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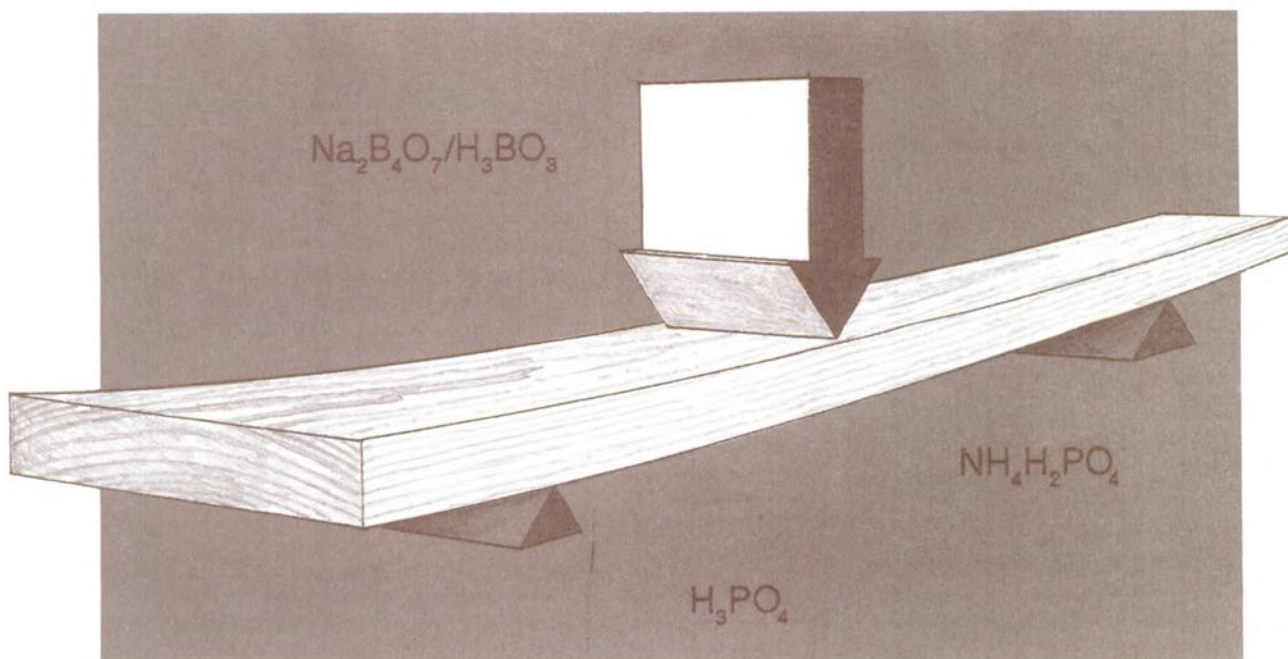
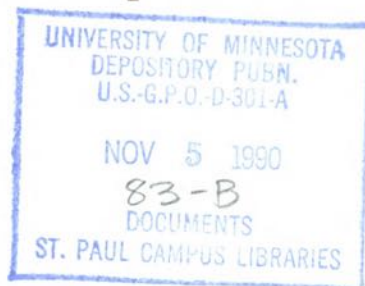
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# Effects of Fire Retardant Chemicals on the Bending Properties of Wood at Elevated Temperatures

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# Abstract

Fire retardant chemicals are designed to lower the temperature at which thermal degradation occurs. When these chemicals are used for roof sheathing, the combination of chemicals, elevated temperatures, and moisture can sometimes prematurely activate the fire retardant mechanism. The objectives of our study were to determine what kind of fire retardant chemicals are most susceptible to accelerating thermal degradation and at what temperature or temperatures this acceleration occurs.

Small, clear Southern Pine specimens were treated with six different fire retardant chemicals and exposed to three environments for up to 160 days. The exposure conditions were (1) 80°F (27°C), 30 percent relative humidity, (2) 130°F (54°C), 73 percent relative humidity, and (3) 180°F (82°C), 50 percent relative humidity. Static bending tests were performed on the treated specimens and untreated controls to determine the effect of treatment and exposure on modulus of

rupture, modulus of elasticity, and work to maximum load.

The phosphoric acid and monoammonium phosphate treatments had the most severe effect on strength. The 180°F (82°C) exposure caused considerable strength loss in wood treated with some chemicals but not others. The 80°F (27°C) exposure had no effect on strength and the 130°F (54°C) exposure a minimal effect. The results indicate that once an elevated temperature has caused a fire retardant chemical to dissociate into its acidic chemical form (the form that provides the fire retardancy mechanism), the rate of wood degradation does not change. Thus, the actual difference between most fire retardant chemical systems is the time required for the chemical to dissociate at some temperature into its acidic chemical form.

Our results show that the effectiveness of acidic fire retardant chemicals rests on achieving a delicate balance between reducing the flammability of the wood and maintaining strength properties.

**Keywords:** Fire retardant treatments, wood degrade, thermal degradation, reduced strength properties

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# Effects of Fire Retardant Chemicals on Bending Properties of Wood at Elevated Temperatures

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## Introduction

Some building codes and insurance companies permit fire-retardant-treated wood to be used as an alternative to noncombustible materials for certain applications. Fire retardant chemicals drastically reduce the rate at which flames travel across the wood surface, thereby reducing the capacity of the wood to contribute to a fire. The chemicals lower the temperature at which thermal degradation occurs (LeVan 1984). They increase the amount of char and reduce the amount of flammable volatiles. Fire retardant chemicals can also reduce the strength of lumber or plywood, an effect related to the nature of the chemicals and to the redrying temperatures used in the treating process (King and Matteson 1961; Jessome 1962; Johnson 1967; Gerhards 1970; Winandy and others 1988). This research indicated that the strength of wood exposed to room temperatures after treatment is reduced between 10 and 20 percent depending on chemical treatment and redrying temperature (Gerhards 1970, Winandy 1988). In addition, more than 30 years of field experience at or near room temperatures have indicated that the initial reduction in strength of fire-retardant-treated wood does not change over time.

However, problems related to reduced strength have developed in some situations where fire-retardant-treated material is exposed to elevated temperatures. The problem has occurred most often when fire-retardant-treated plywood has been used as roof sheathing, but fire-retardant-treated lumber may also be susceptible to strength loss if exposed to elevated temperatures for a sufficient period of time. In the worst cases, roofs made with fire-retardant-treated plywood have required replacement. In these cases, the wood had darkened, was brittle, crumbled easily, and exhibited excessive cross-grain checking. For the

severely degraded roofs brought to our attention, time in service has ranged from 1 to 8 years (APA 1989a).

The magnitude of wood degradation depends on the temperature levels to which the fire-retardant-treated plywood is exposed. High temperature levels can be achieved in processing or when the fire-retardant-treated wood is used in roof systems (Heyer 1963). In addition, the presence of moisture and the particular fire retardant formulation used affect the magnitude of wood degradation. Previous articles by LeVan and Winandy (1990) and LeVan and Collet (1989) describe suspected mechanisms that cause wood failure. We believe that the strength degradation is directly attributable to chemical changes in the constituents that comprise wood. Consequently, we designed and conducted an extensive experimental program to investigate changes in the chemical and mechanical properties of wood treated with fire retardant chemicals under several temperature and relative humidity conditions.

The objective of this report is to discuss research results that show accelerated thermal degradation of strength and chemical composition of wood are functions of fire retardant chemical and temperature.

## Experimental Methods

### Materials

Figure 1 shows an overview of the experimental procedures. Preparation of specimens, selection of fire retardant chemicals, types of environmental exposures, static bending tests, and chemical analysis are described in the following sections.

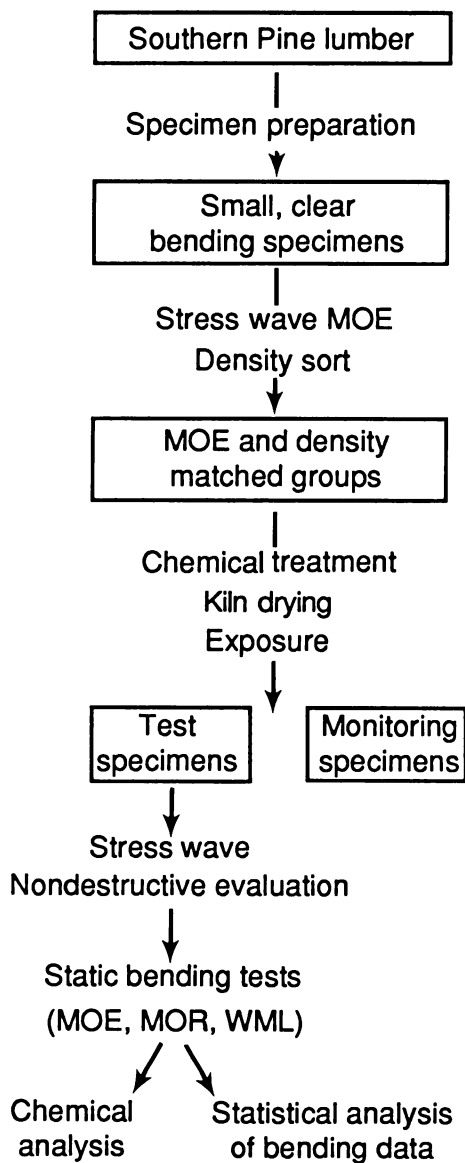


Figure 1—Overview of experimental procedures.

