be fixed in the wood by simultaneously treating the wood with an equal weight of water-soluble phenolic resin, then curing the resin.

Introduction

IT HAS BEEN SHOWN that the dimensions of wood can be stabilized by three different means or combinations thereof (6, 7, 12).³ These are: 1) by reducing the hygroscopicity of the wood so that less water can be taken up, 2) by forming cross links between the interfiber structural units so as to minimize separation of these units and accompanying swelling, and 3) by depositing a bulking agent within the swollen structure so as to reduce shrinkage.

Heating wood to high temperatures for short periods or to moderate temperatures for longer periods of time imparts considerable dimensional stability to wood (8, 10). This was at first believed to be due to the formation of ether cross links by the loss of water of constitution between hydroxyl groups on adjacent cellulose chains (8, 10). It has recently been shown that cross links between the fine structural units are not formed (2). It now appears that the dimensional stabilization is due to the breakdown of the more hygroscopic hemicelluloses and the formation of insoluble polymers from the sugars and furfural formed (2).

Cross linking of polystyrene by polymerization of vinyl benzene with small amounts of divinyl benzene has been shown by Staudinger (17) to

give a polymer with greatly reduced swelling. Tarkow and Stamm (18) have shown that cross links analogous to those formed by the divinyl benzene can be formed in wood by reacting it with small amounts of acidified formaldehyde vapor. Unfortunately, this reaction takes place only under such acidic conditions that the strength properties of the wood are badly impaired. Although other cross linking agents that react with wood under less drastic conditions have been sought, none have yet been found.

When wood is treated with solutions of highly water-soluble chemicals, the solution is taken up within the cell walls in concentrations only slightly less than the bulk concentration (11). When the wood is dried, evaporation of water occurs from the microscopically visible capillary structure, thus building up the chemical concentration and promoting further diffusion of the chemical into the cell walls. The wood in drying is thus prevented from shrinking its normal amount as a result of deposition of the chemical within the fibers (4, 5). The amount of dimensional stability that can be attained between the soaked and the oven-dry condition in this way depends upon the solubility of the bulking chemical and the rate at which the wood is subsequently dried. slow drying promotes more effective diffusion of the chemical into the cell walls.

The reduction of the vapor pressure of water by the chemical also has an effect upon the dimensional stability of wood by bulking. No shrinkage will occur until the prevailing relative humidity has dropped below the relative vapor pressure (in per cent) in equilibrium with the chemical solution within the wood (4). For example, ordinary salt, sodium chloride, when taken up by wood to form a saturated solution reduces

the equilibrium relative vapor pressure to 0.75. In this case shrinkage does not occur until the prevailing relative humidity drops below 75 per cent. Because of this, better dimensional stabilization is obtained between two high relative humidities, one of which is above the equilibrium relative vapor pressure of the saturated salt in the wood, than between two low relative humidities.

Dimensional stabilization by bulking was first demonstrated with inorganic salt solutions (4). Salts, however, are not practical dimension stabilizing chemicals. They can be readily leached from the wood, they are corrosive to machining tools and fastenings, and they reduce the relative vapor pressure of water to such a high degree that the wood is always damp at the higher relative humidities. Sugars are better bulking agents than most salts because of their greater solubility in water (5). They reduce the vapor pressure loss, so they have less tendency to make the wood damp. They are noncorrosive, but they do make wood more subject to decay.

Water-insoluble chemicals can also act as bulking agents if they are deposited within the cell wall structure by a replacing process (9) or put into the fibers from an aqueous solution, dried, and then insolubilized by some chemical reaction (13, 14). The first of these is illustrated by replacing the water in swollen wood with Cellosolve (ethylene glycol monoethyl ether) and replacing the Cellosolve with a wax or fatty acid (9). Such bulking agents cannot be leached from wood with water. They have limitations as dimension stabilizing agents, however, because of the difficulty in carrying out the replacement process and the fact that the treated wood cannot be readily glued or normal finishes applied.

That most successful bulking treatment up to the present time has been the treatment of wood with water-soluble phenolic resins, drying and heat curing of the resin within the cell walls of the wood (12, 13). This process has been successfully used in making Impreg—laminated, uncompresssed, resin-treated wood (12, 13),

¹ A contributed paper.
² Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
³ Numbers in parentheses refer to literature cited.

