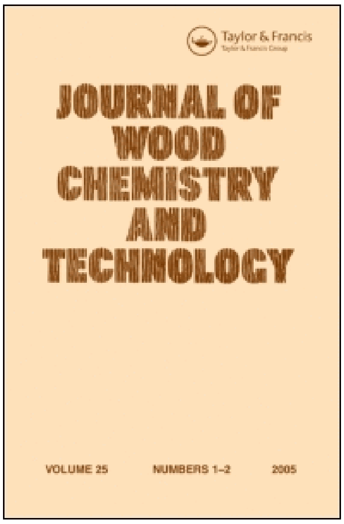

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Guevara, Ruben and Moslemi, A. A.(1983) 'Hygroexpansive and Sorptive Behavior of Wood Modified with Propylene Oxide and Oligomeric Diisocyanate', Journal of Wood Chemistry and Technology, 3: 1, 95 — 114
To link to this Article: DOI: 10.1080/02773818308085153
URL: http://dx.doi.org/10.1080/02773818308085153

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 3(1), 95-114 (1983)

HYGROEXPANSIVE AND SORPTIVE BEHAVIOR OF WOOD MODIFIED WITH PROPYLENE OXIDE AND OLIGOMERIC DIISOCYANATE

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ABSTRACT

Small wood wafers were treated chemically to reduce their hygroexpansive and sorptive behavior. Wood specimens were either ovendried or conditioned to a nominal moisture content of 12 percent, and then treated with several propylene oxide-oligomeric diisocyanate mixtures using a fixed vacuum-pressure schedule. Results indicate that all treatments used reduced the hygroexpansive and sorptive behavior of wood. Resultant anti-swelling efficiency, moisture excluding coefficients, time to half swelling, and ratios of sorption were superior when treatments were applied to ovendry in contrast to wood with an initial moisture content of 12 percent. The best treatment found in the study was a mixture of 9:1 parts of propylene oxide, and oligomeric diisocyanate.

INTRODUCTION

Use of propylene oxide as a wood dimensional stabilizer dates back to the 1960's. Liu and McMillin[1] patented a wood gas treatment using propylene oxide, and ethylene oxide as dimensional stabilizers. Their results claim anti-shrink efficiencies of up to

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80 percent at a 10 percent chemical loading with ethylene oxide but failed to disclose any findings pertaining to propylene oxide. More recently, Rowell and co-workers[2,3,4] have studied the reactivity and effectiveness of propylene oxide as a dimensional stabilizer of wood. Rowell and Gutzmer[3] claimed that the reaction between ovendry wood and propylene oxide is fast, involving formation of strong ether bonds with no by-products. Furthermore, Rowell et al.[4] reported wood swelling variations in a seven-day watersoak test at several chemical loadings using propylene oxide catalyzed with 5 percent of triethylamine. They found that anti-swelling efficiency (ASE) increases with chemical addition up to a point where additional chemical begins disrupting the wood cell wall thereby causing a deleterious response. Best ASE values between 61 to 68 percent were achieved at chemical loadings of 25 to 28 percent.

Studies using oligomeric diisocyanates (MDI) as a wood dimensional stabilizer were not found in the literature. However, a few reports mostly in the late 60's and 70's reported dimensional stability results with various kinds of isocyanates. Baird[5] reacted white pine and Engelmann spruce cross sections pre-soaked in dimethyl formamide (DMF), with ethyl, allyl, butyl, t-butyl, and phenyl isocyanate. Best results were obtained by vapor phase reactions of butyl isocyanate in DMF. ASEs of 47 percent at 14 percent chemical loading, and 67 percent at 31 percent chemical loading were found.

In a report by Rowell and Ellis[6] results from a study using 2, 4- tolylene diisocyanate[7] with pyridine were discussed. ASE of 50 percent were obtained with 21 percent chemical loadings. They also discussed results from their study using methyl isocyanate. They concluded that reaction of methyl isocyanate and southern pine wood was fast, did not require a catalyst, and formed a urethane that was stable to leaching. At chemical loadings of 16 to 28 percent, ASEs of 60 to 70 percent were obtained.

Results from recent studies by the authors[8,9] utilizing propylene oxide, and MDI as wood dimensional stabilizers, showed that these treatments produce complementary responses. On the one hand, propylene oxide enhanced with 5 percent by weight of the crosslinking agent trimethylol propane trimethacrylate (TMPTM) produced excellent efficiency in controlling swelling and water adsorption in water vapor tests. On the other hand, wood of various moisture contents treated with around 12 percent MDI produced excellent liquid water repellency and swelling control.

The main objective of this study was to build on these findings, and combine the effect of both propylene oxide and MDI to reduce wood dimensional stability and water absorption. The complementary effect of both propylene oxide and MDI was expected to provide good control of water vapor and liquid water absorption and thus a reduction in swelling.

