DIMENSIONAL STABILIZATION OF WOOD BY VAPOR PHASE CHEMICAL TREATMENTS[1]

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ABSTRACT

White pine and Engelmann spruce cross sections (approx. 1¾ × 1¾ × ⅛ inches) were treated under various conditions of time, temperature, and moisture content by a vapor phase technique incorporating a number of different reactants. Two of the reactants considered, acetic anhydride and butyl isocyanate, reacted readily with the cell wall material of the wood samples and improved the dimensional stability of the wood by as much as 75%. Sticks 5 × ⅜ × ⅜ inches, with improved dimensional stabilities after reaction of 67%, gave losses in toughness and abrasion resistance of less than 25%. Generally less successful than the butyl isocyanate treatments were those with allyl, t-butyl, ethyl, and phenyl isocyanate.

INTRODUCTION

The hygroscopicity of cellulosic material results in dimensional changes with changes in the surrounding relative humidity. Greater commercial application would undoubtedly be realized and less difficulty would be experienced in many present applications of wood if methods providing adequate control over its swelling and shrinking were to be developed which were not prohibitively costly or detrimental to its strength.

A rather extensive discussion and literature review on the subject of dimensional stabilization of wood and on various techniques capable of imparting dimensional stability are given by Stamm (1964). The method of interest in this research is "bulking," which simply involves depositing nonvolatile materials in the cell walls of fibers when they are in a swollen or partially swollen state so that the cellulose chains in the fiber walls are kept separated as the swelling agent is removed. Thus dimensional stabilization effected by bulking results from restricting the degree of shrinkage rather than the degree of swelling.

The bulking agent may react with the cell wall material as in the reaction of acetic anhydride with the available hydroxyl groups of amorphous cellulose, or it may merely involve deposition of water-soluble salts, sugars, or low-molecular-weight polymers within the cell walls of the fibers (Stamm 1959, 1964). In this research, wood samples were exposed to the vapors of a number of reactants, including acetic anhydride and various isocyanates. Subsequent determinations of the effects of these treatments on the dimensional stability of the samples were made. A vapor phase technique was used in order to reduce problems involving excess chemical take-up during treatment and removal afterward, factors of primary importance in industrial applications.

MATERIALS AND EXPERIMENTAL METHODS

Treating Cell

All treatments reported in this study were conducted in a closed disk-shaped cell with inside diameter of 6¼ inches and depth of 1 inch. The cell was constructed of an aluminum alloy having good resistance to acetic anhydride and acetic acid. An aluminum platform which supported the samples over the treating solution inside the cell contained 33 holes of ⅛ inch radius which permitted the vapors of the solution to move readily through the platform to

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the samples. The cover of the cell was closed tightly by means of wing nuts which screwed on to ten 3/16-inch diameter stove bolts extending through the wall of the cell. The mating surfaces of the cell body, cover, and Teflon gasket were grooved to aid in obtaining an effective seal. A handle which could be attached to the cell before treatment and removed afterward provided a means of easily submerging the cell in, and withdrawing it from, an oil bath, where it rested in a horizontal position during the treatments. The oil bath was equipped with a stirrer, two 500-watt heating coils, and a temperature controller.

Dimensional Stability Tests

White pine (*Pinus strobus* L.) and Engelmann spruce (*Picea engelmann* (*Parry*) *Engelm.*) cross sections, 1/8 inch thick by approximately 1¾ by 1¾ inches in the radial and tangential directions, were used in the study of the effects of the reactions on dimensional stability. They were cut from carefully selected, defect-free specimens of sapwood 1 to 2 ft long with annual rings parallel to two opposite faces. The order of the cross sections from each specimen was maintained during cutting so that optimum matching could be attained in each series of tests. The bulk specific gravity (dry volume basis) of the original white pine specimens varied from 0.34 to 0.42 and the spruce from 0.33 to 0.34. All samples were identified by sets which came from the same original specimen so that variations in dimensions and densities between sets would not confuse the comparison of treatment effects.

