AD-A149 578 REACTION OF EPOIIDES WITH WOOD(U) FOREST PRODUCTS LAB 1/1
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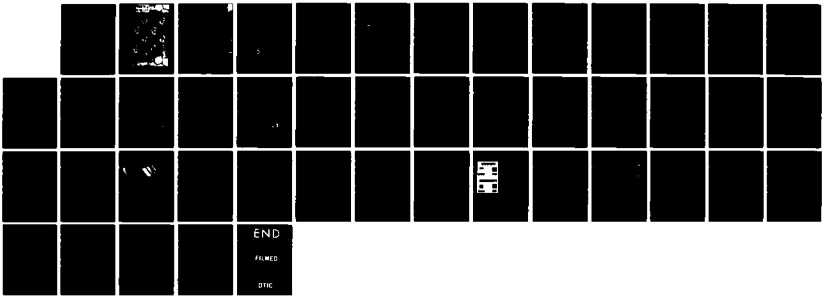

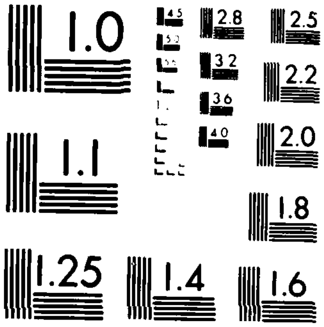

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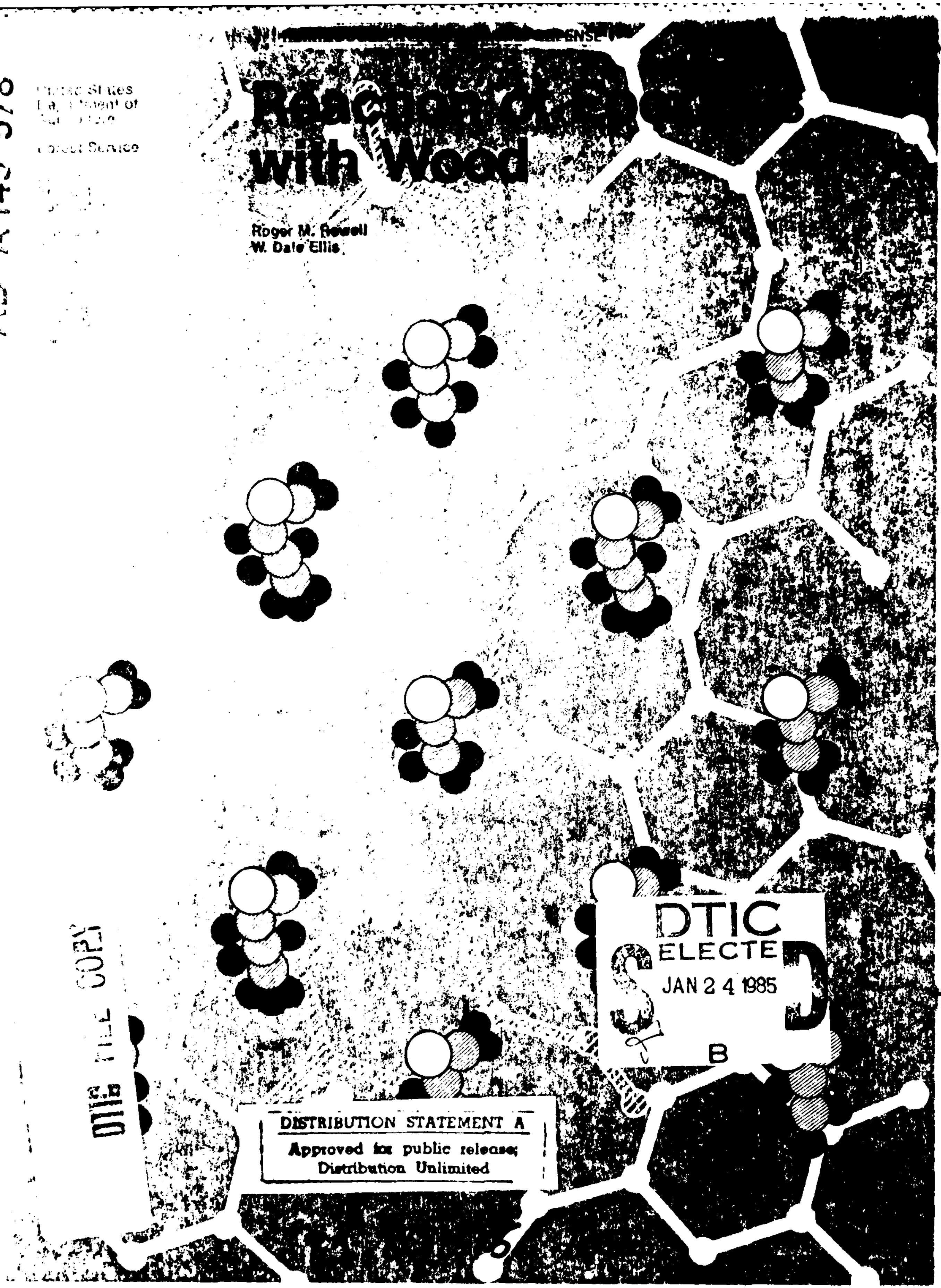
United States
Department of
Agriculture

Forest Service

Reaction of E[illegible]
with Wood

Roger M. Rowell
W. Dale Ellis



Abstract

This report is a summary of an 8-year research program at the Forest Products Laboratory on chemical modification of wood with epoxides. Several species of wood were tested and the reactivity of many mono and difunctional epoxides was determined. The majority of the research concentrated on the reactions of propylene and butylene oxides catalyzed with triethylamine using southern pine.

Low molecular weight epoxides react with wood cell wall polymer hydroxyl groups using a mild alkali catalyst. The chemicals penetrate the cell wall, reaction is fast, there are no byproducts generated with dry wood, and stable chemical bonds are formed. Because reaction takes place in the cell wall, the increase in wood volume from the treatment is proportional to the calculated volume of chemical added. Bulking of the wood, caused by bonded chemical, results in 50 to 70 percent dimensional stability at chemical weight gains of 20 to 30 percent. Above this level of treatment, the increase in added chemical causes the cell wall structure to break down and dimensional stability is lost. Good resistance to biological attack is observed in wood modified to levels of 20 to 30 weight percent gains in laboratory tests with brown- and white-rot fungi, and with termites. Modified wood performs very well in a marine environment. Resistance to biological degradation is thought to be due to changes in chemical conformation of the potential substrate, mainly in the carbohydrate fraction, that result from chemical modification.

Keywords: Epoxides, wood, chemical modification, dimensional stability, biological resistance.

December 1984

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A [redacted] Laboratory publications are sent to over 1,000 libraries in the United States and elsewhere.

The Laboratory is maintained in cooperation with the University of Wisconsin.

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Preface

In 1975, the Forest Products Laboratory initiated a research program to develop new technology in the area of biological resistance of wood. The justification for this research was the need for a less toxic or nontoxic method of protecting wood in adverse environments. In earlier research in the Laboratory it had been found that chemically modified wood was very resistant to attack by biological systems, but the mechanism of effectiveness was not known. New instrumentation technology and interest in this area prompted a new look at chemical modification of wood.

As the research progressed, interest developed from other researchers around the world and a cooperative research program was initiated. During the 8 years this study was active, eight universities, four companies, and six institutes had input into the project. The names of these cooperators are listed in Appendix A. Numerous other companies tested the technology with possible application to their product line.

Much of the data from this research program have been published in scientific journals (see Appendix B) however, some data were not. The total technology developed during this project is presented in this document.

It is hoped that the new advances in the chemical modification of wood presented here will lead to the development of treatments of wood for both improved biological resistance and dimensional stability.

Reaction of Epoxides with Wood

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Introduction

Chemically modifying the cell wall polymers could result in greatly enchanced properties of the composite i.e., wood. The purpose of this research has been to investigate the reactivity of cell wall polymers, changes in the basic chemistry of these polymers, and improvements in wood properties through chemical modification.

A review of the history of chemical modification shows that the bulk of the research conducted was aimed at improving either biological resistance or dimensional stability. Chemical modification of wood for biological resistance is based on the theory that the enzymes (cellulases) must directly contact the substrate (wood cellulose), and the substrate must have a specific configuration. If the cellulosic substrate is chemically changed, this highly selective reaction cannot take place. Chemical modification can also change the hydrophilic nature of wood. In some cases water, a necessity for decay organisms, is excluded from biological sites. The chemicals used for modification need not be toxic to the organism because their action renders the substrate unrecognizable as a food source to support microbial growth. In other words, the organisms starve in the presence of plenty.

By far the greatest amount of research for dimensional stability of wood has been carried out in the area of cell wall treatments. It has been shown that the increase in wood volume upon treatment is directly proportional to the theoretical volume of chemical added. The volume of wood increases with increasing chemical added to about 25 weight percent gain (WPG) at which point the treated volume is approximately equal to green volume. When this bulked wood comes into contact with water, very little additional swelling can take place. This is the mechanism for the effectiveness of dimensional stability bulking treatments.

Background

Wood is a three-dimensional biopolymer composite made up primarily of cellulose, hemicellulose, and lignin (fig. 1). These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Wood is a preferred building/engineering material because it is economical, low in processing energy, renewable, strong, and aesthetically pleasing. It has, however, several disadvantageous properties such as biodegradability, flammability, changing dimensions with varying moisture contents, and degradability by ultraviolet light, acids, and bases. These properties of wood are all the result of chemical reactions involving degradative environmental agents. Wood, for example, is biologically degraded because organisms recognize the polysaccharide polymers in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units. Because high molecular weight cellulose is primarily responsible for strength in wood, strength is lost as this polymer undergoes biological degradation through oxidation, hydrolysis, and dehydration reactions. The same types of reactions take place in the presence of acids and bases.

Wood changes dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. This moisture swells the cell wall, and the wood expands until the cell wall is saturated with water. Water, beyond this point, is free water in the void structure and does not contribute to further expansion. This process is reversible, and shrinkage occurs as moisture is lost.

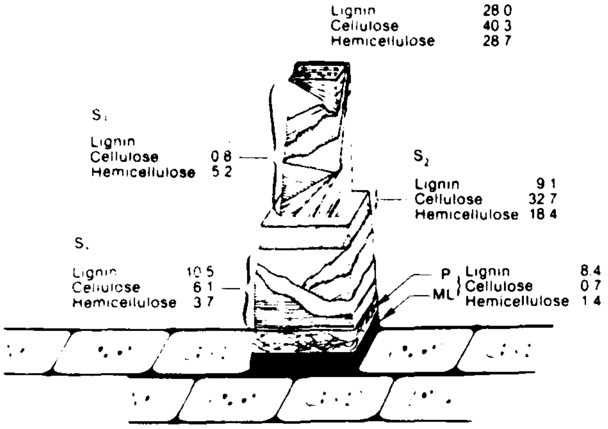


Figure 1.—Chemical composition of the cell wall of scotch pine. (M148913)

Wood burns because the cell wall polymers undergo hydrolytic, oxidation, dehydration, and pyrolytic reactions with increasing temperature, giving off volatile, flammable gases. The lignin component contributes more than do other polymers to char formation, which helps insulate wood from further thermal degradation.

Wood exposed outdoors undergoes photochemical degradation due to ultraviolet light, primarily in the lignin component, which gives rise to characteristic color changes. Because the lignin acts as an adhesive in wood, holding cellulose fibers together, the wood surface becomes richer in cellulose content as the lignin degrades. Cellulose is much less susceptible to ultraviolet degradation and is washed off the surface during a rain exposing new lignin to continue the degradative reactions. This weathering process can account for a significant loss of surface fibers in time.

Because all of these degradative effects are chemical in nature, it should be possible to eliminate or decrease the rate of degradation by changing the basic chemistry of the cell wall polymers. By chemically modifying the cellulose component, for example, the highly specific biological enzymatic reactions cannot take place because the chemical configuration and molecular conformation of the substrate has been altered. Bulking the cell wall with bonding chemicals would reduce the tendency of wood to swell with changes in moisture because the wood would already be in a partially, if not completely, swollen state.

Requirements for Reaction

Penetration

In whole wood, accessibility of the treating reagent to the reactive chemical sites is a major consideration. To increase accessibility to the reaction site, the chemical must penetrate the wood structure. Penetration can be achieved through swelling of the wood structure. If a reagent potentially capable of modifying wood does not swell wood substance, then perhaps a suitable catalyst would. If both reagent and catalyst were unable to swell the wood, a workable cosolvent could be added to the reaction system.

Reactants

Cellulose, the hemicelluloses, and lignin are distributed throughout the wood cell wall. These three polymers make up the solid phase of wood and the hydroxyl groups they contain are the most abundant reactive chemical sites. The void structure or lumens in wood can be viewed as a bulk storage reservoir for potential chemical reactants, used to modify the cell wall polymers. For example, the void volume of southern pine springwood with a density of 0.33 g/cm^3 is 0.77 cm^3 voids/cm^3 wood or 2.3 cm^3/g. For summerwood with a density of 0.70 g/cm^3, the void volume is 0.52 cm^3/cm^3 or 0.74 cm^3/g. The cell wall can also swell and act as a chemical storage reservoir. For southern pine the cell wall storage volume from ovendry to water swollen is 0.77 cm^3/cm^3. These data show that there is more than enough volume in the voids in wood to house sufficient chemical for reaction to take place with the cell wall polymers.

Potential reactants must contain functional groups that will react with hydroxyl groups of the wood components. This may seem obvious, but there are many literature reports of chemicals that failed to react with wood components when, in fact, they did not contain functional groups that could react.

The chemical bond desired between the reagent and the wood component is of major consideration. For permanence, this bond should have great stability to withstand environmental stresses. In such cases, the ether lineage may be the most desirable covalent carbon-oxygen bond. These are more stable than the glycosidic bonds between sugar units in the wood polysaccharides so the carbohydrate polymers would degrade before the bonded ether did. Less stable bonds can also be formed that could be useful for the release of a bonded chemical under environmental stresses. Acetals and esters are less stable than ether bonds and could be used to bond biological agents or fire retardants onto wood to be released under certain conditions.

It is important that 100 percent of the reagent skeleton bond to the wood with no byproduct generation. If a byproduct were formed during the reaction, a recovery system might have to be considered for economic reasons.

A gas reactant creates problems in handling as high pressure equipment is required. The level of chemical substitution is usually lower than liquid systems, and penetration of gaseous reagents can be very difficult. The best success, to date, of chemical systems is with low boiling liquids that easily swell wood. If the boiling point is too high, it is difficult to remove excess reagent after treatment. It is generally true that the lowest member of a homologous series is the most reactive and will have the lowest boiling point.

Some chemicals react with a single hydroxyl group, and the reaction is complete. Such is the case, for example, with methylation using methyl iodide. Other chemicals, in the course of reacting, form a new hydroxyl group which reacts further. Epoxides react in this way. In other words, single-site substitution occurs in cases like methylation while polymer formation from a single graft point occurs in cases like epoxidation. This will be discussed in detail later.

From the standpoint of industrial application of reagents for wood, toxicity, corrosivity, and cost are important factors for chemical selection. The reacted chemicals should not be toxic or carcinogenic in the finished product, and the reactant itself should be as nontoxic as possible in the treating stage. This is somewhat difficult to achieve since chemicals that react easily to wood hydroxyl groups will also easily react with blood and tissue hydroxyl-containing polymers. The reactants should be as noncorrosive as possible to eliminate the need for special treating equipment. In the laboratory experimental stage, high cost of chemicals is not a major consideration. For commercialization of a process for the chemical modification of wood, chemical cost is important.

Reaction Conditions

There are certain experimental conditions that must be considered before a reaction system is selected. The temperature required for complete reaction must be low enough that it causes little or no wood degradation yet the rate of reaction is relatively fast. A safe upper limit is about 120° C since little degradation occurs at this temperature for a short period of time.

It is impractical to dry wood to less than 1 percent moisture, but the water content of the wood during reaction is, in most cases, critical. The hydroxyl in water is more reactive than the hydroxyl groups available in wood components, i.e., hydrolysis is faster than substitution. The most favorable condition is a reaction system in which the rate of reagent hydrolysis is relatively slow.

It is also important to keep the reaction system simple. Multicomponent systems that require complex separation after reaction for chemical recovery should be avoided. The optimum would be for the reacting chemical to swell the wood structure and act as the solvent as well.

Almost all chemical reactions require a catalyst. With wood as the reacting substrate, strong acid catalysts cannot be used as they cause extensive degradation. The most favorable catalyst from the standpoint of wood degradation is a weakly alkaline one, which is also favored as in many cases these chemicals swell the wood structure and give better penetration (see table 2). The catalyst used should be effective at low reaction temperatures, easily removed after reaction, nontoxic, and noncorrosive. In most cases, the organic tertiary amines are best suited.

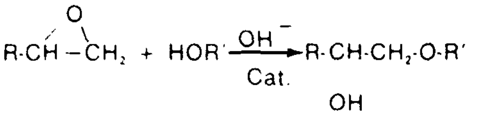
The reaction conditions must be mild enough that the reacted wood still possesses the desirable properties of wood; the strength must remain high, little or no color change (unless a color change is desirable), good electrical insulation, not dangerous to handle, gluable, and paintable.