Swelling and Moisture Relationships

Various expressions have been used to define changes in dimension with a given moisture content, including hygroexpansion coefficient,[10] coefficient of swelling[10,11] differential swelling,[12] ratio of swelling,[13] dimensional change coefficient,[14] and moisture expansion coefficient.[15] In this paper the term hygroexpansion coefficient will be used. This coefficient was defined by Noack et al.[13] as follows:

$$HEC = \frac{\partial S}{\partial M} = \frac{\sum_{i=1}^{n} (Mi - \overline{M})(Si - \overline{S})}{\sum_{i=1}^{n} (Mi - \overline{M})^2} \quad (1)$$

where:

HEC	=	hygroexpansion coefficient
$\frac{\partial S}{\partial M}$	=	change in swelling or shrinkage occurred with a change in the equilibrium moisture content
Mi	=	a given moisture content below the fsp, percent
$\overline{M}$	=	average moisture content over n given Mi
Si	=	swelling obtained at a given moisture content (Mi), percent
$\overline{S}$	=	average swelling, percent

Hygroexpansion coefficients depict relative change in swelling or shrinkage caused by a 1 percent change in moisture content. The relationship is linear over most of the hygroscopic range of moisture contents below the fiber saturation point (fsp).[12]

The relationship between equilibrium moisture content (EMC) and relative humidity is a typical characteristic of the hygroscopicity of wood. The relationship shows different responses depending if the EMC are reached in adsorption or desorption, and the combination forms a closed loop known as sorption hysteresis. Mathematical description of sorption hysteresis is complex,[17] and mostly represented in graphical form. A simple quantification such as the one suggested by Noack[13] is reliable and relatively fast.

$$ROS = \frac{\partial M}{\partial RH} = \frac{\sum_{i=1}^{n} (RHi - \overline{RH})(Mi - \overline{M})}{\sum_{i=1}^{n} (RHi - \overline{RH})^2} \quad (2)$$

where:

ROS = ratio of sorption

$\frac{\partial M}{\partial RH}$ = change in the equilibrium moisture content occurred with a change in relative humidity

i = a given moisture (M) or relative humidity (RH)

n = total number of points considered in the analysis

This relationship holds true at constant temperatures and between about 35 to 85 percent relative humidity.

In a similar manner to the ratio of sorption, changes in dimension for a particular wood species or wood are correlated with variations of relative humidity. Characterization of changes in dimension caused by changes in 1 percent in relative humidity will be called the humidity expansion coefficient (CHE). Noack et al.[13] called this the ratio of swelling.

$$CHE = \frac{\partial S}{\partial RH} = \frac{\sum_{i=1}^{n} (RHi - \overline{RH})(Si - \overline{S})}{\sum_{i=1}^{n} (RHi - \overline{RH})^2} \quad (3)$$

where:

$\frac{\partial S}{\partial RH}$ = change in swelling or shrinkage occurred with a change in relative humidity

Both the ROS and CHE show different values for adsorption and desorption. However, wood in use is usually going from adsorption to desorption and vice versa quite rapidly, which causes a phenomenon known as oscillating desorption. The average ROS or CHE values for adsorption, and desorption in experimental multi-step hysteresis would be a close approximation to expected oscillating desorption (wood in use).

RESULTS AND DISCUSSION

Chemical loadings achieved during treatment are shown in Table 1. Loadings of ovendried specimens were about twice those of specimens with a 12 percent initial moisture content. Also, the amount of chemical absorbed and reacted in ovendry specimens tended to increase with increasing amounts of MDI in the treating solution. This may indicate that the chemical accounted for in the chemical loadings was mainly MDI. This conjecture is supported by chemical loadings achieved in previous studies using identical treating conditions, with propylene oxide or MDI alone.[8,9] In those studies, maximum chemical loading achieved with propylene oxide was 4 percent[8] while with MDI the average chemical loading was around 12 percent.[9]

Tangential Swelling

The effect of the chemical treatments in controlling tangential swelling was measured by antiswelling efficiency, chemical efficiency ratio, time necessary to achieve half of total swelling (t-half), and HEC and CHE values. Results for ASE to water

TABLE 1

Chemical Loadings and Chemical Efficiency Ratios (CER) Achieved by Propylene Oxide-MDI Treatments on Wood Tangential Swelling

Chemical Treatment	Chemical Loading (%)	Chemical Efficiency Ratios for Tangential Swelling[b]	
		Water Vapor	Water-soak
PO95-MDI5-0[a]	12.8	3.40	2.17
PO90-MDI10-0	14.6	2.68	2.51
PO95-MDI15-0	15.3	2.56	1.83
PO95-MDI5-12	8.2	3.22	3.03
PO90-MDI10-12	6.1	5.19	2.28

a A mixture of 95 percent propylene oxide, and 5 percent MDI applied to ovendry wood

b $CER = \frac{\text{antiswelling efficiency}}{\text{chemical loading}}$

vapor, and watersoak exposures are given in Figure 1. Generally, ASE values were superior in water vapor compared with watersoak tests, and for ovendry over semi-moist specimens. Previous studies with propylene oxide,[8] and MDI[9] used separately, show that the alkylene oxide produced better results against water vapor adsorption and swelling control as compared to watersoak, while MDI produced similar results in controlling tangential swelling in both exposures, with the exception of treatments done on wood with a 20 percent initial moisture content.

