Chemical Modification of Wood with Alkylene Oxides, Vinylpirrolidinone and Furans : Effects on Dimensional Stabilization [*2]

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SUMMARY

The effect of propylene oxide, butylene oxide, furan resin, and vinylpyrrolidinone in controlling wood dimensional stability have been examined. Wood in the green or ovendry condition was treated with various chemical treatments using a vacuum-pressure procedure, and treated specimens were tested for tangential sweelling, moisture gain, and changes in sorption hysteresis. Results' indicate that propylene oxide, and butylene oxide enhanced with the crosslinking agent trimethylol propane trimethacrylate and applied to ovendry wood were the most efficient chemical treatments in controlling tangential sweeling caused by liquid water or water vapor, and in reducing water vapor adsorption. The sorption behavior of treated wood as depicted by the ratios of sorption was "very favorable" in most instances. In the particular case of furan resin treatments, ratios of sorption were improved from 25 to 100 percent as compared to those of untreated wood.

KEYWORDS

A/D ratios, antiswelling efficiency, chemical efficiency ratio, moisture excluding coefficient, ratio of sorption, sorption hysteresis.

At the present time, the forest products industry is experiencing an accelerated trend toward the replacement of plywood and lumber by composite products. Profit opportunities exist in replacing plywood applications in house construction and other industrial uses. The availability and the attendant price increases of the raw material for plywood coupled with refinements in composite products technology have made these developments possible.

Additional opportunities to replace lumber in certain applications have become evident. With the growing shortage of high quality knot free timber the need for improved wood fiber-based products that are uniform in strength, dimensionally stable, and that can be better engineered for the particular end use has become apparent. A key requirement — and one of the most difficult to achieve economically — has been dimensional stability.

Dimensional instability of wood and wood products due to relative humidity changes of the surrounding atmosphere has always demanded special

attention in most uses. Wide fluctuations in swelling and shrinkage caused by moisture adsorption and desorption are undersirable. One example is wood and wood products used in the furniture, cabinetry and other related industries where precision dimensions, freedom from warp, and smoothness are important.

The mechanism involved in wood sweeling and shrinkage is reasonably understood. Dimensional changes in wood are attributed to the interaction of water molecules mainly with hydroxyl groups present in the cellulose, hemicellulose, and lignin. When water molecules come into contact with the wood components they become bound through hydrogen bonding (monolayer). With addition of water to the cell wall, swelling occurs proportionately to the volume of water added (polylayer), up to the fiber saturation point (FSP).

In spite of many years of research on the topic of dimensional stability, no practical treatment or procedure has proven to be widely accepted in reducing dimensional instability caused by liquid water and water vapor. The urgency of developing an effective treatment indicates the need to learn from what has been done and to explore avenues which may provide an effective means of improving the needed degree of stability to wood and wood products.

To address this problem logically, an assessment of the effect of several selected treatments on solid wood is important. This should establish whether the treatments used provide for any degree of improvement in stabilizing dimensional changes. The main objective of this study was, therefore, to generate the base knowledge necessary for subsequent applications to composite products.

REVIEW

Efforts oriented at imparting stability to hygroscopic dimensional changes in wood and wood products in the United States are over 40 years old. Most methods have attempted to accomplish one or a combination of the following: cell wall bulking, chemical crosslinking, or coating of wood. Considerable progress has been made in this period.

Most of the methods involve expensive and elaborate treatments that are difficult to apply in a commercial process such as those characteristic of the present wood processing industries.

Extensive discussion and literature reviews on the subject of dimensional stability of wood, and on various techniques capable of imparting dimensional stability is given by Kollmann et al. (1975), Rowell (1975), and Weinhaus et al. (1978).

As mentioned earlier, an effective method to stabilize wood would require blocking most of the free hydroxyls through chemical reactions with a treating reagent. The most common reactions are etherification and esterification. The best known esterification reaction is the acetylation of the hydroxyl groups with acetic acid or acetic anhydride.

Special forms of etherification are the reactions of wood with halogen derivatives of alkalyzed methoxypyridine in which the swelling and adsorption of wood are considerably reduced (Weinhaus et al. 1978). Urethane and acetal formation are also among possibilities reacting with hydroxyl groups in wood.

Another technique used for wood stabilization include impregnation with monomers followed with subsequent polymerization. The most commonly used monomers are styrene, acrylonitrile, vinyl chloride, methyl methacrylate, and vinyl acetate. They all have poor bonding affinity for wood, although graft polymerizations are possible. They all improve the strength, elasticity and swelling resistance of wood.

Some further possibilities for improvement of wood through chemical treatments include maleic acid anhydride (esterification), furfuryl alcohol, phthalic acid, propylene oxide (etherification), and isocyanates (urethane formation).

Research Objectives

This study was designed to test a selected number of chemical treatments to reduce dimensional instability of wood. The treatments were to be enhanced by a crosslinking agent or a reactant to determine if any improvements were made. The

specific objectives of this study were:

1. To determine the effect of several chemical treatments on reducing hygroscopic dimensional changes of wood.

2. To determine the effect of pre-treating the wood with dimethyl formamide (DMF) prior to the chemical treatment.

3. To assess the effect of the crosslinking agent trimethylol propane trimethacrylate (TMPTM) on improving the response of selected chemical treatments on dimensional stability of wood.

