PURCHASED BY THE
U. S. DEPARTMENT OF AGRICULTURE
FOR OFFICIAL USE

Effect of Heat Upon the Dimensional Stabilization of Wood[1]

R: M. SEBORG, HAROLD TARKOW, and ALFRED J: STAMM
Chemists, Forest Products Laboratory,[2] Forest Service, U. S. Department of Agriculture

Describes investigations that disprove the hypothesis that stabilization by heat is a cross-linking reaction: Analyses of tests employed indicate that unless some way can be found to separate the dimension-stabilizing from the embrittling reactions, which does not seem probable at present, the commercial use of wood stabilized in this way will be quite limited:

Introduction

HEATING WOOD TO TEMPERATURES considerably above normal seasoning temperatures is the oldest, simplest, and cheapest means now known for stabilizing the dimensions of wood, but the treatment, unfortunately, embrittles the wood significantly (8, 9, 13).[3]

Dimensional stabilization of wood with heat has been previously shown to be dependent upon a combination of temperature and time. The time required to attain a given antishrink efficiency (dimension change of the control minus the dimension change of a matched heated specimen divided by the dimension change of the control between the oven-dry and the water-soaked conditions, or between two different relative humidities, expressed in percent) increases in a logarithmic fashion with a decrease in temperature *(8)*. An appreciable weight loss accompanies dimensional stabilization. The loss is greater per unit time when the wood has free access to air than when heated beneath the surface of a molten metal (6, *8)*.

Dimensional stabilization by heat is accompanied by a loss of water of constitution of the wood. This fact, coupled with limited data showing that dry heat is more effective than moist heat, was the basis for the hypothesis that stabilization by heat, like the reaction of wood with formaldehyde (12), is a cross-linking reaction (9). The postulated cross linking was pictured as an oxygen linkage (that is, an ether) formed by water splitting off between two hydroxyl groups on adjacent swelling units.

It was felt desirable to check this hypothesis and to find, if possible, means of avoiding the undesirable embrittlement that has thus far prevented the commercial use of this otherwise promising means of stabilizing the dimensions of wood. On the basis of support from the Office of Naval Research, an investigation was initiated at the Forest Products Laboratory to obtain more information on this heat reaction and its control.

Nature of the Thermal Reaction

A series of tests was made to determine if the thermal reaction is really one involving the formation of ether cross links.

Tests were made on the swelling of heated and unheated wood in several different agents that cause normal wood to swell more than it does in water. If ether cross links were formed on heating, the swelling in concentrated sodium hydroxide, morpholine, and pyridine should be significantly less than the swelling of the unheated controls, as none of these liquids is capable of breaking ether linkages. The data given in table 1 for the swelling of unheated and heated spruce and maple cross sections show that with maple, heat treatment reduces the subsequent swelling only in water. In fact, the heated sections of maple swelled more than the controls in all liquids but water. With softwoods (spruce) heat treatment reduced the swelling in water, had a slight effect in reducing the swelling in pyridine, and increased the swelling in sodium hydroxide more than 35 percent. Previous work *(12)* showed that formaldehyde-stabilized wood undergoes less swelling in all of these liquids than does untreated wood. This indicates that the dimensional stability resulting from heat treatment is probably not due to the formation of ether cross links between swelling units, as in formaldehyde treatment.

In order for cross linking to occur between the various swelling units, it would seem that the separation of these units should be within rather definite limits, presumably not more than one molecular diameter of water apart. Cross linking should thus occur readily in dry wood or in wood at low moisture content, but not in completely swollen wood. Experiments were hence conducted on heating both dry and bulked-out (that is, swollen) matched specimens and determining their subsequent antishrink efficiencies.

Preliminary bulking experiments in which diphenyl oxide replaced the acetone in acetone-swollen cross sections of Sitka spruce and glycerine replaced the water in water-swollen sections were inconclusive, as the diphenyl oxide caused more shrinkage than was desired under the heat treatment and the glycerine tended to pulp the wood. The partially bulked specimens heated in diphenyl oxide, however, gave the same subsequent antishrink efficiency as the unswollen sections heated in the same medium. The experiment did show conclusively that oxidation by atmospheric oxygen is not the cause of stabilization, for heating of the swollen specimens was carried out in the absence of both atmospheric and internally occluded oxygen.

The bulking of the wood cross sections was most effectively accomplished by causing potassium iodide to diffuse from a concentrated aqueous solution into the water-swollen cell-wall structure, followed by oven drying to remove the water. The oven-dry specimens retained 65 percent of their water-swollen volume even after drastic heating. This corresponds to an average separation of the swelling units of about three molecular diameters of water, instead of the five for completely swollen wood (7). These specimens, together with unswollen controls, were heated in a bomb at 210° C. for 5 hours. The potassium iodide was leached from the swollen specimens. The antishrink efficiency of

[1] Report of work done under Order No. NAonr 42-47 for the Office of Naval Research. Presented at the Cellulose Division meeting of the Amer. Chem. Soc. in- Milwaukee, April 1, 1952.

[3] Italic figures in parentheses refer to Literature Cited at the end of this report.

[3] Underlined figures in parentheses refer to Literature Cited at the end of this report.

Reprinted from the September issue of the Journal of the Forest Products Research Society.
P.O. Box 2010, Madison 5, Wisconsin.

Table 1.--Swelling of heat-stabilized sugar maple and Sitka spruce cross sections In various liquids compared with the untreated controls

Species	Treatment	Tangential swelling in: Water	18 percent sodium hydroxide	Morpholine	Pyridine
		Percent	Percent	Percent	Percent
Sugar maple...	Unheated control..	9.7	14.1	13.2	12.6
Do.....	Heated 5 hours at 210° C. in air...	5.3	15.6	15.9	13.7
Sitka spruce..	Unheated control..	10.0	13.2	.....	12.5
Do.....	Heated 7 hours at 230° C. in air...	6.6	18.2	.....	11.7

Table 2.--Properties of paper heated under various conditions

Property	Condition during heating	Extent of heat treatment: 180° C. 2 hr.	200° C. 2 hr.	200° C. 5 hr.	220° C. 2 hr.	220° C. 5 hr.	240° C. 2 hr.
Color	S[1]	White	White	White	White	White	White
	D[2]	Tan	Light brown	Brown	Dark brown	Brown black	Brown black
		Percent	Percent	Percent	Percent	Percent	Percent
Relative gain in weight at 90 percent relative humidity	S	93	90	88	86	85	81
	D	93	91	86	88	85	85
Relative fold resistance	S	66	85	43	22	2	3
	D	0	0	0	0	0	0
Relative tensile strength	S	87	92	84	78	70	68
	D	74	51	35	28	19	25

[1]Paper swollen in glycerine. Heated while submerged in glycerine.