#### Wood Specimens

Small, clear 5/8-in.- (15.9-mm-) tangential by 1-3/8-in.- (35-mm-) radial by 12-in.- (305-mm-) long bending test specimens were cut from nominal 1-in.- (25.4-mm-) thick, vertical grain Southern Pine lumber. Although strength loss has been documented for fire-retardant-treated plywood, we chose to use clear Southern Pine specimens to evaluate the fundamental effects of fire retardant treatment on the chemical and mechanical behavior of wood. Southern Pine was chosen because it represents a dominant portion of the structural treated plywood market. We used clear wood because the properties of clear wood are less variable than those of products such as plywood or structural lumber. Consequently, the differences among treatments can be distinguished more readily. We are also conducting

a parallel study to evaluate the effect of several fire retardant chemicals on plywood. These data will be reported at a later date.

To obtain nearly identical sample characteristics for the various treatments and exposures, specimens were sorted according to density and modulus of elasticity (MOE). Stress wave nondestructive testing techniques were used to determine MOE of the specimens. The sort resulted in 161 MOE- and density-matched groups of 30 specimens each. The average density value for each group was about 37 lb/ft<sup>3</sup> (593 kg/m<sup>3</sup>), with a corresponding coefficient of variation of 8 percent. The average stress wave MOE value for each of the groups was  $2.12 \times 10^6$  lb/in<sup>2</sup> (14.6 GPa), with a coefficient of variation of 14 percent. Stress wave MOE values ranged from 1.5 to  $2.7 \times 10^6$  lb/in<sup>2</sup> (10.3 to 18.6 GPa). This report discusses the results of 84 (12 exposures of six fire retardant chemicals and one untreated control) of these matched groups.

#### Fire Retardant Chemicals

The extent of degradation is believed to be due to acid-catalyzed dehydration (LeVan and Winandy 1990), which is influenced by acidity and temperature. Acidity is determined by the pH. The chemicals selected for this research project cover a broad spectrum of acidity and may provide an indication of a property that can be used to predict the extent of acid-catalyzed dehydration. The chemicals selected may or may not be used in commercial formulations. However, the selection of these particular chemicals (all of which provide fire retardancy to wood) indicates which chemicals are activated by temperatures up to 180°F (82°C), which may occur at the top surface of the roof sheathing (Heyer 1963). Table 1 lists the chemicals used and the reasons for their selection.

The specimens were pressure impregnated with the fire retardant chemicals using a full-cell pressure process. A vacuum of 30 inHg (0.102 MPa) of mercury was pulled for 30 min, chemicals were added, and pressure of 150 lb/in<sup>2</sup> (1.03 MPa) was then applied for 60 min. Concentration of the chemical solutions was adjusted to provide retention of approximately 3.5 lb/ft<sup>3</sup> (56 kg/m<sup>3</sup>). Table 2 shows average chemical retentions, including solution concentration in percentage of weight, for each treatment and pH of the chemical solutions before and after treatment.

To minimize premature drying after treatment, the specimens were bundled in polyethylene and stored in a 36°F (2°C) cold room until all specimens could be dried at once. The specimens were then dried in a kiln using the moderate kiln conditions summarized in Table 3.

Table 1—Chemical treatments

Chemical	Chemical classification	Comment
Phosphoric acid (PA)	Inorganic	Phosphoric acid is not used as a sole ingredient in commercial formulations. However, phosphoric acid is a good fire retardant. It was selected as a worst-case control.
Monoammonium phosphate (MAP)	Inorganic	Common chemical used in some commercial formulations.
Borax-boric acid (BBA)	Inorganic	Neutral pH. Used together with other chemicals to buffer some commercial fire retardant systems.
Guanylurea phosphate-boric acid (GUP-B)	Organic	Organic phosphate salt. Used commercially.
Dicyandiamide phosphoric acid formaldehyde (DPF)	Organic	Amino-resin system, sometimes used as exterior fire retardant system (1:1:1 molar ratio).
Diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphate (OPE)	Organic	Phosphonate ester, specifically designed for use as a flame retardant in rigid urethane foams. Selected for this study because of its neutral pH and classification as an organophosphonate ester.

Table 2—Chemical retention and pH levels

Chemical	Average retention (lb/ft <sup>3</sup> (kg/m <sup>3</sup> ))	Concentration (percent wt)	pH before treatment	pH after treatment
Phosphoric acid (PA)	3.64 (58.2)	8.38	1.43	1.35
Monoammonium phosphate (MAP)	3.47 (55.5)	8.14	4.27	4.21
Borax-boric acid (BBA)	3.52 (56.3)	8.14	7.96	8.06
Guanylurea phosphate—boric acid (GUP-B)	3.47 (55.5)	8.19	3.10	3.13
Dicyandiamide phosphoric acid formaldehyde (DPF)	3.55 (56.8)	8.24	3.75	3.75
Diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate (OPE)	3.46 (55.4)	8.14	6.58	5.46

Table 3—Posttreatment drying schedule for small clear wood specimens for all treatments

Days	Dry bulb temperature (°F (°C))	Web bulb temperature (°F (°C))	Airspeed (ft/min (m/min))
9	110 (43)	100 (38)	250–300 (76.2–91.4)
7	120 (49)	112 (44)	250–300 (76.2–91.4)

Table 4—Environmental conditions and exposure times

Temperature (°F (°C))	Relative humidity (percent)	Moisture content (percent)	Exposure time (days)
80 (27)	30	6	3, 160
130 (54)	73	12	3, 7, 21, 60, 160
180 (82)	50	6	3, 7, 21, 60, 160

## Procedures

### Environmental Exposures

Three environmental exposures were selected. Temperature, relative humidity (RH), and exposure time are listed in Table 4. The 80°F (27°C)–30 percent RH exposure represents a common dry-room-temperature condition; 130°F (54°C)–73 percent RH, a warm, moist condition; and 180°F (82°C)–50 percent RH, a hot environment. Both the 80°F (27°C)–30 percent RH and 180°F (82°C)–50 percent RH exposures represent approximately 6 percent equilibrium moisture content (EMC) in untreated wood. The 130°F (54°C) exposure represents an often attainable temperature for roof sheathing (Heyer 1963). The 180°F (82°C) exposure represents a seldom encountered, but possible, maximum-heat exposure (APA 1989b). For the 80°F (27°C)–30 percent RH and 130°F (54°C)–73 percent RH exposures, we used commercial environmental conditioning chambers. For the 180°F (82°C)–50 percent RH exposure, we used a dry kiln.

Specimens were removed from exposure after the appropriate exposure time. For each treatment group, moisture content (ovendry basis) values of five specimens with the highest densities were used to monitor the moisture content of the remaining 25 specimens before reconditioning. In this way, the five density-matched specimens removed from each group maintained the matched characteristics of the remaining 25 specimens. The remaining specimens of each group were then weighed and reconditioned to

constant weight at 73°F (23°C)–65 percent RH, which represents a 12-percent EMC condition for untreated wood. An additional 56 matched groups are being exposed at the Forest Products Laboratory (FPL) in the environmental chamber at 150°F (66°C) and 75 percent RH for exposure times of up to 5 years. Results of tests on these specimens will be the subject of a future report.

### Static Bending Tests

Specimens were tested flatwise, and maximum bending stresses were imposed on the radial faces to minimize variability, attributed to density differences between earlywood and latewood regions. This technique is described by Bendtsen and others (1983) and Winandy and others (1985). A span of 9 in. (0.229 m) was utilized with center-point loading and a loading rate of 0.19 in/min (4.8 mm/min). The length, width, thickness, and weight of each specimen were measured prior to testing. Load-deflection data were continuously monitored and recorded. From this information, static MOE, stiffness (EI), modulus of rupture (MOR), and work to maximum load (WML) were calculated. After testing, moisture content and density were measured for each specimen.

### Chemical Analysis

Each treatment group (defined by type of chemical, exposure condition, and exposure time) consisted of 25 specimens. After static bending tests, a small section was cut from near the failure point of each specimen. A portion of these sections was cut and ground to 40 mesh in a Wiley mill. For each group, we took a fraction of each ground specimen and mixed the fractions together for chemical analysis. Thus, a mixed representative sample was analyzed for each treatment group. Sugar residues, acid-soluble lignin, and klason lignin were analyzed following the procedures of Pettersen and Schwandt (in preparation), TAPPI Standards Useful Method 250 (TAPPI 1982), and Effland (1977), respectively.

## Results and Discussion

### Moisture Content of Unconditioned and Reconditioned Specimens

Figure 2 illustrates average moisture content (MC) of the five specimens from each treatment group that were ovendried immediately on removal from the exposure chamber (monitoring specimens; Fig. 1). The relative difference in MC of treated specimens and untreated controls and the relative trend of each treatment were consistent over time. The MC values

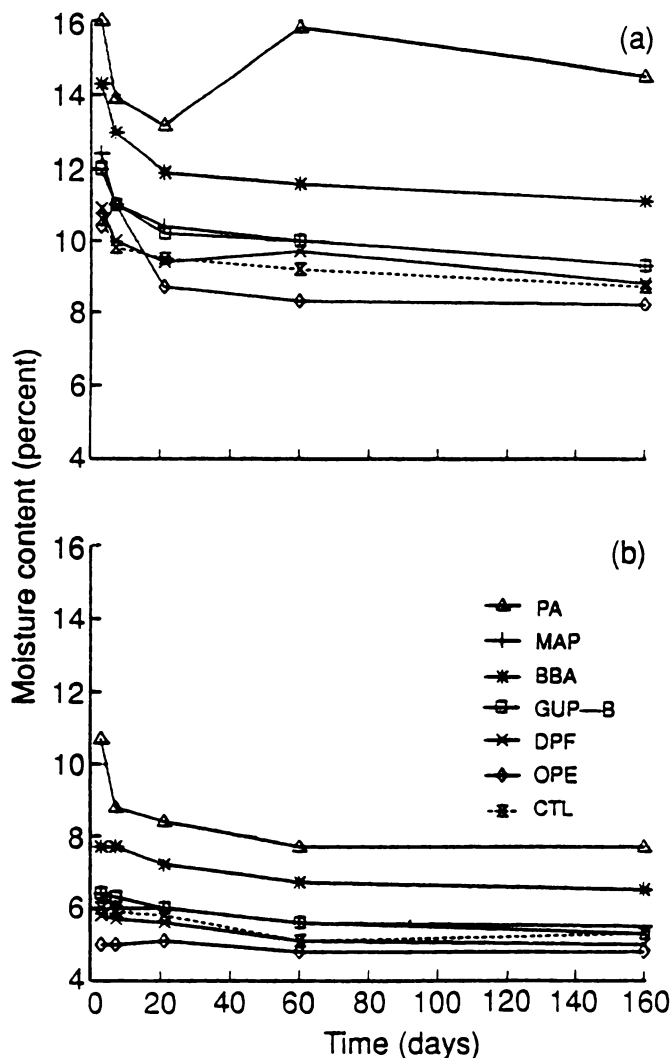


Figure 2—Average moisture content of treated and untreated (control) specimens over time after exposure. Specimens were used to monitor representative moisture content for various exposure times at (a) 130°F (54°C) and 73 percent relative humidity and (b) 180°F (82°C) and 50 percent relative humidity. PA is phosphoric acid, MAP monoammonium phosphate, BBA borax-boric acid, GUP-B guanyurea phosphate-boric acid, DPF dicyandiamide phosphoric acid formaldehyde, OPE organophosphonate ester, and CTL control.