4. To study variations occurring in the rate of dimensional change and equilibrium moisture content (EMC), as well as in the sorption hysteresis of the treated wood.

EXPERIMENTAL PROCEDURES

A paper birch log was used to prepare all the specimens used in this study. Paper birch is a diffuse porous species with small earlywood-latewood variation as compared to most confierous species. These two factors would ensure a more uniform penetration of the chemicals and help reduce variation in the effects of the chemical treatments due to variations in wood characteristics. The high swelling behavoir of paper birch was also desirable.

The chemicals used were furan resin* catalyzed with 5% of a 50% solution of zinc chloride; propylene oxide and butylene oxide catalyzed with 5% of triethylamine; and vinylpyrrolidinone catalyzed with 1% of benzoyl peroxide. The treatment levels and wood moisture contents used for each chemical are shown in Table 1.

Propylene oxide, butylene oxide, and vinyl-pyrrolidinone were pure monomers. The furan resin is an experimental chemical based on bis-hydroxymethyl furan, which contains two hydroxymethyl groups on a major portion of the polymer chain. This resin has few or no difurfuryl either or difurfurylmethane homologues, which are found in significant quantities in most furfuryl based resins. A higher concentration of reactive hydroxyl groups makes this particular resin substantially more reactive than typical furfuryl alcohol

resins as reported by Leitheiser et al. (1981).

Specimen Preparation

Wood wafers 30mm x 30mm x 3mm (longitudinal x tangential x radial) were prepared from the fresh 1.5mm long birch log, as described in Figure 1. All wafers were made from sapwood,
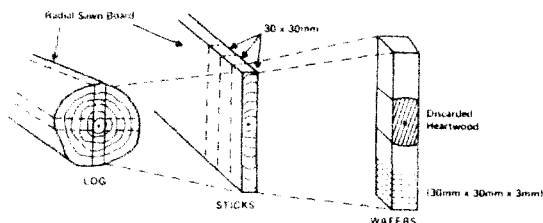

Figure 1.   Specimen preparation technique.

using a VWR Brownwill TSM 77 sawing set-up equipped with a Thurston high speed steel blade (1 mm thick), and following a technique similar to that of Bramhall and McLaughlin (1970).

Adjacent sticks from each radially sawn board, and adjacent wafers from each stick were labeled so that chemical treatments would be applied to adjacent wood wafers, thereby minimizing the effect due to difference in wood characteristics.

After preparation, wafer dimensions were measured using high precision calipers and gauges. Weight was determined with a Mettler H31AR analytical balance. Measurement accuracy was 0.00254mm and weight accuracy was 0.0001 g. Green wafers were stored in plastic bags at $2^{\circ}C$.

Specimen Treatment and Measurement

The wood was treated in batches of six wafers each. The wafers were placed in a plastic vial with small weights on top of the specimens, and the vial was placed in the treating chamber shown in Fig. 2.

The technique followed for the treatment resembles the Bethel wood impregnation method (Kollmann and Cote 1968). A 30 second 100 kPa vacuum was applied prior to introduction of the chemical. Then a 60 second 67 kPa vacuum followed by a 60 second 67 kPa pressure was maintained
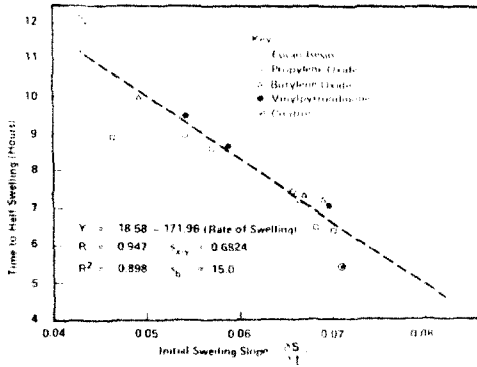
Figure 2. Treating chamber used to apply the chemical treatments.

during the treatment.

The treated wafers were then taken out of the treating chamber, the excess chemical wiped off, and the wafers wrapped in aluminum foil and placed (sandwiched) in a hotpress at 90°C for 45 minutes. A hotpress was preferred to using an oven to polymerize the chemicals in the treated specimens
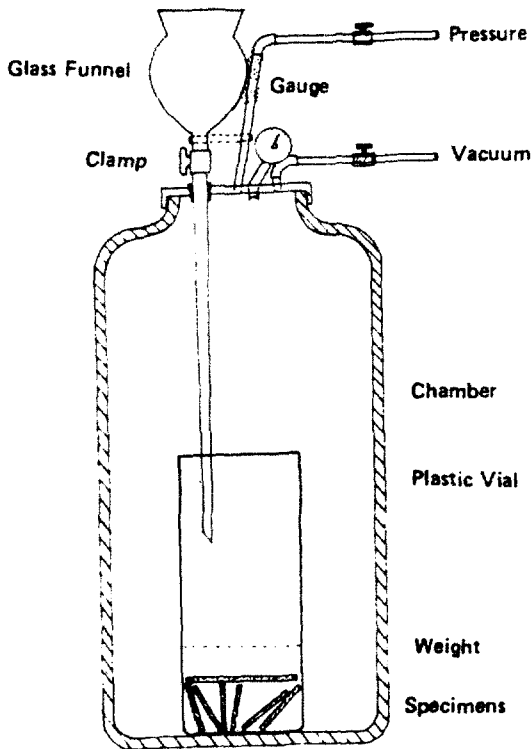