Two cross-sections selected from adjacent positions in the original specimen were used in each treatment. A cross-section to serve as a control was taken from the position between every two pairs of cross-sections designated for treatment. After selection, the samples were dried in a forced-convection oven at 110 C for 4 hr. The oven-dry weight of the samples was then determined to one-thousandth of a gram, and the radial and tangential dimensions to one-thousandth of an inch with a dial gauge. The dry samples were stored in desiccators containing calcium chloride for later treatment. A number of samples to be treated at moisture contents other than oven-dry were stored, over saturated salt solutions or in a conditioned laboratory maintained at 50% relative humidity. Conditioned samples were weighed again before treatment to determine their actual moisture content.

Treatment of the cross sections was carried out with the vapors from 20 ml of reactant solution in the bottom of the cell. The amount was increased to 40 ml for the stick form specimens, as discussed later. (All solution compositions given in this paper are on a per cent by volume basis.) After the assigned treating time, the cell was withdrawn from the bath, cooled in running water for 5 min, emptied and cleaned. After removal from the cell, the cross-sections treated with isocyanates and their controls were washed by soaking in dimethyl formamide for 4 hr, acetone for 1 hr, and water for 12 hr. Acetylated samples were soaked only in water for 12 hr. They were then placed between flat aluminum screens and allowed to air-dry for at least 24 hr before being dried in an oven for 4 hr at 110 C. The dry wood samples were weighed to determine the extent of reaction, and their tangential and radial dimensions were measured. The controls generally lost 1 to 2% in weight because of washing; therefore, the weight loss in per cent of the controls was added to the net weight gain of the corresponding treated samples to give the gross weight gain, which was taken as a measure of the extent of reaction.

The swollen dimensions of the cross sections were measured after the sections had been soaked in distilled water for 24 hr. The per cent swelling of the samples and the anti-shrink efficiency (ASE) obtained by treatment were calculated according to the following equations:

$$\% \text{ directional swelling} = \frac{\left(\begin{matrix}\text{swollen dimension} \\ - \text{dry dimension}\end{matrix}\right)}{\text{dry dimension}} \times 100\%$$

TABLE 1. *Effect of temperature on the vapor phase acetylation of oven-dry white pine cross sections*[1]

Temperature (C)	Weight increase (%)	Antishrink efficiency (%)
110	14.1	43.2
120	17.8	53.3
130	20.5	56.2

[1] Treated with acetic anhydride vapor only for 60 min.

TABLE 2. *Effect of moisture content on the vapor phase acetylation of white pine cross sections*[1]

Moisture content[2] (%)	Weight increase (%)	Antishrink efficiency (%)
0.0	19.8	61.5
4.8	19.0	59.5
11.6	18.1	58.8

[1] Treated with acetic anhydride vapor only for 60 min at 130 C.
[2] Based on the oven-dry weight of the wood.

$$\% \text{ volumetric swelling } (S) = R + T + RT/100$$

$$\% \text{ ASE} = \frac{\left(\begin{matrix}S \text{ of the control} \\ - S \text{ of the treated sample}\end{matrix}\right)}{S \text{ of the control}} \times 100\%,$$

where R = % radial swelling
T = % tangential swelling

Toughness and Abrasion Tests

Five-inch long sticks of white pine and spruce having rings parallel to two opposite faces and radial and tangential dimensions of ¾ inch were used for toughness and abrasion tests. The specific gravity of the pine sticks varied from 0.40 to 0.45 and that of the spruce from 0.33 to 0.34.

The 5-inch samples for treatment and subsequent strength tests and their controls were selected randomly. These samples were dried for 6 hr at 110 C. After their dry weight and dimensions had been recorded, they were stored in desiccators over calcium chloride before treatment. All strength specimens were treated at this dry condition.

The pine sticks were treated at 130 C with vapors of a solution containing 85% acetic anhydride and 15% dimethyl formamide. Spruce sticks were treated at 130 C with vapors of a solution containing 65% butyl isocyanate and 35% dimethyl formamide. A number of these treated samples were cut into five 1-inch sections which were used to determine the variation of specific gravity and dimensional stability from end to end.