[2]Paper not swollen. Heated dry.

both the originally swollen and the unswollen heated specimens was then determined, the former *giving* a value of 33 percent and the latter 31 percent.

If this dimensional stabilization were due to the formation of ether cross linkages, it should have been considerably greater for the heated unswollen wood than for the heated swollen wood because of the much more favorable molecular spacing of the structural units in the unswollen wood. The fact that the antishrink values were practically identical indicates that the dimensional stabilization must be due to some other cause.

As an aid in understanding the transformation occurring when wood is heated, it was of itablest to isolate thok transformations due only to the stable polysaccharide components of wood. For this purpose, the heat treatment of pure carbohydrate material was next considered.

A bleached sulphite paper was cut into 5- by 6-inch sheets. After matched grouping, some of the sheets were swollen in water and the water was replaced with anhydrous glycerine. The swollen and nonswollen sheets were then heated under various temperature-time conditions. After the treatments, they were thoroughly washed, conditioned, and tested for hygroscopicity, fold resistance, and le strength. The data are presented in table 2. The following conclusions may be drawn from the table:

1. Heating paper in the dry condition brings about appreciable darkening. If the paper is swollen in glycerine and heated while submerged, no darkening occurs. With wood, however, equal darkening is obtained under bother conditions. This suggests that the hemicelluloses or lignin in wood are undergoing thermal transformations that do not require oxygen.

2. The relative hygroscopicity (relative weight increase between 0 percent relative humidity and 90 percent relative humidity) is approximately the same regardless of whether the paper is heated while swollen or not. This

fact agrees with the observations made when swollen and nonswollen wood are heated, and adds further weight to the belief that cross linkages do not form on thermal treatment: Again, the data show thar oxidation is not responsible for the reduction in hygroscopicity, for those specimens heated while swollen and submerged were not only out of contact with atmospheric oxygen, but in the process of swelling the specimens, occluded oxygen must have been driven off.

3. The specimens heated while swollen showed a gradual reduction in fold resistance. The specimens heated dry showed an extremely rapid drop in fold resistance to practically zero.

4. The specimens heated while swollen showed a very gradual drop in tensile strength: The specimens heated dry showed a rapid drop in tensile strength.

Cotton fabric that was heated for 6 hours at 200°, 220°, and 240° C. in the dry and in the glycerine-swollen states, like the paper, did- not darken when heated in glycerine, but progressively darkened when heated in air. Appreciable reductions in hygroscopicity occurred in both cases. The fabric swollen in glycerine should not have given the oserved reduction in hygroscopcity if the reaction were one involving the formation of cross links.

Effect of Heating Under Different Conditions Upon the Properties of Wood

In order better to understand the effect of heat upon the dimensional stabilization and physical properties of wood, a number of experiments were performed in which wood was heated in different gaseous media under atmospheric pressure or under confined conditions that allowed the pressure to build up, and under different con• ditions of moisture-content, temperature, and time.

Adjacently cut cross sections of ponderosa pine sapwood were used for the experiments. The sections heated under atmospheescape withoutere 13¼ inches in the radial direction, 1¼ inches in the tangential direction, and ⅛ inch in the fiber direction, except the specimens for toughness tests, which were $\frac{3}{16}$ by $^3/_8$ by 3 inches in the fiber direction. The sections that were heated in pressure bombs were $\frac{3}{16}$ inch thick in the fiber direction by 3 inches in either the radial or the tangential direction and $^3/_8$ inch in the other transverse direction.

Specimens heated in air were suspended in glass jars from metal hooks fastened to loosely fitting asbestos-board tops. In order to avoid spontaneous combustion at the higher temperatures, the air was not circulated. Distillation vapors were, however, able to escape.without appreciable amounts of air entering, hence, no pressure developed in the jars. The jars were suspended in an oil bath, thermostatically controlled to within 1° C. of the desired temperature:

The specimens heated in nitrogen were similarly handled except that the air was removed by a high-vacuum pump and nitrogen was admitted into the jars. During the heat treatment, a slow stream of preheated nitrogen was passed through the jars to avoid the reentrance of air.

Specimens heated in an enclosed system were placed in small brass bombs ½ inch in internal diameter and 3½ inches long. The bombs were heated by immersing them in the oil bath for various periods of time and

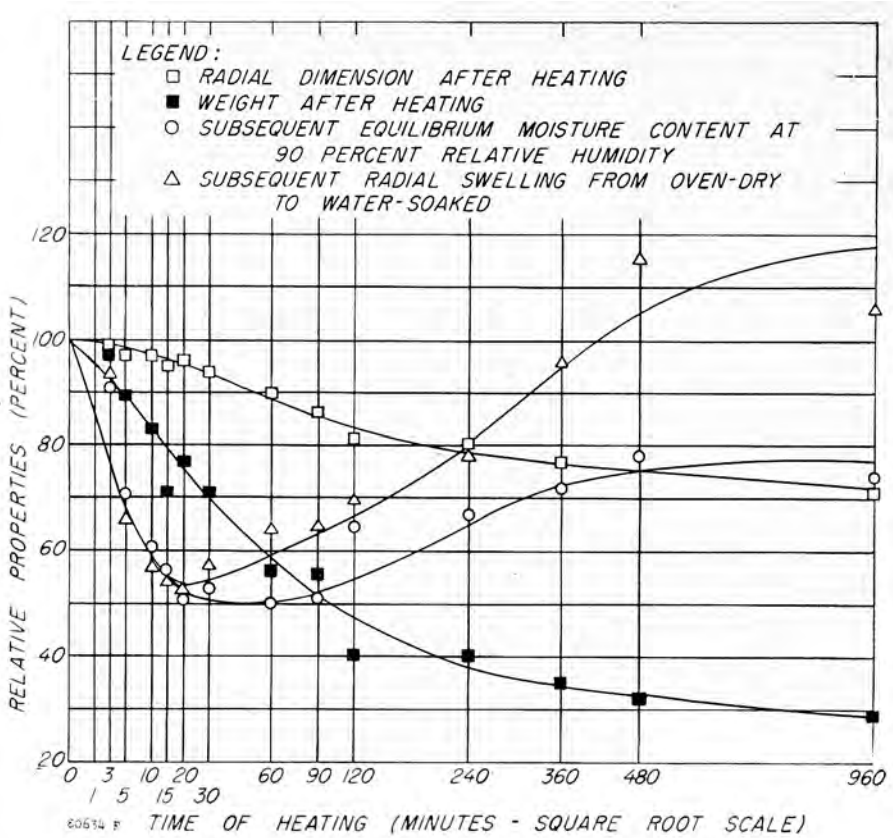

Figure 1.—Effect on properties of ponderosa pine sapwood cross sections when heated at 300° C. in air at atmospheric pressure for different periods of time.