Figure 3. Specimen dimensional and weight measurements for the 76 percent relative humidity chamber.

because a hotpress would ensure a thorough and uniform application of heat to the wafers and prevent them from warping. Intimate contact of the hotpress with the wafers was achieved without the need to apply pressure. Then the wafers were transferred to a circulating oven at 104°C for 18 hours, subsequently unwrapped, and left in the oven for an additional 12 hours to ensure complete dehydration.

The ovendry wafers were remeasured and reweighed as outlined earlier, and placed in conditioning chambers at 20, 50, 76, and 90 percent relative humidity. The 76 percent relative humidity chamber was a set of eight desiccators using a saturated solution of sodium acetate anhydride. The wafers in this chamber were measured and weighed using the set-up shown in Figure 3. This set-up allowed for determining the rates of change in both the dimension and weight. All other conditioning chambers were standard laboratory units.

Data for hysteresis were collected following a procedure similar to that explained by Suchslahd (1980). The adsorption and desorption steps are shown in Figure 4. When equilibrium was reached, the specimen was measured and weighed and
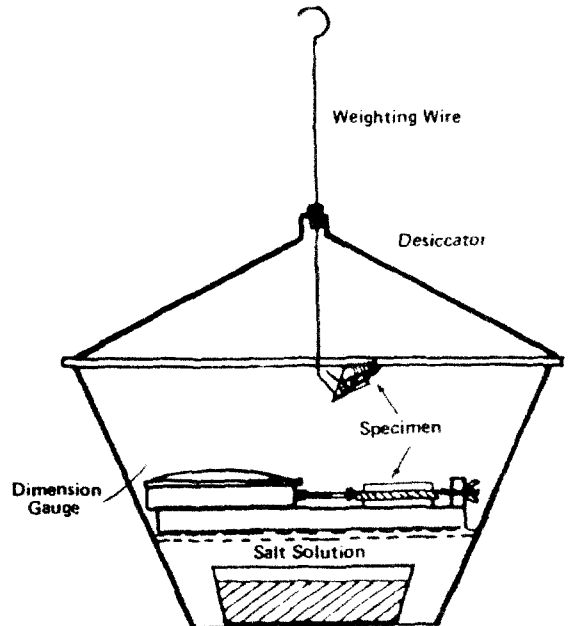

Figure 4. Adsorption-desorption steps followed in the study.

transferred to the next step.

RESULTS AND DISCUSSION

Chemical Loadings

The chemical loading is the amount of chemical that penetrated and remained in the wood specimen. The following equation was used in the calculation:

$$L = \left(\frac{W_t - W_c}{W_c}\right) \times 100 \qquad (1)$$

where:

L = chemical loading, percent

W_t = ovendry weight of treated specimen, grams

W_c = ovendry weight of control (untreated specimen), grams

Table 1. Chemical Loadings in Percent

Chemical	Treatment Level							
	40%-Green [a]	50%-Green	75%-Green	DMF 75% [b]	100%-Green	DMF-100%	100%-Dry	100% D-CA [c]
Furan Resin	3.49	6.84	9.17	4.11	—	—	—	—
Propylene Oxide	—	—	3.79	—	4.00	8.64	5.16	0.91
Butylene Oxide	—	—	—	—	2.40	5.31	3.99	0.68
Vinylpyrrolidinone	—	—	4.34	—	10.05	6.94	—	—

(a)   Signifies using a 40 percent aqueous solution applied to green wood.

(b)   Dimethyl formamide pretreatment followed by treatment with a 75 percent aqueous solution to green wood.

(c)   Addition of 5 percent of the crosslinking agent trimethylol propane trimethacrylate to the chemical and applied to ovendry wood.

Results obtained for each chemical, and treatment levels are shown in Table 1. The treated specimens were impregnated using a fixed vacuum-pressure schedule, which combined with the different viscocity of each treatment produced non-uniform chemical loadings.

Variations in viscocity, reaction rates with wood, and volatility were among the reasons for the non-uniform loadings. The greatest percentage chemical loadings were observed by vinylpyrrolidinone and the lowest ones by propylene oxide and butylene oxide.

Tangential Sweeling

Swelling is defined as the fractional or percent expansion of dry wood with an increase in moisture content. Conversely, shrinkage is the contraction of wood due to a loss in moisture below the FSP. Both swelling and shrinkage are linearly related to the equilibrium moisture content of wood (EMC) up to the FSP (Kollmann and Cote 1968).

