

until the pink color had completely disappeared and the black precipitated manganese dioxide had coagulated and settled. The filtrate was free of manganese so that the calcium could be determined by precipitation as the oxalate and filtered on a sintered glass filter. The oxalate was treated with hot, dilute sulfuric acid and titrated with 0.1 *N* potassium permanganate in the usual manner.

SODIUM. Sodium was separated in one operation from manganese and all but a trace of calcium by reduction of the permanganate with methyl alcohol in ammoniacal solution. A weighed sample of about 5 grams was treated in a 250-ml. beaker with 50 ml. of water, 1 ml. of concentrated ammonia, and 10 ml. of methyl alcohol. The solution was allowed to stand 10-15 minutes and then heated for about an hour on the steam bath. The solution was filtered, and the precipitate (manganese dioxide, calcium carbonate) washed thoroughly and discarded. The trace of calcium was then removed from the combined filtrate and washings with a little ammonium oxalate. After filtration, the solution was acidified with hydrochloric acid, evaporated to dryness in platinum, and ignited to remove ammonium salts. The residue was then extracted with a little water and filtered, and the filtrate collected in a small tared platinum dish. The solution was treated with a few drops of hydrochloric acid, evaporated to dryness, and ignited below a red heat, and the weight of residue (sodium chloride) was obtained.

IRON. Iron was determined colorimetrically as ferric thiocyanate with a Fisher photoelectric colorimeter. Manganese was first removed by the nitric acid treatment described under calcium. From 8 to 10 grams of sample were used.

SULFATE. Since permanganate badly contaminates the barium sulfate precipitate, prior reduction of the permanganate ion is necessary. A weighed sample of about 5 grams was treated with 100 ml. of water and 10 ml. of concentrated hydrochloric acid. The mixture was heated until the pink color was discharged and the manganese dioxide had coagulated. It was then filtered, and the filtrate was neutralized with ammonia and made slightly acid with hydrochloric acid. Barium sulfate was then precipitated in the conventional way.

HYDROGEN ION CONCENTRATION. The calcium or sodium permanganate solutions were diluted to approximately 30% permanganate ion with freshly distilled water of pH 6.1-6.3, and the pH was determined using a glass electrode and the Coleman pH electrometer.

GERMAN MATERIALS

Samples of captured German peroxide and permanganates were analyzed by the methods described. An entire tank car of the peroxide was brought to Huntsville Arsenal, Ala., where the material was sampled; a typical analysis follows:

Hydrogen peroxide	83.4%
Nonvolatile matter (110° C.)	0.11
Acid (as H ₂ SO ₄)	0.24
NH ₄ ⁺	0.03
K ⁺	0.01
Na ⁺	0.01
Al ⁺⁺⁺	Nil (< 0.0002)
Cl ⁻	Absent
NO ₃ ⁻	0.01
PO ₄ ⁻⁻⁻	0.03
SO ₄ ⁻⁻⁻	0.13
SiO ₂	0.01
pH (dilution 1 to 10)	3.1
Density at 25° C., grams/cc.	1.3533

The permanganates were forwarded to us by the AAF Supply Officer, Wright Field. The Germans had a "summer" and a "winter" permanganate. For summer the sodium permanganate was adequate, but its smaller solubility and higher freezing point made it unsuitable for winter temperatures; therefore the much more soluble calcium permanganate was employed.

Summer permanganate was found to be a solution containing 42.11% of sodium permanganate. Both potassium and calcium were absent. The density of the solution at 24° C. was 1.396 grams per cc.; its pH was 7.05 and its freezing point -15° C.