Results shown in Figure 1 depict that best ASE were those achieved with a solution of 90 percent propylene oxide-10 percent MDI applied to ovendry wood. ASE results for this treatment are especially superior to other treatments in the exposures.

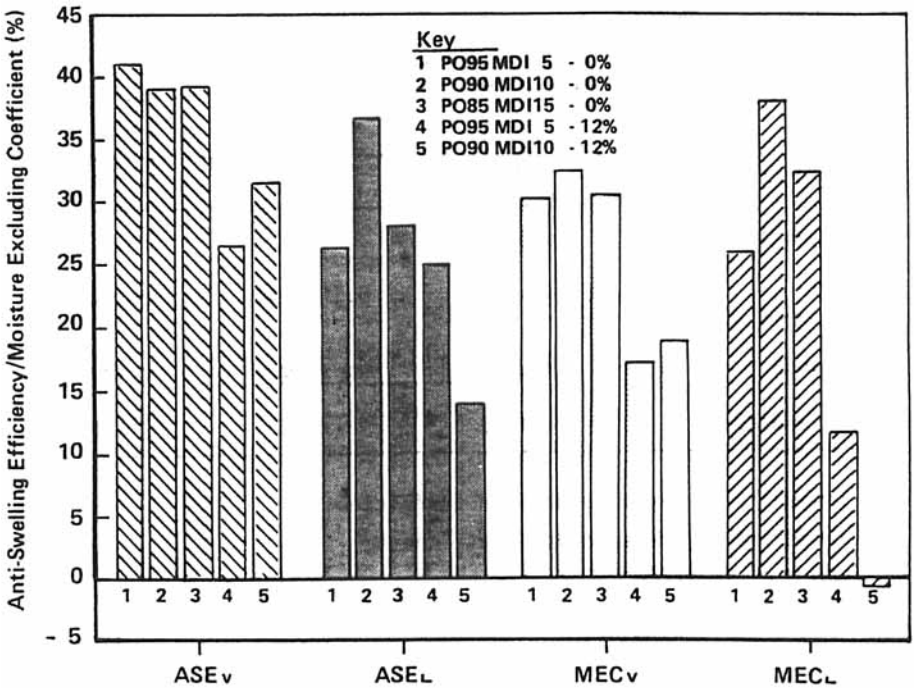

Figure 1. Water vapor, and watersoak antiswelling efficiency (ASE_v, ASE_ℓ), and moisture excluding coefficient (MEC_v, MEC_ℓ) for wood treated with solutions of propylene oxide and MDI.

Chemical efficiencies of each treatment in controlling swelling are shown in Table 1. Results in this case indicate that treatments applied to semi-moist wood were more efficient than those applied to ovendry wood. These results are opposite to those expressed by absolute ASE values. However, efficiency must also take into account values for moisture content, which will be discussed later.

Analyses of CHE, HEC, and ROS results found in this study were done based on the categorization developed by Noack et al.,[13] presented in Table 2. Adsorption, desorption, and average CHE, HEC, and ROS values are given in Table 3. Discussions of the first

TABLE 2

Categorization of Hygroexpansive and Sorptive Behavior of Treated and Untreated Wood According to Noack et al.[13]

Categorization	CHE_T[a]	HEC_T[b]	ROS[c]
Unfavorable	> 0.08	> 0.40	> 0.22
Normal (untreated wood)	0.06-0.08	0.30-0.40	0.18-0.22
Favorable	0.03-0.06	< 0.30	0.16-0.18
Very Favorable	< 0.03	--	< 0.16

[a] Tangential humidity expansion coefficient
[b] Tangential hygroexpansion coefficient
[c] Ratio of sorption

two, which represent hygroexpansive behavior of treated wood will follow. ROS results will be analyzed later under sorption hysteresis.

Most CHE and HEC values fell in the "normal" category, with the exception of the 90 percent propylene-10 percent MDI solution applied to semi-moist wood which fell in the "favorable" category. Overall, CHE and HEC values for ovendry wood were slightly larger than for semi-moist wood, and CHE values in adsorption were generally greater than values for desorption. However, net differences in CHE and HEC values were small and of no major importance for wood in use.