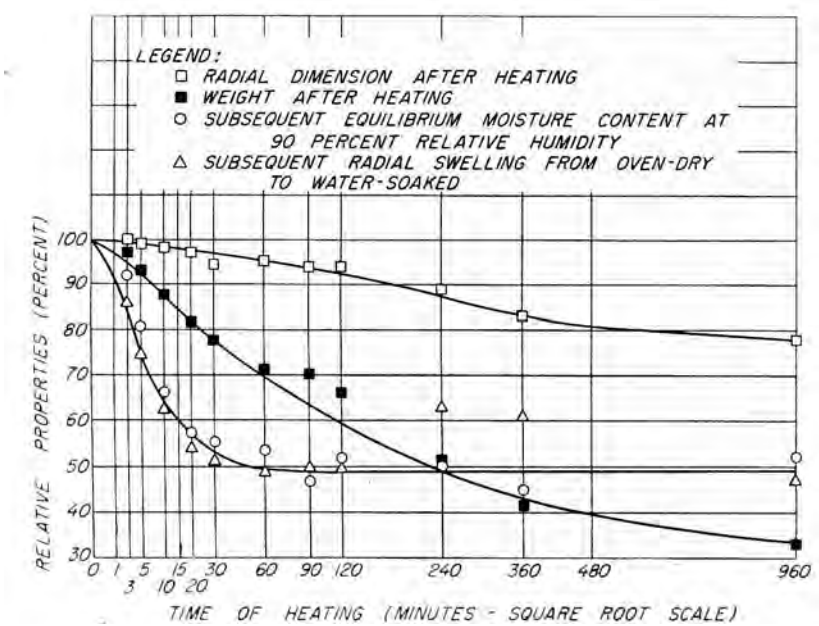

Figure 2.—Effect on properties of ponderosa pine sapwood cross sections when heated at 300° C. in nitrogen at atmospheric pressure for different periods of time.

were then cooled by quickly immersing them in cold water.

Specimens were heated in the bombs under three different moisture-content conditions; oven-dry, in equilibrium with 97 percent relative humidity (about 25 percent moisture content), and in equilibrium with 97 percent relative humidity with additional water added to the bomb in an amount equal to 165 percent of the weight of the wood.

The specimens heated in the bombs were treated with hot water to extract soluble products that might have been formed, and were then air-dried. All specimens were oven-dried, and the loss in weight and the decrease in the long dimension were determined. The specimens wre then subjected successively to 30, 65, and 90 percent relative humidity, and finally to liquid-water immersion followed by conditioning at 90, 65, and 30 percent relative humidity. They were weighed and measured after coming to equilibrium at each relative humidity and were measured after water soaking. Moisture content and dimension changes relative to those for the unheated controls were calculated for each of the exposure conditions. As the relative moisture content at 90 percent relative humidity under adsorbing conditions, and the relative dimension change from the oven-dry to the water-soaked condition, best illustrate the reduction in hygroscopicity and the anti-shrink efficiency that occurs, only this part of the equilibrium data is presented in figures 1 to 5. Figure 6 gives the relation of antishrink efficiency resulting from heating the dry specimens of figures 1 to 5 to the weight loss. Figures 7 and 8 show how the relative equilibrium values change with changes in exposure conditions.

Figure 1 gives the relative property changes that occur on heating oven-dry sections in air at 300° C. for different periods of time. Time is plotted on a square-root scale so as to compress the plot and to make possible the plotting of zero time. The slight inflection in the curves for the shortest heating times is, undoubtedly, due to the fact that a good proportion of this time was required for the specimen to come to the temperature of the oil bath.

All previous heating experiments at this high temperature have been for shorter periods of time *(8)*. The fact that a minimum relative hygroscopicity and relative swelling are finally reached has not been previously observed. It is of interest that the relative hygroscopicity and swelling are equivalent up to about the minimum value, but beyond this, they diverge. It is possible under these conditions actually to obtain a negative dimensional stabilization, that is, a stabilization whereby the heated specimen swells more percentagewise than does the control.

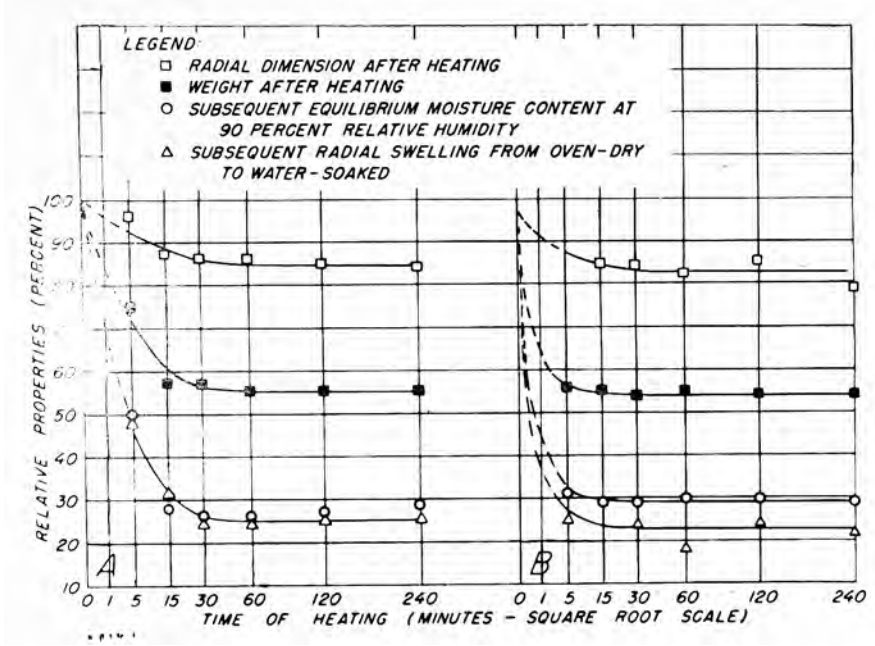

Figure 3.—Effect on properties of ponderosa pine sapwood cross sections when heated at 300° C. in closed containers for different periods of time. A, wood originally oven-dry; B, at 25 percent moisture content.