In summary, the chemicals to be used for chemical modification of wood must be capable of reacting with wood hydroxyls under neutral or mildly alkaline conditions at temperatures below 120° C. The chemical system should be simple and capable of swelling the wood structure to facilitate penetration.

The complete molecule must react quickly with wood components yielding stable chemical bonds, and the treated wood must still possess the desirable properties of untreated wood.

Reactions with Wood

Several chemical systems have been explored for chemical modification of wood. One reaction system that meets the requirements set forth earlier is the base-catalyzed reaction of alkylene oxides with hydroxyl groups.



The reaction is fast, complete, generates no byproducts, forms stable ether bonds, and can be catalyzed by a volatile organic amine. After the initial reaction, a new hydroxyl group originating from the epoxide is formed. From this new hydroxyl, a polymer begins to form. Due to the ionic nature of the reaction and the availability of hydroxyl ions in the wood components, the chain length is probably short due to chain transfer.

The reaction between polysaccharides and alkylene oxides has been known for many years and has often been cited in the literature. The application of this reaction to wood research, however, is somewhat limited.

McMillin (1963) treated hard maple blocks with ethylene oxide catalyzed with trimethylamine in the vapor phase. At 20 percent ovendry weight add-on of ethylene oxide, there was a 60 percent reduction in the water swelling of the treated wood. Using static bending tests, McMillin observed no change in the strength of the treated wood. In a French patent (Aktiebolag 1965), with the same gaseous mixture, treatment of moist wood (14.6 pct H_2O) to 24 percent ovendry weight add-on is described. The treated wood showed reduced swelling in water. Barnes, Choong, and McIlhenny (1969) found that oscillating pressure during treatment rather than maintaining constant pressure gave better results. At weight add-ons of 11 to 12 percent, they found a 42 percent antiswelling efficiency.

Liu and McMillin (1965) patented a process for treating wood with both gaseous ethylene oxide and propylene oxide. Using a vapor phase system with either trimethylamine or triethylamine as catalyst, they treated Douglas fir, hard maple, and persimmon and obtained high levels of dimensional stability. Pihl and Olsson (1968) treated pine and birch with epichlorohydrin and dichlorohydrin with a polyfunctional amine as catalyst and also found greatly reduced swelling due to moisture changes in the modified wood.

The use of ethylene oxide gives a polyethylene oxide polymer in the wood cell wall (Grinbergo 1974; Meyer and Loos 1969; Nikitin and Rudneva 1935; Schuerch 1968; Zimakov and Pokrovskil 1954). Ethylene oxide in trimethylamine is a gaseous reaction, because the compounds have boiling points of 10.7° C and 2.9° C, respectively. This system requires special equipment to handle the liquefied gases. Polyethylene oxide polymers have the disadvantage of being very water soluble especially at low molecular weight (Brandrup 1965).

Polymers from higher members of the 1,2-epoxide homologous series are more hydrophobic than those of ethylene oxide and are much less soluble in water. The monomers are liquids at room temperature which would eliminate the requirement for special gas-handling equipment.

Experimental Design, Results, and Discussion

Reaction Conditions

Propylene oxide (PO) with a triethylamine, (TEA) catalyst was used to modify a known treatable wood species to determine the optimum conditions for treating wood. Southern pine (SP) sapwood blocks, 2 by 2 by 15 cm (*all dimensions shown in this report are* listed in the order radial by tangential by longitudinal), were prepared from freshly cut green logs. All samples were ovendried (OD) at 105° C for 16 hours (hr).

The dry SP blocks were reacted in a stainless steel reactor at 150 lb/in.^{2} nitrogen pressure. The effects of time, temperature, and ratio of epoxide to catalyst on WPG to wood were observed.

The volumetric swelling coefficients for several epoxides, catalysts and solvents, were determined after two different treating conditions: (1) heating an SP block, 2 by 2 by 0.6 cm, with each solution for 1 hr at 120° C, 150 lb/in.^{2} nitrogen pressure, or (2) soaking an SP block, 2 by 2 by 0.6 cm, in each solution for 24 hr at 25° C.

The block volume was determined by measuring dimensions with a flat bed micrometer before each treatment, and after heating or soaking with the solutions. From these measurements the volumetric swelling coefficients were determined.

Ovendried SP blocks were treated with either PO, butylene oxide (BO), or epichlorohydrin (EPI) with TEA (95:5/ v/v) as catalyst at 120° C, 150 lb/in.^{2} for varying lengths of time. Volume of the specimens was determined green before drying, after drying, and after treatment with the epoxide-catalyst mixture to determine the change in wood volume as a result of treatment.

Experiments varying temperature (table 1), reaction time (table 2), and catalyst concentration (table 3 and fig. 2) showed that 120°C, 150 lb/in.^{2} with an epoxide/catalyst ratio of 95:5 (v/v) for 30 to 60 minutes (min) were the optimum reaction conditions for the PO/TEA system. A reaction time of 2 to 4 hr under the same conditions was optimum for BO.

The swelling coefficient for each separate reagent, catalyst, and potential solvent was determined by soaking wood specimens at 120° C under pressure and at 25° C (tables 4-6). Most of the amine catalysts tested swell wood. Triethylamine was selected as the preferred catalyst (even though it does not swell wood) because of its low boiling point for ease of removal after reaction. Many of the solvents tested swell wood very well. If needed in a reaction system, however, many of these would react with the epoxide and could never be used. Propylene oxide swells wood about 50 percent as much as water and BO somewhat less. This ability to swell wood allows the epoxides to react without the need for a cosolvent.

Table 1.—Effect of temperature on propylene oxide (PO)-triethylamine (TEA) treatments of southern pine (*150 lb/in.*^{2}) 95:5, v/v, PO/TEA

Temperature	Time	Weight percent gain
°C	*Hr*	
120	3	50.9
100	3	45.5
80	3	6.3
120	1	32.5
110	1	28.0
100	1	15.0

Table 2.—Effect of time on propylene oxide (PO)-triethylamine (TEA) treatment of southern pine. 120° C, 150 lb/in.^{2}, 95:5, v/v, PO/TEA

Time	Weight percent gain
Hr	
0.25	9.8
.5	26.6
1	32.5
2	39.4
3	50.9
6	50.8
15	61.8

Table 3.—Effect of propylene oxide/triethylamine (PO/TEA) ratio on treatment. 120° C, 3 hours, 150 lb/in.^{2}

PO	TEA	PO/TEA	Weight percent gain
- - - *Pct* - - -			
20	80	1/4	20.4
50	50	1/1	44.5
80	20	4/1	52.9
90	10	9/1	54.8
95	5	95/5	50.9
97	3	97/3	40.0
99	1	99/1	36.6

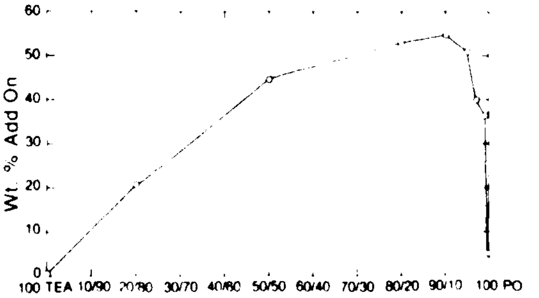


Figure 2.— Effect of propylene oxide/triethylamine ratio on treatment of southern pine, 120° C, 150 lb/in.^{2}, 3 hr (M151128)

Table 4.—Volumetric swelling coefficients (S) for southern pine sapwood in various reagents

Reagent	S[1] 120° C, 150 lb/in.^{2}, 1 hr	S[1] 25° C, soaking
Water	10.0	10.0
Epichlorohydrin	6.9	5.9
Propylene oxide	5.2	5.0
Butylene oxide	4.1	7
Styrene oxide	2.4	---

[1] Value for water set at 10, other values relative to this value.

Table 5.—Volumetric swelling coefficients (S) for southern pine sapwood in various catalysts

Catalyst	S[1] 120° C, 150 lb/in.^{2}, 1 hr	S[1] 25° C, soaking
n-Butylamine	15.5	15.2
Piperidine	13.3	0.0
Dimethylformamide	12.8	12.5
Pyridine	11.3	13.1
Aniline	11.0	.5
Water	10.0	10.0
Diethylamine	5.0	11.0
N-methylaniline	2.6	.8
N-methylpiperidine	2.2	1.6
N,N-dimethylaniline	.3	.5
Triethylamine	– 1	2.1

[1] Value for water set at 10, other values relative to this value.

Table 6.—Volumetric swelling coefficients (S) for southern pine sapwood in various solvents

Solvent	S[1] 120° C, 150 lb/in.^{2}, 1 hr	S[1] 25° C, soaking
Dimethylsulfoxide	13.3	11.7
Dimethylformamide	12.8	12.5
Cellosolve	10.6	10.2
Methyl cellosolve	10.3	10.0
Water	10.0	10.0
Methanol	9.0	9.3
1,4-Dioxane	6.5	6
Tetrahydrofuran	5.4	7.2
Acetone	5.1	5.6
Dichloromethane	3.8	3.3
Methyl ethyl ketone	3.6	5.0
Ethyl acetate	2.4	4.2
Cyclohexanone	2.3	5
4-Methyl-2-pentanone	4	1.5
Xylenes	1	2
Cyclohexane	1	1
Hexanes	2	.2

[1] Value for water set at 10, other values relative to this value.

Under the conditions used here, very little color change takes place on treatment. Southern pine treated with only PO shows no color change; treated with TEA alone, the wood turns to a dark straw color. The combination of PO and TEA gives colors from light to dark yellow. The greatest factor in the darkening of southern pine is in the vacuum heat treatment after reaction. The amine degrades with heat to cause the wood to darken. Wood reacted with EPI/TEA takes on a light-orange color.

Table 7 shows the changes in volume of OD SP after epoxide treatment. At a WPG of approximately 20, the volume of the treated wood was equal to the green volume. Above about 30 WPG, the volume of treated wood was larger than that of the green wood.

To determine the permanence of the chemical treatment, treated specimens were ground to pass a 40 mesh screen and extracted with refluxing distilled water and separate samples with refluxing benzene in a Soxhlet extractor. The OD weight of the ground sample was determined before extraction, after 1 day of extraction, and at the end of 7 days (table 8). Most of the weight loss in modified wood is probably due to unreacted epoxide that was not removed after reaction in the vacuum recovery step. It is interesting to note the extent of weight loss in the control upon extended water extraction at reflux. After 8 days of Soxhlet extraction, 24.6 percent weight loss was observed. This may be due to slow hydrolysis of sugars in the wood. Both the unmodified and modified wood show about the same weight loss in 24 hr of water extraction; however, in the next 7 days the control lost 13.4 additional percent while the modified lost only 2.1 percent.

To determine the reproducibility of the chemical treatments, SP specimens were treated separately with PO/TEA, BO/TEA, and PO-EPI/TEA. Eight separate runs of 24 specimens each were done with 1,900 milliliters (ml) of PO, 100 ml of TEA, at 120°C, 150 lb/in.^{2} for 37 min. Four separate runs of 24 specimens each were done with 1,900 ml of BO, 100 ml TEA at 120° C, 150 lb/in.^{2} for 4 hr. Three separate runs of 24 specimens each were done with 1,425 ml PO, 475 ml EPI, 100 ml TEA at 120° C, 150 lb/in.^{2} for 37 min.

After each of these runs, chemical was drained from the cylinder, and a vacuum applied for 1 hr while the treating cylinder was cooling. All specimens were weighed following vacuum treatment. For each set of samples the mean WPG was determined and standard deviations (SD) calculated. Table 9 shows that the mean for all 8 runs of 24 specimens each for PO was 27.2 with an SD of 2.86. Standard deviations from 1.25 to 5.45 were observed indicating some variation in the treatment. Much less variation was observed in the BO runs. Four runs of 24 specimens each for BO showed a mean of 25.2 with an SD of 1.64.

Method of Drying

The rate of water removal by vapor drying with various benzene-type solvents was measured to determine the effects ovendrying or a solvent drying system (Hudson 1950) had on reactivity. A modified Barrett-type moisture test receiver was used as a vapor-drying chamber.

The content of wood extractives was determined by two different solvent-extraction procedures. Southern pine specimens, xylene-dried or ovendried, were ground to pass a 40-mesh screen. Each specimen was extracted separately in a Soxhlet extractor with the following: (1) benzene/ethanol, 2:1, volume per volume (v/v) for 4 hr, or (2) ether for 4 hr.

To determine the effect of type of drying on the chemical reactivity of wood, 100 SP specimens were either OD or vapor-dried, then reacted with PO in TEA (95:5, v/v) at 120° C, 150 lb/in ^{2}. After ovendrying both sets of treated specimens, the WPG was determined. Fifty separate specimens of SP were prepared as described except they were reacted with BO/TEA (95:5, v/v) for 4 hr at 120° C, 150 lb/in.^{2}.

The results in figure 3 show that the rate of water removal in SP by vapor drying increases with increasing solvent boiling point up to about 150° C. At this temperature, the rate is no longer a function of boiling point but is controlled by the physical limitation of water moving out of the wood structure. If the cost of the solvent and the rate of water removal are the factors considered, xylene is the most satisfactory of the solvents tried.

In the vapor-drying process, the aromatic solvent vapors pass over the wet wood and water vapor is codistilled with the solvent vapor. The mixture is then cooled and, at the lower temperature, the immiscible liquids separate. The water is drained off, and the aromatic solvent can then be recycled.

Table 7.—Changes in volume of southern pine after treatment with alkylene oxides

Compound	Green volume	Ovendry volume before	Ovendry volume after	Weight percent gain
	— — — — —	Cm^3 — — — — —		
Propylene oxide	57 03	53.09	56.04	15.9
Butylene oxide	59 00	53 09	59.00	21.1
Propylene oxide	59.98	56 04	59.98	26.1
Propylene oxide	59 00	54 08	59.98	34.1
Epichlorohydrin	59 00	55 06	60.96	41.0

Table 8.—Soxhlet extraction of southern pine (40 mesh)

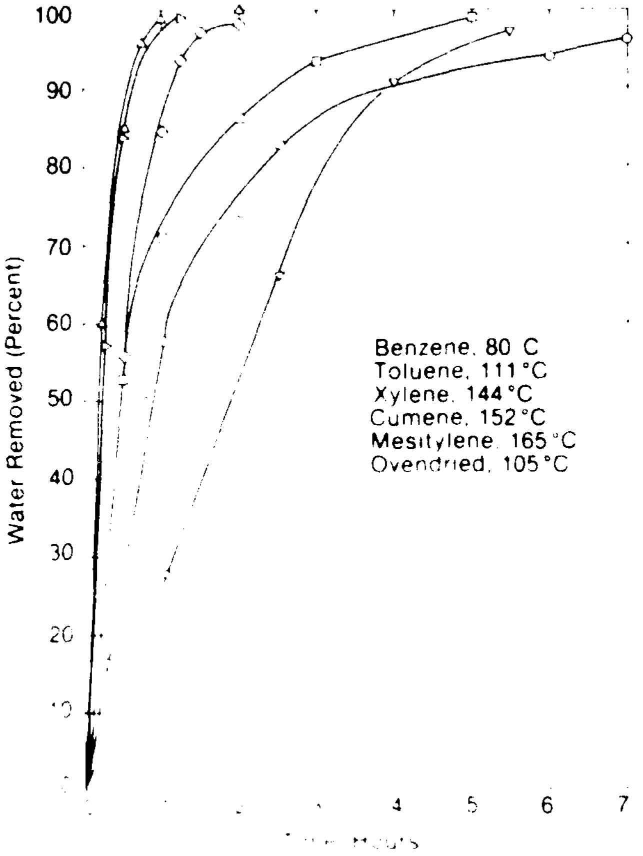
Specimen	Percent lost after extraction for 1 day	 7 days[1]	 Total
	— — — — —	*Pct*	— — — — —
BENZENE			
Control	4.7	0.15	4.9
Propylene oxide, 38 weight percent gain	10.8	76	11.6
WATER			
Control	11.2	13.4	24.6
Propylene oxide, 38 weight percent gain	12.5	2.1	14.6

[1] Additional loss

Table 9.—Reproducibility of epoxide reactions with southern pine

Chemical	Run[1]	Weight percent gain mean $\bar{X}$	Standard deviation
Propylene oxide	I	22.74	3.25
	II	28.81	2.52
	III	26.76	3.42
	IV	27.59	3.89
	V	34.39	1.25
	VI	26.74	1.33
	VII	22.25	1.76
	VIII	28.06	5.45
Average		27.17	2.86
Butylene oxide	I	26.76	2.22
	II	26.64	1.38
	III	22.80	1.64
	IV	24.63	1.30
Average		25.21	1.64
Propylene oxide-epichlorohydrin	I	16.57	2.21
	II	20.79	1.80
	III	21.44	3.08
Average		19.60	2.36

[1] 24 specimens per run.



[illegible] by vapor [illegible] time.

[illegible]

Table 10.—Extractives of southern pine after vapor drying or ovendrying

Sample	Extractives[1]	
	Benzene/ethanol[2]	Ether
	——————Wt. loss	pct——————
Ovendried	5.19	4.25
Vapor dried	4.07	2.47

[1] Based on ovendry weight loss before and after extraction.