Winter permanganate was a calcium permanganate solution of the following composition:

Ca(MnO ₄) ₂	38.00%	Density (24° C.), g./cc.	1.400
NaMnO ₄	1.75	pH	4.01
Mg ⁺⁺	Trace (0.01)	Freezing point, ° C.	-20
SO ₄ ⁻⁻⁻	Trace (0.01)		
K ⁺	Absent		

LITERATURE CITED

- (1) Bellinger, Friedman, *et al.*, *IND. ENG. CHEM.*, 38, 160, 310 (1940).
- (2) Cuthbertson, Matheson, and Maass, *J. Am. Chem. Soc.*, 50, 1120 (1928).
- (3) Kargin, V. A., *Z. anorg. allgem. Chem.*, 183, 77 (1926).
- (4) Linton and Maass, *Can. J. Research*, 4, 322 (1931).
- (5) Maass and Hatcher, *J. Am. Chem. Soc.*, 42, 2548 (1920).
- (6) Maass and Herzberg, *Ibid.*, 42, 2560 (1920).
- (7) Maass and Hibert, *Ibid.*, 46, 2693 (1924).
- (8) Matheson and Maass, *Ibid.*, 51, 674 (1929).

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STAYBWOOD... Heat-Stabilized Wood

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HHEATING wood under drying conditions at higher temperatures or for longer periods of time than are normally encountered in kiln drying has been shown to reduce appreciably the hygroscopicity and subsequent swelling and shrinking (5, 6, 7, 10, 12, 16). Staybwood is uncompressed wood that has been dimensionally stabilized by heat alone. It differs from staypak, a heat-stabilized compressed wood (8), in that the hygroscopicity of the wood is reduced as a result of the more drastic heating.

The importance to antishrink efficiency of heating originally dry wood, or green wood that dries in a small fraction of the total heating time, has been demonstrated by experiments at this laboratory. Matched dry-wood specimens were heated in sealed bombs, one containing no free moisture and the other having more than enough free water in the bomb to saturate the specimen. Under heating conditions that gave a rather large re-

duction in the hygroscopicity of the dry wood, there was no reduction in hygroscopicity of the wood heated in the presence of an excess of moisture (12). This, together with the fact that water of constitution is lost when wood is heated at elevated temperatures, led to the hypothesis that the loss in hygroscopicity and the reduction in swelling and shrinking are due to the splitting out of water between two adjacent hydroxyl groups with the formation of an ether linkage (12). This hypothesis is in keeping with the facts that ethers are less hygroscopic than alcohols, that cross bridging reduces swelling (16), and that the presence of an excess of water inhibits reactions involving the loss of water (12).

Other experiments in which the specimens were heated in bombs containing different gases indicate that the nature of the gas has only a minor effect upon the resulting hygroscopicity, an