This study involved both swelling and shrinkage measurements. The equation used in the computation of wood swelling from an overdry condition to equilibrium at a given relative humidity is as follows:

$$S = \left(\frac{D' - D}{D}\right) \times 100 \qquad (2)$$

where:

S = swelling at a given relative humidity, percent

D = ovendry dimension, mm

D' = swollen dimension at a given relative humidity, mm

For maximum sensitivity, tangential swelling was used as a measure of cell wall moisture adsorption. Absolute dimension results do not take into consideration the efficiency of each treatment in controlling tangential swelling. A simple method to measure treatment efficiency is by computing the ratio of ASE over the chemical loading. This ratio will be called the chemical efficiency ratio (CER), and computed as follows:

$$ASE = (\frac{S_c - S_t}{S_c}) \times 100 \qquad (3)$$

and

$$CER = \frac{ASE}{L} \qquad (4)$$

where:

ASE = antiswelling efficiency of a given treatment, percent

S_t = total swelling of treated specimen at a given relative humidity, percent

S_c = total swelling of the control at a given relative humidity, percent

CER = chemical efficency ratio

L = chemical loading, percent

CER results for each chemical level are shown in Table 2. Using this approach, the most efficient treatments were pure propylene oxide enhanced with the crosslinking agent and applied to ovendry wood, and butylene oxide enhanced with the crosslinking agent and applied to ovendry wood. The

Table 2. Chemical Efficiency Ratios (CER) in Controlling Tangential Swelling

Chemical	Treatment Level	ASE $_v$/L [a]	ASE ℓ/L [b]
Furan Resin	40-Green	5.87	8.47
	50-Green	6.35	5.16
	75-Green	4.36	3.93
	DMF-75	10.82	5.69
Propylene Oxide	75-Green	8.93	1.47
	100-Green	10.03	1.94
	DMF-100	5.50	0.57
	100-Dry	8.33	6.26
	100-Dry-CA	67.89*	50.20*
Butylene Oxide	100-Green	10.60	4.80
	DMF-100	6.70	2.30
	100-Dry	11.80	7.81
	100-Dry-CA	58.80*	51.50*
Vinylyrrolidinone	75-Green	7.90	6.31
	100-Green	3.27	2.78
	DMF-100	6.38	2.37

(a) Antiswelling efficiency for water vapor divided by the chemical loading.

(b) Antiswelling efficiency for watersoak divided by the chemical loading.

* Depicts highest CER responses for each case.

least efficient treatment was pure vinylpyrrolidi-
none applied to green wood. Overall, butylene
oxide was the most efficient chemical, followed
closely by propylene oxide.

A previous study, dealing with chemical im-
provement of wood swelling using alkylene oxides
(Rowell et al. 1976) used ASE as the main para-
meter to quantify the effectiveness of the chemical

treatments in controlling swelling. Treatments with
alkylene oxides such as propylene oxide and butyl-
ene oxide gave a liquid water ASE of 70 percent
at chemical loadings between 20 and 22 percent
(Rowell et al. 1976). These results would produce
a CER of approximately four, which is consider-
ably smaller than those obtained in this study
(Table 4). CER differences with Rowell's study

Table 4. Equilibrium Moisture Content of Birch Wafers Treated with Various Levels of Furan Resin,
Propylene Oxide, Butylene Oxide, and Vinylpyrrolidinone, and Exposed to Various Relative Humidites
and the Water Soaking.

| Chemical | | Relative Humidity (%) | | | | 24-hr Soaking Time |
	Level	20	50	76	90	
Furan Resin	40-Green	3.14	6.15	10.03	15.08	46.50*
	50-Green	2.88	5.80	9.25	13.82*	50.09*
	75-Green	2.13*	5.44	9.76	14.20	51.61*
	DMF-75	2.58	5.78	9.11	14.39	57.73
Propylene Oxide	75-Green	2.71	4.83*	9.66	14.78	56.93
	100-Green	1.86*	5.07	7.08*	13.48*	58.69
	DMF-100	1.92*	4.56*	6.60*	13.35*	62.93
	100-Dry	2.59	5.73	10.57	16.45	72.86
	100-Dry-CA	2.50	5.45	10.39	16.04	72.89
Butylene Oxide	100-Green	2.96	6.52	10.36	15.23	54.61
	DMF-100	2.67	5.95	9.97	15.31	59.97
	100-Dry	3.11	6.47	11.57	17.49	52.67
	100-Dry-CA	2.63	5.68	10.37	15.87	61.89
Vinyl-pyrrolidinone	75-Green	2.40	5.27	9.65	15.40	64.71
	100-Green	2.41	5.22	9.88	17.31	64.02
	DMF-100	2.13*	4.47*	8.52*	15.00	62.53
Control		3.60	7.49	12.02	18.03	55.89

* Depicts lowest equilibrium moisture contents.

are particularly large if compared with those obtain-
ed with pure propylene oxide enhanced with a
crosslinking agent or pure butylene oxide applied to
ovendry wood, and pure butylene oxide applied to
green wood. All other CER values are not as
different, especially in the case of propylene oxide.