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and in making Compreg—laminated resin-treated compressed wood (15). Impreg is finding us in patterns and die models (3); Compreg is used in forming dies, tooling jigs, picker sticks, shuttles, cutlery handles, and clarinets (7, 12).

The highest dimensional stabilization of wood thus far attained has

been by acetylation; that is, replacing the hydroxyl groups in the cellulose and lignin of the wood by acetate groups (16). Although this process appears as if the dimensional stabilization is attained by reducing hygroscopicity, this, too, is a bulking process. When the dimensional stabilization obtained by acetylation is com-

pared to that obtained by butyralation, it is found that the volume of acid groups introduced rather than the number of hydroxyl groups replaced determines the stability attained (16).

Treatment with Carbowaxes

Even though water-soluble bulking agents can be leached from wood, they may find several special practical applications if good dimensional stabilization can be attained. Both the inorganic salts (4) and the sugars (5) previously used have limiting solubilities; hence they will stop diffusing into the cell walls when the water in the cell walls becomes saturated. It appeared desirable to test a series of nonvolatile organic chemicals that are soluble in water in all proportions to determine if greater diffusion into the cell walls than was previously obtained with invert sugar is possible.

A series of Carbowaxes⁴ was chosen for these tests. Carbowaxes are polyethylene glycols. They are available in molecular weights ranging from 200 to 6,000. The fractions with molecular weights of 200 through 600 are liquids and are soluble in water in all proportions. Even the Carbowax with a molecular weight of 6,000 is soluble in water to the extent of 50 per cent by weight.

The tests were made on cross sections of Sitka spruce $\frac{1}{8}$ inch in the fiber direction and 2.25 inches in the two other directions. The specimens from which they were cut were chosen on the basis of the straightness of the annual rings and were dressed so that the rings were parallel to two opposite faces. Cross sections were used because they furnish the best possible means of matching wood specimens and because of the ease of treating which eliminates all treating variables.

Pairs of oven-dry specimens were weighed and the tangential and radial dimensions measured with a dial gage to one-thousandth of an inch. They were then soaked in water and in 25 per cent by weight aqueous solutions of glycerine and each of the Carbowaxes. To insure saturation, the submerged specimens were put into a vacuum desiccator that was then evacuated; when the vacuum was released, the specimens became completely saturated. The specimens were left submerged over the weekend to attain diffusion equilibrium. They were then blotted, rapidly weighed and measured, and transferred to a humidity room held at 80° F. and 90 per cent

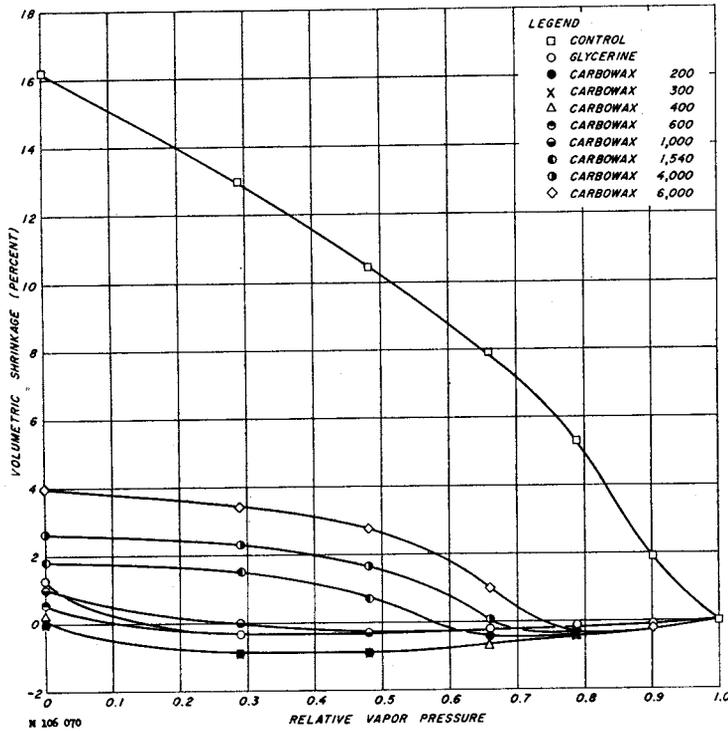


Fig. 1.—The effect of Carbowaxes on the volumetric shrinkage of Sitka spruce cross sections at various relative vapor pressure levels. The specimens were saturated with 25 per cent by weight aqueous solutions of glycerine and each of the Carbowaxes. The average molecular weights of the Carbowaxes are given in the legend.