[2] Benzene/ethanol 2:1 mixture, v/v 4

[3] [illegible]

Table 11.—Weight percent gain (WPG) of vapor-dried and ovendried southern pine

Reaction system	Drying method[1]	
	Oven (WPG)	Vapor (WPG)
[illegible]	26.2	26.4
Butyl [illegible]	25.7	27.6
Propylene oxide [illegible]	22.5	21.4

[1] Average of all samples [illegible]

Volume Changes in Wood as a Result of Modification

The dimensions of 50 SP [illegible] using a flat bed micr[illegible] calculated [illegible] were then OD [illegible] measured an[illegible] their volume [illegible] treated with PO/TEA [illegible]

[illegible]

Ovendrying untreated SP caused a shrinkage of 6 to 10 percent from the original green volume (table 12). At a WPG of approximately 20, the volume of modified wood was equal to the green volume before the specimens were initially OD. The volume expansion in the wood was nearly equal to the calculated volume of chemical added (table 13). This is strong evidence that the chemicals have ended up in the cell wall, but the results of these tests do not indicate whether or not the chemical is bonded.

Dimensional Stability of Modified Wood

A double water soak method was developed to determine volumetric swelling coefficient (S), and antishrink efficiency (ASE). Southern pine blocks, 2 by 2 by 0.6 cm, both treated and untreated, were submerged in distilled water and evacuated in a vacuum desiccator. Vacuum was continued for 30 min, released for 1 hr, reapplied for 30 min, then released for 24 hr. Fresh distilled water was then added and this process repeated. After each 24 hr, wet volume of the block was determined. This was continued for 7 days. The S and ASE were calculated. The samples were then resoaked for 7 days, volume was determined, and then they were reovendried followed by a final volume determination. Volumetric swelling coefficient is calculated from.

$$S = \frac{V_2 - V_1}{V_1} \tag{1}$$

where
V2 = wood volume after wetting with liquid water
V1 = wood volume of ovendried sample before wetting,
and ASE is calculated from

$$ASE = \frac{S_1 - S_2}{S_1} \tag{2}$$

where
S2 = treated volumetric swelling coefficient
S1 = untreated volumetric swelling coefficient.

Both the ASE and S values are usually reported as percent. In that case, the ASE and S values from equations (1) and (2) are multiplied by 100.

Southern pine blocks, 2 by 2 by 10 cm, were treated at 120° C, 150 lb/in.² nitrogen pressure with PO/TEA or BO/TEA (95:5, v/v). By varying the reaction time, specimens with WPGs of 4 to 45 were prepared for dimensional stability determination.

Table 12—Changes in volume of southern pine upon drying and modification with propylene oxide

A	B	B – A	C	Weight percent gain	C – B	C – A
Green volume	Ovendry volume	B ΔV	After treatment ovendry volume		B ΔV	A ΔV
Cm³	*Cm³*	*Pct*	*Cm³*		*Pct*	*Pct*
57.0	53.1	6.9	56.0	15.9	+5.3	1.7
59.0	53.1	10.0	59.0	21.1	+10.0	0
60.0	56.0	6.6	60.0	26.1	+6.6	0
59.0	54.1	8.3	60.0	34.1	+9.8	+1.6
59.0	55.1	6.7	61.0	41.0	+9.7	+3.3

Table 13.—Volume changes in southern pine upon treatment with epoxides

Weight percent gain	Increase in wood volume with treatment	Calculated volume of chemical added[1]
	Cm³	*Cm³*
	EPICHLOROHYDRIN	
14.9	4.26	4.42
22.7	5.41	6.06
	BUTYLENE OXIDE	
25.3	6.88	6.88
	PROPYLENE OXIDE	
26.5	7.05	7.54
28.8	6.39	7.21
32.4	7.70	8.36
34.3	8.36	8.03
36.2	8.85	9.01

[1] Density 1.01 g/ml for D = M/V

Table 14.—Volumetric swelling coefficients (S) and antishrink efficiency (ASE) of modified southern pine as determined by the water-soaking method

Treatment	Weight percent gain	S^1_1	ASE^2_1	S^3_2	ASE^4_2	Weight loss[5]	S^6_3	ASE^7_3	S^8_4	ASE^9_4	Additional weight loss
						Pct					*Pct*
Propylene oxide	0	15.8	—	15.8	—	0.6	15.9	—	15.9	—	2.3
	29.2	6.0	62.0	9.0	43.8	4.0	7.8	50.9	7.9	50.3	1.7
Butylene oxide	0	13.6	—	12.4	—	5	12.4	—	12.9	—	2.4
	26.7	3.5	74.3	5.5	55.6	1.6	5.0	59.7	5.4	48.1	3.0
	27.0	3.6	73.5	5.7	54.0	1.6	5.2	58.1	5.6	56.6	2.6

[1] Volumetric swelling coefficient determined from initial ovendry volume and first waterswollen volume. Equation (1).

[2] Antishrink efficiency based on S_1. Equation (2).

[3] Determined from first waterswollen volume and reovendrying.

[4] Based on S_2.

[5] Percent weight loss based on the difference between initial ovendry weight and ovendry weight after first water soaking.

[6] Determined from reovendry volume and second waterswollen volume.

[7] Based on S_3.

[8] Determined from second waterswollen volume and second reovendrying.

[9] Based on S_4.

Additional weight loss based on ovendry weight.

Table 14 shows the results of a repeated water wetting test for determining dimensional stability. Propylene oxide and BO specimens show an ASE of about 70 on the first wetting cycle. Because of a small loss of chemical upon leaching, ASE drops during the second wetting cycle. The ASE value calculated from the first wet volume to the second ovendry volume is almost always a lower value than any subsequent ASE values. This is because the new OD volume is smaller than original OD volume because of leached chemical that had bulked the original sample. Because of the slight loss of chemical in the first water soak test in the calculation of ASE in the water leaching test, it is recommended that the OD volume after the first water leach be used for V_1 in equation (1), and the waterswollen volume in the second wetting be used as V_2. This will give a more meaningful measurement of the dimensional stability of a bonded treatment in liquid water.

In almost all tests described for water swelling, a soaking time of 1 week is used. Within 24 hr, the S is within experimental error of what it will be in 7 days (table 15). Soaking beyond 24 hr will not increase the S, but it will influence the amount of material leached out.

All specimens used in these soaking tests were 0.6 cm in the longitudinal direction, permitting easy access of the water into the interior of the specimens. This insured rapid swelling and rate of leaching. All specimens had parallel sides and annual rings parallel to two faces. If the rings were not parallel to two faces, the specimens would have gone out of square during water swelling. Attempts to measure an out-of-square wet block with the flat bed micrometer introduce a very large error in volume measurements.

Since determination of dimensional stability is based on a comparison between an untreated and a treated specimen, it is critical that the treated sample come from the same source as the control. The blocks can serve as their own controls if they are subjected to a soaking-drying cycle prior to treatment. The S for SP springwood is 6 to 9, while summerwood is 17 to 20. The average S for a sample will, therefore, depend on the proportion of summerwood to springwood. If a different control is used to compare with a treated specimen and they differ in the percent of summerwood, then the values obtained for the ASE are nearly useless.

Table 16 and figure 4 show the effects of chemical loadings on the ASE. For PO, the maximum ASE observed is about 60 while BO maximum ASE is over 70 percent at WPG between 21 to 33. The difference between these two may be due to the greater hydrophobicity of BO and the difference in molecular weight. Both treatments show a downward trend in ASE above 33 percent.

Specimens for photo micrographic study were cut from modified or unmodified SP blocks, hand split in the radial direction and mounted on circular (9-mm diameter) specimen holders with a mixture of silver paint and cellulose acetate cement. The stub holders then were transferred to a high vacuum evaporating unit and coated with approximately 100 to 200 Angstroms (Å) of gold. The specimens were examined with a Cambridge Stereoscan Electron Microscope at 20 kilovolts (kV).

Additional specimens were infiltrated with celloiden to fill all cavities and interstices, thereby holding the cellular components in place during sectioning and free-hand cutting and splitting. This was done to demonstrate that the effects observed were due to the chemical treatment and not to specimen preparation.

Table 15.—Rate of water swelling of southern pine

Treatment	Weight percent gain	Volumetric swelling coefficient, S			
		1 day	2 days	4 days	7 days
Control	0	18.9	18.9	19.0	19.0
	0	15.8	15.8	15.8	15.8
Propylene oxide	29.2	6.1	6.1	6.0	6.0

Table 16.—Antishrink efficiencies (ASE) of modified southern pine as a function of weight percent gain (WPG)

Butylene oxide		Propylene oxide	
WPG	ASE	WPG	ASE
	Pct		*Pct*
3.6	16.0	—	—
7.1	22.0	—	—
13.9	52.7	14.0	12.0
—	—	19.7	38.9
21.1	68.8	20.4	51.3
23.0	71.0	—	—
25.4	73.3	25.5	61.4
27.0	73.8	27.1	63.8
—	—	28.0	68.1
—	—	29.5	67.1
—	—	32.6	60.4
33.2	72.2	33.7	63.5
—	—	33.9	57.7
—	—	37.7	35.4
39.4	51.5	39.6	36.1
—	—	45.3	15.1

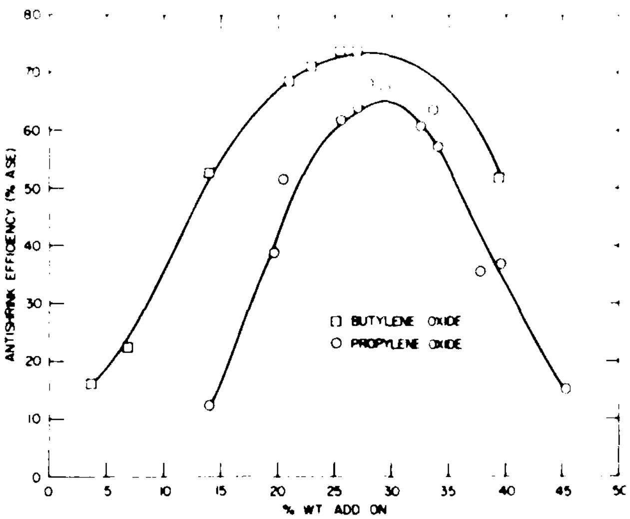


Figure 4.—Relationship between antishrink efficiency and chemical add-on due to epoxide modification. (M151131)

The electron micrographs clearly show the effects of high chemical add-on. Figure 5A shows a radial-split specimen of unmodified SP. Shown in figure 5B is a radial-split specimen of SP modified with PO to 29.5 WPG. The tracheid walls are intact, and no effects of the chemical added can be seen. In figure 5C, the same type of specimen is shown except at 32.6 WPG: checks are starting to form in the tracheid walls. In figure 5D, at 45.3 WPG, the checks in the tracheid wall are very large. The splitting is always observed in the tracheid wall, not in the intercellular spaces; in some cases the splits go through the border pits.

Most of the checks occur in the summerwood portion of the modified wood. The less dense springwood may be able to accommodate more chemical before the cell wall ruptures. It is also possible that there is less chemical add-on in the springwood. If so, and since the WPG is an average for the whole sample, the WPG in the summerwood would be higher than 33 when cell wall rupture occurs.

Only the epoxide treatments have been reported to add to wood cell wall components to such a degree that they cause the wood structure itself to break apart. All other reported chemical substitution treatments of wood components add to wood up to about 35 WPG, and no cell wall rupture has been observed. The epoxide system seems to swell the cell wall, react with it, and continue to swell and react to the point of cell wall rupture and beyond.

Distribution of Bonded Chemicals

Ovendry SP sapwood was treated with PO-EPI (2:1, v/v) with TEA as the catalyst (95:5, epoxide/TEA, v/v) at 120° C, 150 lb/in.². Treated wood specimens were prepared varying the radial and tangential dimensions from 1.2 by 1.2 cm up to 5 by 5 cm. All specimens were 45 cm long with the grain parallel to one face. After treatment, each specimen was taken apart for analysis as described in the following. For determining ASE, 1.0 cm cross-sectional specimens were removed 10 cm from one end and in the center of a sample block. On either side of these cross sections, additional 1.0 cm samples were cut for chlorine analysis. The samples removed for chlorine analysis were cut in three equal sections from the outside to the center. These were analyzed for chlorine as outside, middle, and inner samples.

All chlorine analyses were done by the X-ray fluorescence method. Separate SP blocks, 3.7 by 3.7 by 7.5 cm, were prepared from freshly cut logs and OD. Three types of samples were prepared: (a) sapwood with two to three annual rings per sample with each ring comprised predominantly of springwood with very thin summerwood bands; (b) sapwood with 11 to 12 annual rings per sample with 2- to 3-mm wide bands of summerwood and nearly equal volumes of springwood; and (c) mixed heartwood and sapwood with 22 to 24 annual rings per sample and equal volumes of summerwood and springwood.

These blocks were treated with equal amounts of PO and EPI with TEA as the catalyst (95:5 epoxide/TEA, v/v). Specimens with chemical WPGs of 6 to 36 were prepared by varying the reaction time. Some of the treated specimens were cut into sections of essentially all summerwood or springwood. Volumetric swelling coefficient and ASE were determined.

Separate specimens 3.7 by 3.7 by 7.5 cm were treated with the PO-EPI/TEA system, reovendried, separated into springwood, summerwood, sapwood, and heartwood and ground to pass a 20-mesh screen. Half of the specimen was used to determine chlorine content by x-ray fluorescence; the remainder was extracted with benzene for 2 hr in a Soxhlet extractor, ovendried, and the chlorine content determined.

There is no direct way to determine the degree of chemical substitution with the PO and the BO treatments. Reporting the chemical pickup as a WPG may be in error due to the possible extraction of some hemicelluloses and lignin during the treatment. A direct measurement of epoxide bonding is possible by chlorine analysis of EPI modified wood determined by x-ray fluorescence. Epichlorohydrin with a molecular weight of 92.53 grams per mole (g/mole) is 38.3 percent chlorine. With a ratio of PO-EPI of 1:1 (v/v), the relationship between WPG and chlorine was calculated as (WPG/0.383)/2 = percent chlorine. This calculation assumes equal amounts of PO and EPI, and the ratio is actually 1.12:1 on a mole/mole basis.

In one specimen in which the polymer weight gain was 6.14 g in 21.13 g of wood, the chlorine content was calculated at 11.1 percent. By x-ray fluorescence, 10.5 percent was found. In several other specimens, the percent found was within 1 percent of the calculated chlorine content based on WPG.

Apparently there is some preferential reactivity with epichlorohydrin in samples in which mixtures of PO and EPI were used. For example, in a 1:1 sample (PO/EPI, v/v) at 24.1 WPG, the theoretical chlorine content is 3.8 percent. Chlorine determined by fluorescence gives 4.6 percent. Similarly, at a 2:1 ratio, 18.7 percent add-on calculated Cl 2.4, found 2.9; at 3:1, 16.6 percent calculated Cl 1.6, found 2.8; at 3:1, 24.8 percent calculated Cl 2.4, found 3.4; at 4:1, 27.7 percent calculated Cl 2.1, found 3.5; and 8:1, 24.3 percent calculated Cl 1.0, found 3.1.

It was important to show that the chlorine was not lost during the reaction. It has been shown that under strong alkaline condition, the chlorine is lost through reepoxidation from the chlorohydrin (fig. 6). If the chlorohydrin formed did undergo further reaction to the epoxide, hydrochloric acid would be formed as a byproduct. Under reaction conditions employed, no loss of chlorine was observed during reaction.

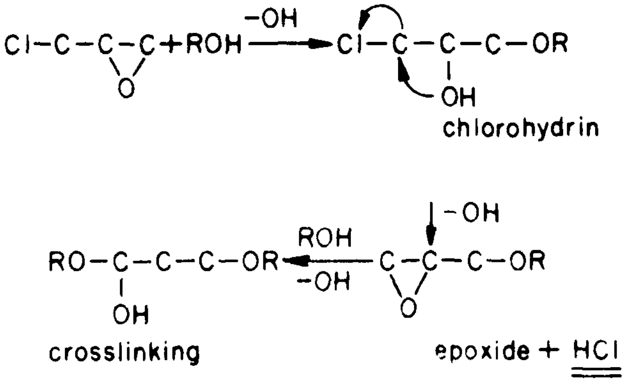


Figure 6.—Reaction of epichlorohydrin in alkali. M 151 1[illegible]

Table 17.—Chlorine distribution and antishrink efficiency of propylene oxide/epichlorohydrin (2:1, v/v) treated southern pine

Sample size	Weight percent gain	Chlorine							Antishrink efficiency	
		Theoretical	End			Center				
			Outside	Middle	Inside	Outside	Middle	Inside	End[1]	Center[2]
Cm		*Pct*								
1.2 by 1.2	28.8	3.7	—	4.5	—	—	4.5	—	65	65
2.5 by 2.5	24.8	3.2	5.34	5.21	5.40	5.83	5.41	5.36	70	69
3.7 by 3.7	20.9	2.7	4.05	3.90	3.75	4.15	3.70	3.30	49	49
5 by 5	28.1	3.6	4.20	4.15	4.40	4.30	4.15	4.15	62	59

[1] 10 cm from sample end.

[2] 22.5 cm from sample end.

In the EPI-treated specimens, the chlorine was confirmed to be in the cell wall by energy-dispersive analysis of x-ray spectra generated in the scanning electron microscope. The greatest percentage of chlorine is in the S_2 layer, which is the thickest cell wall component and contains the most cellulose.