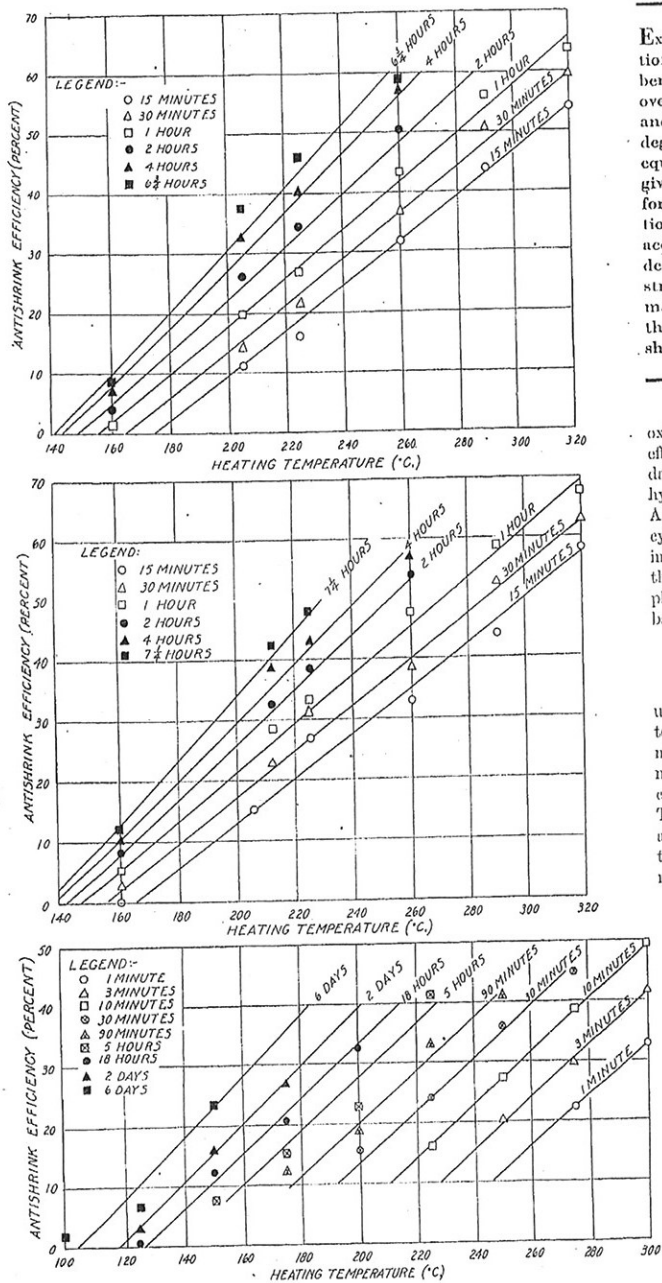


Figure 1. Antishrink Efficiency Obtained by Heating Specimens under Molten Metal at Different Temperatures for Various Times

Top. Western white pine cross sections, 1/2 inch thick in the fiber direction.
 Center. Flat-sawn western white pine, 1 3/32 inch thick.
 Bottom. Sitka spruce rotary-cut veneer, 1/16 inch thick.

Extensive data are presented on the reduction in hygroscopicity of wood when heated beneath the surface of a molten metal over the temperature range 120° to 320° C. and time range of 1 minute to 1 week. The degree of reduction in hygroscopicity and equilibrium swelling and shrinking for a given time of heating is practically doubled for each 10° C. rise in temperature. Reductions in hygroscopicity are shown to be accompanied by appreciable increases in decay resistance and significant losses in strength. Serious losses in strength for many possible uses are not obtained until the reductions in hygroscopicity and antishrink efficiency exceed 50%.

oxidizing atmospheres being only slightly more effective than a reducing atmosphere. Previous data also show that the effect of heat upon the hygroscopicity of wood is permanent (10, 12). After an initial humidification-dehumidification cycle or soaking-drying cycle subsequent to heating, no gain in hygroscopicity occurs within the time or number of cycles tested. The phenomenon thus cannot be explained on the basis of a hysteresis effect.

HEATING IN MOLTEN METAL

It seemed desirable to extend heating measurements over a much broader range of heating temperatures and times in order to analyze the nature of the phenomenon better and to determine the practicability of such a process for commercially stabilizing the dimensions of wood. To minimize oxidation and its effect on strength and to make possible rapid heat transfer so as to avoid making corrections for the length of time required to attain the desired temperature in high temperature-short time combinations, a method of heating wood beneath the surface of molten metal was adopted (10). A lead-tin-cadmium alloy (approximately 50% tin, 30% lead, and 20% cadmium) with a melting point of about 150° C. (302° F.) was used. This alloy had but little tendency to stick to the specimens when they were removed from the bath except when used at temperatures only slightly above its melting point. Any small amount of adhering metal was readily scraped off with a steel spatula. In later work Wood's metal was tried in order to determine if it could be used at lower temperatures. This metal tended to stick to the wood sections and hence its use was abandoned.

The experiments with western white pine were made by heating the wood in an iron pan containing the molten metal with a steel weight having an insulated handle for holding the specimens immersed. The pan was heated with two Bunsen burners. The bath, with the weight immersed, was heated to about 2° C. (3.6° F.)

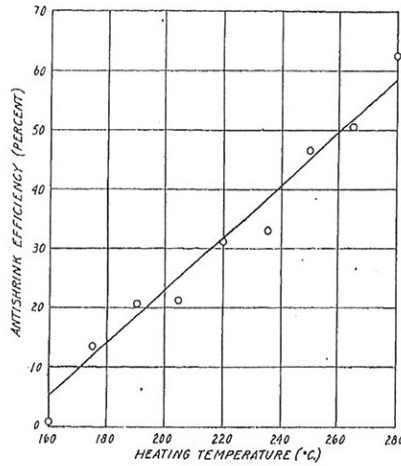


Figure 2. Antishrink Efficiency Obtained by Heating Eastern White Pine Specimens, $6 \times 2 \times 15/16$ Inch, under Molten Metal at Different Temperatures for 2 Hours