Probable explanations for the differences be-
tween the CERs in this study and Rowell's are the

difference in testing technique, and the size of the
specimens used. The specimens used in Rowell's
study were 20 mm x 20 mm x 150 mm (radial,
tangential, and longitudinal) and were water soaked
for 7 days, while specimens used in this study were
30 mm x 30 mm x 3 mm (tangential, longitudinal,
and radial) and were soaked for 24 hours only.
Differences in results are expected under these dif-

ferent testing and specimen conditions used in both experiments. The addition of the crosslinking agent TMPTM in the present study might have also contributed to the outlined differences.

The effectiveness of propylene oxide and butylene oxide in controlling water vapor swelling is attributed to the reaction of these chemicals with available hydroxyls in the wood cell wall. This reaction produces ether bonds and imparts a high degree of dimensional stability to the wood (Rowell and Gutzmer 1975).

The addition of the crosslinking agent TMPTM to propylene oxide and butylene oxide added substantially to the efficiency of the chemical treat- ~nt in reducing water vapor swelling. According to Kenaga (1970), TMPTM is a reactive crosslink- ing agent that would increase the reaction rate of vinyl monomers. In the present case, TMPTM not only increased the reaction rate of propylene oxide, but also improved the reactivity of the chemical with hydroxyls in wood. Furthermore, TMPTM might have promoted the formation of strong and stable crosslinks thus producing high chemical efficiencies at low chemical loadings. This could _.plain the greater CER achieved by propylene oxide and butylene oxide enhanced with the cross- linking agent, in controlling both liquid water and water vapor tangential swelling.

Another factor considered in this study was the rate of change of tangential swelling over time, from the ovendry condition to equilibrium at a 90 percent relative humidity. Two important values in the evaluation of changes in tangential swelling over time are the initial slope of the change (IS) and the time to half swell (t-half). The initial swelling slope would quantify the initial rate of swelling over time, which is an important indicator of the effectiveness of a chemical treatment to control swelling. This slope was computed from plots of Δs, the fractional tangential swelling, versus time.

The t-half is an indicator of water vapor diffu- sion through the treated wood. The association of t-half with vapor diffusion is possible by using the Boltzmann's form of Fick's general diffusion law

when applied to wood, and expressed as:

$$D = \frac{\tau l^2 \Delta s^2}{16t} \qquad (5)$$

where:

D = Diffusion coefficient, in $mm^2 \ sec^{-1}$

l = Specimen dimension in flow direction, mm

Δs = Increase in tangential dimension (as a fraction of maximum dimension) in time t, in seconds

From equation (5) D is invesely proportional to t. If the remainder of the terms in equation (5) are kept constant for a defined set of experimental conditions, the values of t-half are inversely propor- tional to moisture diffusion coefficients, and may be used as an indicator of diffusion through wood, on a relative basis.

Results obtained for initial swelling slopes and t-half are given in Table 3. The highest t-half values were achieved by the furan resin treatments, indicating that the specimens treated with these chemical had the lowest vapor diffusion coefficient. Conversely, all DMF pretreated specimens generally had the lowest t-half values. A likely explanation is that the swelling characteristics of DMF (Ashton 1973) made the wood more permeable, therefore producing higher diffusion coefficients (lower t- half).

The treated specimens were exposed to various levels of relative humidity without coating any of the faces. For this reason, the diffusion coefficients obtained using the t-half method are indicators of mainly radial diffusion. The radial dimension was the smallest one, thereby being responsible for the quickest access of water vapor into the wood. A limited degree of tangential and particularly longi- tudinal diffusion was also likely.

An examination of the initial swelling slopes and t-half values given in Table 3 shows that there exists a strong negative correlation between these two factors. The statistically fitted equation for this relationship is given in Figure 5. Even though the slopes for the various chemicals are different, equation (6) is a good estimator of t-half for any of

Table 3. Fractional Swelling Date:
Initial Slope, and Time to Half Swelling Obtained from Fractional Swelling Versus Time

| Chemical | | Swelling Rates Data | | Ratio of Treated to Control T-Half |
	Level	Initial Slope	T-Half	
Furan Resin	40-Green	0.0541	8.914	1.64
	50-Green	0.0438	11.991	2.21*
	75-Green	0.0430	12.132	2.25*
	DMF-100	0.0656	7.399	1.36
Propylene Oxide	75-Green	0.0465	8.841	1.63
	100-Green	0.0680	6.442	1.19
	DMF-100	0.0842	4.492	0.829
	100-Dry	0.0703	6.316	1.16
	100-Dry-CA	0.0570	8.622	1.59
Butylene Oxide	100-Green	0.0670	7.334	1.35
	DMF-100	0.0690	7.234	1.33
	100-Dry	0.0493	9.933	1.83
	100-Dry-CA	0.0666	7.161	1.32
Vinylpyrrolidinone	75-Green	0.0545	9.415	1.74
	100-Green	0.0589	8.689	1.60
	DMF-100	0.0693	7.092	1.27
Control		0.0708	5.421	1.00