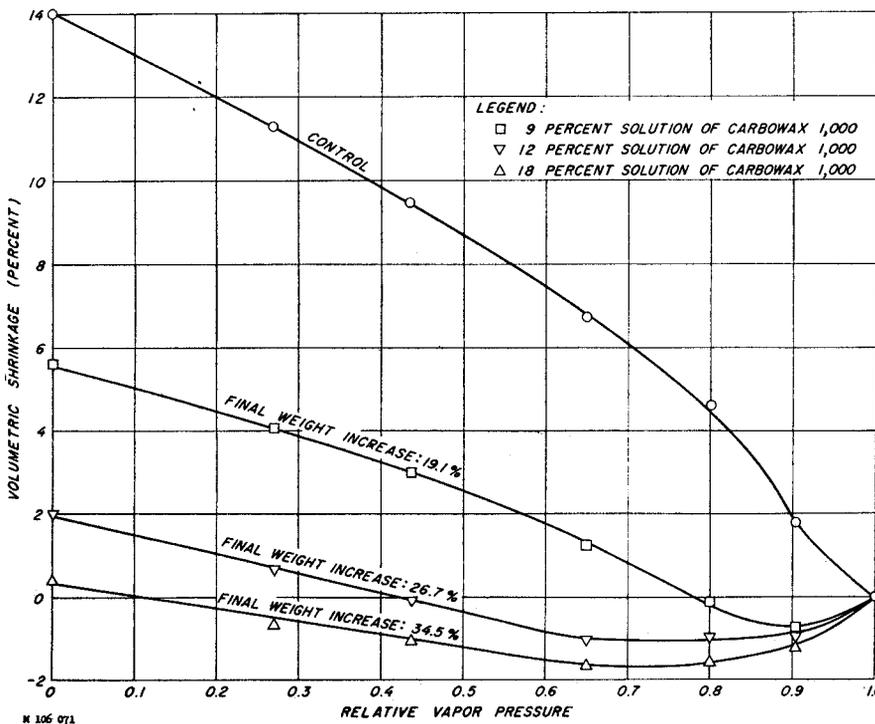


Fig. 2.—Effect of the concentration of Carbowax 1000 solution on the volumetric shrinkage of Sitka spruce cross sections at various relative vapor pressure levels. The specimens were soaked in 9, 12, and 18 per cent solutions of Carbowax 1000. Percentage figures on the curves indicate the weight of Carbowax taken up per unit dry weight of the untreated wood.

⁴A recent patent by the Upson Company (U. S. 2,629,674) discloses the use of Carbowaxes for stabilizing fiberboards. Their work implies recognition of the impermanence of the treatment in the presence of liquid water. To overcome this, the Upson Company recommends treatment with equal parts of the Carbowax and a thermosetting resin.

relative humidity. Humidities were checked with an electric hygrometer.

The specimens were weighed and measured after 7 days and again after 10 days drying. Differences between the readings for the two times of drying were small. The specimens were transferred to a humidity room held at 80° F. and 79 per cent relative humidity, then successively to humidity rooms at 66 per cent, 48 per cent, and 29 per cent after attaining virtual weight and shrinkage equilibrium in each room. The specimens were then oven-dried, weighed and measured. The weight increase of the specimens due to deposition of Carbowax in the structure averaged about 56 per cent.

The data for the volumetric shrinkage (sum of tangential and radial shrinkage) are plotted in Fig. 1. All of the treatments reduce the shrinkage of the wood to a considerable degree. The poorest reduction between the soaked and the oven-dry condition was to 25 per cent of normal by Carbowax 6000. The dimensional stabilization improved with decreasing molecular weight of the Carbowax to Carbowax 600. Below this value there is little change. The dimensions of the oven-dry specimens treated with Carbowaxes 200 to 600 are virtually the same as the original soaked dimensions. To attain this, water within the cell walls of the swollen specimens must be entirely replaced by Carbowax. This is not surprising since other polar liquids, notably Cellosolve, have been previously shown to completely replace water (9).