above the desired point for temperatures below 270°C . (518°F). The weight was rapidly lifted, the specimens were placed on the molten-metal surface, and the weight was put on them to immerse them in the molten metal. The wood specimens cooled the bath by about 2°C , and thus minimized the necessary manual adjustment of the burners. When the heating temperature was above 270°C . (518°F .) the exothermic reaction was sufficiently great so that one of the burners could be removed, slightly before or at the time the specimens were put into the bath, and not replaced for a period of 2 to 5 minutes. This agrees with the findings of Kobe and Goin (4) who found 273°C . (523°F .) to be the temperature at which exothermic decomposition of wood becomes appreciable.

The temperature control by this manual method was accurate to only $2\text{--}5^\circ \text{C}$. ($3.6\text{--}9.0^\circ \text{F}$). It was not suitable for long-

period heating. For this reason the Sitka spruce veneer specimens and the larger eastern white pine specimens were electrically heated in a bomb with automatic temperature control. The bomb lid was designed to hold the specimens immersed. The molten metal could not be used for heating at temperatures below 175°C . (347°F). Therefore, the veneer specimens were heated at 125° and 150°C . (257° and 302°F .) in sand with dry nitrogen slowly circulating through the sand to prevent oxidation. Veneer specimens were also heated in an electrically heated oven at 125° , 150° , and 175°C . (257° , 302° , and 347°F .) to determine the extent to which oxidation affects the results.

HYGROSCOPICITY AND DIMENSIONAL STABILITY

The heated specimens, when removed from the heating medium, were cooled in a desiccator, scraped free of any adhering metal, weighed, and measured. They were then subjected to relative humidity cycles in which they were successively brought to equilibrium with 90% and 30% relative humidity in rooms held at 26.7°C . (80°F .) Matched unheated controls went through the same relative humidity cycles and were then oven-dried to determine the weight at the conclusion of the measurements.

The western white pine cross-section specimens were all cut from a single flat-sawn board, 1 inch thick and $4\frac{1}{4}$ inches wide, into pieces $\frac{1}{2}$ inch in the fiber direction. Every seventh specimen was used as a control. The flat-sawn western white pine specimens were also cut from a single board, $\frac{13}{16}$ inch thick, into strips $1\frac{1}{4}$ inches wide in the tangential direction. The strips were cut into 6-inch lengths. All the specimens heated at a given temperature, together with two controls taken from the two ends, were cut from a single stick to assure optimum matching. The rotary-cut $\frac{1}{16}$ -inch Sitka spruce veneer specimens were $5\frac{7}{8}$ inches long and 1 inch wide. They were similarly matched except that specimens 1, 6, 11, and 16, all cut from a single 1-inch-wide strip, were used as controls. The eastern white pine specimens were cut into 8-inch lengths from a single stick, 2 inches wide and $\frac{15}{16}$ inch thick. The two end specimens were used as controls.

The specimens were put through three complete relative humidity cycles of 90% to 30% to 90%, with the exception of the eastern white pine; sufficient time was allowed under each condition (about 2 weeks) for moisture equilibrium to be reached,

The percentage reduction in hygroscopicity and the percentage increase in the dimensional stability (antishrink efficiency) was calculated for each half cycle of 90 to 30% and 30 to 90% relative humidity. The percentage reduction in hygroscopicity is equal to 100 times the difference between the weight change of the control and the relative weight change of the heated specimen divided by weight change of the control. The percentage increase in the dimensional stability is equal to 100 times the difference between the dimension change of the control and the relative dimension change of the heated specimen, divided by the dimension change of the control. The percentage reduction in hygroscopicity and the antishrink efficiency are practically equal under the experimental conditions of this research. In view of this equality and inasmuch as the accuracy of weighing is greater