The acetylated samples and the corresponding controls were washed by soaking in water for 12 hr; the samples treated with the isocyanate solution and controls were washed by soaking for 4 hr in dimethyl formamide, 1 hr in acetone, and 12 hr in water. These samples were conditioned for 7 days to a moisture content in equilibrium with 50% relative humidity. The conditioned samples were tested for toughness on a Forest Products Laboratory Intermediate Toughness Tester using the weight in the low position, 4-inch span and 60° angle. The pull was in the tangential direction. One-inch sections were cut from the ends of the broken toughness samples and were abraded with the abrasion tester devised by Loos (1966). This tester consisted of a disk wood sander mounted on a lever arm designed to apply a 500 g load on the test specimen. The sander was geared down to 85 rpm. The radial surface of the specimen was abraded using no. 80 grit disks. The abrasion resistance of the samples was taken as the reciprocal of the change in tangential dimension after 200 revolutions.

RESULTS AND DISCUSSION

Treatment with Acetic Anhydride

Most of the work reported in the literature on the acetylation of wood has been liquid phase, or partially liquid phase, as in the impregnation of wood with a swelling agent or catalyst and then exposure to vapors of acetic anhydride. Any impregnation step which involves extreme liquid absorption generally requires a considerable time and results in a waste of chemical. For this reason, acetylation was included in this study to determine its applicability to a completely vapor phase, relatively high

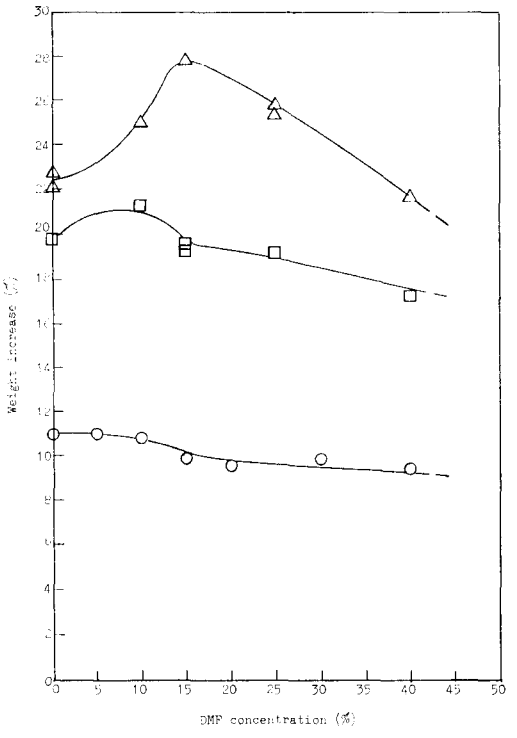

FIG. 1. Relationship between the per cent weight increase of oven-dry white pine cross sections and the concentration of DMF in the liquid treating solution for vapor phase acetylation at 130 C. Circles: 20-min treating time, Set A samples. Squares: 60-min treating time, Set B samples. Triangles: 120-min treating time, Set B samples.

temperature system. It was also included as a means of judging the performance of the other reactions investigated.

Results of acetylation reactions conducted between 110 and 130 C are given in Table 1. The normal boiling points of acetic anhydride and dimethyl formamide (DMF) are 140 and 153 C, respectively. The relationship between treating rate and temperature would be expected to vary appreciably with treating time, *i.e.*, at lower levels of treatment, the effect of increasing temperature on the rate should be more pronounced.

The effect of sample moisture content on the extent of acetylation is shown in Table 2 for several 60-min treatments. Increasing the moisture content of the cross sections before treatment caused a decrease in the concentration of the acetic anhydride in the wood and in the vapor surrounding the wood during treatment and resulted in a slight decrease in the reaction rate. The rate-depressing effect of the moisture is not serious. It is evident that air-dried wood which generally has a moisture content of less than 15% can be acetylated readily. However, because of the reaction of the anhydride with water to form acetic acid, it is desirable to have the moisture content as low as possible.