Values for t-half in swelling achieved from the ovendried to equilibrium conditions in a 90 percent relative humidity chamber varied from 1.6 hours for the control to 18.2 hours for the 90 percent propylene-10 percent MDI solution applied to ovendry wood (Figure 2). Lowest t-half, 10.3 hours, was obtained with the same solution applied to wood with a 12 percent initial moisture

TABLE 3

Humidity Expansion and Hygroexpansion Coefficients, and Ratios of Sorption for Wood Treated with Solutions of Propylene Oxide and MDI

Chemical Treatments	Adsorption			Desorption			A/D Average		
	CHE[a]	HEC[b]	ROS[c]	CHE	HEC	ROS	CHE	HEC	ROS
PO95-MDI5-0[d]	0.0611	0.366	0.167	0.0599	0.349	0.172	0.0605	0.358	0.170
PO90-MDI10-0	0.0624	0.370	0.169	0.0603	0.348	0.173	0.0614	0.359	0.171
PO85-MDI15-0	0.0624	0.349	0.179	0.0618	0.340	0.182	0.0621	0.344	0.181
PO95-MDI5-12	0.0603	0.380	0.159	0.0611	0.319	0.192	0.0607	0.350	0.176
PO90-MDI10-12	0.0555	0.342	0.162	0.0636	0.337	0.189	0.0596	0.340	0.176
Control	0.0644	0.342	0.188	0.0654	0.357	0.206	0.0650	0.350	0.197

[a] Humidity expansion coefficient

[b] Hygroexpansion coefficient

[c] Ratio of sorption

[d] A solution of 95% of propylene oxide and 5% MDI applied to ovendry wood

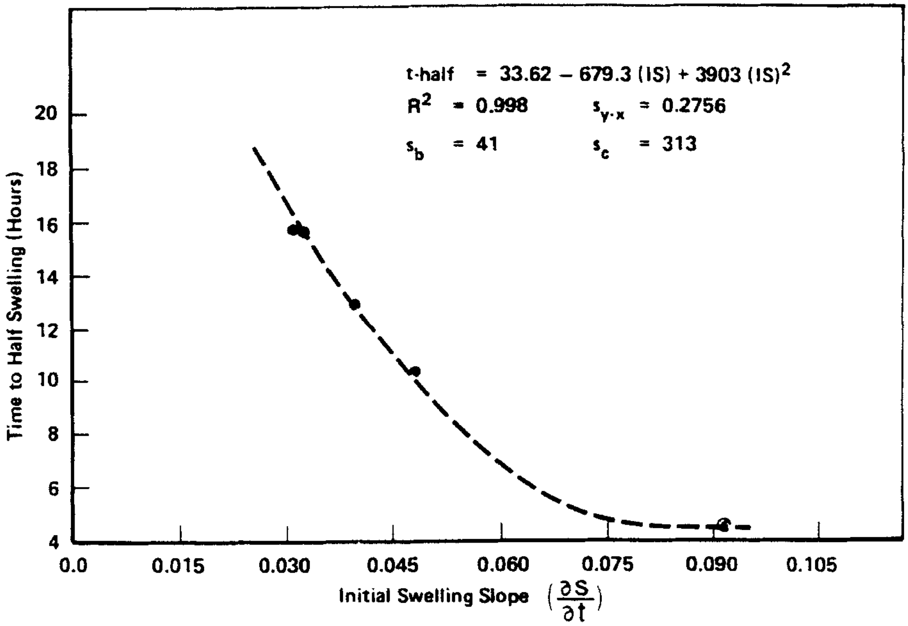

Figure 2. Relationship between the initial rate of swelling and time required to achieve half of total swelling for propylene oxide-MDI treated, and untreated wood. Dots - treated wood; circle - untreated wood.

content. Even the lowest t-half value is considerably higher than the one obtained for the control, which indicates a substantial reduction in the rate of swelling of treated vs. untreated wood.

The relationship between the initial swelling slope and t-half is shown in Figure 2. This relationship is well represented by the second degree polynomial shown. The authors found a similar relationship for a mixture of treatments using MDI, styrene, and divinylbenzene.[9] In another study, however, the relationship between initial swelling slope and t-half for chemical treatments with alkylene oxides, furan resin, and vinylpyrrolidinone was linear.[8] Reasons why these differences occurred were not apparent.

Equilibrium Moisture Content

Equilibrium moisture content obtained during water vapor and watersoak tests is expressed as the average moisture excluding coefficient for vapor (MEC_v) and liquid water (MEC_ℓ). The mathematical approach and reasoning for using MEC instead of EMC to evaluate moisture gain have been discussed in an earlier paper.[8] MEC values are a relative measure of moisture gain of treated vs. untreated specimens in contrast to EMC, which is an absolute value.