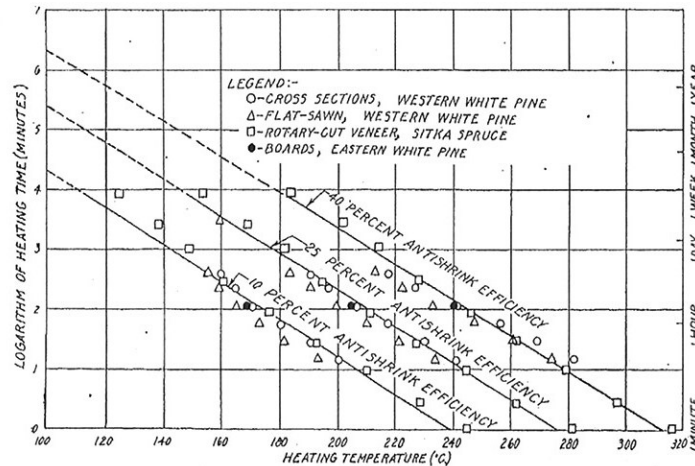


Figure 3. Heating Time and Temperature Necessary to Obtain Antishrink Efficiencies of 10, 25, and 40%

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than that of measuring, the values recorded in this paper are actually the reduction in hygroscopicity as found by weighing, except for eastern white pine. In this case dimension changes between the water-soaked and the oven-dry condition were measured.

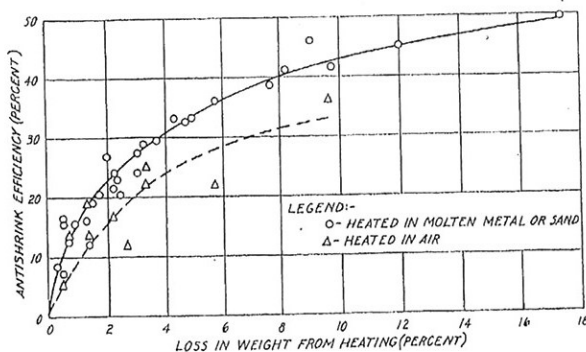


Figure 4. Antishrink Efficiency vs. Loss in Weight on Heating, for Rotary-Cut Sitka Spruce Veneer

Figure 1 gives the average antishrink efficiencies for the complete second and third cycles plotted against heating temperature for several different times of heating, obtained on western white pine cross sections and flat-sawn specimens and the rotary-cut Sitka spruce veneer. Figure 2 shows the antishrink efficiency values from a water-soaked to an oven-dry condition for the specimens of eastern white pine. These measurements were made on 1/8-inch-thick cross sections cut from the ends of the larger specimens. An approximately linear relationship exists between the antishrink efficiency and the temperature for each time of heating, the lines becoming slightly steeper with increasing time.

When wood is heated at temperatures and for periods sufficient to give an appreciable antishrink efficiency, it is materially darkened. The light-colored softwoods used in these experiments darkened to about the color of walnut.

Theoretically, for the minimum heating times used in these experiments (15 minutes for the 1/2-inch and 13/12-inch western white pine and 1 minute for the 1/16-inch Sitka spruce veneer) the temperature rise at the center of the wood is at least 95% of that at the surface in a fraction of the total time. Practically, uniform antishrink efficiencies should result throughout the thickness of the wood, even in these short heating times.

Figure 3 shows the data of Figures 1 and 2 plotted as the logarithm of heating time against the heating temperature necessary to obtain three different antishrink efficiencies. The slope of the lines is such that the reaction rate practically doubles for each rise in temperature of 10° C. (18° F.).

Figure 4 shows the relationship between the antishrink efficiency and the loss in weight caused by heating, for the data of Figure 1 on Sitka spruce veneer. The loss in weight per unit antishrink efficiency obtained is greater when the wood is heated in air than in the molten metal. Evidently a greater degree of oxidation occurs in air; this contributes less, if at all, to the antishrink efficiency than the postulated ether-linkage formation.