for specimens exposed to 180°F (82°C) (Fig. 2b) were essentially uniform for the various fire retardant chemicals over the exposure times. The MC of controls was reduced about 1 percent after 60 days. At 130°F (54°C), the phosphoric acid (PA) and borax-boric acid (BBA) treatments showed the largest deviation in MC over the exposure times. The MC of controls was reduced about 2 percent after 60 days. For both the 130°F (54°C) and 180°F (82°C) exposures, MC apparently did not change between 60 and 160 days of

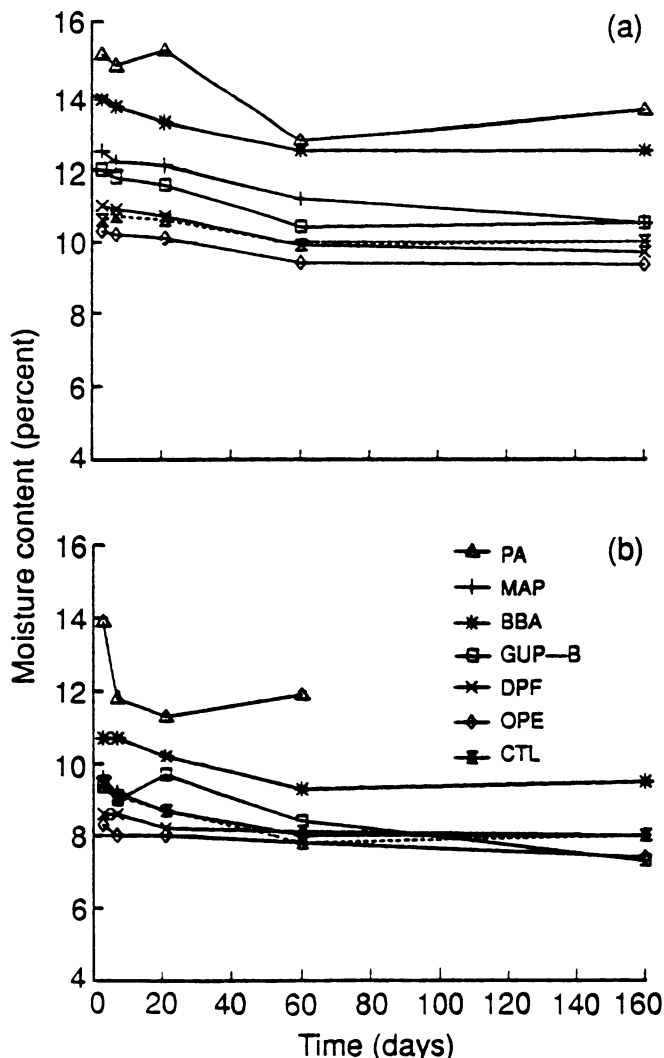


Figure 3—Average moisture content of treated and control specimens after reequilibration and bending tests for various exposure times at (a) 130°F (54°C) and 73 percent relative humidity and (b) 180°F (82°C) and 50 percent relative humidity. See legend to Figure 1 for definition of treatment abbreviations.

exposure. The ordered rank of MC values for specimens treated with the various fire retardant chemicals was found to be the same as that of MC values of the specimens after reconditioning to 73°F (23°C) and 65 percent RH (Fig. 3).

Mean, median, and 10th, 25th, 75th, and 90th percentile MC values were determined for the test specimens. No distributional trends or differential skewness of the MC distribution were observed. Consequently, further discussion will focus on mean MC values after reequilibration.

Mean MC values are summarized in Table 5. These specimens do not include the five monitoring specimens of each group. These values were obtained after the specimens were reequilibrated to 73°F (23°C) and 65 percent RH. Note that for each treatment group at 80°F (27°C), no change in MC was observed between the 3- and 160-day exposure times. At the higher temperatures, all MC values were slightly reduced with time (Fig. 3). Exposure to 130°F (54°C) and 180°F (82°C) was previously shown to result in EMC values of 12 and 6 percent, respectfully, in untreated, unexposed Sitka spruce (USDA 1987). In our study, these respective exposures resulted in 10 and 6 percent EMC in untreated Southern Pine. The differences between these results may be related to species differences or equipment difficulties in maintaining 73 percent RH at 130°F (54°C). Nevertheless, the relative difference between each treatment group and untreated controls and the relative trend of each treatment over the exposure times are consistent.

The relative rank of MC values was found to be dependent upon chemical treatment. In general, the descending order of MC values for the various treatments was as follows: phosphoric acid (PA), borax-boric acid (BBA), monoammonium phosphate (MAP), guanylurea phosphate-boric acid (GUP-B), dicyandiamide phosphoric acid formaldehyde (DPF), control, and organophosphonate ester (OPE). Inorganic chemicals tended to increase MC more than did the organic salts when compared to controls. The OPE treatment, however, resulted in slightly reduced MC values at all temperatures and RH conditions compared to that of controls.

Each fire retardant chemical system alters the EMC of the wood. The magnitude of this alteration depends on the attraction of the fire retardant chemical for water. Bendtsen (1966) found that most inorganic salts increased the EMC of wood 3 to 5 percent depending on the chemical treatment. The differences between untreated controls and specimens treated with PA and BBA are in agreement with Bendtsen's results; the differences between the controls and the specimens treated with MAP, GUP-B, DPF, and OPE are less similar to Bendtsen's results, although generally within 1 percent of the control. Because some fire retardant chemicals, but not others, permanently altered the EMC in our study, the effect of the chemicals on EMC should be considered as part of the treatment. Thus, strength properties were not adjusted to the same MC level because strength should be compared at a constant environment rather than at a constant MC. Furthermore, equations are not available for adjusting strength properties of treated wood for MC.

The MC results shown in Figure 3 also indicate a permanent reduction in EMC over the exposure time. This trend presents another reason for not adjusting the strength values for MC. Overall, the magnitude of this permanent reduction in EMC was about 1 to 2 percent. This effect was more pronounced for the specimens subjected to the higher EMC conditions (130°F (54°C)-73 percent RH). The MC values of the monitoring specimens indicated similar negative trends in EMC at 130°F (54°C)-73 percent RH (Fig. 2a) and 180°F (82°C)-50 percent RH (Fig. 2b).

Two possible explanations for this negative trend are as follows: (1) RH conditions in the exposure chambers and reconditioning rooms changed over a period of several months, or (2) long high-temperature exposures resulted in a permanent loss in the capacity of the specimens to absorb water. Although RH conditions of the conditioning chambers could change over a long period, we doubt that this occurred because the trends in MC between unconditioned and reconditioned specimens are nearly identical (Figs. 2 and 3). We believe the negative MC trends are due to a permanent loss in the water-holding capacity (hygroscopic affinity for water) of the specimens after long high-temperature exposure. This loss in hygroscopic affinity for water is primarily due to degradation of the hemicelluloses (Skaar 1972). We believe the slight deviations between MC values over time do not affect the general trends in the strength property data.

## Modulus of Elasticity

As with MC values, mean, median, and various percentile values for MOE and EI were determined. No distributional trends or differential skewness of the MOE or EI distributions were observed. The MOE and EI values showed parallel trends. Accordingly, our discussion will focus solely on mean MOE values. Overall MOE data are summarized in Table 6, and mean values are shown graphically in Figure 4. Table 7 shows the reduction in bending properties of the treated specimens over the exposure time. The MOE of all untreated specimens (controls) showed no change after 160 days for all exposures.

For PA, the 180°F (82°C) exposure resulted in an initial reduction in MOE of almost 45 percent when compared to the MOE of controls (Table 7). A significant rate of reduction in MOE compared to that of controls became apparent after only 7 days of exposure. The degradation of the PA-treated specimens exposed for 160 days at 180°F (82°C) was so severe that the specimens broke during handling, which precluded mechanical testing.