MEC results for treatments applied to ovendry wood were greater than those applied to wood with a 12 percent initial moisture content, as shown in Figure 1. Best MEC_v and MEC_ℓ were obtained by the 90 percent propylene oxide-10 percent MDI treatment applied to ovendry wood. In contrast, lowest MECs were obtained with the same treatment applied to wood at a 12 percent initial moisture content. These results follow the same pattern as those exhibited by ASE discussed earlier. These findings indicate that the treatments are very sensitive to the initial moisture content of wood. Availability of free reactive sites in wood with a relatively high initial moisture content, i.e., 12 percent, would be theoretically zero. This would cause most of the propylene oxide and MDI to react with water molecules thus reducing their effectiveness in controlling swelling and moisture gain. Furthermore, formation of links connecting propylene oxide and MDI would also be less likely under a semi-moist wood condition because of the higher affinity between MDI and water.[9]

Similarly to ASE values, MEC results would show how effective a particular chemical treatment was. For this reason, the chemical efficiency of each treatment in controlling water vapor and liquid water gained was computed. Results are shown in Table 4. Best CER results were obtained by treatment with a solution of 90 percent propylene oxide-10 percent MDI applied to ovendry wood. Comparing CER values from this study and those previously obtained with MDI[9] or propylene oxide[8] alone indicate that application of both chemicals mixed in a solution is not really efficient. MDI showed

TABLE 4

Chemical Efficiency Ratios (CER) in Controlling Moisture Gain by Wood Treatments with Solutions of Propylene Oxide and MDI

Chemical Treatments	Chemical Efficiency Ratios for Moisture Gain[b]	
	Water Vapor	Water-Soak
PO95-MDI5-0[a]	2.48	2.14
PO90-MDI10-0	2.21	2.61
PO85-MDI15-0	1.98	2.11
PO95-MDI5-12	2.09	1.41
PO90-MDI10-12	3.11	-0.12

a A mixture of 95 percent propylene oxide and 5 percent MDI applied to ovendry wood

b $CER = \frac{\text{moisture excluding coefficient}}{\text{chemical loading}}$

CERs of over 4.0 for liquid water exposures, and propylene oxide produced CERs of 3.6 and above for water vapor exposures. The only advantage of mixing these two chemicals is in producing an even effect in controlling swelling and moisture gain in both water vapor and watersoak tests. MDI or propylene oxide were effective in either one or the other test situation.

Water vapor diffusion in wood specimens can be calculated from adsorption or desorption data.[18] An approximation to the integral diffusion coefficient could be determined from the initial adsorption or desorption stages by the following formula:

$$E = \frac{Mt}{M\infty} = \left[\frac{4}{\pi^{(1/2)}}\right]\left[\frac{Dt}{L^2}\right]^{1/2} \qquad (6)$$

where:

E = fractional moisture content

M_t = amount of moisture adsorbed or desorbed at time, t, seconds

M_∞ = total moisture adsorbed or desorbed at equilibrium

L = thickness (mm)

t = time (sec)

D = diffusion coefficient ($mm^2\ sec^{-1}$)

This approximation to diffusion through wood is subject to certain boundary conditions as follows: (1) Moisture is initially uniformly distributed through specimen; (2) Surface of specimen immediately reaches the equilibrium concentration at $t > 0$; (3) Concentration at center of specimen does not change appreciably.

Plots of E vs. $\sqrt{t}$ or E^2 vs. t are commonly used to compute adsorption or desorption diffusion coefficients. Figure 3 shows the relationship of E vs. $\sqrt{t}$ for treated and untreated specimens exposed to water vapor from the ovendry to equilibrium in a 90 percent relative humidity chamber. The average diffusion coefficient can be computed from this figure by using a modification of equation (6) as follows:

$$D = \left(\frac{E}{\sqrt{t}}\right)^2 \left(\frac{L^2}{5.093}\right) \tag{7}$$

where:

D = average adsorption diffusion coefficient ($mm^2\ sec^{-1}$)

$\frac{E}{\sqrt{t}}$ = slope of E vs. $\sqrt{t}$ for any $E < 0.6$

L^2 = specimen thickness, (mm)

Calculation of exact diffusion coefficients from the data shown in Figure 3 would not be possible because the specimens were