Figure 5 gives the relationship between toughness and antishrink efficiency of the flat-sawn western white pine specimens in equilibrium with 30% relative humidity. The measurements were made on the Forest Products Laboratory toughness machine (1), using a 4-inch span. The toughness values are for the actual cross section of the specimens corrected, for the slight variation

in thickness and width, to an area of 0.53 square inch by considering the toughness directly proportional to the cross-sectional area. As expected, the toughness of the wood was appreciably decreased by the heat treatment. The reduction in toughness of wood on heating is not attributable to the reduced moisture content at test which results from the reduced hygroscopicity of the wood. The variation in toughness of wood with changes in moisture content is small compared to the loss in toughness obtained on heating. The loss in toughness must thus be due to embrittlement of the fiber itself.

Figure 6 shows the relationship between the face hardness and antishrink efficiency of the eastern white pine specimens as determined by the A.S.T.M. method, in which the load required to embed a 0.444-inch diameter ball to half its diameter is measured. The specimens were preconditioned at 65% relative humidity. The hardness is reduced significantly at the higher degrees of heating, but not so much as the toughness.

Figure 7 shows the relationship between the antishrink efficiency of spruce veneer and the modulus of rupture in equilibrium with 30% relative humidity. The measurements were made on a cantilever-beam stiffness tester (3, 17). The veneer heated in the molten metal showed a much smaller decrease in modulus with increase in antishrink efficiency than did the veneer heated in air.

The modulus of elasticity is also decreased by the heating process, but to an appreciably lesser degree than the modulus of rupture. Heating in air again causes a greater loss in strength than does heating beneath the surface of molten metal. It is thus of considerable importance to heat wood in the absence of air in any commercial operation aimed at stabilizing wood for uses in which moderate strength is important.

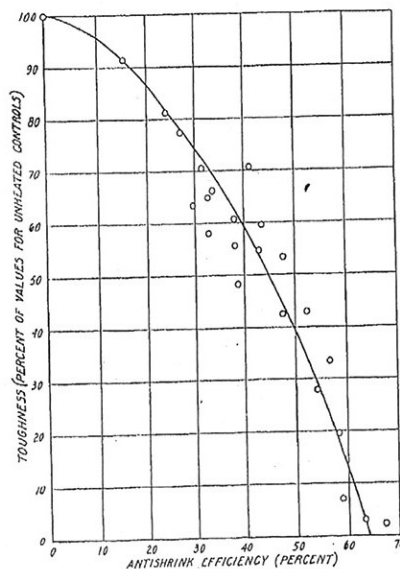


Figure 5. Toughness vs. Antishrink Efficiency Obtained by Heating Flat-Sawn Western White Pine Specimens as Indicated in Figure 1

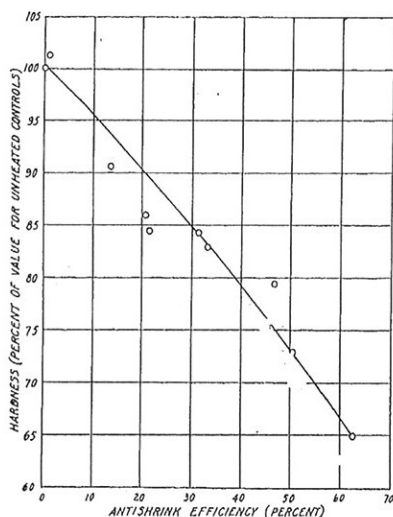


Figure 6. Hardness vs. Antishrink Efficiency Obtained by Heating Eastern White Pine Specimens as Indicated in Figure 2

A few preliminary pure-culture decay tests were made on the flat-sawn western white pine specimens. Both the heated specimens and controls were cut into 2-inch lengths, oven-dried, weighed, and placed in jars containing a good growth of the wood-destroying fungus, *Trametes serialis*. The jars were held under favorable growth conditions for 2 months. The fungus grew over the surface of all the specimens. This growth was carefully removed and the specimens were again oven-dried and weighed. The controls sustained an average weight loss of 28.4%. Heated specimens with antishrink efficiencies of 30 to 33% gave an average weight loss of 12.5%. Specimens with antishrink efficiencies of 33 to 38% gave weight losses of 0 to 4.5%. All the specimens with antishrink efficiencies of 40% or more gave no weight loss.