Glycerine, the second member of the Carbowax series, gives a somewhat greater shrinkage than the low molecular weight Carbowaxes, presumably because some of it vaporized from the wood in the final oven-drying process.

It is of interest to note that all of the treated specimens swelled slightly in the initial stages of drying. This is due to the fact that wood swells in these concentrated solutions slightly more than in water alone and that diffusion continues into the cell walls as drying progresses. In the case of the Carbowaxes that are soluble in water in all proportions, this diffusion continued down to equilibrium with a relative vapor pressure of about 0.5. With the less-soluble Carbowaxes, diffusion into the cell walls ceased when the solution in the coarse capillary structure became saturated. It thus appears that the inferiority of the higher molecular weight Carbowaxes compared to the lower for dimensional stabilization of wood is due to loss in solubility rather than to molecular size.

Fig. 2 gives similar data for a different set of specimens that were

soaked in 18, 12, and 9 per cent solutions of Carbowax 1000 giving final weight increases of 34.5, 26.9 and 19.1 per cent. These specimens were left in the higher humidity rooms for longer periods of time (at least 3 weeks). This accounts for the greater extent of diffusion into the cell walls and for the greater swelling in the early stages of drying.

If the fiber saturation point of the wood is assumed to be 30 per cent and the specific gravity of the Carbowax is 1.125, the maximum volume of Carbowax that could enter the cell wall per gram of wood is 0.307, 0.237, and 0.168 for the three concentrations. These values are 100, 80, and 57 per cent of saturation. From the per cent shrinkage to the oven-dry condition relative to the control, the amount of bulking should be 98, 85, and 60 per cent. These values are near the maximum amount that could be taken up within the cell walls, indicating that diffusion into the cell walls must be quite complete. This is in agree-

ment with the microscopic indication that diffusion of water-soluble phenolic resin into wood below the saturation concentration is so complete that no resin deposit can be detected on the cell walls (12).

Fig. 3 gives isotherms for the desorption of water vapor from the Sitka spruce and from the Carbowax 1000. Also plotted are the observed values for Sitka spruce containing 0.345 gram of Carbowax 1000 per gram of dry wood and the values calculated from the data for the wood and the Carbowax on the basis of the mixture law. The observed moisture contents are somewhat less than the calculated values. The data show that the wood containing Carbowax is more hygroscopic than the untreated wood only above a relative humidity of 80 per cent. Only above 90 per cent relative humidity does the wood feel real damp.

A few attempts were made to fix the Carbowax in the wood by treating with water-soluble phenolic resin. Table 1 shows the effect of the concen-

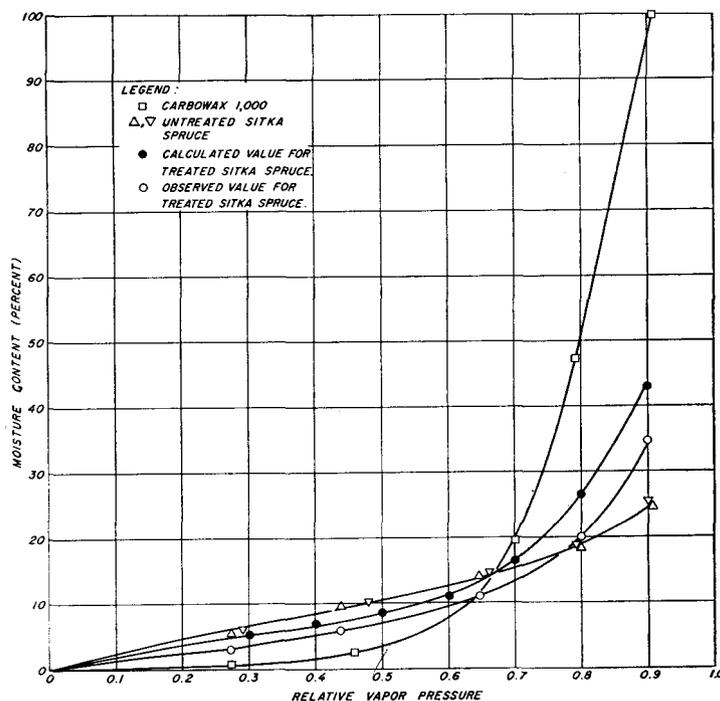


Fig. 3.—Desorption isotherms at 80° F. for Sitka spruce, Carbowax 1000, and Sitka spruce treated to contain 0.345 gram of Carbowax 1000 per gram of dry wood.