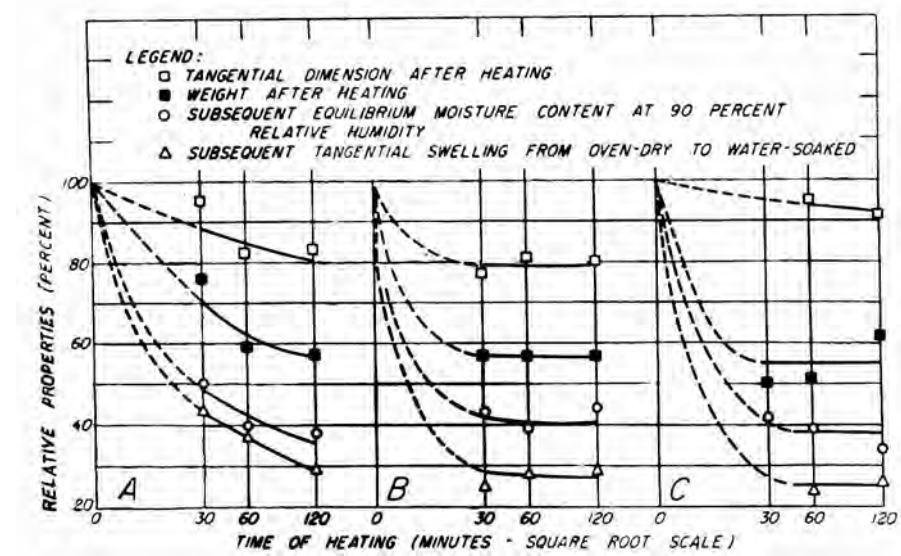

Figure 4.—Effect on properties of ponderosa pine sapwood cross sections when heated at 260° C. in closed containers for different periods of time. A, wood originally oven-dry; B, at 25 percent moisture content; C, at 165 percent moisture content.

Figure 2 gives the corresponding data for heating oven-dry specimens at the same temperature in nitrogen. The relative weights are but slightly higher than when the specimens were heated in air. Had an appreciable amount of air been available in the experiments shown in figure 1, considerably greater weight losses would have occurred. It is of interest that the relative radial dimensions, although slightly higher than for the specimens heated in air, are practically the same when the comparisons are made at the same relative weight.

The relative hygroscopicity and relative swelling reach about the same minimum value as when the specimens are heated in air, but they remain at this value even though there is still a continued loss in weight with increasing time. In this case, relative hygroscopicity and relative swelling are practically equivalent over the entire range.

Figure 3 gives the data for heating of the oven-dry and humidified specimens in the small sealed bombs at 300° C. It is of interest that under these conditions minimum relative weight, radial dimension, hygroscopicity, and swelling values are rapidly attained and that they remain constant with continued heating. The values attained for dry and for moist wood are

practically the same. The more rapid attainment of the minimum values when moisture is present, is presumably due to the better thermal conductivity of moist wood.

Figure 4 gives similar data to figure 3, except that the heating temperature was lower, namely, 260° C. The results were similar except that a longer time was required to attain the minimum relative property values. When large amounts of water were present (fig. 4, C), the tangential dimension was, for some unexplainable reason, abnormally high.

Figure 5 gives the data for heating in the bombs at 205° C. In this case, the final relative weights and tangential dimensions are quite similar for the specimens heated dry, for the specimens heated at a moisture content of '25 percent, and for the specimens heated in the presence of a large excess of water. It is of interest that the relative hygroscopicity and swelling increase quite appreciably with an increase in moisture content. Stamm and Hansen (9) found that at a still lower temperature (165° C.) a negligible antishrink efficiency was obtained when water was added to the bomb, whereas significant antishrink efficiencies were obtained when the wood was heated in the dry condition. It was partially on the basis of this finding that they postulated the formation of ether cross links. The fact that the presence of an excess of moisture.does not reduce the resulting antishrink efficiency at 260° to 300° C., as is shown in figures 3 and 4, is, however, not compatible with the old hypothesis.

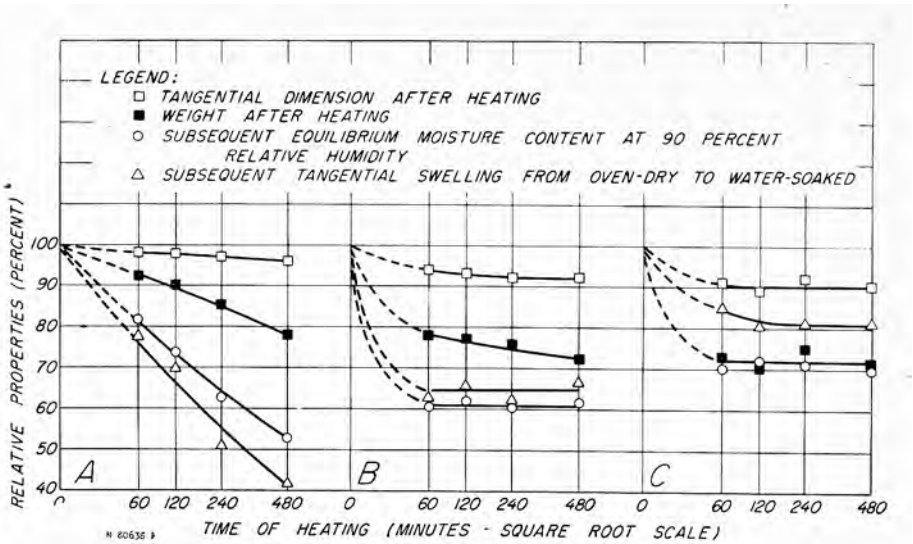

Figure 5.—Effect on properties of ponderosa pine sapwood cross sections when heated at 205° C. in closed containers for different periods of time. **A,** wood originally oven-dry; **B,** at 25 percent moisture content; **C,** at 165 percent moisture content.