Decay resistance produced by heating the wood is similar to that resulting from resin treatment in that the resistance results largely from the inertness of the material rather than to the presence of a toxic ingredient. The decay resistance in both is presumably due to either or both the reduced hygroscopicity, whereby sufficient water is prevented from entering the cell-wall structure to support decay, or to a chemical change occurring within the wood that made it no longer susceptible to fungus attack (18).

CONCLUSIONS

It appears feasible to impart an appreciable degree of stabilization of dimensions and decay resistance to wood commercially by means of a simple heat treatment which materially reduces the hygroscopicity. Such a heat treatment causes a loss in strength properties varying from a rather large loss in toughness to a small loss in modulus of elasticity in bending. It appears that the practical limitations on the degree of dimensional stabilization obtainable will, in large measure, be controlled by the acceptable loss in toughness. In general, it is felt that an antishrink efficiency of 40 to 50% is as high as is practical. Under these conditions the toughness is less than half that of the original wood, according to data thus far obtained.

In the strength properties tested, the loss in strength per unit antishrink efficiency obtained is greater when the wood is heated

in the presence of air than when air is excluded by heating under a molten metal. This suggests that lumber might be fed through a trough of electrically heated molten metal under a series of rollers to convey it through the trough. The process could be made rapid for half-inch or thinner stock, and need not be prohibitively long for 1-inch or somewhat thicker stock (11). If the trough were well insulated, the energy consumption would involve only a small fraction of the cost of dimensionally stabilizing wood by known chemical means (2, 9, 11, 13, 14).

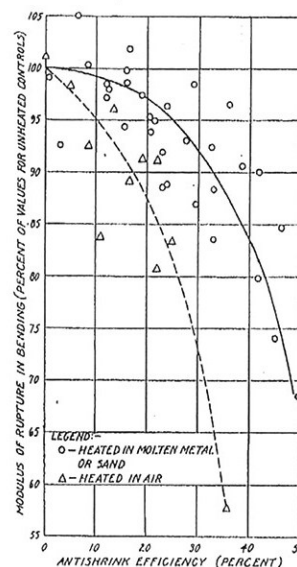


Figure 7. Modulus of Rupture in Bending vs. Antishrink Efficiency Obtained by Heating Rotary-Cut Sitka Spruce Veneer Specimens as Indicated in Figure 1

Before any large-scale tests are undertaken, further work should be done to determine the abrasion resistance and other strength properties and also the gluing and painting qualities of heat-stabilized wood. Additional species should also be studied.

LITERATURE CITED

- (1) Forest Products Lab., *Repl.* 1308 (1941).
- (2) *Ibid.*, R1277 (1943).
- (3) Jungmann, E. C., Turner, H. D., and Buhr, H. K., *Ibid.*, 1388 (1944).
- (4) Kobo, K. A., and Goin, T. L., *IND. ENG. CHEM.*, 31, 1171 (1939).
- (5) Koehler, A., and Pillow, M. Y., *Southern Lumberman*, Dec. 19, 1925, 219.
- (6) Merritt, R. W., and White, A. A., *IND. ENG. CHEM.*, 35, 207 (1943).
- (7) Pillow, M. Y., *Wood Working Ind.*, Oct., 1929, 8.
- (8) Soborg, R. M., Millott, M. A., and Stamm, A. J., *Mech. Eng.*, 67, 25 (1945).
- (9) Stamm, A. J., *IND. ENG. CHEM.*, 29, 833 (1937).
- (10) Stamm, A. J., U. S. Patent 2,296,310 (1942).
- (11) Stamm, A. J., and Hanson, L. A., *IND. ENG. CHEM.*, 27, 1480 (1935).
- (12) *Ibid.*, 29, 831 (1937).
- (13) Stamm, A. J., and Soborg, R. M., *Ibid.*, 31, 897 (1939).
- (14) Stamm, A. J., and Soborg, R. M., *Trans. Am. Inst. Chem. Engrs.*, 37, 365 (1941).
- (15) Staudinger, H., *Trans. Faraday Soc.*, 32, 323 (1936).
- (16) Tiemann, H. D., *Lumber World Rev.*, 28 (7), 10 (1915).
- (17) Tinius Olsen Testing Machine Co., *Bull.* 11.