The distribution of chlorine as a function of wood thickness was determined on wood specimens varying the radial and tangential dimensions from 1.2 by 1.2 cm up to 5 by 5 cm as described previously. Table 17 shows little difference in chlorine concentration between outside, middle, and inner (fig. 7) samples; however, a slight chemical concentration difference between the outside layer and the inner layer occurs in the 3.7-cm sample. Table 17 also shows little difference in ASE values even in the 5- by 5-cm samples. The ASE for both the end sample and the center sample are lower than expected for the WPG. From tests to date, a sample with 28 WPG should have an ASE of 65 to 70.

The data here are not conclusive because, although the chlorine concentration is very low in the 5- by 5-cm inner sample, the ASE of that same sample is not lowered to the same degree. This could mean that in the EPI-PO mixture the PO is preferentially penetrating. This would give a higher ASE value than the chlorine analysis would predict. These results indicate that EPI does not penetrate wood deeper than 2 cm (the center of a 3.7- by 3.7-cm sample), but that PO does.

The chlorine content found is higher than the theoretical content based on a dilution factor of 2 to 1 (table 17). There is a preferential reactivity of the EPI. This may also explain why the chlorine content decreases as the thickness increases.

A final observation from table 17 is that in some cases the chlorine content of the inner layer is greater than in the middle layer. This may be due to the high exothermic heat generated by the EPI reaction that creates a hot spot in the center of the wood due to poor heat transfer. This will result in a faster reaction rate in that zone and will apply especially to the larger samples with high end grain penetration of EPI. These hot spots were observed in 5- by 10-cm samples treated with pure EPI or a 1 to 1 (v/v) mixture of EPI and PO. In these specimens, the heat of reaction caused charring in the center, and in some cases, the entire specimen was carbonized. This has not been observed in either PO or BO treatments in samples up to 7.5 by 7.5 cm.

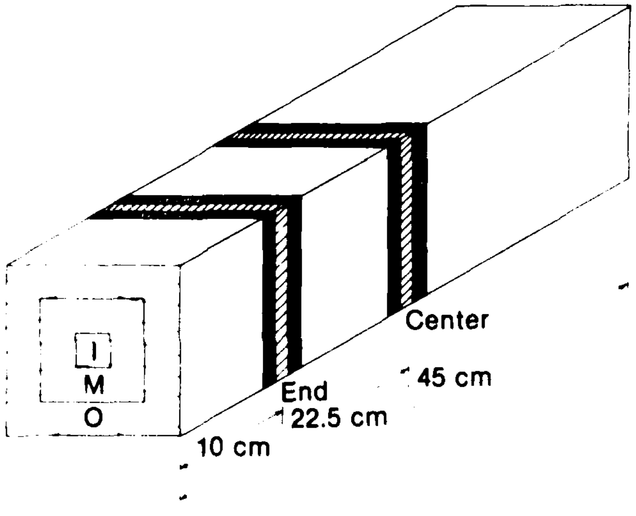


Figure 7.—Scheme for removing sections of southern pine for chlorine analysis and antishrink efficiency determinations. (Samples: I, inner; M, middle; and O, outer.) (M151129)

Separate SP specimens were modified with the PO/EPI system (table 18) to determine the distribution of chlorine in springwood, summerwood, sapwood, and heartwood. For untreated SP summerwood from sample B, S was more than twice that of springwood from sample A (table 19). This was due to the differences in density of the two sections (1, 2, 16). Sample B, which was over half summerwood, achieved a WPG of 20.1 after 2 hr of treatment (table 18). At this same treatment time, sample A, which had a high springwood content, was treated to a WPG of 35.9. This indicated that it was much easier to treat springwood than summerwood. The summerwood sample with a WPG of 20.9 split in the radial direction during treatment. Table 19 also shows that the treated summerwood had an S of 7.4. Even though this represents an ASE of 60.7 compared with unreacted summerwood, it still indicates a swelling equivalent to that of untreated springwood. This means that chemicals used to control swelling must effectively react with the summerwood, for this is the largest contributor to the swelling of wood.

Table 20 shows the reactions of the PO-EPI/TEA system on SP which was mainly springwood (sample A). At the lower weight gain, the amounts of chlorine found were greater in all samples than the theoretical amounts calculated based on EPI. This preferential reaction does not seem to occur at the high WPG.

In the A samples (table 20), summerwood bands were so thin they were not easily separable from springwood. For this reason, the data in table 20 are for isolated springwood bands and for summerwood/springwood mixtures in ratios of 1:1 to 1:3. Even in these summerwood/springwood mixtures, there is a lower chlorine content.

Table 18.—Reaction of southern pine with propylene oxide-epichlorohydrin/triethylamine (120° C, 150 lb/in.^{2})

Reaction time	Weight percent gain		
	Sample A	Sample B	Sample C
Min			
25	19.6	6.7	13.3
38	23.4	11.2	16.9
45	27.0	15.9	19.4
60	27.3	18.6	23.2
120	35.9	20.1	29.8

Table 19.—Four characteristics of summerwood and springwood of southern pine treated with propylene oxide

Samples	Density	Weight percent gain	Volumetric swelling coefficients (S)	Antishrink efficiency (ASE)
			Pct	
Springwood (A)	0.33	0	7.8	—
		24.2	2.1	73.1
		33.5	1.6	79.5
Summerwood (B)	.70	0	18.8	—
		20.9	7.4	60.7

Table 20.—Chlorine determination on southern pine treated with propylene oxide-epichlorohydrin/triethylamine (samples A)

Isolated sections[1]	Weight percent gain	Chlorine based on weight percent gain	Chlorine found	Weight percent gain based on chlorine found	Percent weight loss on extraction
		Pct	*Pct*		*Pct*
Sp NE	19.6	3.76	5.42	28.3	—
E	—	—	4.57	23.9	4.9
Su/Sp NE	—	—	4.98	26.0	—
E	—	—	4.40	23.0	4.0
Sp NE	27.0	5.18	6.02	31.4	—
E	—	—	5.01	26.2	2.5
Su/Sp NE	—	—	5.30	27.7	—
E	—	—	4.77	24.9	2.8
Sp NE	35.9	6.89	6.88	35.9	—
E	—	—	6.11	31.9	6.9
Su/Sp NE	—	—	6.12	32.0	—
E	—	—	5.08	26.5	5.3

[1] Sp, springwood; Su, summerwood, E, extracted with benzene; NE, no extraction.

Table 21.—Chlorine determination on southern pine treated with propylene oxide-epichlorohydrin/triethylamine (samples B)

Isolated sections[1]	Weight percent gain	Chlorine based on weight percent gain	Chlorine found	Weight percent gain based on chlorine found	Percent weight loss on extraction
		——— Pct ———			—Pct—
Sp NE	6.7	1.28	3.33	17.4	—
E	-	—	3.65	19.1	3.9
Su NE	-	—	1.46	7.6	—
E	—	—	1.34	7.0	1.4
Sp NE	18.6	3.57	6.12	32.0	—
E	—	—	5.42	28.3	2.9
Su NE	—	-	4.20	21.9	—
E		—	3.29	17.2	1.5
Sp NE	20.1	3.87	5.58	29.1	—
			5.33	27.8	2.4
Su NE		—	4.00	20.9	—
E			3.80	19.8	1.5

[1] Sp, springwood; Su, summerwood; E, extracted with benzene; NE, no extraction.

Table 22.—Chlorine determination on southern pine treated with propylene oxide-epichlorohydrin/triethylamine (samples C)

Isolated sections[1]	Weight percent gain	Chlorine based on weight percent gain	Chlorine found	Weight percent gain based on chlorine found	Percent weight loss on extraction
		——— Pct ———			—Pct—
S NE	13.3	2.55	3.29	17.2	—
E	—	—	3.17	16.6	1.5
H NE	—	—	4.54	23.7	—
E	—	—	3.33	17.4	4.3
S NE	19.4	3.72	4.89	25.5	—
E	—	—	3.87	20.2	1.7
H NE	—	—	4.84	25.3	—
E	—	—	2.85	14.9	4.9
S NE	23.2	4.45	5.02	26.2	—
E	—	—	4.00	20.9	1.4
H NE	—	—	5.63	29.4	—
E	—	—	3.35	17.5	5.2
S NE	29.8	5.71	5.53	28.9	—
E	—	—	3.78	19.7	2.3
H NE	—	—	5.66	29.6	—
E	—	—	3.44	18.0	6.0

[1] S, sapwood; H, heartwood; E, extracted with benzene; NE, no extraction.

The B samples (table 21) were from sapwood that had about equal amounts of summerwood and springwood. Here the bands were wide enough that good separation was possible. The data in table 21 clearly show preferential reactivity in the springwood. At a WPG of 6.7, over 100 percent more reacted chemical was in the springwood and, at a WPG of 20.1, there was 40 percent more reacted in springwood than in summerwood. Almost twice as much weight loss on benzene extraction was observed in the springwood as in the summerwood.

Part of the explanation why springwood contains more bound chemical than summerwood may be found in a consideration of the distribution of reacting chemical within the wood. The void volume of the wood gives an indication of the vacant space within the wood that the entering chemical can occupy. The greater the void volume, the greater will be the amount of chemical that can be contained by the wood. Assuming the voids are evenly distributed and totally accessible to the chemical, the greater the void volume, the greater will be the content of reacting chemical within a unit quantity of wood. The relative void volume of ovendried SP as given before is 0.77 cm³ voids/cm³ or 2.3 cm³/g for springwood and 0.52 cm³/cm³ or 0.74 cm³/g for summerwood. This means that there is 1.5 times more void volume in springwood than in summerwood on a total volume basis. On a weight basis, springwood has 3.1 times more void volume per gram than summerwood. These void spaces would allow a greater content of chemical within the springwood. With the thinner, more easily penetrated springwood walls, it would be expected that more reaction would occur.

The differences in chemical pickup in SP modified with the PO-EPI/TEA system showed greater uptake in heartwood before benzene extraction (table 22). However, almost three times as much weight loss was observed after extraction of the heartwood samples with benzene. After extraction, the amount of nonleachable chemical observed in the heartwood was lower than in sapwood in all samples except in the lowest weight percent gain sample. Obviously then caution must be taken in interpreting the results of chemical uptake in species with significant extractives content.

Epoxides Reacted

Nine epoxides (figs. 8 and 9) other than PO, BO, and EPI were selected for evaluation. Southern pine specimens 2.5 by 2.5 by 0.6 cm were cut from a board which had 10 to 12 growth rings per inch with rings parallel to one edge. Ovendried specimens in duplicate were submerged in 25 ml of 95/5 epoxide/TEA (v/v) in a 150-ml stainless steel cylinder. The specimens were treated at 120 °C (150 lb/in²) for varying lengths of time. Volumetric swelling coefficient and ASE were calculated from untreated and treated specimens.

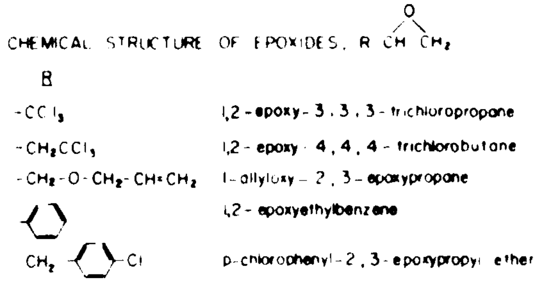


Figure 8 – Chemical structure of monofunctional epoxides $\overset{O}{R\text{-}CH\ CH_2}$ *(M151132)*

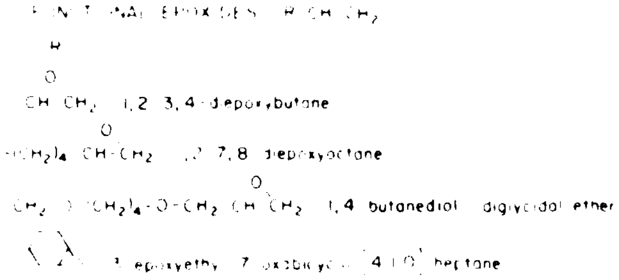


Figure 9 – Chemical structure of difunctional epoxides $\overset{O}{R\ CH\ CH_2}$ *(M151133)*

Table 23 shows that 1.2-epoxyethylbenzene reacts more slowly with wood than either BO, PO, or EPI. After 6 to 16 hr of reaction with 1.2-epoxyethylbenzene-TEA, good dimensional stability was achieved with very little loss of bonded chemical after two water soak tests. 1-Allyloxy-2.3-epoxypropane also reacted well with wood, giving good nonleachable weight gains and moderately high ASE values. 1.4-Butanediol diglycidal ether and 1.2:3.4-diepoxybutane gave high nonleachable weight gains but no dimensional stability. This means that these two epoxides polymerized in the cell lumen and did not react with hydroxyl groups in the cell wall. p-Chlorophenyl 2.3-epoxypropyl ether, 3-epoxyethyl-7-oxabicycloheptane, and 1.2:7.8-diepoxyoctane did not react very well with wood and therefore gave only low levels of dimensional stability. It was hoped that the difunctional epoxides would undergo crosslinking between hydroxyl groups on different polymer chains which would result in good dimensional stability at relatively low weight gains. This was found not to be the case. Since 3-epoxyethyl-7-oxabicycloheptane did not react with wood, it can be assumed that the epoxide group on the cyclohexane ring is not reactive under the conditions used. This would mean that the reactive epoxide in 3-epoxyethyl-7-oxabicycloheptane is the epoxyethyl group and not the epoxide on the cyclohexane ring.

Table 23.--Properties of modified southern pine

Chemical	Reaction time	Weight percent gain	S_o[2]	ASE$_1$[3]	ASE$_2$[4]	Weight percent gain retained[5]
	Min		*Pct*	*Pct*	*Pct*	
1,2-epoxyethyl benzene	60	7	0.4	0	2	3
	240	10	2.6	22	19	9
	390	26	9.3	66	63	25
	450	23	9.4	66	66	21
	1.080	30	12.0	78	76	27
1-allyloxy-2,3-epoxypropane	15	4	1.5	15	8	0
	25	17	10.2	48	37	14
	45	20	7.5	48	45	18
	60	26	9.5	56	41	19
	120	32	11.0	59	56	29
1,4-butanediol diglycidal ether	15	8	8	2	0	6
	20	7	1.2	5	0	4
	25	16	2.1	14	15	7
	27	23	5.0	19	7	9
	30	39	2.8	3	0	37
[illegible] ether	15	4	.9	2	4	1
	60	19	4.4	36	27	11
	120	14	1.6	4	0	12
	240	20	.8	7	2	17
	360	14	1.4	12	10	11
[illegible]	30	3	.9	5	0	0
	60	4	1.1	6	0	0
	300	17	4.0	31	15	9
	450	17	4.9	24	10	11
	1.080	12	1.3	9	3	4
[illegible]	15	16	1.8	23	13	9
	22	8	2.5	0	0	4
	25	8	3.8	5	0	1
	30	37	4.5	22	21	35
	60	64	1.7	8	0	61
[illegible]	30	9	6.6	24	11	3
	60	17	3.5	22	18	12
	180	11	3.6	22	10	8
	240	20	7.6	41	33	14

[1] [illegible] weight of [illegible] treated ovendry wood

[2] [illegible] reacted chemical remaining in wood after solvent extraction and ovendrying

[3] [illegible] treated wood in liquid water compared to untreated wood in first 7 day soak

[4] [illegible] treated wood in liquid water compared to untreated wood after second 7 day soak

[5] [illegible] after two 7 day water soak periods, based on weight of untreated ovendry wood

[illegible]

Wood Species Modified

Thirteen different species of wood (table 24), 2 by 2 by 15 cm, were treated with either PO or BO with TEA as catalyst (95:5, v/v) at 120° C, 150 lb/in.^{2}. Weight percent gain was determined on an OD basis before and after treatment. ASE was determined from a single water soak test.

It can be seen in table 24 that many species will react under the conditions used. Most species tested gave weight gains similar to SP and showed equivalent dimensional stability resulting from the modification. Of the species tested there were two which gave unexpected results. Both red oak and teak reacted with the PO and BO systems but neither resulted in any dimensional stability. Teak is very high in extractives that may interfere with the reaction. This may give rise to nonbonded homopolymer in lumens and no reaction in cell wall. Oak, on the other hand, is low in extractives so that the weight gains should be cell wall bonded chemical.

It is easy to generalize on the type of wood that can be modified and extrapolate information to an untried species with the rationale that if it worked on one it will work on the other. The data collected so far would indicate that this is a dangerous assumption. The parameters of chemical modification as they relate to species differences are not known at this time. Each species must be tested separately without any assumptions on treatability.

Effects of Moisture on Epoxide Reactions

One of the greatest concerns in considering chemical modification as a viable commercial process is how dry the wood must be before the reaction chemicals come into contact with the wood. Since the epoxides react with any hydroxyl group, the hydroxyl group in water will also react. This would result in glycol formation from the reaction of epoxide with water. The epoxide would then be lost for bonding to wood. It is not possible or practical to dry wood to zero percent moisture, so it was important to determine the effects of low levels of moisture in wood on reactivity and resulting properties with the PO and BO systems.