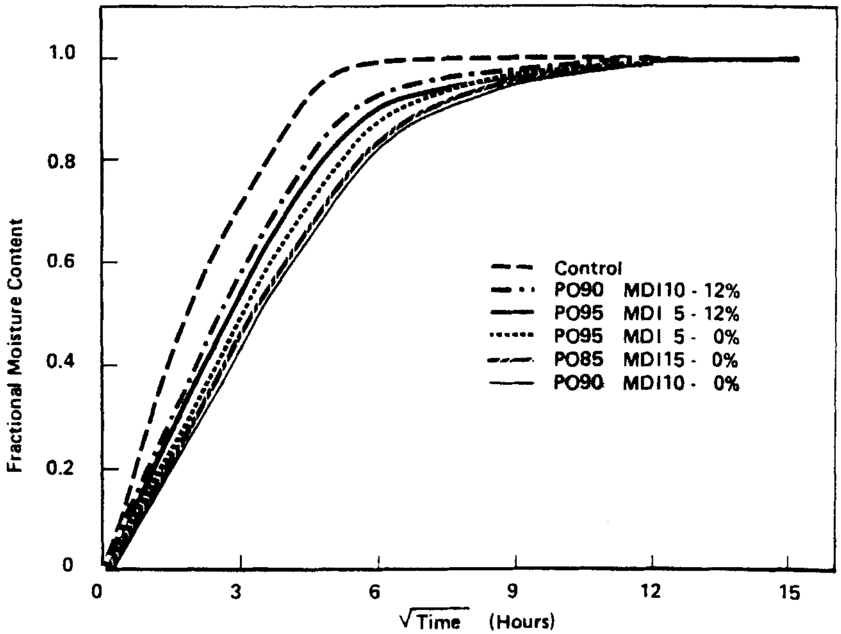

Figure 3. Relationship between fractional moisture content E and square root of time for propylene oxide-MDI treated, and untreated wood.

not edge-sealed hence making impossible the use of specimen thickness as a variable in equation (7). However, the relative values of the slope of E vs. $\sqrt{t}$, in seconds, is a good indicator of diffusion into treated and untreated wood. Slopes of E vs. $\sqrt{t}$ where t is expressed in seconds were computed and results are shown in Figure 3. These values show that a 90 percent propylene oxide-10 percent MDI treatment to ovendry wood produced the lowest results. Also, a comparison of these slopes with t-half values discussed earlier would show a close correlation between t-half and E vs. $\sqrt{t}$ slopes. This is not surprising as explained earlier.[9] Values of t-half are good indicators of diffusion coefficients as expressed in equations (5) and (6).

Sorption Hysteresis

Sorption hysteresis curves for treated and untreated wood initially ovendried or at 12 percent moisture content are shown in Figures 4a and 4b, respectively. All treatments applied to ovendry wood produced a substantial shift of adsorption and desorption points. Historically, wood treatments have tended to produce a shift in the sorption isotherms of wood. One such example is reductions in EMC in adsorption and desorption caused by heat treatments,[19] causing a shift in the sorption hysteresis loop. Chemical modification of wood such as affected by propylene oxide or MDI reactions are also expected to produce a shift in sorption hysteresis. This was the case in the present study.

Slope of sorption curves was expressed as the ROS shown in Table 3. Adsorption ROS were consistently smaller than desorption ROS, which indicates that changes in EMC produced by every 1 percent increase in relative humidity are smaller than changes in EMC caused by 1 percent relative humidity decrease. Most average ROS fell in the "favorable" categorization shown in Table 2.

Separation or relative distance of the adsorption from the desorption semi-loops of hysteresis curves were measured by the adsorption over desorption EMC generally known as the A/D ratios. Table 5 shows A/D ratios for treated and untreated wood. Values ranged from 0.769 to 0.843, and were consistently smaller at 50 than at 76 percent relative humidity. Comparing these values with those obtained by Spalt[20] for eight hardwoods and eight softwoods over the entire hygroscopic range, indicate that even though responses to the treatments produced both lower and higher ratios than the control, all values fell within the margins expected for most wood species.

EXPERIMENTAL METHODS

Wood wafers (30 mm x 30 mm x 3 mm in the tangential, longitudinal, and radial directions) were prepared from the sapwood of a freshly felled birch log. Specimen preparation followed a