Table 5—Effect of temperature and exposure time on moisture content and specific gravity of treated Southern Pine specimens

Chemical <sup>a</sup>	Temperature (°F(°C))	Exposure time (days)	Moisture content (percent)		Specific gravity <sup>b</sup>	
			Mean	Range	Mean	Standard deviation
Control	80 (27)	3	10.5	9.3 – 11.3	0.55	0.04
		160	10.5	9.6 – 11.4	0.56	0.04
	130 (54)	3	10.5	9.3 – 11.3	0.56	0.04
		7	10.6	9.6 – 11.4	0.54	0.04
		21	10.5	9.2 – 12.7	0.54	0.04
		60	9.8	9.1 – 10.9	0.55	0.04
	180 (82)	160	9.9	9.3 – 10.4	0.52	0.10
		3	9.4	9.2 – 9.8	0.54	0.04
		7	9.0	8.5 – 9.4	0.52	0.05
		21	8.7	8.5 – 9.0	0.55	0.04
		60	8.0	7.8 – 8.7	0.57	0.05
		160	7.9	7.6 – 8.4	0.55	0.05
PA	80 (27)	3	14.0	12.4 – 15.4	0.54	0.04
		160	13.9	12.9 – 15.3	0.54	0.05
	130 (54)	3	15.0	13.1 – 16.5	0.54	0.05
		7	14.7	13.1 – 16.4	0.53	0.05
		21	15.2	13.6 – 19.5	0.54	0.06
		60	12.8	11.4 – 14.1	0.55	0.04
	180 (82)	160	13.6	12.0 – 15.5	0.56	0.05
		3	13.9	11.0 – 16.4	0.54	0.04
		7	11.8	9.8 – 13.8	0.55	0.05
		21	11.2	9.6 – 13.6	0.52	0.04
		60	11.8	9.9 – 14.2	0.54	0.05
		160	(c)	(c)	(c)	(c)
MAP	80 (27)	3	11.9	11.5 – 12.4	0.57	0.03
		160	11.7	11.3 – 12.0	0.57	0.04
	130 (54)	3	12.5	12.0 – 13.0	0.56	0.06
		7	12.2	11.6 – 12.9	0.56	0.04
		21	12.0	11.2 – 12.9	0.56	0.04
		60	11.1	10.9 – 11.4	0.58	0.05
	180 (82)	160	10.5	9.8 – 11.3	0.56	0.09
		3	9.5	9.1 – 10.0	0.57	0.04
		7	9.2	9.0 – 9.9	0.56	0.05
		21	8.7	8.2 – 9.3	0.57	0.04
		60	8.0	7.2 – 8.5	0.57	0.05
		160	8.0	7.7 – 8.5	0.55	0.04
BBA	80 (27)	3	13.7	12.5 – 14.2	0.55	0.04
		160	13.4	13.1 – 13.9	0.56	0.05
	130 (54)	3	13.8	13.6 – 14.2	0.55	0.04
		7	13.6	12.2 – 14.1	0.56	0.04
		21	13.3	12.5 – 13.6	0.56	0.03
		60	12.5	12.2 – 12.8	0.57	0.04
	180 (82)	160	12.5	11.9 – 12.9	0.54	0.09
		3	10.7	9.7 – 11.2	0.57	0.05
		7	10.7	10.2 – 11.0	0.56	0.05
		21	10.1	10.0 – 10.3	0.57	0.05
		60	9.3	9.1 – 10.0	0.59	0.04
		160	9.4	9.1 – 9.8	0.56	0.04

Table 5—Effect of temperature and exposure time on moisture content and specific gravity of treated Southern Pine specimens—concluded

Chemical <sup>a</sup>	Temperature (°F (°C))	Exposure time (days)	Moisture content (percent)		Specific gravity <sup>b</sup>	
			Mean	Range	Mean	Standard deviation
GUP-B	80 (27)	3	11.6	11.3 – 11.8	0.56	0.04
		160	11.5	11.3 – 11.8	0.56	0.04
	130 (54)	3	12.0	11.7 – 12.3	0.56	0.04
		7	11.7	11.4 – 12.0	0.55	0.04
		21	11.6	11.1 – 11.9	0.57	0.03
		60	10.4	10.3 – 10.6	0.55	0.04
		160	10.4	10.2 – 10.8	0.57	0.03
	180 (82)	3	9.2	9.0 – 9.4	0.57	0.04
		7	9.0	8.9 – 9.2	0.57	0.04
		21	8.6	8.5 – 9.0	0.57	0.04
		60	8.3	8.0 – 8.7	0.59	0.04
		160	7.2	7.1 – 7.4	0.57	0.04
DPF	80 (27)	3	10.7	10.4 – 11.1	0.57	0.05
		160	10.7	10.6 – 10.9	0.59	0.05
	130 (54)	3	10.9	10.6 – 11.2	0.57	0.04
		7	10.8	10.6 – 11.2	0.56	0.03
		21	10.7	10.2 – 11.1	0.58	0.07
		60	9.9	9.6 – 10.2	0.57	0.05
		160	9.7	9.4 – 9.9	0.59	0.04
	180 (82)	3	8.5	8.4 – 8.8	0.58	0.05
		7	8.5	8.2 – 8.8	0.58	0.04
		21	8.2	8.1 – 8.5	0.57	0.04
		60	8.0	7.7 – 8.4	0.58	0.04
		160	8.0	7.8 – 8.2	0.56	0.05
OPE	80 (27)	3	10.2	10.0 – 10.5	0.55	0.04
		160	10.3	10.0 – 10.5	0.56	0.04
	130 (54)	3	10.3	10.1 – 10.7	0.57	0.04
		7	10.1	9.7 – 10.5	0.56	0.04
		21	10.0	9.6 – 12.3	0.57	0.04
		60	9.4	9.2 – 9.8	0.55	0.04
		160	9.3	9.1 – 9.6	0.58	0.05
	180 (82)	3	8.3	8.0 – 8.6	0.56	0.05
		7	8.0	7.8 – 8.3	0.56	0.04
		21	8.0	7.8 – 8.2	0.57	0.04
		60	7.8	7.7 – 8.0	0.58	0.04
		160	7.4	4.4 – 7.9	0.55	0.11

<sup>a</sup>PA is phosphoric acid; MAP, monoammonium phosphate;  
BBA, borax-boric acid; GUP-B, guanyurea phosphate-boric acid;  
DPF, dicyandiamide phosphoric acid formaldehyde;  
and OPE, diethyl-N, N-bis (2-hydroxyethyl) aminomethyl phosphate.

<sup>b</sup>Based on oven-dry, treated conditions.

<sup>c</sup>These specimens were not tested in bending because of excessive degradation, and moisture content values were thus not determined.

Table 6—Effect of fire retardant treatments on modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load (WML)<sup>a</sup>

Chemical <sup>b</sup>	Tempera- ture (°F (°C))	Exposure time (days)	MOE (×10 <sup>6</sup> lb/in <sup>2</sup> (GPa))		MOE COV <sup>c</sup> (%)	MOR (lb/in <sup>2</sup> (MPa))		MOR COV (%)	WML (in-lb/in <sup>3</sup> ) <sup>d</sup>		WML COV (%)
			Mean	Standard deviation		Mean	Standard deviation		Mean	Standard deviation	
Control	80 (27)	3	2,019 (13.92)	0.201 (1.39)	9.9	17,024 (117.4)	1,874 (12.9)	11.0	14.68	6.03	41.1
		160	2,099 (14.47)	0.276 (1.90)	13.1	18,550 (127.9)	1,618 (11.2)	8.7	16.91	2.94	17.4
	130 (54)	3	2,011 (13.87)	0.189 (1.30)	9.4	18,003 (124.1)	1,898 (13.1)	10.5	15.98	3.96	24.8
		7	1,996 (13.76)	0.271 (1.87)	13.6	16,964 (117.0)	1,835 (12.7)	10.8	14.29	1.45	10.1
		21	1,953 (13.47)	0.270 (1.86)	13.8	17,341 (119.6)	2,011 (13.9)	11.6	14.68	3.98	27.1
		60	2,003 (13.81)	0.185 (1.28)	9.2	17,590 (121.3)	1,375 (9.5)	7.8	14.72	1.94	13.2
	180 (82)	160	2,017 (13.90)	0.261 (1.80)	12.9	17,422 (120.1)	2,030 (14.0)	11.7	14.40	3.06	21.3
		3	1,953 (13.47)	0.228 (1.57)	11.7	17,260 (119.0)	1,846 (12.7)	10.7	16.25	4.38	27.0
		7	2,027 (13.98)	0.158 (1.09)	7.8	18,133 (125.0)	1,489 (10.3)	8.2	15.27	3.61	23.6
		21	2,132 (14.70)	0.235 (1.62)	11.0	18,011 (124.2)	2,275 (15.7)	12.6	14.71	4.80	32.6
		60	2,034 (14.02)	0.193 (1.33)	9.5	17,219 (118.7)	1,728 (11.9)	10.0	12.24	3.87	31.6
		160	2,000 (13.79)	0.214 (1.48)	10.7	15,187 (104.7)	2,907 (20.0)	19.1	8.42	3.54	42.0
PA	80 (27)	3	1,667 (11.49)	0.255 (1.76)	15.3	8,460 (58.3)	2,301 (15.9)	21.2	3.27	1.59	48.6
		160	1,648 (11.36)	0.236 (1.63)	14.3	8,252 (56.9)	1,913 (13.2)	23.2	3.14	1.30	41.4
	130 (54)	3	1,716 (11.83)	0.282 (1.94)	16.4	8,097 (55.8)	1,771 (12.2)	21.9	2.69	1.07	39.8
		7	1,621 (11.18)	0.236 (1.63)	14.6	7,665 (52.9)	1,731 (11.9)	22.6	2.57	1.23	47.9
		21	1,913 (13.19)	0.480 (3.31)	25.1	8,036 (55.4)	2,078 (14.3)	25.9	2.77	1.24	44.8
		60	1,558 (10.74)	0.262 (1.81)	16.8	7,362 (50.8)	2,156 (14.9)	29.3	2.75	1.41	51.3
	180 (82)	160	1,646 (11.35)	0.296 (2.04)	18.0	7,603 (52.4)	2,141 (14.8)	28.2	2.57	1.27	49.4
		3	1,533 (10.57)	0.272 (1.88)	17.7	5,942 (41.0)	2,179 (15.0)	36.7	1.83	1.24	67.8
		7	1,509 (10.40)	0.266 (1.83)	17.6	6,322 (43.6)	1,519 (10.5)	24.0	1.81	0.77	42.5
		21	1,245 (8.58)	0.241 (1.66)	19.4	4,478 (30.9)	1,624 (11.2)	36.3	0.95	0.59	62.1
		60	1,104 (7.61)	0.230 (1.59)	20.8	2,960 (20.4)	999 (6.9)	33.8	0.49	0.24	49.0
		160	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
MAP	80 (27)	3	1,807 (12.46)	0.351 (2.42)	19.4	14,767 (101.8)	1,598 (11.0)	10.9	11.80	2.94	24.9
		160	1,841 (12.69)	0.223 (1.54)	12.1	15,012 (103.5)	1,451 (10.0)	9.7	11.50	2.33	20.3
	130 (54)	3	1,808 (12.47)	0.257 (1.77)	14.2	13,935 (96.1)	1,965 (13.5)	14.1	11.11	3.81	34.3
		7	1,769 (12.20)	0.258 (1.78)	14.6	14,388 (99.2)	1,491 (10.3)	10.4	11.27	2.30	20.4
		21	2,266 (15.62)	0.246 (1.70)	10.9	14,305 (98.6)	1,751 (12.1)	12.2	9.08	2.58	28.4
		60	1,825 (12.58)	0.259 (1.79)	14.2	13,910 (95.9)	1,819 (12.5)	13.1	9.44	2.55	27.0
		160	1,919 (13.23)	0.272 (1.88)	14.2	13,186 (90.9)	2,640 (18.2)	20.0	6.42	2.33	36.3
			(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)