Table 1.—EFFECT OF TREATING SITKA SPRUCE CROSS SECTIONS WITH CARBOWAX 600 AND WATER-SOLUBLE PHENOLIC RESIN (BAKELITE 15100) TO FIX THE CARBOWAX

Composition by weight of treating solution	After drying and curing*		After 3 days of leaching†		After 6 days of leaching‡	
	Treating† solid content Per cent	Antishrink§ efficiency Per cent	Treating† solid content Per cent	Antishrink§ efficiency Per cent	Treating† solid content Per cent	Antishrink§ efficiency Per cent
30 per cent resin	77.0	78.4	77.2	78.5	77.4	79.7
50 per cent Carbowax 15 per cent resin	139.0	93.0	74.3	82.8	33.6	69.6
16.7 per cent Carbowax 15 per cent resin	70.4	82.0	68.7	2.7	66.2	59.5
8.3 per cent Carbowax 7.5 per cent resin	38.4	68.0	37.6	60.0	37.3	59.6

*Oven-dried and cured for 2 hours at 150° C.

†Leached in water, then dried.

‡Average weight increase after oven-drying over the original untreated oven-dry weight of two specimens.

§Reduction in volumetric shrinkage below that of the control divided by that of the control.

tration of the treating solutions on leachability and dimensional stability.

The specimens treated with phenolic resin alone contained enough resin to completely stabilize the wood if the resin acted the same as the Carbowax. The lower dimensional stabilization is due to loss of water of constitution from the resin in the curing process. Because of this, the optimum antishrink efficiency obtainable is 82 per cent (reduction in volumetric shrinkage below that of the control, divided by that of the control). The antishrink efficiency obtained is thus quite close to the optimum value.

The specimens treated with 50 per cent Carbowax and 15 per cent of phenolic resin gave a high initial antishrink value, 93 per cent. The theoretical optimum value is 96 per cent. Because of the more rapid drying in this case compared to the data of Fig. 1, the attained antishrink efficiency would be expected to be slightly low because of incompleteness of diffusion into the cell walls. These specimens lost about half of their treating solids on the first cycle of leaching and another quarter on the second leaching. If it is assumed that the resin is not leached, practically all of the Carbowax is lost after the second leaching. This assumption seems justified in that the final antishrink efficiency is about what would be expected for the residual solids content being entirely resin (1).

Specimens treated with 16.7 per cent of Carbowax and 15 per cent of resin and those treated with 8.3 per cent of Carbowax and 7.5 per cent of resin gave lower initial antishrink efficiencies, as would be expected. In both of these cases the weight loss due to leaching is quite small. The first leaching caused some loss in antishrink efficiency, but the second leaching caused little. It appears that the resin can fix about its own weight of Carbowax. When more Carbowax is originally present, the Carbowax is not as well fixed initially so that practically all of it can be leached from the wood.

A few tests showed that inorganic salts are not as effectively fixed in wood by phenolic resin as the Carbowaxes. This could be explained on the basis of an insoluble addition compound being formed between Carbowax and phenolic resin. There is still insufficient evidence to prove whether this or physical enveloping is the cause of the fixing of the Carbowax.

Conclusions

Carbowaxes are excellent bulking and dimension stabilizing agents for

wood because of their high solubility in water and their nonvolatility. Carbowaxes 200 through 600 are soluble in water in all proportions and as a result can completely replace water in the swollen structure on slow drying to give the wood virtually perfect dimensional stability. Diffusion into the cell walls continues down to an equilibrium relative vapor pressure of 50 per cent for the Carbowaxes that are soluble in water in all proportions. The less effective dimensional stabilization by Carbowaxes 1000 to 6000 is due to their limiting solubility in water.

When the wood contains less Carbowax than that needed to saturate the structure, practically all of the Carbowax diffuses into the cell walls, as indicated by the degree of bulking.