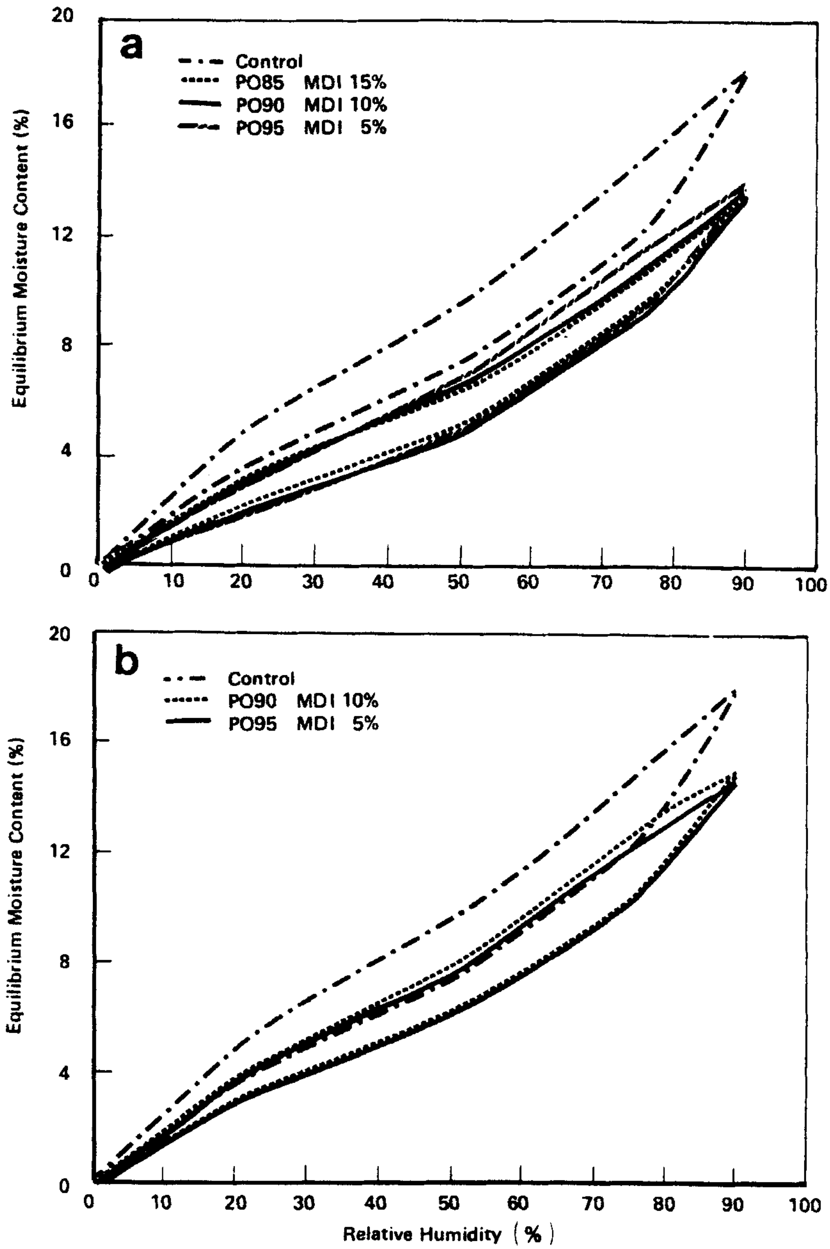

Figure 4. Sorption hysteresis for propylene oxide-MDI treated and untreated wood. a. Treatment applied to ovendry wood. b. Treatment applied to wood with a 12 percent initial moisture content.

TABLE 5

A/D Ratios of Treated and Untreated Wood Exposed to Relative Humidities of 50 and 76 percent

Chemical Treatment	Adsorption-Desorption Ratio		
	50%	76%	Average
PO95-MDI5-0[a]	0.809[b]	0.877	0.843
PO90-MDI10-0	0.742	0.838	0.790
PO85-MDI15-0	0.714	0.823	0.769
PO95-MDI5-12	0.803	0.813	0.808
PO90-MDI10-12	0.821	0.837	0.829
Control	0.763	0.817	0.790

a Solution of 95 percent propylene oxide and 5 percent MDI applied to ovendry wood

b EMC in adsorption divided by EMC in desorption at a given RH

technique similar to that used by Bramhall and McLaughlin,[16] and described in detail by the authors in a prior paper.[8]

Half of the wood wafers were placed in an oven for ovendrying and half in a 65 percent relative humidity conditioning chamber for conditioning to zero and 12 percent nominal equilibrium moisture contents respectively. Treatment of specimens was done in a treating chamber using a vacuum-pressure schedule described earlier.[8] The treating solution consisted of propylene oxide enhanced with 5 percent by weight of trimethylol propane trimethacrylate (TMPTM), and 5 percent by weight of the catalyst triethylamine, plus MDI. Once treated with this solution, the specimens were wiped, wrapped in aluminum foil, and placed (sandwiched) in a 90°C hotpress for reaction and polymerization. After 90 minutes in the hotpress, the wafers were transferred to a circulating oven at 103°C for further reaction, and dehydration.

After 24 hours, the specimens were unwrapped and left in the oven four more hours. They were then weighed, measured, and transferred to conditioning chambers for the hysteresis and swelling tests, or to a large glass container for a 24-hour watersoak test. The multi-step schedule followed to compute swelling and moisture content in hysteresis is shown in Figure 5. Rate of change during original adsorption was recorded for both tangential swelling and moisture content (Figure 5). A detailed description of experimental methods can be found in an earlier study.[8]

CONCLUSIONS

The combination of propylene oxide and MDI in a solution successfully reduced the hygroexpansive and sorptive behavior of wood to liquid and water vapor. This was particularly the case when