Table 24.--Wood species treated at 120°C, epoxide/triethylamine (95:5, v/v) 150 lb/in.^{2}

Species	Treatment[1]	Time	Weight percent gain	ASE[2]
		Min		
Red oak	PO	30	21.8	0
	PO	40	25.6	2.1
Hard maple	PO	35	27.3	41.1
	BO	60	18	52.2
	BO	180	32	61.0
Teak	PO	30	20.5	0
	PO	60	20.7	0
Walnut	PO	3	26.2	46
	BO	240	28.3	53
Elm	PO	40	28.2	46.3
Cativo	PO	40	29.7	42.2
	BO	240	22.8	64.2
Persimmon	BO	180	22	—
	BO	240	33	—
Eucalyptus obligva	BO	240	22	46.4
Radiata pine (sapwood)	PO	40	34.2	67.3
(heartwood)	PO	40	32.1	52.3
Southern pine (sapwood)	PO	40	35.5	68.3
(heartwood)	PO	40	24.6	59.7
Ponderosa pine	PO	40	26.9	36.5
Douglas-fir	BO	300	20.7	—
	BO	360	24.6	—
Spruce	PO	40	32.6	—
	BO	360	30.4	—

[1] PO—propylene oxide; BO—butylene oxide.

[2] Antishrink efficiency after one water soak.

Table 25.—Repeated reactions of propylene oxide with ovendried and moist ponderosa pine

Specimen	Equilibrium moisture Content when treated	Weight percent gain	Dimensional Stability: Water soak ASE_1	Dimensional Stability: Water soak ASE_2	Dimensional Stability: 27° C, 90 percent relative humidity ASE_1	Dimensional Stability: 27° C, 90 percent relative humidity Equilibrium moisture content	Extraction of 20-mesh sample with benzene:EtOH weight loss	Weight gain remaining after extraction	Wood weight loss 14 days at 105° C
	Pct								
1-0-PO	~0 OD	26.0	52.8	11.1	3.8	20.2	—	--	4.1
2-0-PO	~0 OD	38.0	67.7	34.3	96.6	20.5	13.4	19.4	5.1
3-0-PO	~0 OD	39.0	57.0	22.0	—	—	—	—	5.2
4-0-PO	~0 OD	38.4	64.0	34.3	—	—	13.3	20.1	5.3
5-0-PO	~0 OD	31.9	61.0	25.1	—	—	—	—	5.1
6-0-PO	~0 OD	32.7	62.7	29.8	26.4	20.4	14.2	13.8	5.1
7-0-PO	~0 OD	40.4	68.8	42.0	—	—	—	—	5.4
8-0-PO	~0 OD	33.3	60.8	12.6	32.1	20.2	14.5	14.0	5.3
9-0-PO	~0 OD	40.3	59.3	20.3	77.4	19.1	—	—	5.3
10-0-PO	~0 OD	32.0	58.2	13.8	17.0	20.4	15.4	11.8	4.9
1-5-PO	5.6	47.4	88.1	29.3	0.0	21.6	28.3	5.8	16.5
2-5-PO	5.7	54.1	76.4	18.5	77.4	28.1	26.5	13.3	15.5
3-5-PO	5.5	52.0	83.4	24.4	—	—	27.2	10.7	16.4
4-5-PO	5.5	53.2	84.5	33.4	—	—	29.4	8.2	16.6
5-5-PO	5.7	53.2	79.6	23.7	64.2	28.1	28.5	9.5	16.9
1-10-PO	10.8	59.0	85.6	16.5	79.2	34.5	35.6	2.5	20.2
2-10-PO	10.0	49.6	88.1	0	77.4	32.3	31.1	3.1	19.8
3-10-PO	10.6	61.1	87.0	24.1	83.0	34.3	33.7	6.9	20.4
4-10-PO	10.7	49.5	80.6	27.1	71.7	31.5	31.6	2.3	16.3
5-10-PO	10.0	39.3	72.3	0	64.2	28.0	25.1	4.3	14.0
Average controls						19.4	3.9		

Forty ponderosa pine (PP) specimens, 2 by 8 by 16.5 cm, were prepared. Twenty were ovendried, 10 were equilibrated at 30 percent relative humidity (RH) 27° C, and 10 were equilibrated at 65 percent RH, 27° C. These specimens were used to run a series of epoxide reactions as follows: One OD sample was treated with either 1,500 ml PO/TEA or BO/TEA (95/5 v/v) at 120° C, 150 lb/in². At the end of this treatment, a second specimen was treated with the same treating solution made back up to 1,500 ml with fresh epoxide/TEA mixture (approximately 200 ml). This procedure was repeated for a total of 10 runs for the OD specimens, 5 runs each for the specimens equilibrated at 30 percent RH and 65 percent RH.

After reaction, each specimen was OD for 14 days at 105° C and weight loss determined. Each specimen was then cut and ASE determined in both the water soaking test and at 90 percent RH at 27° C. A portion of each specimen was ground to pass a 20-mesh screen, extracted with refluxing benzene/ethyl alcohol (2:1 v/v) for 2 hr, and weight loss determined.

A 10-ml sample of each treating solution was collected at the end of each run and submitted for gas chromatographic analysis. The gas chromatograph was a Varian 3700 with a thermal conductivity detector. A helium carrier was used with a 400-cm by 2-mm column packed with 60/80-mesh Porapak QS. Starting temperature was 75° C, program temperature rise of 4° C/min to a final temperature of 230° C. The ratio of epoxide to TEA was determined along with percent water and volatile unknowns. The percentage of butylene glycol was also determined on the BO samples.

It can be seen in tables 25 and 26 that 10 runs of PO or BO at zero percent wood moisture gave consistent results. The ASE values for PO go from 58 to 70 percent in the first soak cycle to 11 to 42 percent on the second water cycle. The ASE values for BO are higher than PO on the first soak cycle and do not drop as much on the second. Part of the weight gain is lost on continuous ovendrying and through extraction.

Table 26.--Repeated reactions of butylene oxide with ovendried and moist ponderosa pine

Specimen	Equilibrium moisture Content when treated	Weight percent gain	Dimensional Stability				Extraction of 20-mesh sample with benzene:EtOH weight loss	Weight gain remaining after extraction	Wood weight loss 14 days at 105° C
			Water soak			27° C, 90 percent relative humidity			
			ASE_1	ASE_2	ASE_1	Equilibrium moisture content			
	Pct								
1-0-BO	~0 OD	33.6	69 2	58.7	60.4	12.9	--	—	5.1
2-0-BO	~0 OD	26 3	68.1	56 5	--	—	13.7	9.0	4.2
3-0-BO	~0 OD	33.1	68.1	59 1	—	—	—	—	5.0
4-0-BO	~0 OD	23.4	39.9	25.5	0.0	14.5	15.4	4.5	4.1
5 0-BO	~0 OD	29.7	57.2	42.9	-	—	—	—	5.9
6-0-BO	~0 OD	38.0	75.4	65.2	—	--	18.4	12.6	6.7
7-0-BO	~0 OD	21 2	58.2	52.8	37 7	14 3	—	—	3.0
8-0-BO	~0 OD	32.7	75.5	58.1	—	—	16.2	11.2	4.1
9-0-BO	~0 OD	29 6	70 2	59.8	41.5	14 7	—	—	5.0
10-0-BO	~0 OD	36.4	75.4	68.8	—	--	17.3	13.2	5.4
1-5-BO	4.9	50.7	91.8	49.7	66.0	14.4	34.8	- 1.7	14.6
2-5-BO	5.1	52 6	91.9	46.6	94.0	14.3	33.1	2.1	15.7
3-5-BO	5.5	71.8	100.0	62.0	77.4	14.4	38.1	6.3	18.5
4 5-BO	5.4	65.8	100.0	66.2	—	—	36.5	5.3	17.7
5-5-BO	[illegible]	70.8	96.4	57.5	73.6	14.8	38.1	5.7	20.0
1-10-BO	10.5	69.7	98.8	50 0	—	—	39.7	2.4	24.4
2-10-BO	10.4	77.8	97.6	53.5	—	—	43.6	.3	25 7
3-10-BO	9.8	77 3	93.0	43.7	58.5	16.5	43.7	- .2	25 9
4-10-BO	10 3	91.1	100.0	57 9	88.7	17.7	47.2	.8	27 8
5-10-BO	10.0	68.3	90.8	35.2	67.9	16.4	39 4	1.9	24 3
Average control						19.4	3.9		

At both 5 and 10 percent moisture levels PO-modified wood specimens (table 25) show high initial dimensional stability, but very little in a second soak cycle. This finding coupled with the high amount of chemical lost to both extraction in benzene/ethanol and continuous ovendrying would indicate that cell wall penetration has taken place but little or no bonding. Similar results were obtained with BO-modified wood (table 26) except there is not as much drop in dimensional stability in continuous soak cycles.

It is interesting to note that a control specimen conditioned at 27° C, 90 percent RH has a moisture content of 19.4 percent while BO-modified wood has a somewhat lower average moisture (17 pct). Propylene oxide-modified specimens on the other hand have an average moisture content of over 32 percent. This would indicate that the PO-modified wood was somewhat hygroscopic while the BO-modified wood is hydrophobic.

Little difference in specimen properties was observed on repeated use of the treating solution. The effects of the moisture are seen in the first specimen treated, and subsequent treatments do not compound the effects of accumulated moisture.

Gas chromatographic examination of the treating solutions (tables 27 and 28) also shows no buildup of water in reusing the solutions up to five times on moist specimens. With the BO solutions there is an increasing amount of butylene glycol as the treating solution is reused, showing that some of the BO is hydrolyzed to the glycol.

Table 27.--Gas chromatographic analysis of propylene oxide/triethylamine solutions used to treat ponderosa pine

Specimen No.	Propylene oxide/ triethylamine ratio	Water	Volatile unknown	Total
		Pct		
1-0-PO	21.4	0.03	0.04	92.04
2-0-PO	21.5	.04	.06	92.67
3-0-PO	20.5	.05	.22	93.42
4-0-PO	19.8	.22	1.62	97.52
5-0-PO	19.6	.09	.18	96.04
6-0-PO	18.9	.04	.13	92.08
7-0-PO	19.6	.17	.14	90.63
8-0-PO	19.0	.08	.13	91.06
9-0-PO	18.1	.06	.31	91.38
10-0-PO	16.7	.15	.23	84.44
1-5-PO	17.5	.09	.07	88.73
2-5-PO	19.3	.18	.16	82.63
3-5-PO	19.2	.11	.06	77.84
4-5-PO	20.1	.12	.06	76.67
5-5-PO	20.6	.08	.03	68.44
1-10-PO	23.4	.23	.85	90.07
2-10-PO	23.9	.08	.07	78.07
3-10-PO	24.1	.08	.05	71.16
4-10-PO	21.2	.17	.11	60.32
5-10-PO	23.7	.34	.54	50.53
Starting solution	19	0	0	

A starting ratio of PO/TEA or BO/TEA is 95:5, v/v, or 19. After one treatment of wood at zero percent moisture the ratio is up to 21 to 22 for both PO and BO, and then decreases with subsequent runs to 15 to 16. This means that the epoxide is removed and TEA is increasing as new 95:5 mix is added to make up the volume for the next run. When moisture is present in the wood, the ratio of epoxide/TEA increases somewhat.

There is very little change in the amount of unknown volatile material in the solutions, however, the total accountable materials decreases significantly with continuous solution use. This means that nonvolatile homopolymers are being formed. These homopolymers will not react with wood and therefore do not end up as bonded cell wall chemical. If polymer is formed in the cell wall and if the wood does not come into direct contact with liquid water, then the polymer would act as a nonbonded cell wall bulking agent and could provide a high degree of dimensional stability.

Table 28.--Gas chromatographic analysis of butylene oxide/triethylamine solution used to treat ponderosa pine

Specimen No.	Butylene oxide/ triethylamine ratio	Butylene glycol	Water	Volatile unknown	Total
		Pct			
1-0-BO	22.1	0.035	0.028	0.337	93.59
2-0-BO	19.1	.075	.029	.313	94.59
3-0-BO	17.9	.0719	.233	.606	94.08
4-0-BO	15.8	.074	.119	.396	93.28
5-0-BO	15.0	.097	.130	.360	91.90
6-0-BO	14.0	.128	.344	.371	90.78
7-0-BO	15.2	.015	.096	.485	84.89
8-0-BO	15.5	.125	.179	.454	89.68
9-0-BO	16.4	.112	.125	.295	90.31
10-0-BO	16.3	.125	.181	.335	90.06
1-5-BO	21.0	.023	.259	.224	95.65
2-5-BO	21.3	.046	.969	.175	91.98
3-5-BO	22.1	.060	.071	.232	85.39
4-5-BO	21.3	.073	.448	.431	81.75
5-5-BO	22.5	.076	.629	.346	78.52
1-10-BO	21.6	.015	.113	.385	89.94
2-10-BO	22.3	.038	.099	.388	80.80
3-10-BO	22.7	.045	.091	.267	73.79
4-10-BO	21.3	.023	.093	.276	67.08
5-10-BO	24.4	.043	.055	.334	58.70
Starting solution	19.0				

Decay and Termite Tests

Laboratory—Decay.

Standard soil-block tests were run according to specifications as outlined in the American Society for Testing and Materials (ASTM) D 1413 (1973). Southern pine blocks, 2 by 2 by 2 cm, untreated or modified with PO, BO, EPI, or styrene oxide were placed in test with either the fungus Madison 534 (*Lentinus lepideus*), Madison 617 (*Gloeophyllum trabeum*), or Madison 697 (*Coriolus versicolor*). Specimens were removed at 6 and 12 weeks, and the extent of decay was determined as OD weight loss.

Separate samples were leached for 7 days with distilled water before being placed in test.

It can be seen in table 29 that PO-modified SP is resistant to attack by *Lentinus lepideus* at WPG of 24. This brown-rot fungus is not as destructive to SP as is *Gloeophyllum trabeum*. Table 30 shows that PO-modified SP is not very resistant to attack by *Gloeophyllum trabeum* even at high WPG. Butylene oxide and EPI modified wood is resistant to attack at WPG over about 23. Very little weight loss occurs with the white-rot fungus *Coriolus versicolor* even in control specimens. Both PO- and BO-modified wood is resistant to attack by this fungus at weight gains above 20 percent (table 31).

Results from soil-block tests on leached blocks show that effectiveness of bonded BO was due to [illegible] substrate modification and not toxicity of the bonded chemical. If the bonded epoxide was toxic to the fungus, decay resistance would have been [illegible] at much lower WPG. Resistance to decay by *Gloeophyllum trabeum* of SP modified with BO or pentachlorophenol are shown in figure [illegible]. Attack was essentially stopped at about 24 WPG for BO and the level required for pentachlorophenol [illegible] 0.5 WPG. The curve for pentachlorophenol [illegible] shows what effect a highly toxic chemical has on fungal growth.

Theoretically the degree of substitution (DS) of bonded chemicals on the cell wall components would be the most important factor in the effectiveness of chemically modified wood in controlling attack by micro-organisms. While the degree of polymerization (DP), after initial grafting to cell wall components, increases bulking in the cell wall and contributes positively to dimensional stability. DP does not seem to contribute to decay resistance except perhaps to exclude water from the enzyme-substrate site which is required for attack to take place.

Laboratory—Unsterile Soil

Ovendried wood of PP 19 by 19 by 152 mm were reacted with BO/TEA (95:5, v/v) at 120° C and 150 lb/in². By varying the reaction time, three different WPG specimens were obtained: 8, 15, and 23.7. Small blocks, 5 by 5 by 10 mm, were cut from the larger blocks.

Three small unleached wood blocks from each treatment were incubated at approximately 22° C in moist unsterile compost soil (garden refuse compost). A set of unmodified PP blocks was also placed in the soil. The blocks were removed from the soil after 6 weeks exposure and transverse, radial and tangential sections were cut for microscopic examination. The unmodified wood blocks were studied after 4 weeks exposure.