Figure 6 gives the compiled data taken from figures 1 through 5 for the antishrink efficiency measured between the oven-dry and the water-soaked condition plotted against the loss in weight. The antishrink efficiency for losses in weight up to 20 percent is dependent upon the loss in weight irrespective of whether the wood was heated in air, nitrogen, or in a closed system. Beyond 20 percent loss in weight, the curves deviate greatly. The antishrink efficiency obtained by heating in the bomb continues to increase with increasing° weight loss. The antishrink efficiency obtained by heating in nitrogen remains virtually constant, and the antishrink efficiency obtained by heating in air decreases for weight losses exceeding 20 percent. A similar relationship holds for the relative hygroscopicity at 90 percent relative humidity. The fact that relatively large

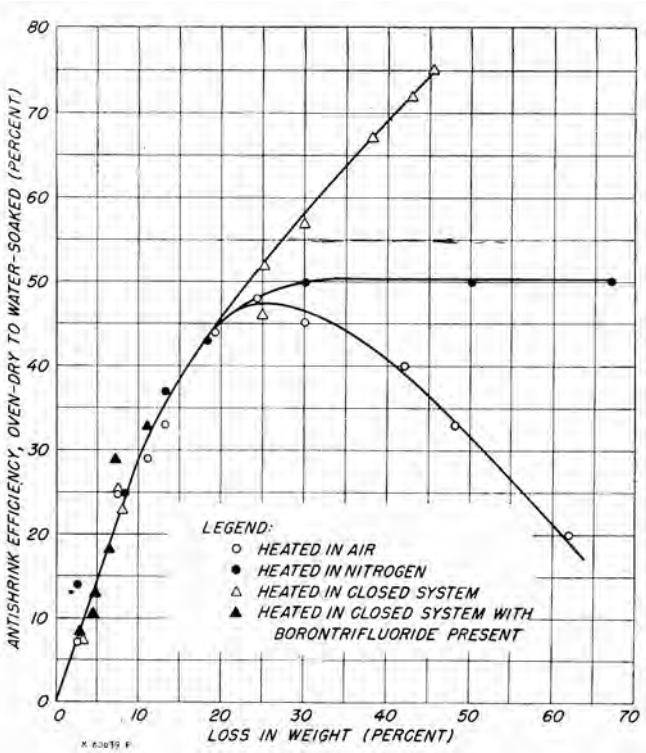

Figure 6.—Relation of antishrink efficiency resulting from heating the dry specimens of figures 1 to 5 to the weight loss.

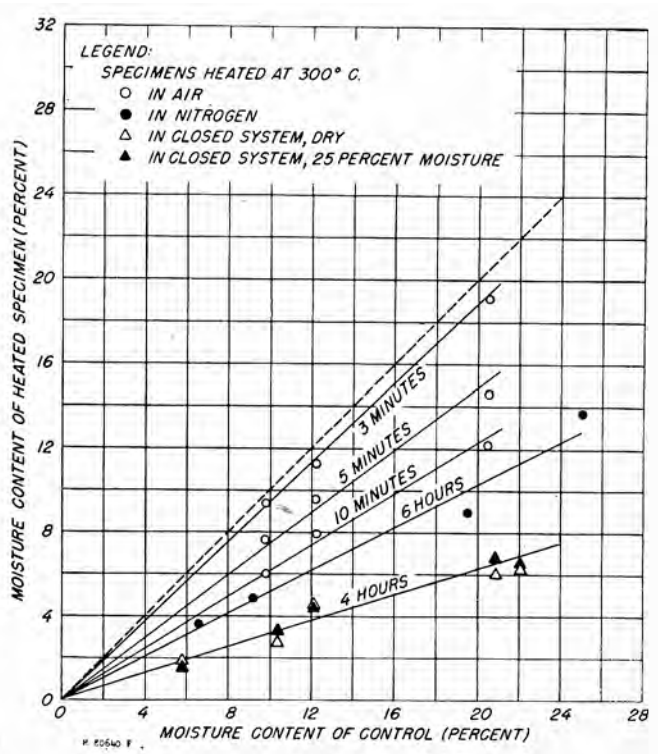

Figure 7.—Relation of equilibrium moisture content of specimens heated under different conditions at 300° C. for different periods of time to the equilibrium moisture content of the control specimens, which had been exposed to the same relative humidities as the heated specimens.

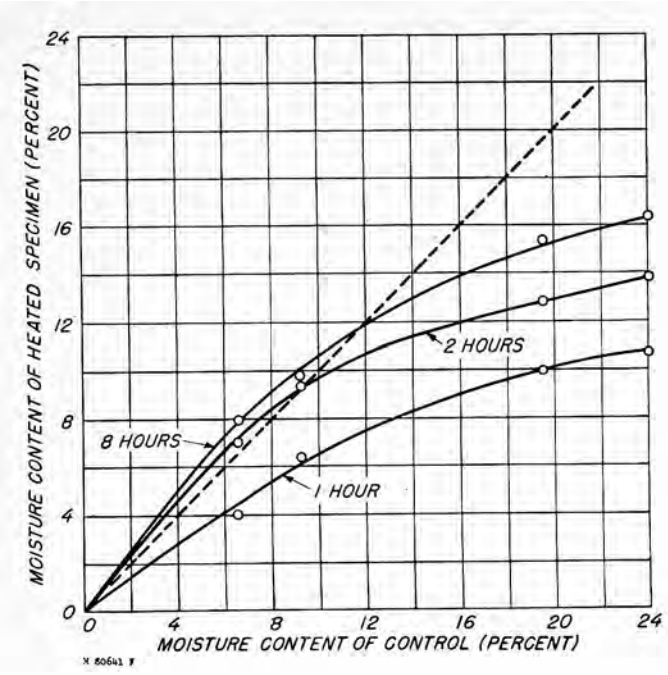

Figure 8.—Relation of equilibrium moisture content of specimens heated for 1 to 8 hours in air at 300° C. to the equilibrium moisture content of the control specimens, which had been exposed to the same relative humidities as the heated specimens.