The hygroscopicity of wood containing just sufficient Carbowax to give it virtually complete dimensional stability exceeds that of untreated wood only at equilibrium with a relative vapor pressure of 0.80 or above. It becomes damp only above 0.90 relative vapor pressure.

Carbowax can be readily leached from the wood. The treatment should hence not be used for dimensional stabilization of wood to be subsequently subjected to uses under leaching conditions. The Carbowax can, however, be fixed within the structure with an equal weight of phenolic resin.

No data are as yet available on the effect of Carbowax treatment on other properties. It is felt, however, that the strength properties will be similar to those of green wood. The treatment will probably introduce gluing and finishing difficulties.

The treatment at present appears suitable for stabilizing the dimensions of initially water swollen wooden objects that do not require subsequent gluing or painting, that have sufficient strength in the green condition, and that will not be subjected to leaching conditions. It should be possible to stabilize cross sections of trees for display purposes or for table tops to prevent them from developing radial cracks that invariably develop on drying due to the greater tangential than radial shrinkage. It should likewise be suitable for treating of green bolts of wood for art carving. In this case it would not be necessary to carry the replacement to completion before carving. It is conceivable that after a reasonable depth of penetration has been attained by soaking, the bolt could be removed for carving each

day and returned to soaking in the solution at night. Data on different size bolts would be needed for several different carving species before the total time of soak prior to air-drying could be determined.

The method should also be suitable for preserving unearthened waterlogged wooden objects of historical value. Frequently such objects, though free from decay, are very refractory because some hydrolysis has occurred. Such objects on drying frequently collapse so badly that they go all to pieces. Soaking in Carbowax solution for some time prior to air-drying should prevent this.

Literature Cited

1. Millett, M. A. and Stamm, A. J. 1946. Treatment of wood with urea resin-forming systems: dimensional stability. *Modern Plastics* 24:150.
2. Seborg, R. M., Tarkow, H., and Stamm, A. J. 1953. Effect of heat upon the dimensional stabilization of wood. *J. For. Prod. Res. Soc. III* (3):59.
3. — and Vallier, A. E. 1954. Application of impreg for patterns and die models. *J. For. Prod. Res. Soc. IV* (5):305.
4. Stamm, A. J. 1934. Effect of inorganic salts upon the swelling and shrinking of wood. *J. Am. Chem. Soc.* 56:1195.
5. —. 1937. Minimizing wood shrinkage and swelling, treatment with sucrose and invert sugar. *Ind. Eng. Chem.* 29:833.
6. —. 1946. Modified woods. *Am. Wood Pres. Assoc. Proc.* 42:150.
7. —. 1948. Modified woods. *Modern Plastics Encyclopedia*, p. 725.
8. —, Burr, A. K., and Kline, A. A. 1946. Staywood: heat-stabilized wood. *Ind. Eng. Chem.* 38:630.
9. — and Hansen, L. A. 1935. Minimizing wood shrinkage and swelling by replacing the water with nonvolatile materials. *Ind. Eng. Chem.* 27:1480.
10. — and Hansen, L. A. 1937. Minimizing wood shrinkage and swelling, effect of heating in various gases. *Ind. Eng. Chem.* 29:831.
11. Stamm, A. J. and Hansen, L. A. 1938. Surface-bound versus capillary condensed water in wood. *J. Phys. Chem.* 42:209.
12. — and Harris, E. E. 1953. *Chemical processing of wood*, pp. 196-263, Chemical Pub. Co., N. Y.
13. — and Seborg, R. M. 1936. Minimizing wood shrinkage and swelling, treatment with synthetic resin-forming materials. *Ind. Eng. Chem.* 28:1164.
14. — and Seborg, R. M. 1939. Resin-treated plywood. *Ind. Eng. Chem.* 31:897.
15. — and Seborg, R. M. 1941. Resin-treated-laminated compressed wood.
16. — and Tarkow, H. 1947. Dimensional stabilization of wood. *J. Phys. and Colloid Chem.* 31:493.
17. Staudinger, H. and Heuer, W. 1934. Über hochpolymere verbindungen, 94 über ein unlösliches polystyrol. *Ber.* 67:1164.
18. Tarkow, H. and Stamm, A. J. 1953. Effect of formaldehyde treatments upon the dimensional stability of wood. *J. For. Prod. Res. Soc. III* (2):33.