Table 6—Effect of fire retardant treatment on modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load (WML)<sup>a</sup>—continued

Chemical <sup>b</sup>	Tempera- ture (°F (°C))	Exposure time (days)	MOE (×10 <sup>6</sup> lb/in <sup>2</sup> (GPa))			MOE COV <sup>c</sup> (%)	MOR (lb/in <sup>2</sup> (MPa))			MOR COV (%)	WML (in-lb/in <sup>3</sup> ) <sup>d</sup>		WML COV (%)
					Standard deviation				Standard deviation				
			Mean				Mean				Mean	Standard deviation	
BBA	180 (82)	3	1.888 (13.02)	0.288 (1.99)	15.3	12,945 (89.3)	2,037 (14.0)	15.7	6.63	1.67	25.2		
		7	1.784 (12.30)	0.188 (1.30)	10.5	11,244 (77.5)	2,191 (15.1)	19.5	4.86	1.93	39.7		
		21	1.930 (13.31)	0.209 (1.44)	10.8	11,020 (76.0)	2,314 (16.0)	21.0	4.21	1.67	39.7		
		60	1.818 (12.54)	0.243 (1.68)	13.4	8,856 (61.1)	2,838 (19.6)	32.0	3.06	1.85	60.5		
		160	1.526 (10.52)	0.207 (1.43)	13.6	6,194 (42.7)	1,484 (10.2)	24.0	1.63	0.68	41.7		
	80 (27)	3	1.797 (12.39)	0.293 (2.02)	16.3	16,777 (115.7)	2,569 (17.7)	15.3	10.05	2.56	25.5		
		160	1.930 (13.31)	0.294 (2.03)	15.2	16,731 (115.4)	2,895 (20.0)	17.3	9.49	3.05	32.1		
		130 (54)	3	1.874 (12.92)	0.177 (1.22)	9.4	15,386 (106.1)	1,985 (13.7)	12.9	8.36	2.33	27.9	
			7	2.009 (13.85)	0.155 (1.07)	7.7	16,736 (115.4)	2,361 (16.3)	14.1	9.02	2.61	28.9	
			21	2.322 (16.00)	0.354 (2.44)	15.2	16,990 (117.1)	1,665 (11.5)	9.8	8.67	2.22	25.6	
GUP-B	180 (54)	60	1.952 (13.46)	0.171 (1.18)	8.8	18,353 (126.5)	2,458 (17.0)	13.4	12.52	3.45	27.6		
		160	1.986 (13.69)	0.220 (1.52)	11.1	17,801 (122.7)	2,348 (16.2)	13.2	10.28	2.63	25.6		
		3	2.113 (14.57)	0.194 (1.34)	9.2	17,861 (123.2)	2,456 (17.0)	13.8	9.70	2.45	25.3		
		7	2.106 (14.52)	0.217 (1.50)	10.3	19,020 (131.1)	2,627 (18.1)	13.8	11.15	2.38	21.3		
		21	2.096 (14.45)	0.227 (1.57)	10.8	19,244 (132.7)	2,717 (18.7)	14.1	10.72	2.85	26.6		
	80 (27)	60	2.146 (14.80)	0.264 (1.82)	12.3	20,180 (139.1)	3,228 (22.3)	16.0	12.92	4.00	31.0		
		160	2.071 (14.28)	0.168 (1.16)	8.1	17,989 (124.0)	1,786 (12.3)	9.9	10.03	2.07	20.6		
		130 (54)	3	1.764 (12.16)	0.215 (1.48)	12.2	15,685 (108.1)	1,580 (10.9)	10.1	12.01	2.76	23.0	
			160	1.821 (12.56)	0.191 (1.32)	10.5	15,631 (107.8)	1,705 (11.8)	10.9	11.70	2.60	22.2	
			3	1.826 (12.59)	0.194 (1.34)	10.6	15,577 (107.4)	1,750 (12.1)	11.2	12.24	3.31	27.0	
7	1.944 (13.40)		0.203 (1.40)	10.4	15,732 (108.5)	1,729 (12.0)	11.0	11.25	2.37	21.1			
21	1.814 (12.50)		0.179 (1.23)	9.9	15,612 (107.6)	1,566 (10.8)	10.0	10.96	2.30	21.0			
GUP-B	180 (82)	60	1.865 (12.86)	0.194 (1.34)	10.4	15,114 (104.2)	1,651 (11.4)	10.9	10.44	2.64	25.3		
		160	1.892 (13.05)	0.209 (1.44)	11.0	15,166 (104.6)	1,859 (12.8)	12.3	9.44	2.32	24.6		
		3	1.961 (13.52)	0.179 (1.23)	9.1	16,110 (111.1)	1,710 (11.8)	10.6	10.17	2.53	24.9		
		7	1.861 (12.83)	0.192 (1.32)	10.3	15,998 (110.3)	2,046 (14.1)	12.8	10.05	2.42	24.0		
		21	1.935 (13.34)	0.203 (1.40)	10.5	15,224 (105.0)	2,022 (13.9)	13.3	7.99	2.35	29.4		
	130 (54)	60	1.945 (13.41)	0.200 (1.38)	10.3	12,144 (83.7)	3,153 (21.7)	26.0	5.40	2.78	51.5		
		160	1.808 (12.47)	0.283 (1.95)	15.7	9,615 (66.3)	2,631 (18.1)	27.4	3.65	2.09	57.3		

Table 6—Effect of fire retardant treatment on modulus of elasticity (MOE), modulus of rupture (MOR), and work to maximum load (WML)<sup>a</sup>—concluded

Chemical <sup>b</sup>	Temperature (°F (°C))	Exposure time (days)	MOE (×10 <sup>6</sup> lb/in <sup>2</sup> (GPa))			MOR (lb/in <sup>2</sup> (MPa))			WML (in-lb/in <sup>3</sup> ) <sup>d</sup>		
			Mean	Standard deviation	COV <sup>c</sup> (%)	Mean	Standard deviation	COV (%)	Mean	Standard deviation	COV (%)
DPF	80 (27)	3	1.732 (11.94)	0.165 (1.14)	9.5	15,412 (106.3)	1,618 (11.2)	10.5	12.02	2.73	22.7
		160	1.802 (12.42)	0.227 (1.57)	12.6	15,870 (109.4)	1,790 (12.3)	11.3	12.19	2.47	20.3
	130 (54)	3	1.799 (12.40)	0.180 (1.24)	10.0	14,960 (103.1)	1,524 (10.5)	10.2	10.81	2.49	23.0
		7	1.799 (12.40)	0.276 (1.90)	15.3	15,347 (105.8)	1,651 (11.4)	10.8	11.08	2.94	26.5
		21	1.870 (12.89)	0.158 (1.09)	8.4	15,810 (109.0)	1,815 (12.5)	11.5	11.18	2.88	25.8
		60	1.861 (12.83)	0.234 (1.61)	12.6	15,832 (109.2)	2,102 (14.5)	13.3	11.82	3.12	26.4
	180 (82)	160	1.883 (12.98)	0.254 (1.75)	13.5	15,419 (106.3)	2,046 (14.1)	13.3	10.42	2.38	22.8
		3	1.917 (13.22)	0.223 (1.54)	11.6	16,462 (113.5)	1,818 (12.5)	11.0	11.34	2.53	22.3
		7	1.891 (13.04)	0.196 (1.35)	10.4	16,252 (112.1)	1,933 (13.3)	11.9	10.67	2.15	20.1
		21	1.851 (12.76)	0.182 (1.25)	9.8	14,946 (103.1)	2,333 (16.1)	15.6	8.42	2.54	30.2
OPE	80 (27)	60	2.599 (17.92)	0.318 (2.19)	12.2	13,091 (90.3)	2,847 (19.6)	21.7	6.36	2.71	42.6
		160	1.796 (12.38)	0.255 (1.76)	14.2	10,217 (70.4)	2,759 (19.0)	27.0	4.14	2.12	51.2
		3	1.716 (11.83)	0.173 (1.19)	10.1	14,480 (99.8)	1,715 (11.8)	11.8	12.56	2.82	22.5
		160	1.730 (11.93)	0.201 (1.39)	11.6	14,844 (102.3)	1,646 (11.3)	11.1	13.05	2.50	19.2
	130 (54)	3	1.723 (11.88)	0.184 (1.27)	10.7	14,336 (98.8)	1,898 (13.1)	13.2	12.70	3.55	28.0
		7	1.801 (12.42)	0.215 (1.48)	11.9	14,472 (99.8)	1,725 (11.9)	11.9	12.10	2.59	21.4
		21	1.696 (11.69)	0.168 (1.16)	9.9	14,609 (100.7)	1,589 (11.0)	10.9	12.86	3.51	27.3
		60	1.774 (12.23)	0.190 (1.31)	10.7	14,771 (101.8)	1,868 (12.9)	12.6	12.65	2.88	22.8
	180 (82)	160	1.755 (12.10)	0.231 (1.59)	13.2	15,345 (105.8)	2,415 (16.7)	15.7	13.48	3.29	24.4
		3	1.768 (12.19)	0.239 (1.65)	13.5	15,501 (106.9)	2,524 (17.4)	16.3	12.19	2.93	24.0
		7	1.823 (12.57)	0.207 (1.43)	11.4	15,825 (109.1)	1,934 (13.3)	12.2	12.89	2.91	22.6
		21	1.787 (12.32)	0.228 (1.57)	12.8	15,552 (107.2)	2,232 (15.4)	14.4	11.32	3.12	27.6
		60	2.162 (14.90)	0.506 (3.49)	23.4	14,892 (102.7)	1,956 (13.5)	13.1	9.51	2.51	26.4
		160	1.851 (12.76)	0.236 (1.63)	12.7	12,727 (87.8)	2,165 (14.9)	17.0	6.11	2.25	36.8