Table 29.—Soil-block tests on propylene oxide treated southern pine inoculated with *Lentinus lepideus*

Weight percent gain	Percent weight loss	
	6 weeks	12 weeks
0	24.3	44.2
5.1	8.1	17.5
24.0	3.2	4.8
36.6	2.6	4.6
44.5	3.4	7.3
50.9	3.7	5.3

Table 30.—Soil-block tests on epoxide-modified southern pine inoculated with the fungus *Gloeophyllum trabeum*

Specimen	Weight percent gain	Percent weight loss after			
		Nonleached		Leached	
		6 weeks	12 weeks	6 weeks	12 weeks
Control	0	44.6	62.9	44.9	68.7
Propylene oxide	20	12.9	40.0	26.7	38.6
	24	10.3	35.5	17.3	50.4
	37	8.4	28.7	14.2	23.6
	50	6.5	25.2	12.7	25.0
Butylene oxide	7	5.2	18.8	7.0	16.8
	14	2.9	12.4	1.3	11.9
	23	3.2	3.8	2.7	2.0
Epichlorohydrin	17	4.9	7.2	6.2	9.7
	25	2.6	5.1	2.4	—
	35	2.2	5.9	2.0	4.1
	41	—	—	3.7	4.0

Table 31.—Soil-block tests on epoxide-modified southern pine inoculated with *Coriolus (Polyporus) versicolor*

Specimen	Weight percent gain	Percent weight loss after 12 weeks
Control	0	3.43
Propylene oxide	16.2	4.54
	25.2	1.06
	30.5	.88
Butylene oxide	17.3	.26
	25.9	[illegible]
	29.8	[illegible]

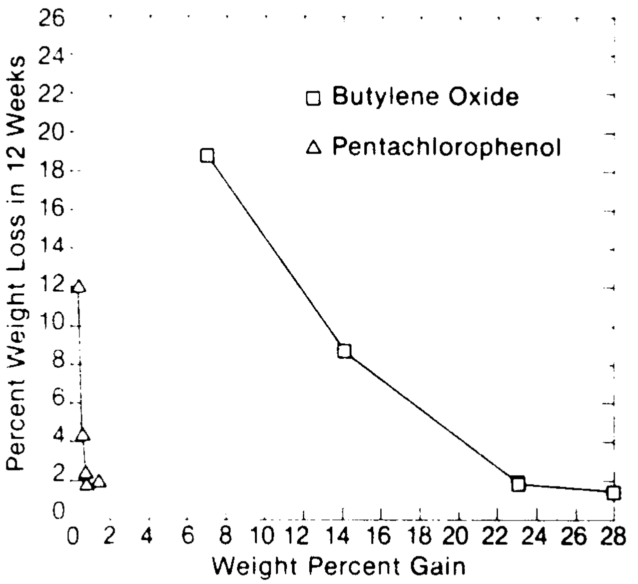


Figure 10.—Resistance of modified southern pine exposed to the fungus ***Gloeophyllum trabeum****. (M151134)*

A simple study was done on unmodified PP blocks in order to try to demonstrate pathways for solutions in the wood structure. The blocks were placed in a 2 percent solution of crystal violet with the transverse surface downwards in the solution. The depth of the solution was approximately 3 mm. The solution was allowed to soak through the wood blocks by capillary forces. The process was stopped when the first signs of stain appeared on the upper transverse faces of the wood blocks. The blocks were then left to dry overnight and were subsequently leached in water until no more stain was given off. Transverse sections were cut and the distribution of the violet stain was studied with a light microscope.

The untreated wood blocks were attacked by soft rot. Typical soft-rot cavities were found in both earlywood and latewood tracheids. The heaviest attack occurred in the latewood tracheids where the cavities were more or less randomly distributed in the radial and tangential walls.

The surfaces of the wood blocks with a weight gain of 8 percent were softened and severe decay by soft rot fungi and "tunneling" bacteria was observed in the outermost parts of the blocks. The tunneling bacteria is a special group of wood-degrading bacteria which penetrate into the wood fiber walls where they form tunnels and later complete destruction of the cell wall structure. These bacteria appear to be much more tolerant to preservatives than soft-rot fungi. The bacterial attack in the treated wood blocks was most pronounced in the latewood tracheids where the radial walls and [illegible] parts of fiber walls were attacked.

The soft-rot decay pattern was very unusual, because all cavities were confined to the radial walls in the latewood tracheids. However, most of the radial walls that were seen next to rays in the microscope sections were not attacked. Cavity initials (T-branches) were observed in the tangential walls but further development seemed to have stopped.

There are two immediate explanations to the uneven distribution of the soft-rot cavities. The first one is that chemical differences between the tangential and radial walls in the tracheids have resulted in different types or different degrees of reaction with the BO. The radial walls contain a higher proportion of lignin than the tangential walls. This could possibly affect the type or degree of reaction.

The most likely explanation is that the radial walls have not been completely penetrated by the solution of BO/TEA. The radial walls in the latewood are nearly twice as thick as the tangential walls. Microscopic studies of sections from the wood blocks that had been partially stained with crystal violet showed that only the inner halves of the radial walls in the latewood tracheids were stained while the tangential walls were completely penetrated by the stain. Most of the radial walls adjacent to the rays were also generally well stained. The penetration of the stain was observed to be slower in the radial walls than in the tangential walls in some of the latewood tracheids.

The staining experiment showed that areas which remained unstained coincide with the areas where heavy soft-rot attack occurred. This strongly indicates that the peculiar distribution of soft-rot attack is due to incomplete penetration of the radial walls by the solution of BO/TEA.

Very few soft-rot cavities were found in wood blocks with a weight gain of 15 percent. The superficial decay observed was caused by tunneling bacteria. Their attack in the wood blocks now showed the same uneven distribution as the soft-rot attack in wood blocks with 8 WPG. The distribution of bacteria was not affected by the chemical modification at the lower weight gain probably because of their greater tolerance to toxicants. But at the higher weight gain they became restricted to the radial walls in the latewood tracheids, which again probably are less well treated compared with the tangential walls. No attack could be found in wood blocks with a weight percent gain of 23.7.

The results obtained so far indicate important distribution differences in connection with chemical modification of PP with BO. The same problems are likely to occur in other softwoods as well.

Laboratory—Termite

Blocks of SP, 4.5 by 4.5 by 15 cm, were OD and treated with either PO/TEA or BO/TEA (95:5, v/v) at 120° C, 150 lb/in². Specimens were prepared as 9, 17, and 34 WPG for PO and 27 and 34 WPG for BO. A sixth specimen from the same board was used untreated as a control.

The control and treated pieces were sawed into seven smooth-faced 0.4- by 4.5- by 15-cm strips. Two blocks, 0.4 by 2.5 by 2.5 cm, were cut from the middle of each of the three central strips. Five of these, designated interior blocks, were randomly selected for testing. Four blocks of the same dimensions were cut from the two strips initially on the surface of the starting piece. Five of these, designated surface blocks, were randomly selected for testing.

Individual sets of five interior and five surface blocks from each treatment, and the control, were leached in a Soxhlet extractor for 2 hr with benzene/ethanol (2:1 v/v) and, after drying, for another 2 hr with water. The leaching process was designed to remove any toxic residual unreacted reagents. The leached blocks were dried overnight in a 105° C oven.

Reticulitermes flavipes (Kollar) subterranean termites, were collected at Janesville, Wis., and maintained in a 20-gallon metal container prior to use (Esenther 1977). In a preliminary test, approximately 87 percent of the termites placed in containers with control blocks survived over a 4-week period, indicating that the termites would be acceptable for further experimental usage.

An exposure method was selected (Esenther 1969) where the treated wood was the only source of nutrients for the termites because this would reveal whether unpalatability might be an antitermitic property of the epoxide-modified wood. Dry, washed sand (10 ml) was placed [illegible] in a clear plastic container (inside dimensions 5 cm diameter and 3.5 cm deep). The sand was wetted with 2.5 ml distilled water, and a leached, OD weighed SP block was placed on the sand (with the 2.5- by 2.5-cm surface in contact with the sand). Each of the 55 experimental blocks (25 interior, 25 surface, and 5 controls) were placed in such units—one per unit. Five [illegible] without wood blocks were also prepared [illegible]. One-gram groups of termites [illegible] were placed in each unit. The number of termites in various caste forms (workers, nymphs, and soldiers) were counted in three of every five replicate containers. The termite group consisted mainly of the worker form, the form that actually attacks wood. The average number of termites in the groups was [illegible] ([illegible] percent workers, [illegible] percent nymphs, and 1.5 percent soldiers). The test units with [illegible] were stored in a 25° C incubator.

Table 32.—Percent weight loss in control and modified southern pine blocks after 2 weeks exposure to subterranean termites

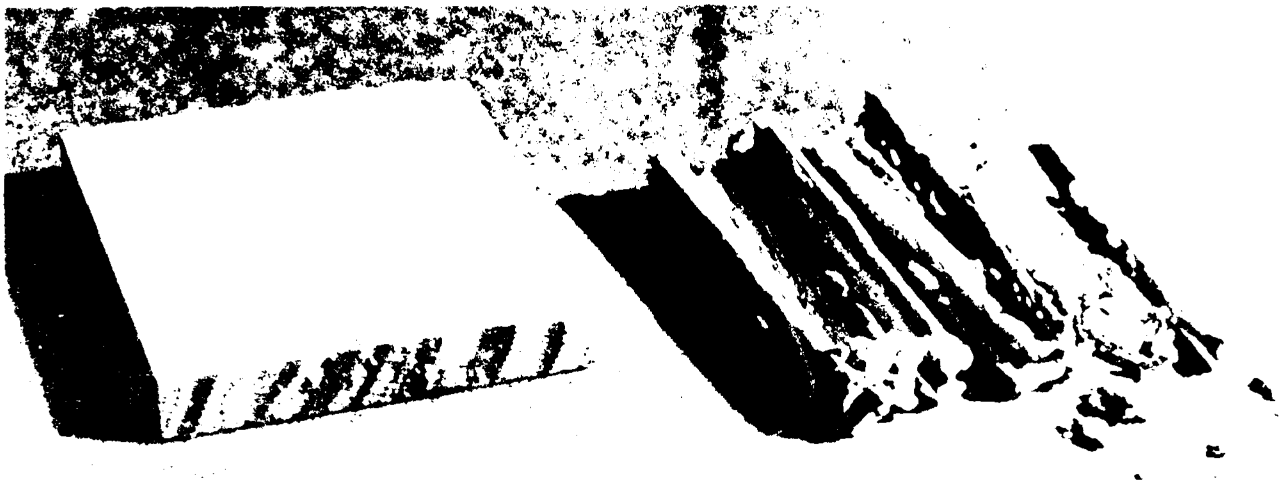
Specimen	Weight percent gain	Block location[1]	Wood weight loss
			Pct
Control	0	—	31
Propyelene oxide	9	Interior	24
		Surface	19
	17	Interior	15
		Surface	13
	34	Interior	5
		Surface	8
Butylene oxide	27	Interior	4
		Surface	4
	34	Interior	3
		Surface	3

[1] In piece of wood after treatment.

Units were inspected at 4, 10, and 13 days after setup to determine if the experiment was proceeding normally. The experiment was terminated at the end of 2 weeks because the earlywood from the control samples was almost completely gone. To continue the experiment would have introduced a starvation condition in this control set. Termites counted previously in units were recounted and reweighed. The percentage survival of the different termite forms and the total group, as well as final percentage group weight, was calculated. After being brushed free of debris, the individual wood blocks were OD at 105° C overnight, weighed, and percentage weight loss of the block sets was calculated.

In a preliminary termite exposure of PO- or BO-modified wood not leached previously, the termites moved as far from the blocks as possible. Apparently, unreacted monomers vaporized causing lethal fumigation of the termites in the small containers within 1 day. Those blocks were then extracted with benzene/ethanol followed by water and the units reset with fresh termites. This time the termites exhibited no abnormal behavior. Because of these findings, subsequent termite tests were conducted only on extracted blocks.

The average percent weight losses from corresponding interior and surface block sets differed by 5 percent or less (table 32), demonstrating the uniformity of resistance at both the surface and the interior of the treated wood. This agrees with earlier findings that wood treated with EPI is modified evenly throughout the wood up to 2 by 4 cm in cross section. Figure 11 illustrates that weight loss in BO blocks was due to slight termite attack.



[illegible] control (right) after [illegible]

[illegible] Theoretically [illegible] that has [illegible] with the wood should not be [illegible] weight gains of about [illegible] the wood resistant to [illegible]

Table 33 — Average termite survival and group weight after 2 weeks attack on control and modified southern pine blocks

Specimen	Weight percent gain	Wood block	Termite survival	Termite group weight
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Possible explanations for the observed resistance to subterranean termite damage are numerous; epoxide-modified wood can be: (a) toxic, (b) repellent, (c) distasteful, (d) undigestible and, therefore, unsuitable as food, or (e) epoxide-modified wood fibers are stiffer and physically more difficult to eat. Explanations (c), (d), and (e) are aspects of unpalatability.

Ethylene and propylene oxides are used as biological sterilants so any free unreacted oxide remaining in the treated wood might be toxic or repellent to termites. Repellency and lethal fumigation occurred in the preliminary study with epoxide-treated wood. After solvent extraction of this wood, neither repellency nor fast-acting toxicity were noted.

The resistance of the modified wood seems attributable primarily to its unpalatability. Up to 39 WPG, the higher weight gains from epoxide treatments virtually eliminated attack on the wood by termites. A delayed mortality of termites occurred; although it was greater than that occurring in groups of starved termites, it was similar except for blocks treated to 34 percent BO. That greater mortality may be attributable to either an enhanced starvation effect or a slow-acting toxic effect. These two options will remain difficult to assess because proliferation of pathogenic microbes in groups of starvationally weakened termites will confound interpretation of results.

Field Tests—Decay and Termite

Standard field stake tests were run according to specifications as outlined in ASTM D 1758 (1974). Southern pine or ponderosa pine stakes unmodified and modified with PO, BO, or EPI were placed in test in the ground in either Madison, Wis., or Saucier, Miss. Inspection of the stakes occurred semiannually. Specimens were graded for both decay and termite damage as follows:

Rating	Description of Condition
10	Sound
9	Trace of decay or attack
7	Moderate
4	Heavy
0	Failure

Field stake tests on epoxide-modified wood showed decay was much less severe in the northern climate of the United States (table 34) than in southern exposures (table 35). There was virtually no termite damage at the Madison site, and after 7 years, control specimens have a fungal decay rating of 7, while the epoxide-modified wood rates either 9 or 10. After only 2 years at the southern exposure site, most of the control specimens were destroyed by fungi and attacked by termites. BO-modified specimens rate higher than controls, but both fungal attack and termite attack took place.

Table 34.—Field exposure of southern pine stakes (4.8 x 9.6 x 43.2 cm) modified with propylene oxide, butylene oxide, or epichlorohydrin initiated June 1975 in Madison, Wis.

Specimens (No. of specimens)	Weight percent gain	Decay rating after 7 years
Controls (4)	0	7
(1)		0
Propylene oxide (6)	20-37	10
(6)		9
(1)		
Butylene oxide (5)	19-40	10
(4)		9
Epichlorohydrin (4)	12-23	10

Table 35.—Field exposure of ponderosa pine stakes (4.8 x 9.6 x 43.2 cm) modified with butylene oxide, initiated September 1978 in Saucier, Miss.

Specimen	Weight percent gain	Rating after 2 years	
		Decay	Termite
Controls	0	0	0
		7	7
		4	4
		0	0
		7	7
Butylene oxide	27	9	10
	28	7	9
	31	9	9
	33	10	10
	34	7	9
	35	9	9

Marine Tests

Standard marine exposure tests were run according to specification as outlined in ASTM D 2481 (1976). Southern pine specimens, 3.7 by 0.6 by 15 cm, untreated and modified with either PO or BO were placed in test in the coastal Atlantic waters off Key West, Fla. The specimens were inspected semiannually. Marine borer attack on each panel was rated as follows:

Rating	Description of Condition
10	No more than trace attack
9	Light attack
7	Moderate attack
4	Heavy attack
0	Destroyed by attack

Table 36.—**Marine tests of southern pine panels (3.7 x 0.6 x 15 cm) modified with propylene oxide, initiated June 1975 or butylene oxide, initiated December 1977 in Key West, Fla.**

Specimens (No. of specimens)	Weight percent gain	Rating after year				
		1	2	4-1/2	5-1/2	7
Control	0	0				
Butylene oxide (10)	24-31		10	10		
	21-26		10	10		
Propylene oxide (6)	20-32				10	
(3)					9	
[illegible]					10	
(2)					9	

Some loss of springwood due to wave action

Table 36 shows the results of epoxide-modified wood in a marine environment. Unmodified control specimens were destroyed in less than 1 year while epoxide-modified wood has been in test for over 7 years with very little marine borer attack. After about 3 years of exposure, modified specimens showed some loss of lower density springwood which was the result of the mechanical action of the waves. The mechanism of effectiveness of modified wood in resisting attack by marine organisms is unknown. Unpalatability, as with termites, may play an important part in this mechanism.

Mechanical Properties

Specimens of sugar maple (*Acer saccharum* March.), 2.5 by 2.5 by 47.5 cm, were prepared from two boards cut from the same log with the grain oriented parallel to two faces. Ten specimens were treated with PO/TEA (95:5, v/v at 120° C, 150 lb/in.²). Because permanent swelling occurred during treatment all specimens were replaned to 2.5 by 2.5 cm.

In general, mechanical tests of modified specimens followed specifications as outlined in ASTM D 143 (1976). Sample sizes varied somewhat from standards, and strict application of ASTM standard procedures was not followed as the mechanism of failure may differ from untreated controls.

Bending tests were conducted on specimens 2.5 by 2.5 by 27.5 cm at 20° C and 65 percent RH. Specimens were placed on the testing machine supports with the tangential surface nearest the pith toward the center loading block and loaded with a crosshead feed rate of 0.10 in./min. A deflection measuring device was placed under a nail driven horizontally into the specimens at midlength and midheight. In this way, the testing machine produced a load-versus-deflection graph of the test. The modulus of elasticity in bending (MOE) (lb/in.²) was calculated as:

$$\mathrm{MOE} = \frac{dP/dx\ L^3}{4.0\ bh^3}$$

where

dP/dx = slope of load-versus-deflection graph within the elastic limit (lb/in.)

L = length of specimen between supports (9.75 in.)

b = width of specimen (tangential) (~1 in.)

h = height of specimen (radial) (~1 in.)

The modulus of rupture (MOR) (lb/in.²) was calculated as

$$\mathrm{MOR} = \frac{P_{max}\ 1.5L}{bh^2}$$

where

P_{max} = maximum load (lb).