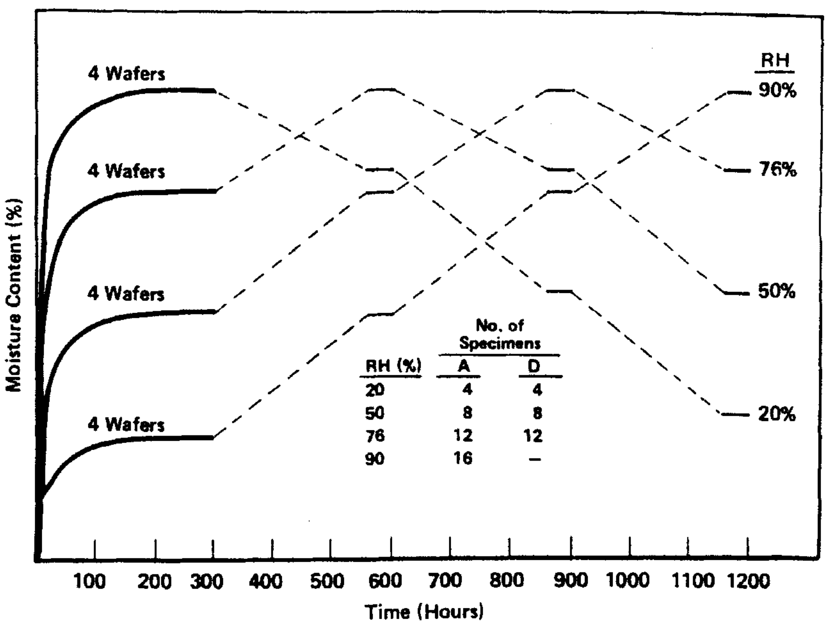

Figure 5. Schedule used to obtain equilibrium moisture content in treated and untreated wood sorption hysteresis.

the treatments were applied to ovendry wood. Resultant ASE, MEC, t-half, and ROS indicate the superiority of treatments applied to ovendry wood, with special reference to a solution of 90 percent propylene oxide-10 percent MDI. Chemical efficiency as measured by CERs suggested that the propylene oxide-MDI solution was not as effective as application of single chemicals in previous studies[8,9]. Possible reason might be that the two chemicals began reacting with each other prior to their application to wood, reducing the possibilities of chemical reaction and crosslinking with wood, and the different chemical loadings achieved in each case. Nevertheless, CER values are high enough to indicate that a limited amount of chemical reaction took place. This perhaps provides a reason for the effectiveness of the treatment in reducing swelling and moisture adsorption in water vapor exposure tests.

Use of HEC and CHE as quantifiers of hygroexpansive behavior of treated wood did not provide enough sensitivity to detect downward shifts in the responses. If the slope of the relationships is the main affected factor resulting from wood chemical treatments, such as the case of bulking agents or water repellents, then Noack's[13] categorization is useful in classifying the effect of these kinds of treatments. Further studies are necessary to explore the interaction of propylene oxide and MDI, and means to increase their reactivity with wood.

ACKNOWLEDGEMENTS

We are very grateful with Weyerhaeuser Company of Tacoma, Washington for their generous contributions and financial support of this research. We are also very thankful to Dr. Frank C. Beall for his suggestions at the beginning of this project, and to Drs. W. F. Lehmann, D. C. Johnson, and R. W. Rowell for their reviews of this manuscript.

REFERENCES

1. C. Liu, C. W. McMillen, U.S. Patent No. 3,183,114 (1965).

2. R. M. Rowell, Wood Sci., 10, 193 (1978).

3. R. M. Rowell, D. I. Gutzmer, Wood Sci., 7, 241 (1975).

4. R. M. Rowell et al., Wood Sci., 9, 51 (1976).

5. B. R. Baird, Wood and Fib., 1, 54 (1969).

6. R. M. Rowell, W. D. Ellis, Wood Sci., 12, 52 (1979).

7. H. H. Wakita et al., Zairyo, 26, 460 (1977).

8. R. Guevara, Holzforschung, In revision (1982).

9. R. Guevara, A. A. Moslemi, Wood Sci. Technol., In revision (1982).

10. C. Skaar, Water in Wood, Syracuse University Press, Syracuse, New York, 1972.

11. H. N. Rosen, Wood Sci. Technol., 8, 283 (1974).

12. R. Keylwerth, Holz Roh- Werkstoff, 20, 252 (1962).

13. D. Noack et al., Wood Sci. Technol., 7, 218 (1973).

14. Anon., Wood Handbook, U.S. Dept. of Agriculture Handbook No. 72, Washington, D.C., 1974.

15. A. Chomcharn, Ph.D. Diss. SUNY, Syracuse, 1975.

16. W. T. Simpson, Wood and Fib., 5, 299 (1974).

17. G. Gramhall, T. A. McLaughlin, Wood and Fib., 2, 40 (1970).

18. G. L. Comstock, For. Prod. J., 13, 97 (1963).

19. M. A. Millett, C. C. Gerhards, Wood Sci., 4, 193 (1972).

20. H. A. Spalt, For. Prod. J., 7, 331 (1957).