<sup>a</sup>Each value represents the mean or standard deviation of 25 specimens.

<sup>b</sup>See Table 5 (footnote a) for definitions of treatment abbreviations.

<sup>c</sup>Coefficient of variation.

<sup>d</sup>1 in-lb/in<sup>3</sup> = 6.8947 kJ/m<sup>3</sup>.

<sup>e</sup>These specimens were not tested because of extreme degradation, and moisture content values were thus not determined.

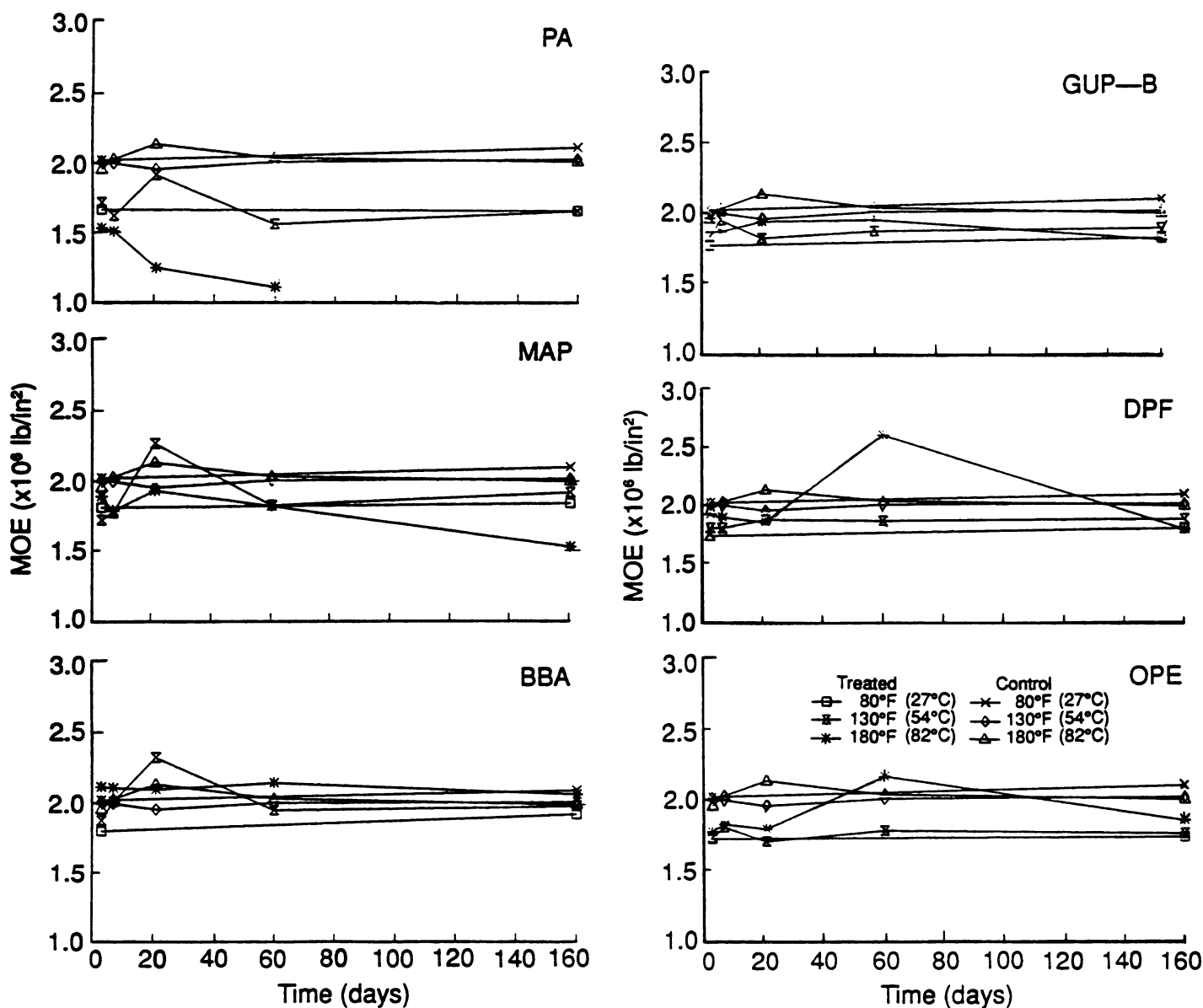


Figure 4—Average modulus of elasticity (MOE) of treated and control specimens exposed for various times to different temperature and relative humidity conditions. See legend to Figure 1 for definition of treatment abbreviations. ( $10^6 \text{ lb/in}^2 = 6.895 \text{ GPa}$ )

The MAP-treated specimens showed an initial reduction in MOE of about 11 percent, which did not change over the exposure time for the 80°F (27°C) and 130°F (54°C) exposures (Fig. 4, Table 7). At 180°F (82°C), MOE was reduced 24 percent over the exposure time compared to that of controls. The MAP-treated specimens exhibited a consistent reduction in MOE after 21 days of exposure at the high temperature.

The initial reduction in MOE of specimens treated with BBA, GUP-B, DPF, and OPE apparently did not change over the exposure time for all exposure temperatures (Fig. 4, Table 7).

The MOE values of the various treated specimens, except the PA-treated specimens, were generally unaffected by almost all temperatures and exposure times. This stability in the effect of treatment on MOE clearly supports historical adjustment factors (NFPA 1986) that assume that the relative performance of treated compared to untreated wood over time at room-temperature conditions is constant after accounting for the initial treatment effect. Evaluation of treatment effects based solely on MOE would not give a realistic evaluation of the impact of chemical type, exposure conditions, and exposure time.

Table 7—Reduction in bending properties of treated wood over exposure time

Treatment and exposure (°F (°C))	Reduction in property (percent)					
	Modulus of elasticity		Modulus of rupture		Work to max. load	
	Initial	Final	Initial	Final	Initial	Final
Control						
80 (27)	0	0	0	0	0	0
130 (54)	0	0	0	0	0	0
180 (82)	0	0	0	11	0	43
PA						
80 (27)	17	17	50	50	78	78
130 (54)	17	17	50	50	78	78
180 (82)	17	45	50	(a)	78	(a)
MAP						
80 (27)	11	11	13	13	20	20
130 (54)	11	11	13	22	20	56
180 (82)	11	24	13	64	20	89
BBA						
80 (27)	13	13	0	0	32	32
130 (54)	13	13	0	(b)	32	32
180 (82)	13	13	0	(b)	32	32
GUP-B						
80 (27)	13	13	8	8	18	18
130 (54)	13	13	8	8	18	36
180 (82)	13	13	8	44	18	75
DPF						
80 (27)	13	13	9	9	16	16
130 (54)	13	13	9	9	16	16
180 (82)	13	13	9	40	16	72
OPE						
80 (27)	13	13	15	15	16	16
130 (54)	13	13	15	15	16	16
180 (82)	13	13	15	25	16	58

<sup>a</sup>Specimens not tested because of extreme degradation.

<sup>b</sup>Values increased by approximately 5 percent.

## Modulus of Rupture

As with the MOE values, no distributional trends or differential skewness of the MOR distributions were observed. Accordingly, our discussion will focus on mean MOR values. The MOR data are summarized in Table 6, and mean values are shown graphically in Figures 5 and 6. Table 7 shows the reduction in MOR over the exposure time.