Dimethyl formamide (DMF) is miscible with acetic anhydride and lends itself readily to a one-step vapor phase treating process (1957). The effect of varying the concentration of DMF in the liquid acetylating solution on the degree of reaction for three different treating times is shown in Fig. 1. For the lower degrees of reaction, DMF exhibited little influence on the reaction except at higher concentrations where the corresponding reduction in anhydride concentration reduced the reaction rate. DMF concentrations up to 15% exerted a slight positive effect on the 60-min reaction and concentrations up to 35% considerably increased the degree of reaction for treatments for 120 min. The appearance of a maximum in the curves and the shift of this maximum toward 15% DMF with increasing reaction times suggests that the factor controlling the extent of the reaction is the degree to which the cell wall structure is opened up, *i.e.*, the number of reaction sites or hydroxyl groups exposed. It is felt that at shorter reaction times the acetic acid formed as a by-product of the acetylation of wood swells the amorphous cell wall material and exposes a sufficient number of hydroxyl groups to permit a weight increase of approximately 20%. As is shown by Fig. 2, acetylation without DMF proceeds very slowly above 20% weight increase, whereas acetylation incorporating 15% DMF in the liquid reaction solution continues quite rapidly toward 28% weight increase. Measurement of the volumetric swelling of white pine cross sections from oven dry to saturation in acetic acid, acetic anhydride, and DMF showed that the swelling of the

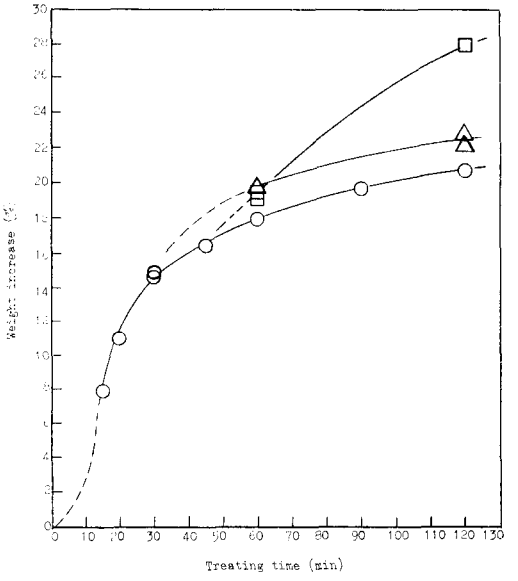

FIG. 2. Relationship between the per cent weight increase of oven-dry white pine cross sections and the treating time for vapor phase acetylation at 130 C. Circles: Set A cross sections, 0.0% DMF. Triangles: Set B cross sections, 0.0% DMF. Squares: Set B cross sections, 15.0% DMF.

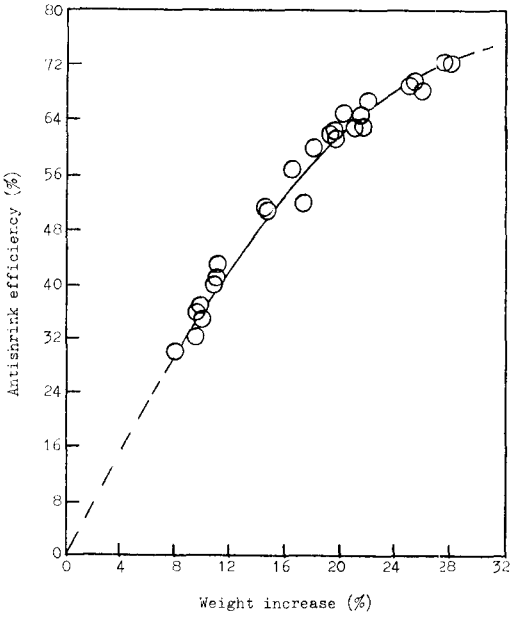

FIG. 3. Relationship between the antishrink efficiency and the oven-dry weight increase of white pine cross sections upon acetylation.

cross sections in these chemicals relative to that in water was 87% for acetic acid, 20% for acetic anhydride, and 133% for DMF.

The relationship between the antishrink efficiency and the per cent weight increase of the white pine cross sections upon acetylation is given in Fig. 3 and is in agreement with results reported by Tarkow, Stamm, and Erickson (1955). Approximately 30% weight increase, corresponding to about 75% ASE, appears to be the maximum obtainable by acetylation.

Table 3 shows the variation in the fiber direction of specific gravity and antishrink efficiency of two 5-inch pine sticks having different levels of treatment. The radial and tangential dimensions of these sticks were $\frac{3}{8}$ inch. The degree of treatment as reflected both by the specific gravity and the antishrink efficiency decreased from the ends to the centers of the sticks. The existence of this treatment gradient supports the conclusion of previous investigators (Goldstein et al. 1961) that vapor phase treatment of wood is probably feasible for only thin specimens. Because of the slow rate of diffusion of the reactants into the wood, treatment of thicker specimens requires a longer time and yields less uniform results.