Treatments that achieved the lowest t-half as related to the control. The initial slope was obtained using fractional swelling up to 18 hours, following a least-squares technique.
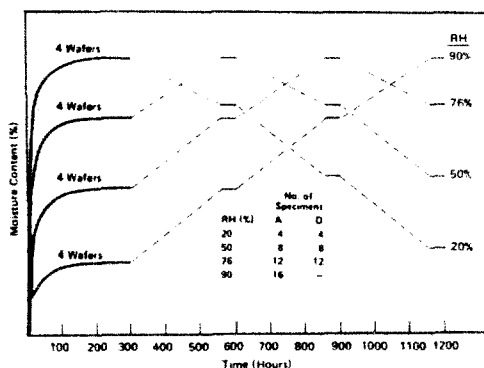

Figure 5. Relationship between initial swelling slope and time required to achieve half the total swelling.

these chemicals (Figure 5), and therefore, a good indicator of the vapor diffusion coefficients. There fore, the IS versus t-half relationship is of importance to provide an indication of water vapor diffusion into wood. The computation of the initial fractional swelling slope would require short times, making the computation of equation (6) simple, therefore providing with a valuable means to infer about water vapor diffusion in treated or untreated wood.

Moisture Content

Average adsorption EMC achieved by all chemical treatments at various relative humidity, and in watersoaking are shown in Table 4. The lowest overall EMCs for water vapor adsorption were ob-

tained by propylene oxide applied to green wood and pretreated with DMF. The lowest overall EMC in water soaking were achieved by the furan resin treatments.

An examination of watersoak EMCs for propylene oxide, butylene oxide and vinylpyrrolidinone shows that these values are generally higher than the control. However, the corresponding water vapor EMC, and most important, the corresponding water soaking swelling are lower than the control. A presumed reason for this behavior is an increase in the liquid water permeability of the wood, which could be brought about by the strong solvent action of propylene oxide, and vinylpyrrolidinone ￵ the extractives present in wood (Rowe and Conner 1979, Nicholas 1977). This could cause liquid water to enter more voids within the wood without a subsequent increase in swelling.

Propylene oxide and butylene oxide can also react with free hydroxyls present in the wood,

which could in turn improve liquid permeability, particularly in the case of ovendry wood. Therefore, there is a presumption that both of these permeability improvement methods took place during treatments with propylene oxide, butylene oxide, and vinylpyrrolidinone. This explains the unusual behavoir observed in the relationship between swelling due to water soaking and EMC, of treated and untreated specimens.

Chemical efficiency in controlling moisture sorption, as expressed by EMC, was computed in a similar fashion as for tangetial swelling. However, instead of ASE the moisture excluding coefficient (MEC) was used. MEC was computed as follows:

$$MEC = (\frac{EMC - EMC'}{EMC}) \times 100 \qquad (7)$$

where:

EMC'= equilibrium moisture content of treated specimens at a given relative humidity

Table 5. Chemical Efficiency Ratios (CER) in Controlling Moisture Content

Chemical	Treatment Level	$MEC_v/L^{(a)}$	$MEC_\ell/L^{(b)}$
Furan Resin	40-Green	3.70	4.81
	50-Green	2.89	1.52
	75-Green	2.52	0.84
	DMF-75	6.91	-0.71
Propylene Oxide	75-Green	6.83	-0.34
	100-Green	8.80	-1.25
	DMF-100	5.21	-1.46
	100-Dry	3.60	-5.88
	100-Dry-CA	31.13*	-42.83
Butylene Oxide	100-Green	4.30	0.96
	DMF-100	3.60	-1.37
	100-Dry	2.50	8.50
	100-Dry-CA	4.06	-2.69
Vinylpyrrolidinone	75-Green	5.67	-3.63
	100-Green	2.56	-1.47
	DMF-100	4.77	-1.71

(a) Moisture excluding coefficient for water vapor divided by the chemical loading.

(b) Moisture excluding coefficient for watersoak divided by the chemical loading.

* Depicts highest CER responses for each case.

EMC = equilibrium moisture content of controls, at a given relative humidity

The acronym CER (Equation 3) was also used for the resultant variable and results are shown in Table 5. The most efficient treatments in controlling water vapor adsorption were pure propylene oxide enhanced with the crosslinking agent and applied to ovendry wood, and pure propylene oxide applied to green wood. The most efficient treatment in controlling liquid water adsorption was pure butylene oxide applied to ovendry wood. Generally, efficiency in controlling water vapor adsorption was greater in the case of propylene oxide and butylene oxide. However, propylene oxide was the least efficient chemical in controlling liquid water absorption.

Comparing the CER for propylene oxide treatments in controlling tangential swelling, and reducing EMC in the case of liquid water, opposite responses are observed. The most efficient treatment in reducing tangential swelling is simultaneously the least efficient in controlling liquid water absorption. This behavoir indicates that pure propylene oxide enhanced with the crosslinking agent and applied to ovendry wood might be producing stable bonds with the wood, (which would reduce tangential swelling), and improving the liquid permeability as explained earlier (which would increase the EMC).