The controls exhibited no reduction in MOR after 160 days of exposure at 80°F (27°C) (Tables 6 and 7) or 130°F (54°C) (Tables 6 and 7, Fig. 5a). However,

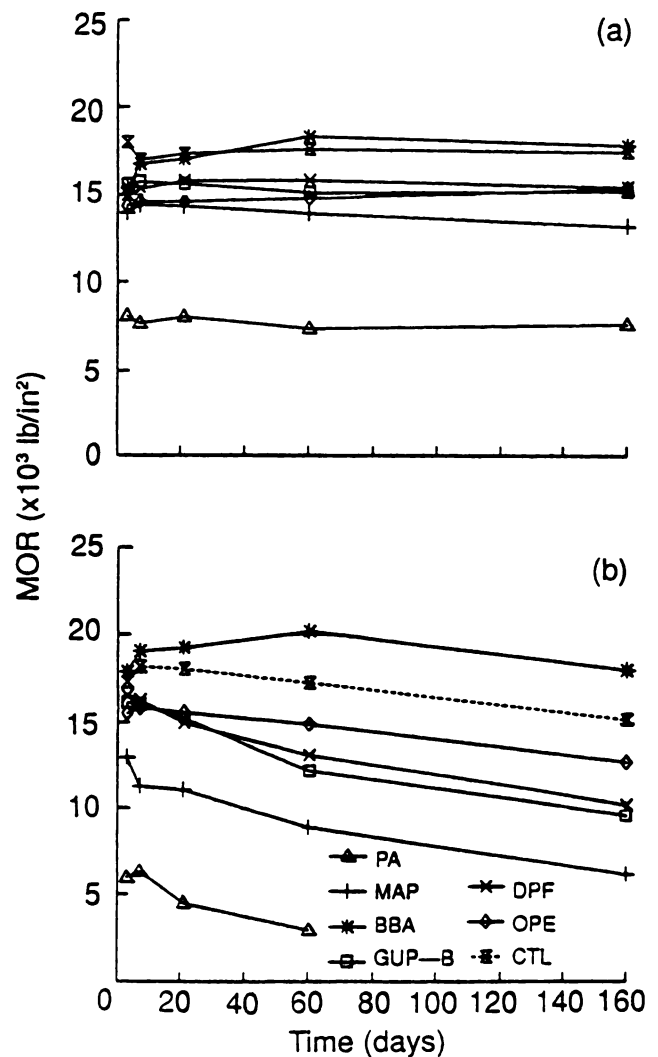


Figure 5—Effect of various treatments on average modulus of rupture (MOR) for two exposure conditions: (a) 130°F (54°C) and 73 percent relative humidity, and (b) 180°F (82°C) and 50 percent relative humidity. See legend to Figure 1 for definition of treatment abbreviations. ( $10^3 \text{ lb/in}^2 = 6.895 \text{ MPa}$ )

the MOR of controls was reduced 11 percent after 160 days of exposure at 180°F (82°C) (Fig. 5b).

The PA-treated specimens showed an initial reduction in MOR of 50 percent compared to that of controls (Table 7, Fig. 6). At 80°F (27°C) and 130°F (54°C), this reduction in MOR did not change for the duration of exposure. However, after 160 days at 180°F (82°C), PA-treated specimens were degraded to such an extent they broke on handling. A significant rate of reduction in MOR for PA-treated specimens was apparent after only 7 days when compared to the MOR of controls. This loss in MOR agrees with the results for MOE.

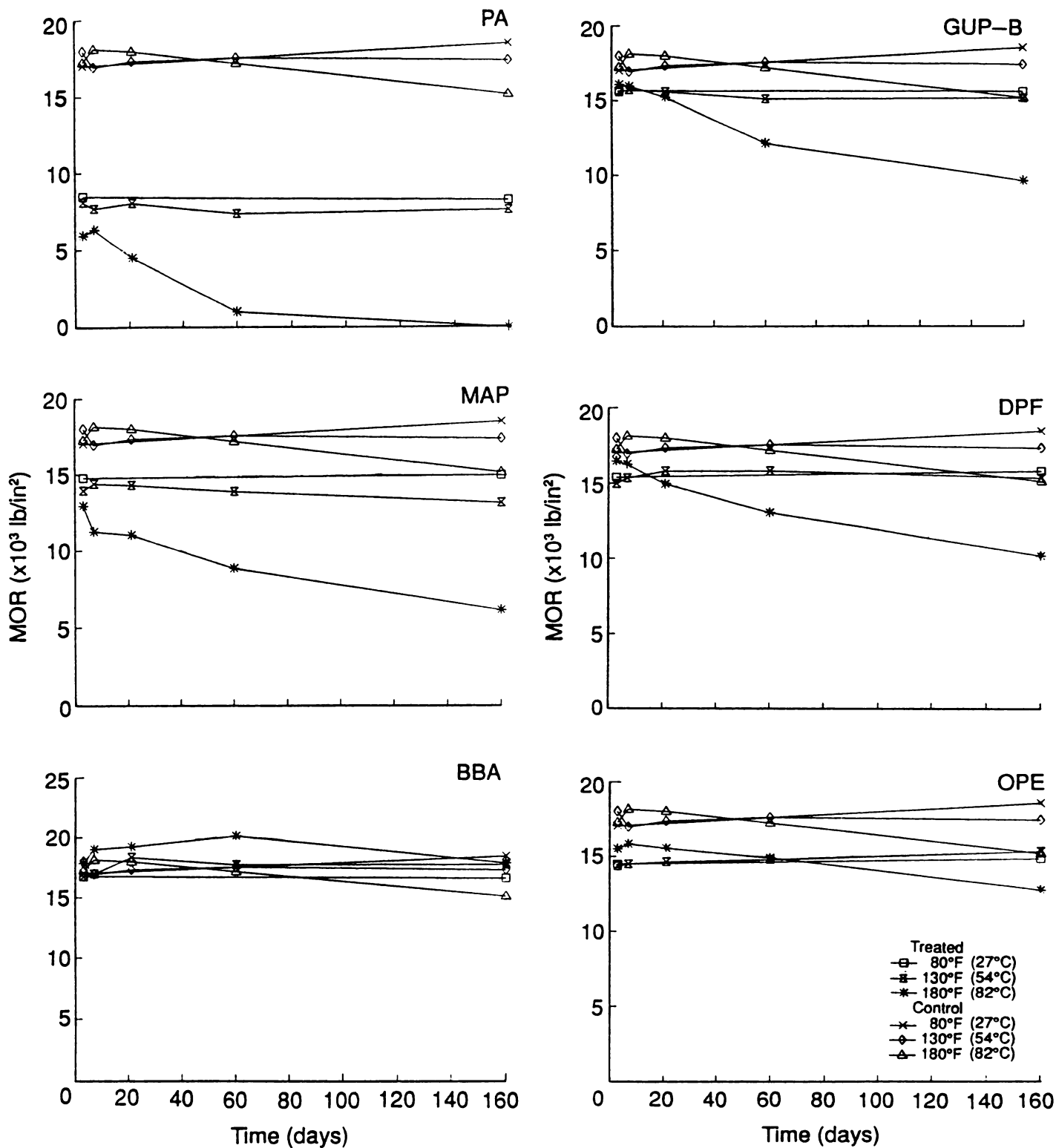


Figure 6—Average modulus of rupture (MOR) of treated and control specimens exposed for various times to different temperature and relative humidity conditions. See legend to Figure 1 for definition of treatment abbreviations. ( $10^3 \text{ lb/in}^2 = 6.895 \text{ MPa}$ )

The initial reduction in MOR of MAP-treated specimens did not change over the exposure time at 80°F (27°C) (Table 7, Fig. 6). At 130°F (54°C), MOR values apparently decreased slightly over the exposure time, but this difference was not statistically significant. At 180°F (82°C), MOR values were significantly reduced compared to that of controls after only 7 days.

The BBA-treated specimens showed no significant decrease in MOR values compared to control MOR values for all temperature exposures (Table 7, Fig. 6). In fact, MOR values at both 130°F (54°C) and 180°F (82°C) increased by approximately 5 percent. We suspect these increases were a result of crosslinking of some carbohydrates. Further research is underway at FPL to explain this anomaly.

The other three treatments, GUP-B, DPF, and OPE, resulted in an initial MOR reduction of 8, 9, and 15 percent, respectively, compared to that of controls after 3 days of exposure at 80°F (27°C) (Table 7, Fig. 6). This reduction was constant over the exposure time at 80°F (27°C) or 130°F (54°C). At 180°F (82°C), however, the treated specimens showed a significant rate of reduction in MOR over the exposure time (Table 7, Fig. 5b).

Modulus of rupture was more sensitive to treatment effects than was MOE and shows differences between most treatment groups. As with MOE, the PA treatment had the most deleterious initial and thermal-induced effects on MOR, especially at 180°F (82°C). Although not as severe as the effects of PA treatment, the MAP treatment also had deleterious initial and thermal-induced effects on the strength properties of the wood. All other treatments clearly showed an initial effect on MOR. While thermal-induced effects were apparent at 180°F (82°C), these effects were not as severe as those resulting from PA and MAP. Also note that a similar thermal-induced effect on MOR was apparent for the controls after 160 days at 180°F (82°C).

Most importantly, note that after the thermal-induced reduction in MOR at 180°F (82°C) was initiated (<60 days) and eventually stabilized ( $\geq 60$  days), the rate of strength degradation (slopes of the lines) was similar for treated and untreated material even though large differences in strength occurred (Fig. 5b). This suggests that once an elevated temperature has caused a fire retardant chemical to dissociate into its acidic chemical form, this form catalyzes strength deterioration in the wood in a similar manner with all chemicals. Thus, the actual difference between most fire retardant chemical systems is the time required for the chemical to dissociate at some temperature.