Compression tests parallel to the grain were conducted on 2.5 by 2.5 by 6 cm specimens at 20° C, 65 percent RH. The specimens were placed on a spherical bearing and loaded in the longitudinal direction with a crosshead feed rate of 0.007 in./min. A deflection measuring device was placed against the feed head. In this way, the testing machine produced a load-versus-deflection graph of the test. The fiber stress at the proportional limit (FSPL) (lb/in.²) was calculated as:

$$\mathrm{FSPL} = \frac{Ppl}{bh^2}$$

where

Ppl = maximum load within the elastic region (lb).

The maximum crushing strength (MCS) (lb/in.²) was calculated as:

$$\mathrm{MCS} = \frac{P_{max}}{bh}$$

Hardness tests were conducted on specimens 2.5 by 2.5 by 6 cm at 20° C and 65 percent RH. Hardness was determined by the load required to penetrate a test ball (0.444-in. diameter) approximately half of its diameter into the specimen. The rate of penetration was 0.25 in./min. The index was determined on each surface.

Diffusion coefficient tests were conducted on specimens 2.5 by 2.5 by 1 cm. The radial and tangential surfaces were coated with a silicone rubber sealant to restrict water-vapor diffusion to the longitudinal direction during the test. Ovendried specimens were placed in a conditioning cabinet at 20° C and 65 percent RH and weighed at specified time intervals. The moisture content of each specimen was

Table 37 — Modulus of elasticity and rupture for propylene oxide-modified maple (average values of 10 specimens)

Treatment	Modulus of elasticity			Modulus of rupture		
	Pounds per square inch	95 Percent confidence interval	Coefficient of variation	Pounds per square inch	95 Percent confidence interval	Coefficient of variation
[illegible]	[illegible]	[illegible]	8	[illegible]	1,963	15
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 38 — Fiber stress at proportional limit and maximum crushing strength for propylene oxide-modified maple (average of 10 specimens)

Treatment	Fiber stress at proportional limit			Maximum crushing strength		
	Pounds per square inch	95 Percent confidence interval	Coefficient of variation	Pounds per square inch	95 Percent confidence interval	Coefficient of variation
[illegible]	[illegible]	488	7	9,420	461	7
[illegible]	[illegible]	420	7	8,450	422	7

Table 39 — Radial, tangential, and longitudinal hardness of propylene oxide-modified maple

Treatment	Radial hardness index			Tangential hardness index			Longitudinal hardness index		
	Pounds	95 Percent confidence interval	Coefficient of variation	Pounds[2]	95 Percent confidence interval	Coefficient of variation	Pounds	95 Percent confidence interval	Coefficient of variation
[illegible]	[illegible]	[illegible]	9	403	16	9	825	23	6
[illegible]	[illegible]	[illegible]	4	40[illegible]	19	10	822	24	6

[illegible] depth of 0.05 in.

[illegible]

[illegible] The ratio (W') of water [illegible] have been [illegible] was calculated as

$$[illegible]$$

where

[illegible] = [illegible] content at time t (percent)
[illegible] = [illegible] of the moisture content within the specimen at time zero (percent)
[illegible] = [illegible] of the moisture content under equilibrium conditions (percent)

The values of W' were plotted against the values of time (t), and the diffusion coefficient (D), in square centimeter second (cm²/sec) was calculated as

$$D = \frac{\pi a^2 (W'/t)}{16}$$

where
W'/t = slope of the initial straight line portion of the plot of W' versus time
a = longitudinal dimension (cm)

Tables 37 to 41 show the effect of epoxide modification on the mechanical properties of sugar maple.

Table 40.—Diffusion coefficients of propylene oxide-modified maple (average of 10 specimens)

Treatment	Diffusion coefficient
	10^{-6} cm^2/sec
None	6.269
Propylene oxide	8.109

Table 41.—Summary of the percent change in properties of maple due to modification with propylene oxide

Property	Percent change
Modulus of elasticity	−14
Modulus of rupture	−17
Fiber stress at proportional limit	−9
Maximum crushing strength	−10
Radial hardness index	+5
Tangential hardness index	0
Longitudinal hardness index	0
Diffusion coefficient	+29

Specimens used in these tests had an average level of chemical add-on of 20 to 22 WPG. Test results on sugar maple for MOE, MOR, fiber stress at proportional limit, and maximum crushing strength all show a similar trend (tables 37 and 38). Those specimens modified with PO show a loss of 9 to 17 percent in these properties as compared to an unmodified control. This shows the effect cell wall bulking has on the mechanical properties of wood. One would anticipate a loss in strength and stiffness due to bulking, even if the treatment was completely inert with the wood substrate.

Results from the hardness tests show PO-modified wood to be roughly equivalent in hardness to unmodified maple on all surfaces (table 39). Diffusion tests show that PO-modified wood resulted in a more open structure than that of unmodified wood since the diffusion coefficient is 29 percent higher for modified wood than unmodified wood. Table 41 shows a summary of the percent change in mechanical properties of modified maple tested as compared to unmodified maple.

Accelerated Weathering

Southern pine sapwood blocks, 2.5 by 0.6 by 2.5 cm, were prepared from a freshly cut log. All specimens were OD at 105° C for 20 hr. Two sets of five controls were prepared: one set received no treatment and one set was extracted with benzene/ethanol (2:1, v/v) for 2 hr in a Soxhlet extractor before use.

Ovendried blocks (five each) were reacted in a stainless steel vessel at 120° C, 150 lb/in.^{2} nitrogen pressure, with BO/TEA (95:5, v/v). Specimens with weight gains of 25 to 30 percent were used in weathering tests.

The radial faces of all test specimens were exposed to a 6,500-watt xenon arc light source (which closely approximates natural sunlight spectrum in the visible and ultraviolet regions) in an enclosed chamber at 45° to 50° C and 50 percent RH. Exposure to this radiation alternated with a spray of distilled water at ambient temperatures with the light off. One week of accelerated weathering consisted of seven 24-hr cycles. Each cycle consisted of 4 hr of distilled water spray followed by 20 hr of light. Exposure time is expressed as hours of exposure to light. Erosion of earlywood was measured using the technique as described for vertical-grained specimens (Feist and Mraz 1978). The rate of erosion of earlywood was determined after 600, 1,200, and 1,800 hr of light. After weathering, all blocks were reovendried and weighed.

Separate specimens both unmodified and modified with butylene oxide were exposed to the same light source under the same conditions except 1,800 hr of light only.

Selected specimens, both unweathered and artificially weathered, were mounted on circular (9-mm diameter) specimen holders with a mixture of silver paint and cellulose acetate cement. The stub holders were then transferred to a high vacuum evaporating unit and coated with approximately 100 to 200 Å of gold. The specimens were examined with a scanning electron microscope (Cambridge Stereoscan) at 20 kV.

Table 42.—Rate of accelerated weathering and overall weight loss of southern pine sapwood after 1800 hours light exposure

Specimen	Weight percent gain	Ovendry weight loss		Erosion rate, microns per hour[1]			
				Springwood		Summerwood	
		Light	Light/water	Light	Light/water	Light	Light/water
		Pct	*Pct*				
Control	0	0.5	5.7	0.008	0.150	0.008	0.042
Butylene oxide	28	1.3	6.4	.033	.183	.017	.067

[1] Erosion rate determined between 1200 to 1800 hr, expressed in microns per hour of light exposure.

Three separate specimens were used for chemical analyses for each modification. The first was the unexposed wood. The second was the outer 0.5 mm of wood (removed by slicing with a razor) exposed in the accelerated weathering chamber (referred to as outer specimen). The third specimen was the remainder of the exposed specimen after removal of the 0.5 mm of exposed wood surface (referred to as inner specimen). All specimens were ground to pass a 40-mesh screen and ovendried for 16 hr at 105° C prior to chemical analysis.

Lignin determinations were by a method similar to Technical Association of the Pulp and Paper Industry (TAPPI) Standard T 13 (1954). Samples were treated with 72 percent sulfuric acid for 1 hr at 30° C and 3 percent sulfuric acid for 4 hr at reflux temperature. Wood carbohydrates are thus hydrolyzed and solubilized. The insoluble residue was measured gravimetrically as lignin. The hydrolysate from the lignin determination was used for the reducing sugar analyses. All values shown are uncorrected for extractives, chemical add-on from modification, and for the small amount of degradation during hydrolysis.

Chemical modification of the cell wall components of wood should theoretically give increased resistance to weathering due to the blocking of lignin hydroxyls so they do not undergo a quinone-type reaction. In addition, modification blocks holocellulose hydroxyl groups, which decreases the hygroscopicity in the carbohydrate component. This tendency to resist water pickup reduces swelling and shrinking. By reducing the extent of lignin degradation and water pickup, chemical modification could play a very important role in controlling the natural weathering process.

Measuring the erosion of springwood compared to summerwood as a function of time provides a good method of determining the rate of weathering. The use of an accelerated weathering chamber increases the rate such that 1,800 hr of light are roughly equivalent to 3 to 4 years of outdoor weathering. Very little erosion of high density summerwood occurs during this time.

Table 42 shows the rate of accelerated weathering and overall weight loss of SP sapwood after 1,800 hr of light exposure only, and light exposure combined with water. Weight loss is low in the ultraviolet (UV) light-only exposure since there is no leaching of degraded products by water. Weight loss values for cell wall-modified specimens were higher than that observed for unmodified control specimens. This greater loss may be the result of residual bound monomer being slowly vaporized or by slow degradation of grafted polymer.

Weight loss values for specimens in the UV light/water exposure study were from 2 to 11 times greater than for specimens in the *UV light-only* exposure. All these weight loss values, whether for light only or light/water exposure, indicate loss of wood substance only from the surface of the exposed specimen since UV light does not penetrate wood deeply, and the weathering process is a surface phenomenon.

The maximum erosion value for all specimens, modified or unmodified, after 1,800 hr of light-only exposure was 40 microns, the minimum was 10 microns. These erosion values were observed for springwood (summerwood was approximately one-half that of springwood) and compare to values of 60 to 330 microns for specimens in the light and water cycle exposures. Without the action of water (leaching, washing) degraded wood substance will still adhere to the wood surface, and wood modified or unmodified will erode or wear away slowly.

The summerwood of specimens chemically modified with BO eroded faster than unmodified controls when exposed to UV light and water cycles. Chemical modification with BO was ineffective in controlling erosion. For both springwood and summerwood, chemical modification of SP sapwood with BO yielded a modified wood in which the overall erosion of wood substance was increased during accelerated weathering.

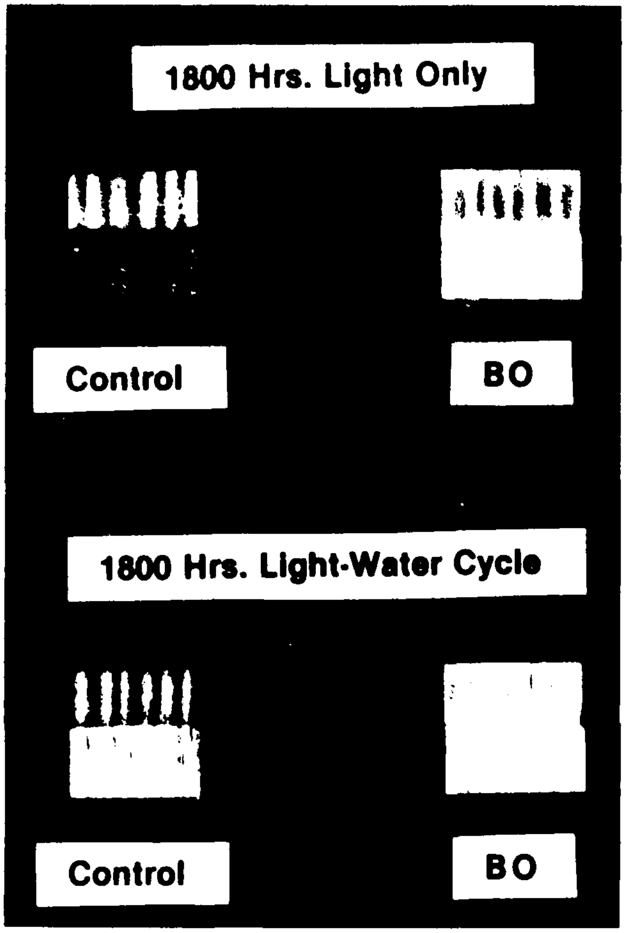


Figure 12.—Southern pine specimens after 1800-hr exposure to UV light plus alternating water spray or UV light alone. Upper half of each specimen was protected with a stainless steel plate. (M151123)

Specimens used for erosion measurements had thin stainless steel covers over their top half to prevent UV light degradation and to provide an unexposed base for optical measurement purposes. Representative samples of all exposed specimens are shown in figure 12 where physical changes for the exposed wood can be observed. The difference in color between UV light-only and UV light/water exposure is the most obvious change occurring after exposure. The color of exposed wood in the UV light-only exposure is darker than those of the protected wood in all cases except specimens chemically modified with BO. Light colored woods like SP usually darken on exposure to UV light. Butylene oxide modified specimens become lighter in color on exposure to UV light.

Table 43 shows the chemical analysis of unweathered and weathered wood. In the control sample the sum of the lignin and carbohydrate components (lignin, plus total sugars) accounts for almost all of the wood substance.

The BO-modified specimens show a much lower total sugar content which, in turn, accounts for the lower total mass balance (lignin, plus total sugars). The reason for this is not known, but perhaps part of the explanation is how modified sugars react in the sugar analysis. A sugar unit that is substituted may not undergo the same colorimetric reactions as an unsubstituted sugar. The ratio of sugars is lower in the BO specimens as compared to the controls. The sugars in the hemicellulose fraction are the ones which are lost. It is possible that these more accessible sugars are more highly substituted and again do not respond to the colorimetric analysis. The loss of hemicellulose sugars may also be due to the stability of the ether linkage in the BO modified specimens and the dissolution of substituted sugars in the separation step. The sugars would be absent in the sugar analysis and would appear to have been degraded by the test conditions, but in fact were present in a modified form which did not survive the separation procedure. Because of the real or apparent loss of sugars in the BO-modified woods, the total mass balance for these treatments is very low (lignin, plus total sugars).

Lignin values were always lower for the exposed outer surface wood than for unexposed specimens or inner portions of the exposed specimens. This effect has been observed previously (Meyer and Loos 1969) and reflects the degradation and solubilization of the lignin component.

Scanning electron micrographs of the exposed radial surfaces and split tangential surfaces of unmodified and modified SP, before and after accelerated weathering (1,800 hr of light or 1,800 hr of light, plus water spray), gave additional interesting information about the role of chemical modification in providing resistance to UV light degradation. The upper left photograph in figure 13 shows the planed radial surface of unmodified SP before accelerated weathering. The middle left photograph shows an unmodified radial wood surface after 1,800 hr UV light exposure. Pit degradation is apparent and some mild check formation. The upper right photograph in figure 13 shows BO modified wood before exposure while the middle right photograph shows a BO-treated radial surface after 1,800 hr UV only. Slightly more degradation of pits is visible, although overall wood element degradation is relatively small.

Table 43.—Chemical analyses of chemically modified southern pine after accelerated weathering

Specimen[1]	Weight percent gain	Lignin[2]	Total sugars[3]	Lignin + sugars	Sugar ratios				
					Glucose	Xylose	Mannose	Arabinose	Galactose
		Pct	Pct	Pct					
Control (C)									
Unexposed	—	28.6	66.3	94.9	65.0	10.2	16.1	2.8	5.9
Light									
Outer	—	26.9	65.7	92.6	67.0	9.8	15.9	2.6	4.7
Inner	—	29.1	66.3	95.4	64.3	11.1	15.0	2.9	6.7
Light/water									
Outer		24.8	70.6	95.4	69.3	8.7	14.3	1.8	5.9
Inner	—	28.3	67.5	95.8	65.9	10.0	16.9	2.2	5.0
Butylene Oxide									
Unexposed	31.0	29.6	34.1	63.6	87.9	6.1	4.5	.7	.8
Light									
Outer	28.4	30.1	35.1	65.2	83.9	6.7	6.5	1.4	1.5
Inner	28.4	32.5	34.9	67.4	83.9	6.9	6.4	1.3	1.5
Light/water									
Outer	30.3	27.9	36.7	64.6	87.5	5.9	4.7	.8	1.1
Inner	30.3	31.6	33.8	65.4	87.7	6.3	4.6	.6	.8

[1] Outer = 0.5 mm thickness of exposed surface.
Inner = Portion under exposed surface.

[2] Material insoluble in 72 pct H_2SO_4, expressed as percent of ovendry sample.

[3] Reducing sugars dissolved by acid hydrolysis, expressed as percent of ovendry sample.