Sorption Hysteresis

The amount of moisture held by cellulosic materials such as wood, is not only dependent upon the equilibrium relative humidity, but also dependent upon the direction from which equilibrium is approached. This phenomena is known as sorption hysteresis, and has been extensively studied by several investigators (Spalt, 1956; Urquhart, 1960).

A more favored theory for sorption hysteresis of wood is based on the hydroxyl availablity theory, which attributes the effect to a change in the availability of polar hydroxyl groups in wood due to drying. In the original green condition, the hydroxyl groups in wood are almost entirely satisfied by sorbed water. When wood is dried, a number of hydroxyl groups are freed, and as shrinkage occurs, they are drawn closely together as to satisfy each other. Upon subsequent adsorption, part of the hydroxyls are mutually satisfied preventing hydrogen bonding with water molecules and resulting in a decreased adsorption. The process repeats itself during cycling of relative humidities, forming a more or less repetitive hysteresis loop.

The magnitude of the hysteresis effect can be expressed as the ratio of adsorption to desorption EMCs or A/D ratios. The A/D ratio varies with relative humidity reaching its lowest value around 55 to 65 percent relative humidity. However, the ratios for relative humidity between 45 and 75 percent are the most important as an indicator of wide shrinking and swelling fluctuations, because the adsorption-desorption curves are farthest apart in this region.

Lower A/D ratios indicate wider differences in the sorption isotherms. Wider differences in the sorption isotherms are good indicators of wide fluctuation in the shrinking and swelling behavoir of wood exposed to constantly changing environmental conditions. This information is particularly important in the early stages of the sorption cycles, before the sorption isotherms reach a more stable (less flucturating) loop.

A/D ratios at relative humidity of 50 and 76 percent for all chemical treatments are given in Table 6. The furan resin treatments generally produced lower A/D ratios than the control, and the vinylpyrrolidinone treatments achieved higher A/D ratios than the controls. DMF pretreated specimens in the cases of furan resin, propylene oxide, and vinylpyrrolidinone produced ratios considerably larger than the control or any other treatments.

The A/D ratios for the control are close to those found by Prichananda (1966) in a study involving yellow birch. He found A/D ratios of 0.819 for a multi-step adsorption, and 0.861 for a single-step adsorption. The similarity between the multi-step A/D ratios found by Princhananda (1966) and those found in this study indicate that

Table 6. Adsorption-Desorption Ratios for Chemical Treatments at 50 and
76 percent Relative Humidities

Chemical	Treatment Level	Adsorption-Desorption Ratios		
		50%	76%	Average
Furan Resin (FR)	40-Green	0.710	0.785	0.748
	50-Green	0.731	0.871	0.801
	75-Green	0.742	0.887	0.814
	DMF-75	0.915	0.867	0.891
Propylene Oxide (PO)	75-Green	0.752	0.917	0.834
	100-Green	0.689	0.741	0.715
	DMF-100	0.912	0.989	0.951
	100-Dry	0.753	0.837	0.795
	100-Dry-CA	0.774	0.864	0.819
Butylene Oxide (BO)	100-Green	0.748	0.802	0.775
	DMF-100	0.792	0.856	0.824
	100-Dry	0.720	0.818	0.769
	100-Dry-CA	0.749	0.859	0.804
Vinylpyrrolidinone (VP)	75-Green	0.792	0.889	0.841
	100-Green	0.806	0.924	0.865
	DMF-100	0.895	0.884	0.890
Control	–	0.811	0.835	0.823

e adsorption-desorption shcedule shown in Figure 5 and used in this study was appropriate to simulate sorption hysteresis of wood in use.

Another important variable in wood moisture sorption analysis is the slope of the sorption isotherms or what Noack et al. (1973) call the ratio of sorption. The ratio of sorption is generally computed for relative humidity between 35 and 85 percent, where the sorption isotherms could be reasonably represented by a linear relation as follows:

$$EMC = (ROS \times RH) + b \qquad (8)$$

where:

ROS = ratio of sorption

If equation (8) is rearranged, and the coefficient b (intercept) dropped from the relationship, the representation of ROS for relative humidities of 50 and 76 percent becomes:

$$ROS = \frac{\Delta EMC}{\Delta RH} = \frac{EMC76 - EMC50}{RH76 - RH50} \qquad (9)$$

If more than two terms are used in computing ratios of sorption then a least-squares fit using equation (8) is necessary. The ratio of sorption indicates the amount the EMC will change when the RH changes by $\Delta RH = 1$ percent. This ratio gives evidence of the sorption behavior of wood in the treated and untreated state.

Adsorption and desorption ratios of sorption were computed, and relative humidities of 20, 50, and 76 percent were included. However, the discussion of the results was based on the average ratio of sorption at 50 and 76 percent RH for reasons explained earlier. The average ratios of sorption for adsorption and desorption of treated and untreated (control) were computed using equation (8), and the results are presented in Table 7.