Other investigators have shown that the physical strengths of wood are not seriously affected by acetylation and are actually improved in some cases (Stamm 1964). The toughness and abrasion resistance of 5-inch samples acetylated in this study by a vapor phase procedure are shown in Table 4. Samples treated to 43 and 67% ASE retained at least 90% of their original toughness and over 80% of their original abrasion resistance. The fact that the samples treated to 67% ASE exhibited a relative abrasion resistance of 1.09 cannot be considered significant because of the large variance associated with this group of samples.

Treatment with Isocyanates

The vapor phase treatment of spruce cross sections with phenyl isocyanate was confounded by the polymerization of this

TABLE 3. *Longitudinal variation of specific gravity and antishrink efficiency of 5-inch white pine sticks after vapor phase acetylation at 130 C*[1]

Sample	Weight increase (%)	Section[2]	Oven-dry specific gravity[3]	ASE (%)
1	13.3	1	0.42	63
		2	0.41	53
		3	0.41	47
		4	0.41	53
		5	0.42	59
2	23.9	1	0.52	73
		2	0.49	70
		3	0.49	71
		4	0.48	64
		5	0.49	80

[1] The liquid acetylating solution consisted of 15% DMF and 85% acetic anhydride; treating times were 2 hr for sample 1 and 5 hr for sample 2.

[2] Sections were 1 inch long and were numbered consecutively from end to end of the stick.

[3] The oven-dry specific gravity before treatment of sample 1 was 0.40 and that of sample 2 was 0.42.

chemical on the inside of the treating cell and on the surfaces of the wood samples. Because of this polymerization, the results for any given set of treating conditions were unpredictable. The phenyl isocyanate did not polymerize appreciably unless DMF was present in the treating solution; however, without DMF the cross sections would remain unswollen and the isocyanate could not enter and bulk the wood structure. Although this one-step treating process was unsatisfactory, samples which were soaked in DMF prior to treatment with vapors of phenyl isocyanate exhibited a bulking effect of the order expected from their chemical content, indicating a relatively small amount of isocyanate polymerized outside the cell walls. (A weight increase of 65% resulted in antishrink efficiencies of 77%.) The impregnation of wood samples with liquid DMF followed by exposure to phenyl isocyanate vapor was the treating procedure used successfully by Clermont and Bender (1957).

Butyl isocyanate was found to be much more adaptable to a completely vapor phase treating process than was phenyl isocyanate. Some of the conditions and results of the butyl isocyanate treatments of spruce cross sections are given in Table 5. The data indicate that the most effective concentration of DMF in the treating solution was about 35%. Only a slight change in per cent weight increase of the samples resulted from varying the DMF concentration from 25% to 45% for either the 120 min treatments or the 60-min treatments.

Table 5 shows that the cross sections, dry or containing moisture, cannot be adequately treated with butyl isocyanate unless DMF, or possibly some other swelling agent which is also a solvent for the isocyanate, is present. The moisture in one sample caused it to be partially swollen; but since butyl isocyanate is not soluble in water, the treat-

TABLE 4. *Effect of vapor phase acetylation on the toughness and abrasion resistance of white pine*[1]

	Low level treatment		High level treatment	
	Control	Treated	Control	Treated
Number of samples[2]	4	5	4	5
Treating time (min)	0	90	0	240
Weight increase (%)	0	12.4	0	23.3
Antishrink efficiency[3] (%)	0	43	0	67
Toughness (inch-lb)	11.51	10.78	10.72	9.99
Standard deviation	1.63	1.69	0.78	1.73
Abrasion resistance	22.4	18.7	20.0	21.8
Standard deviation	2.8	2.7	2.0	4.0
Values relative to controls				
Toughness	1.00	0.94	1.00	0.93
Abrasion resistance	1.00	0.83	1.00	1.09

[1] Oven-dry samples were acetylated at 130 C with vapors of an acetic anhydride solution containing 15% DMF.

[2] The samples for the two levels of treatment were from different longitudinal positions in the original specimen; however, the nine samples within each level were from laterally adjacent positions and were randomly designated to serve as a control or to be treated.

[3] Antishrink efficiencies were predicted from Fig. 3.