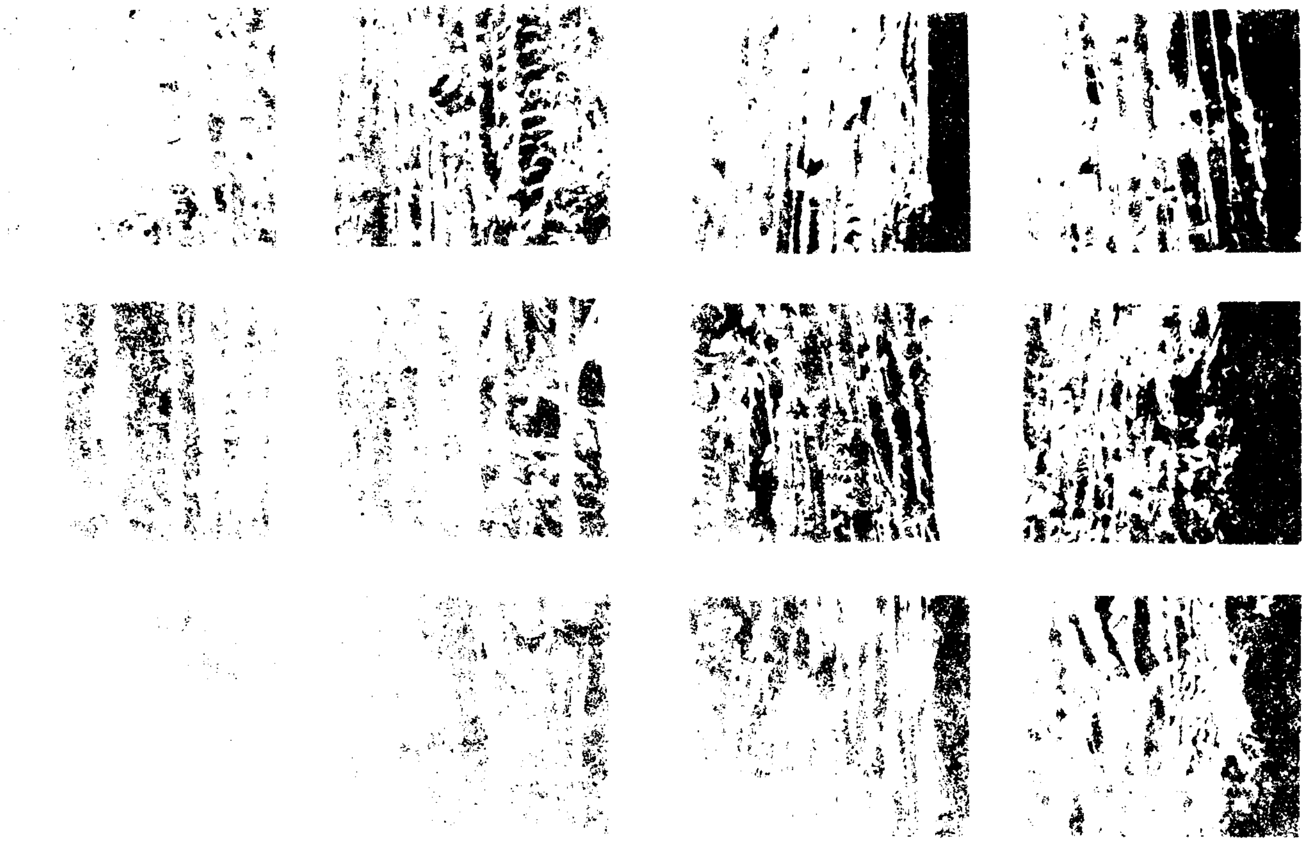
When unmodified wood is exposed to both UV light and water cycles, significantly more surface degradation is apparent than with UV-light-only exposure (lower left photo, fig. 13), and both horizontal and longitudinal checking along with loss of surface fibers is apparent. BO-modified radial wood surfaces exhibit more severe degradation (lower right photo), consistent with the weight loss and erosion data discussed earlier. Severe checking is apparent on these ordinarily planed, smooth surfaces.

Figure 14 shows scanning electron micrographs of tangential [illegible] the specimen with a razor after UV light exposure. The upper left photo shows a control specimen before exposure, and the upper right photo shows a BO-modified specimen before exposure. The center left photo is a control sample exposed to 1,800 hr of UV light only. Very little surface damage is observed while somewhat more surface damage is seen in the right middle photo for BO-modified wood exposed to light only. Considerably more deterioration is seen in both control and BO-modified wood in the lower photo for UV light and alternating water spray. The deterioration is only three or four wood fibers deep, and fibers below these are essentially unchanged.

Thermal Properties

Southern pine and PP ovendried blocks (2 by 2 by 5 cm) were reacted with PO/TEA or BO/TEA at 120° C, 150 lb/in². Specimens were prepared at 32 WPG with PO for both SP and PP, and at 22 WPG and 29 WPG with BO for SP and PP, respectively. Each specimen along with an unmodified control, was ground to pass a 40-mesh screen, extracted with benzene/ethanol (2:1, v/v) for 2 hr, air dried, and finally OD at 105° C for 16 hr.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGS-2 thermogravimetric system. A Hewlett Packard data acquisition system measured sample mass to 0.1 µg and run time to 0.004 sec. Furnace temperature was programed by the data system through a digital-to-analog converter. Samples of 5 ± 0.5 milligrams (mg) were charred to a temperature of 500° C under nitrogen flowing at 0.2 liter per minute (ℓ/min).



[illegible]

[illegible]

Propylene oxide is a very flammable [illegible] liquid. Bonding this chemical to wood [illegible] change the burning characteristics of wood [illegible] less flammable. It [illegible] after bonding [illegible] alter the thermal properties of wood. Thermogravimetric analysis of a [illegible] modified with PO to 32 WPG and BO to [illegible] WPG [illegible] (fig. 15) that epoxide-modified wood [illegible] degrade at a slightly higher temperature than unmodified wood. There was a [illegible] with epoxide-modified wood than unmodified. Figure 16 shows that the temperature [illegible] of weight loss is the same for modified and unmodified wood. Control specimens show two [illegible] the weight loss plots, one at 325° C and one at [illegible] C. The 325° C maximum scan in the control is thought to be due to hemicellulose degradation. This scan was missing in the modified wood, which may mean that the hemicellulose sugars have been somewhat stabilized to thermal degradation and degrade along with the cellulose at a higher temperature.

While the TGA data did not show any significant differences between modified and unmodified wood, it is not possible to learn from this analysis if the products from the combustion of modified wood were more or less flammable than combustion products from unmodified wood. Thermogravimetric analysis was done on PP unmodified and modified with PO to 32 WPG and BO to 29 WPG. Figure 17 shows the heat of combustion of combined volatile decomposition products based on its equivalence of the quantity of oxygen used in combustion. A control specimen showed a heat of combustion of 2.8 kcal/g. This is based on an original fuel basis. For BO-modified wood, the heat of combustion was 4 kcal/g and PO-modified wood 4.1 kcal/g. These results show that the volatiles coming from epoxide-modified wood are somewhat more flammable than volatiles from unmodified wood. This is probably due to the lower oxygen content of the epoxide added to the wood, as compared to the oxygen content of the wood cell wall polymers. It would require more oxygen in combustion to convert the epoxide combustion products to CO_2 and H_2O. Figure 18 shows the temperature of the maximum rate of oxygen consumption. The control has two peaks at 325° C and 375° C while the epoxide-modified wood showed only one at 375° C. This is similar to the TGA data in figure 16.

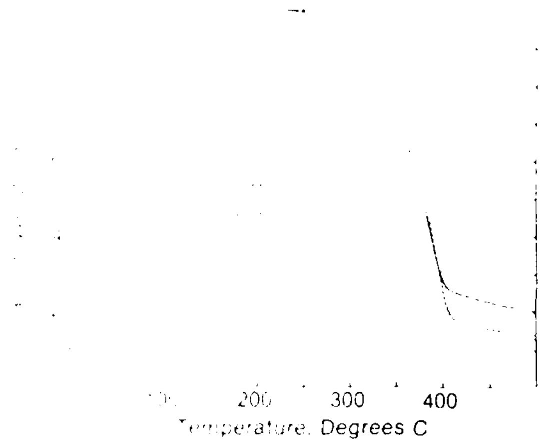


Figure 15.—Thermogravimetric analysis of epoxide-modified southern pine. Fraction of weight remaining as a function of temperature. (M151[illegible])

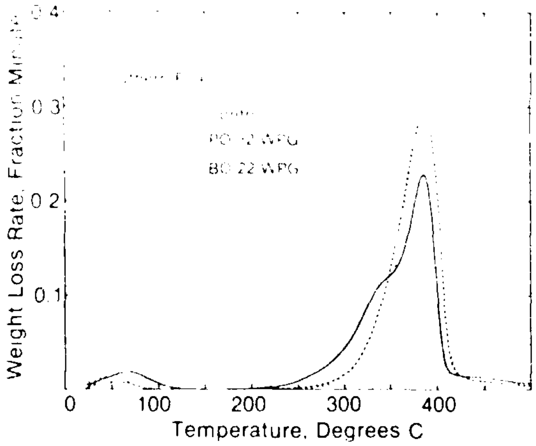


Figure 16.—Thermogravimetric analysis of epoxide-modified southern pine. Rate of weight loss as a function of temperature. (M151126)

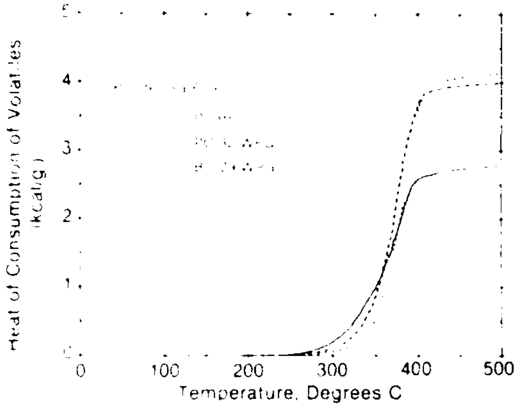


Figure 17.—Evolved gas analysis of expoxide-modified ponderosa pine. Heat of combustion of volatile as a function of temperature. 151124)

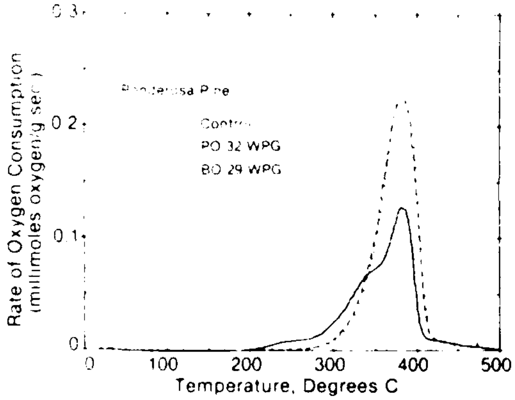


Figure 18.—Evolved gas analysis of epoxide-modified ponderosa pine. Rate of oxygen consumption as a function of temperature (M151125)

Table 44.—Adhesive shear strength of epoxide-modified southern pine laminated with phenol resorcinol[1]

Specimen	Weight percent gain	Stress at failure	Wood failure
		$Lb/in.^2$	*Pct*
Control	0	1,670	52
Propylene oxide	38.1	1,360	81
Butylene oxide	35.2	1,295	92

[1] Average of 35 specimens of each type.

Adhesive Bond Strength

Standard tests for strength properties of adhesive bonds in shear by compression loading were run according to specifications as outlined in ASTM D 905 (1976). Specimens of SP (2 by 6.2 by 30 cm), with grain parallel to the longitudinal face were prepared. The specimens were OD and treated with either PO/TEA or BO/TEA at 120° C, 150lb/in.^{2}. The average WPG for all specimens modified with PO was 38.1 and with BO 35.2.

Specimens for adhesive bond strength were prepared from the above modified wood and unmodified controls (4.5 by 3.7 cm). Two specimens were laminated with Koppers 4411 phenol resorcinol, double spread, pressed at 175-lb/in.^{2} pressure overnight at 23° C. Test specimens were placed in a standard block shearing tool, and a load applied with continuous travel of a movable head at a rate of 0.015 in./min to failure. The shear area was 2.8125 in.^{2}.

Adhesive shear strength of PO- and BO-modified SP laminated with phenol resorcinol was determined. Table 44 shows that while a control specimen failed at 1,670 lb/in.^{2}, epoxide-modified specimens failed at about 1,300 lb/in.^{2}. This 20 percent reduction in adhesive bonding strength is due to failure in the wood, not in the glue joint. In an average of 10 control specimens only 52 percent of the joint failure was due to wood failure, but in epoxide-modified wood over 80 percent joint failure was due to wood failure. This probably means that because the wood fibers are bulked, the forces holding them together are reduced.

Public Exposure

A piece of epoxide-modified American black walnut was aboard the American-Soviet space mission in July 1975. The wood was used to make a small box, given to the Soyuz crew during the flight exchange, containing genetically superior spruce tree seeds. Several of these boxes were made and given to the U.S. astronauts and Soviet cosmonauts involved in the mission as well as several major television announcers. The box exchanged in space is now in the U.S.S.R. Space Museum in Moscow, and a replica is in the U.S. Space Museum in Washington, D.C.

As a result of this public exposure, the epoxide process received wide press coverage in 1975 and 1976. A patent on the BO process was issued during 1976 to the United States government. News from the space mission and the public disclosure of the patent resulted in over 10,000 letters from people wanting information on the process.

Conclusions

Since the epoxides react quickly with wood cell wall polymers. With dry wood, there are no byproducts generated in the reaction, there is complete chemical addition, and the chemical bonds formed are stable. Because chemical reaction takes place in the cell wall, the increase in wood volume from the treatment is proportional to the volume of chemical added. Bulking of the cell wall with bonded chemical results in 50 to 70 percent dimensional stability at chemical add-ons of 20 to 30 percent. Because of the high levels of chemical addition necessary to achieve good dimensional stability, the procedure is expensive and may see only limited industrial application except for specialty uses. Overtreatment results in a loss in dimensional stability due to cell wall rupture.

Good resistance to attack by fungi and termites was achieved with BO-modified wood in laboratory tests. In actual inground tests, the level of resistance was not as good. Epoxide-modified wood might perform very well in above ground application where dimensional stability and biological resistance are desired. Preliminary testing of above ground exposed wood in Saucier, Miss., shows promise; however, full-scale testing is needed.

The most significant finding in this research program is the resistance of epoxide-modified wood in a marine environment. Except for a small amount of mechanical wave damage, epoxide-modified wood has resisted attack by marine borers for about 7 years. Unmodified control specimens usually last less than 1 year and many times only a few months. At this time, the continuing resistance to attack by marine borers of epoxide-modified wood is the most promising aspect for further industrial development.

Wide varieties of wood species are treatable with the epoxide procedure. It is an excellent swelling/reactive system and penetrates heartwood of several species known to be difficult to treat. A wide variety of epoxides can be used in the reaction, however, those of low molecular weight, low boiling point, and low cost have the most promise of commercialization. Epoxide-modified wood is somewhat more flammable than unmodified wood but not to a great extent. Due to the bulking action of the bonded chemical in the cell wall, epoxide-modified wood has slightly lowered mechanical properties. The modification does not result in plugging up the voids in the wood, so porosity is not reduced. This means that modified wood should still be paintable, stainable, and gluable. The cell wall bulking also results in reduced inter-fiber bonding so there is more wood failure in an adhesive bond between two pieces of modified wood. Epoxide modification was found to have no effect in improving the resistance to UV light in the weathering process.

Resistance to attack of modified wood by organisms is speculated to be due to modification of the carbohydrate components such that very specific biological reactions cannot take place. Lignin substitution does not seem to play a major role in the protection mechanism to biological attack. For this reason, substituting the lignin component is a waste of chemical in the modification process.

It does not seem likely that a completely nontoxic means of treating wood for biological resistance will ever be as effective as treating wood with toxic chemicals as is presently done. As the concern for the environment increases, however, the use of these toxic chemicals may be restricted or even banned. The need to extend our timber supply by using less new wood due to increased service life from treated wood in use will require that alternatives to these toxic procedures be developed in the future. Bonding of nonleachable chemicals to wood may provide a possible solution.

Most of the research done on chemical modification of wood has been done on ovendried material. If wet wood is used, reacting chemical is lost due to hydrolysis and is not available for substitution. As long as the end product is to be used as a bulked, dimensionally stabilized product with no direct water contact, the hydrolyzed chemical would not be lost and would still act as a cell wall bulking agent. If bonding is necessary, as in the case of biological resistance, then any hydrolyzed chemical reagent is lost, and this adds to the cost of treatment without any benefits.

The future of chemical modification of wood with epoxides lies in end product property enhancement. If, for example, fire retardancy is important in a wood material, the fire retardant could be bonded permanently to the cell wall through the epoxide bonding system. If the level of chemical addition were high enough, dimensional stability and some degree of resistance to biological attack would also be achieved at no additional cost. The greatest single application of the research would be in reconstituted products in which standard operating procedures call for dry wood materials, spray chemical addition for maximum distribution, small sample size for good penetration, and high temperature and pressure in product formation. These are exactly the procedures required for successful chemical modification. Permanently bonded chemicals that provide fire retardancy, UV stabilization, color changes, dimensional stability, and resistance to biological attack to wood products may be possible through chemical modification.

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Appendix A

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Appendix B

Chronological listing of publications resulting from epoxide modification research program 1975-1984.

1. **Rowell, R. M., and D. I. Gutzmer.** 1975. Chemical modification of wood: Reactions of alkylene oxides with southern yellow pine. Wood Sci. 7(3):240-246.
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Appendix C

Glossary of terms used in epoxide modification.

ASE	Antishrink efficiency
BO	Butylene oxide
DP	Degree of polymerization
DS	Degree of substitution
EGA	Evolved gas analysis
EPI	Epichlorohydrin
OD	Ovendry or ovendried
PO	Propylene oxide
PP	Ponderosa pine
RH	Relative humidity
S	Volumetric swelling coefficient
SD	Standard deviation
SP	Southern pine
TEA	Triethylamine
TGA	Thermogravimetric analysis
UV	Ultraviolet
WPG	Weight percent gain

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