The analysis of ratios of sorption from Table 7 will be summarized in a categorization developed

**Table 7. Ratios of Sorption (ROS) Corresponding to Relative Humidities of 20, 50, and 76
percent for all Chemical Treatments**

| Chemical | Treatment Level | Adsorption | | Desorption | | A–D |
		50-76%	20-50-76%	76-50%	76-50-20%	Mean
Furan Resin	40-Green	0.149	0.124	0.158	0.149	0.154*
	50-Green	0.133	0.113	0.063	0.121	0.098*
	75-Green	0.166	0.136	0.111	0.124	0.138*
	DMF-100	0.128	0.116	0.161	0.139	0.144*
Propylene Oxide	75-Green	0.186	0.123	0.134	0.129	0.160·
	100-Green	0.077	0.106	0.193	0.176	0.135*
	DMF-100	0.078	0.084	0.064	0.080	0.071*
	100-Dry	0.186	0.142	0.193	0.161	0.190
	100-Dry-CA	0.190	0.140	0.191	0.154	0.190
Butylene Oxide	100-Green	0.148	0.132	0.161	0.154	0.154*
	DMF-100	0.155	0.129	0.159	0.149	0.157*
	100-Dry	0.196	0.150	0.198	0.172	0.197
	100-Dry-CA	0.180	0.137	0.172	0.150	0.176·
Vinyl-pyrrolidinone	75-Green	0.165	0.129	0.161	0.140	0.163·
	100-Green	0.179	0.132	0.162	0.146	0.171·
	DMF-100	0.156	0.113	0.178	0.129	0.167·
Control		0.174	0.150	0.199	0.169	0.186

*   "Very favorable" sorption characteristics.

·   "Favorable" sorption chracteristics.

by Noack et al. (1973) where the following evalua-
tion scale was established for the average sorption
behavoir:

ROS	Sorption Behavior
>0.22	Unfavorable
0.18 – 0.22	Normal (untreated wood)
0.16 – 0.18	Favorable
<0.16	Very Favorable

Following this categorization, half of the treat-
ments have "very favorable" sorption character-
istics, especially a 50 percent water solution of
furan resin applied to green wood, and propylene
oxide with a DMF pretreatment. The most ef-
ficent treatments in controlling tangential swelling,
pure propylene oxide enhanced with the crosslink-
ing agent and applied to ovendry wood, and pure
butylene oxide applied to vendyr wood have
"normal" sorpition characteristics.

Values for ratios of sorption are not common
in the literature. Most studies dealing with wood
hysteresis show the results in graphical form. How-
ever, Chomcharn (1975), and Noack et al. (1973)
presented results using ratios of sorption, and con-
cluded that the information generated is easier to
analyze and provides a better means to compare
sorption behavior among species or between chemi-
cal treatments.

Chomcharn (1975) studied the effect of the
adsorption-desorption cycling time on the value of
the ratio of sorption. He found out that as the cycl-

ing time increased the ratio of sorption decreased asymtotically, approaching a constant value. However, he notes that his results ". . . . are only about half the slopes of the static sorption isotherm in the humidity range 40-80 percent because of the hysteresis loop." When a sample is exposed to cyclically changing humidities between two fixed relative humidities, its total moisture content change may be considerably less than would be the case when the specimen is allowed to reach equilibrium. His ratio of sorption values for untreated yellow birch varied between 0.101 to 0.126. Noack et al. (1973) compiled his data from previous studies in Western Europe. He shows ratio of sorption values for treated and untreated European birch to range from 0.08 to 0.25, respectively. The treatments included were methyl-methacrylate and polyester. Ratio of sorption values for furan resin were 0.098, which is very close to the best value shown by Noack et al. (1973).

CONCLUSIONS

Results from this study indicate that propylene de, and butylene oxide plus TMPTM, applied to ovendry wood were the most efficient chemical treatments in controlling tangential swelling caused by liquid water or water vapor, and in reducing water vapor adsorption. The degree of dimensional stability gained by these treatments might indicate that there was chemical reaction between the treatments and the available hydroxyls in wood. Furthermore, there is the possibility that propylene oxide enchanced with TMPTM might have produced strong and stable chemical crosslinks, which imparted a high degree of dimensional stability at low chemical loadings. Pretreatment with DMF did not provide a greater chemical efficiency in controlling either swelling or moisture adsorption. However, DMF increased the A/D ratios indicating a reduction in the fluctuation of wood dimensions exposed to varying humidity conditions. Reasons for these increase in the A/D ratios of wood are presumed to be the powerful reactivity of this reagent and, to a limited degree, to the delayed released of free

DMF from wood over time.

The addition of the crosslinking agent TMPTM improved the response of propylene oxide and butylene oxide treatments significantly. The response was unchanged or slightly increased in all other cases.

The sorption behavior of treated wood as depicted by the ratios of sorption was "very favorable" in most instances. In the particular case of furan resin treatments the ratios of sorption were improved from 25 to 100 percent as compared to those of untreated wood. These improvements are good indicators of considerable reductions in the equilibrium moisture content of wood over a wide range of varying relative humidity conditions.

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