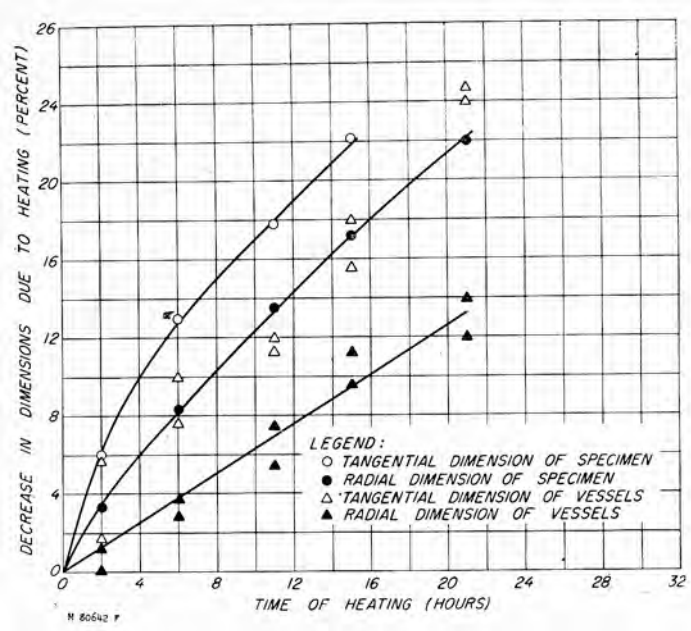

Figure 9.—Effect of heating 30-micron cross sections of sugar maple in air at 206° C. for different periods of time upon the subsequent specimen and vessel dimensions measured at 20 percent relative humidity.

weight losses are required to obtain appreciable reductions in hygroscopicity supports the view that cross linking is not responsible for stabilization of wood by heat treatment.

Figure 7 gives a plot of the equilibrium moisture content of the heated specimens against those of the controls under the same exposure conditions. The data given in this figure in all cases are fairly well represented by straight lines through the origin. This means that the relative hygroscopicity (mois:ure content of the heated specimen divided by that of the control) is practically independent of the exposure conditions. This is usually true for all woods stabilized by resin treatments *(10)* and by acetylation (11). Antishrink efficiencies are also virtually independent of the exposure conditions for dimensionally stabilized woods produced by any of the three methods.

Figure 8 shows that in the case of wood heated in air for periods of time such that the loss in weight exceeds 20 percent (fig. 6), the relationships of figure 7 no longer hold. The curves are not only displaced upwards with increasing time of heating instead of being displaced downwards, but distinct curves rather than straight lines are obtained. For low moisture contents, the relative hygroscopicity is actually increased for wood heated for 2 hours or more at 300° C. The relative hygroscopicity, however, decreases appreciably with increasing moisture content.

Internal Dimension Changes

On comparing the decrease in dimensions with the decrease in weight (figs. 1 to 3), it should be kept in mind that the decrease in dimensions refers to that in the radial direction. It would be more appropriate to compare the percentage decrease in weight with the percentage decrease in volume. Since dimension changes in the radial direction are about half of the values in the tangential direction for the ponderosa pine wood, and since changes in the longitudinal direction can be neglected, the weight changes in figures 1, 2, and 3 should be compared with values corresponding to about 3 times the radial change. The percentage volumetric change is approximately equal to the sum. of the percentage change in the tangential direction and the radial direction. If the tangential change is assumed to be twice the radial change, the volumetric change is 3 times the radial change. It will be noted now that on this basis the weight changes and volume changes are of the same order of magnitude. Thus, according to figure 1, after heating at 300° C. for 30, 60, and 120 minutes, the weight changes are 30, 41, and 53 percent, respectively, and the volume changes are 20, 33, and 51 percent, respectively. Such large volume changes are surprising. On drying wood, the percentage volume change is generally less than 50 percent that of the percentage weight change. If it is assumed that additional voids are created on heating wood, then the corresponding external volume change would be expected to be a small fraction of the weight change. It must be assumed, then, that in addition to a loss of volume due to the removal of wood substance, there occurs a decrease in volume of the cell cavities, which decrease is transmitted to the external volume of the wood.

To check this, microscopic observations were made of 30-micron-thick cross sections of alpine fir, maple, and ailanthus. The latter species was chosen because of its large, easily measurable vessels. Selected cell cavities were measured before and after heat treatment. The specimens were mounted in a special microscope cell through which humidified air was passed. The specimens were first conditioned at 20 percent relative humidity, following which the tangential and the radial dimensions of each whole specimen between marked points, the tangential and the radial dimensions of several marked vessels of the hardwoods, and of several marked lumina of tracheids of the softwood were measured with an ocular micrometer. The specimens were then conditioned at 90 percent relative humidity, measured, and again conditioned at 20 percent relative humidity and measured. The sections were placed between pieces of platinum gauze to keep them flat and were heated in a jacketed tube (Abderhalden flask) with nitrobenzene vapors (206° C.) for various periods of time. After cooling, they were again placed in the microscope cell and taken through a 20 to 90 percent relative humidity cycle to

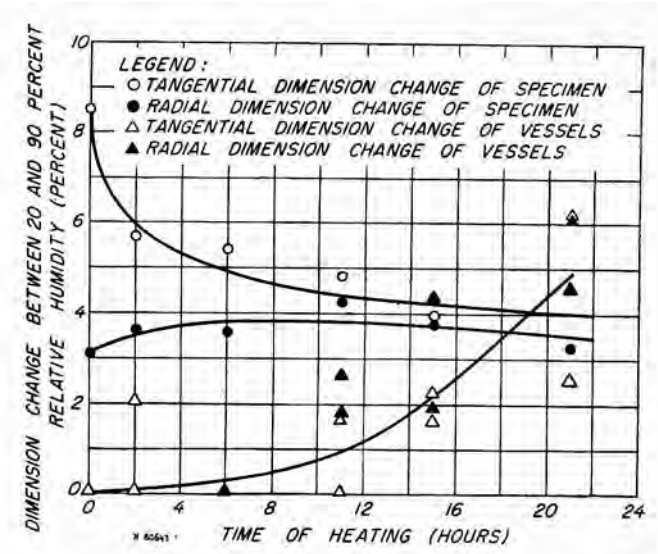

Figure 10.—Effect of heating 30-micron cross sections of sugar maple at 206° C. for different periods of time upon the subsequent dimension changes of the specimen and of the vessels between 20 and 90 percent relative humidity.

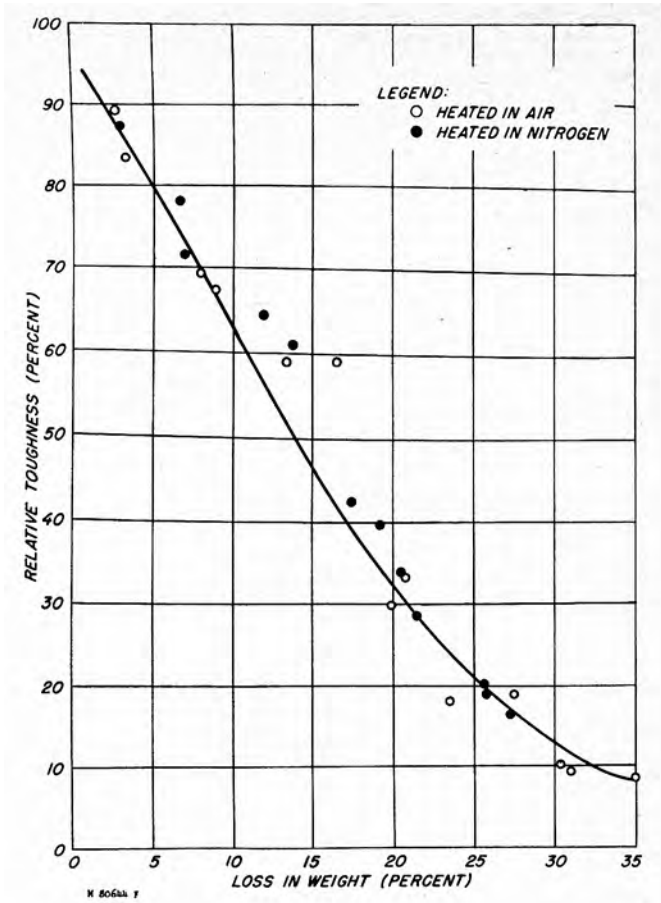

Figure 11.—Relationship between relative toughness (ASTM method) and weight loss for ponderosa pine sapwood cross sections that were heated at 300° C.

release thermal stresses resulting from heating. The specimens were then measured while at equilibrium with 20 percent and 90 percent relative humidity.

Figure 9 gives the dimension changes of sugar maple heated in air at 206° C. for different periods of time. The vessels show a definite decrease in diameter due to heating, which is somewhat less than for the specimens as a whole. The same is qualitatively true for the lumina of the softwood specimens, which, because of their smaller size, could not be measured with as great accuracy. Thus the cell cavities do decrease in size on heating. The externally observed decrease in volume must be due to both a removal of wood substance from the cell walls and to the decrease in volume of the cell cavities. It is not very likely that additional void volume is created in the cell walls.

The experiment was repeated with the cross sections heated after thorough evacuation with a high vacuum pump. For a given period of heating, these specimens did not darken as much as did the specimens heated in the presence of air. The decrease in tangential dimension of both the whole specimen and of the cell elements was less than that of the specimens heated in the presence of air; however, the ratio of the decrease in tangential dimension of the whole specimen to that of the cell cavities was approximately independent of whether the specimen was heated in the presence or absence of air. Had the heat treatment of the evacuated specimen been continued until it had darkened to the same degree as the specimen heated in air (that is, until the weight losses were the same), the reductions in dimensions of the whole wood and of the cell cavities would very likely have been the same as those of the wood heated in air.

Figure 10 shows the dimension changes of the maple specimens as a whole and of the vessels between 20 and 90 percent relative humidity for unheated specimens and specimens heated for several different periods of time at 206° C. Heating up to 10 hours had but a slight effect upon the subsequent change in dimensions of the vessels, whereas continued heating caused larger relative dimension changes than occurred in the specimens as a whole.

Different pores do not change dimensions by the same amount. Pores nearest to the annual rings, in general, change more than those somewhat removed from the annual rings. This same phenomenon has been observed for the lumina of unheated wood (1, 5), in which case stresses caused by different swelling tendencies of the different zones within the annual ring cause individual lumina to respond differently, even though statistically they do not change significantly in size with swelling and shrinking of the wood.

Similar results were obtained with other samples of sugar maple and with ailanthus.

Dimension changes for the lumina of the softwood, because of their smaller size, could not be followed as accurately as the dimension changes of the vessels. Qualitatively, however, the results appear to be similar.

It is thus apparent that with variations in relative humidity, not only is the corresponding dimension change of the cavities in unheated wood small, but it is also small for cavities in mildly heated wood. With prolonged heating, however, the dimension changes of the cell cavities become pronounced with variations in relative humidity. Perhaps this accounts for the peculiar behavior of the relative swelling curve in figure 1. After mild heating, the cell cavities do not change in size on exposing the wood to different relative humidities. In such wood, the reduced swelling tendency is due to the reduced hygroscopicity of the wood substance. With prolonged heating, some of the restraints to dimension change of the cell cavities are removed. Although the swelling tendency of the wood substance is reduced, this is more than compensated for by the pronounced

Table 3.--Effect of heating wood in molten metal upon the abrasive wear and hardness modulus

Species	Temperature	Time	Approximate anti-shrink efficiency	Wear due to abrasion[1]	Hardness modulus (14)
	° C.	Min.	Percent	Inches per 1,000 revolutions	P.s.i.
Douglas-fir...	.....	0	0	0.05	2,580
Do.....	250	3	20	.06	2,730
Do.....	300	3	40	.09	2,520
Yellow birch..	.....	0	0	.02	5,450
Do.....	250	3	20	.05	5,720
Do.....	300	3	40	.07	5,310

[1]Measurements made on Navy abrader (2).

Table 4.--Effect of heating basswood in air and in a bomb with steam upon the abrasive wear

Heating medium	Temperature	Time	Approximate anti-shrink efficiency	Wear due to abrasion[1]
	° C.	Min.	Percent	Inches per 1,000 revolutions
.....	.....	0	0	0.10
Air.....	300	10	45	.29
Do.....	300	20	50	.42
Do.....	300	60	40	.78
Steam.....	193	5	10	.22
Do.....	193	30	15	.18
Do.....	193	240	20	.21

[1]Measurements made on Navy abrader (2).

increase in dimensions of the cell elements during swelling. This increase in dimensions of the cell cavities is transmitted to the external dimensions and is reflected in an increase in relative swelling. The swelling of severely heated wood is comparable to the swelling of a film of gelatin having a hole in it. The hole gets larger during swelling, as do the cell cavities during swelling of the wood. No explanation can be offered for the difference in bestill or of the relative swelling curves for wood heated in air (fig. 1) and for wood heated in nitrogen (fig. 2).

A few tests were made, while it was sill thought that the loss of water caused ether cross bridges to form between cellulose chains, to see if boron trifluoride added to the sealed bombs in which wood was heated, might catalyze the desired reaction. The data in figure 6[4] show that the same anti-shrink efficiency is obtained per unit weight loss as for the controls, even though the rate of loss of weight was accelerated. There is thus no advantage in, adding boron trifluoride.

[4] Thanks are due to Dr. M. A. Millett for obtaining these data.

Effect of Heat Upon the Toughness and Abrasion Resistance of Wood

Figure 11 gives the relative toughness (ASTM method) versus the weight loss for wood heated at 300° C. for various periods of time. It shows that there is no significant difference in the results obtained by heating in air and by heating in nitrogen. Specimens heated in air, in nitrogen, and in sealed bombs so as to give weight losses significantly grea:er than tho e at which the curve of figure 6 diverge, became so brittle that they were difficult to handle without break-

ing. Hence no measurements were made on such specimens:

Wood heated so as to attain a practical antishrink efficiency, between 28 and 45 percent, undergoes a weight loss of 10 to 20 percent (fig: 6). This corresponds to relative toughness values of 63 to 32 percent. As in the case of formaldehyde-treated wood *(12),* the toughness loss is, however, presumably due to a break-down of the cellulose chains rather than to a stiffening of the fiber.

This type of embrittlement is much more serious than that caused by stiffening of the fibers by resin treatment *(3)*, as is shown by the loss in abrasion resistance. Tables 3 and 4 show that wear under abrasive action increases greatly on heating: Wood that gives an antishrink efficiency of 40 percent on heating abrades 1.8 to 3.5 times as readily as the unheated wood. In contrast, resin treatment causes only a slightly greater rate of wear under abrasion conditions than that for the untreated wood:

Table 3 also gives values for the modulus of hardness *(14).* The hardness is at first increased somewhat on heating. Very little loss in hardness occurs even after heating under conditions that give a 40 percent antishrink efficiency. It has been claimed that for normal wood, hardness is a good index of the abrasion resistance. In the case of heated wood this statement is far from true.

It has been previously shown that the modulus of rupture and modulus of elasticity in bending are not seriously reduced when wood is heated to obtain a significant antishrink efficiency *(4, 8).* Qualitative tests indicate that the shear strength of wood may be as seriously reduced by heating as the toughness and the abrasion resistance. On account of the serious loss in these three properties, it is not probable that stabilizing the dimensions of wood by heating will find many commercial uses, especially as no technique for avoiding the embrittlement and poor abrasion resistance have been found.

Conclusions

It has been shown that the dimensional stabilization of wood caused by heating under more drastic conditions than those used in seasoning is not due to an ether cross-linking reaction, as was earlier supposed:

Data for the heating of both paper and wood in the presence and in the absence of air indicate that air is not needed to cause dimensional stabilization. Up to a weight loss for wood of about 20 percent, the reduced hygroscopicity and dimension changes are dependent upon the weight loss and not upon the medium in which the wood is heated. The presence of air, however, does accelerate other secondary changes, such as changes in strength, and on prolonged heating it causes. a reversal in the stabilization.

Antishrink efficiencies exceeding about 45 percent are not obtainable by heating either in air or in nitrogen. Wood heated in nitrogen, unlike that heated in oxygen, maintains this optimum antishrink efficiency on prolonged heating even though the wood continues to lose weight. Higher antishrink efficiencies can be attained by heating in a closed system: For any one temperature, a constant weight loss and antishrink efficiency are rapidly attained, which do not increase with time. Presumably, when the reaction products are not removed from the reacting system, a decomposition equilibrium is attained.

If moisture is present, the same equilibrium values are usually attained at high temperatures as when moisture is absent, but at a more rapid rate, presumably because of the improved heat transfer. At lower temperatures (160° to 205° C.), the presence of moisture in the wood at the time of heating causes the attainment of a lower antishrink efficiency than when the wood is heated in the dry condition. The reason for this is still unknown:

The percentage loss of volume on heating is unusually large: This contraction must be due in part to a reduction in the volume of the cell cavities. Microscopic observations have shown that the cell cavities do decrease in dimensions during heat stabilization. For a given loss of weight, the reduction in size of these cavities seems to be independent of whether heating is done in the presence or absence of air: It is not necessary to assume the formation of submicroscopic voids in the cell walls, since such formation would require that the reduction in size of the cell cavities be greater than is actually observed.

The great loss in toughness and in abrasion resistance and probably in the shear resistance of wood that has been given a significant dimensional stabilization by heating, does not appear to be due to oxidation, but it is inherently associated with the other chemical reactions that cause dimensional stabilization. Unless some way can be found to separate the dimension-stabilizing from the embrittling reactions, which does not seem probable at present, the commercial use of wood stabilized in this way will be quite limited.

Literature Cited

1. Beiser, W: Kolloid Z. 65:203 (1933).
2. Cizek, A. W:, Jr., Kailas, D: H., and Nesttem, H. Amer: Soc: Testing Materials Bull. 132 (1945):
3. Erickson, E: C. 0. U. S: Forest Products Laboratory Rept. R1639 (1947):
4. MacLean, J. D. U. S. Forest Products Laboratory Rept: R1471 (1945).
5. Schwalbe, C: G., and Beiser, W. Papier-Fabr. 50:655 (1933):
6. Stamm, A. J. U: S. Patent 2,296,316 (1942)
7. _____, "Wood Chemistry," ed. by L. E: Wise, Pt. IV, p. 464, Reinhold Publishing Corp. (1944):
8. _____, Burr, H. K., and Kline, A. A. Ind. Eng: Chem: 38:630 (1946):
9. _____, and Hansen, L: A. Ind. Eng. Chem. 29:831 (1937):
10. _____, and Seborg, R: M. Ind. Eng. Chem. 28:1164 (1936).
11. ____ , and Tarkow, H. J. Phys. Colloid Chem: 31:493 (1947):
12. Tarkow, H: and Stamm, A: J. Forest Products Research Soc. V. 3: No. 2 (1953).
13. Tiemann, H: D: Lumber World Review 28:(7) 10 (1915).
14. Weatherwax, R. C:, Erickson, E. C. O., and Stamm, A: J: Amer. Soc. Testing Materials Bull: 153, 84 (1948):