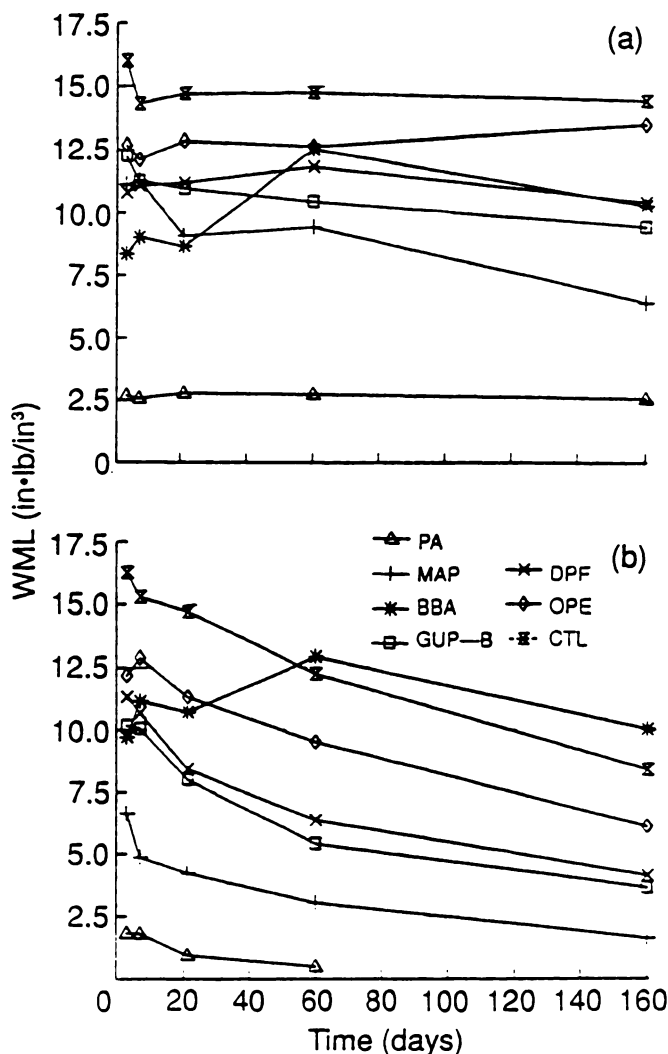


Figure 7—Effect of various treatments on average work to maximum load (WML) for two exposure conditions: (a) 130°F (54°C) and 73 percent relative humidity, and (b) 180°F (82°C) and 50 percent relative humidity. See legend to Figure 1 for definition of treatment abbreviations. (1 in-lb/in<sup>3</sup> = 6.8947 kJ/m<sup>3</sup>)

## Work to Maximum Load

As with the other properties, the distributions of WML for each treatment group were evaluated. No distributional trends or differential skewness of the WML distributions were observed. Accordingly, our discussion will focus on mean WML values. The WML data are summarized in Table 6, mean values are shown graphically in Figures 7 and 8, and the reduction in WML over the exposure time is shown in Table 7.

The WML of the untreated wood (control) was relatively unchanged over the 160-day exposure at 80°F

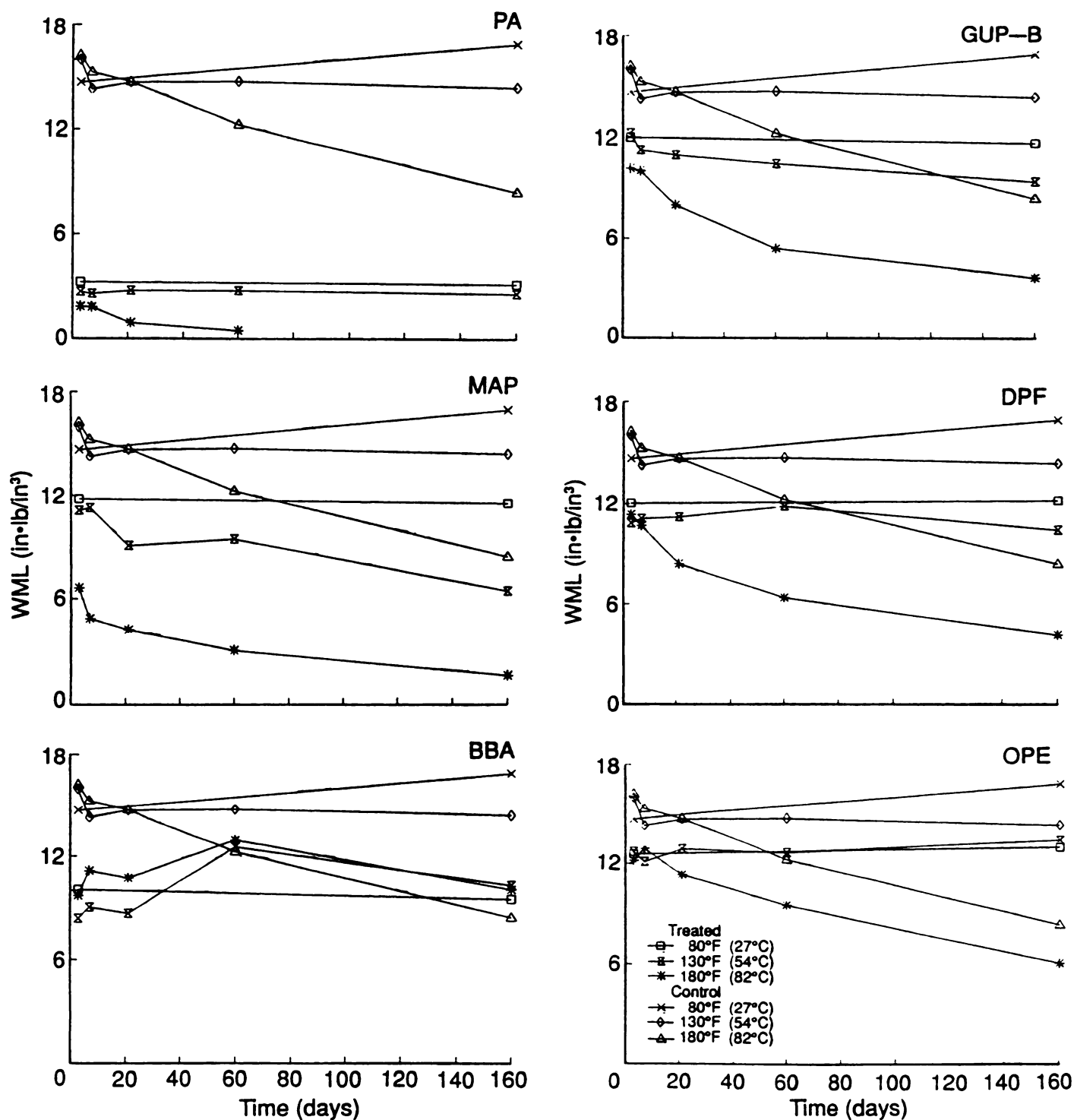


Figure 8—Average work to maximum load (WML) of treated and control specimens exposed for various times to different temperature and relative humidity conditions. See legend to Figure 1 for definition of treatment abbreviations. ( $1 \text{ in}\cdot\text{lb}/\text{in}^3 = 6.8947 \text{ kJ}/\text{m}^3$ )

(27°C) (Table 7) or 130°F (54°C) (Table 7, Fig. 7a). However, the WML of controls was significantly reduced by about 43 percent after 160 days of exposure at 180°F (82°C) (Table 7, Fig. 7b).

The PA-treated specimens showed an initial reduction in WML of approximately 78 percent compared to that of the controls after 3 days of exposure at 80°F (27°C) (Table 7, Fig. 8). At 80°F (27°C) and 130°F (54°C), this reduction was constant over the exposure time. However, after 160 days at 180°F (82°C), the PA-treated specimens could not be tested because the specimens were too brittle to handle.

The WML of the MAP-treated specimens was initially reduced approximately 20 percent compared to that of controls (Table 7, Fig. 8). At 80°F (27°C), WML did not change over the exposure period. Both the 130°F (54°C) and 180°F (82°C) exposures caused a significant reduction in WML over the exposure time (Table 7).

The BBA-treated specimens showed an initial reduction in WML of approximately 32 percent compared to that of controls (Table 7, Fig. 8). This reduction was essentially constant for all three exposure temperatures although an anomalous increase in WML occurred at 130°F (54°C) and 180°F (82°C) after 60 days (Fig. 8). Although the results with BBA look promising on a quantitative basis, the specimens treated with this chemical experienced ceramic-like failures during the bending test—they experienced sudden rupture and smooth, almost glass-like fractures. This embrittlement is a matter for concern because wood is assumed to undergo ductile or plastic-like failure, rather than brittle failure. Ductile failure is often cited as a structural advantage for wood.

Specimens treated with GUP-B showed an initial reduction in WML of approximately 18 percent compared to that of controls (Table 7, Fig. 8). These WML values did not change over time at 80°F (27°C), but they were further reduced at the other exposure temperatures (Table 7). The reduction in WML for GUP-B-treated specimens was not as severe as the reduction for specimens treated with PA or MAP.

The initial reduction in WML for specimens treated with DPF or OPE was generally constant for both the 80°F (27°C) and 130°F (54°C) exposures over the exposure time (Table 7, Fig. 8). For the 180°F (82°C) exposure, WML was reduced a total of 72 and 58 percent for DPF- and OPE-treated specimens, respectively, over the exposure time (Table 7). At the high exposure temperature, the rate of change in WML for both DPF- and OPE-treated specimens paralleled the rate of change for controls. The DPF and OPE performance was very similar to that of GUP-B.

Work to maximum load is sensitive to the influence of chemical type, exposure conditions, and exposure time. The WML is an indication of the brittleness of materials, and treatments tend to cause embrittlement (Winandy and Rowell 1984). The PA treatment had the greatest detrimental effect on WML, followed by MAP. All other treatments were not as severe as PA and MAP. However, except for BBA-treated specimens, all other treated specimens and the untreated controls had reductions in WML over time at 180°F (82°C).

## Chemical Analysis

The chemical analysis data revealed a pattern of degradation for several treatments (Table 8). Because we were looking for patterns in the degradation of the sugar residues, we ran only one chemical analysis per group. Consequently, the differences between control and specimen groups should be viewed as relative estimates only. Further chemical analysis is necessary to establish the quantitative changes in sugar residue percentages from the untreated controls. Examination of the degradation patterns provides some clues as to the causes of strength degradation and gives a starting point for further extensive chemical investigation. In addition, degradation patterns in the wood constituents appeared primarily for the exposures at 180°F (82°C). Therefore, the following discussion deals with trends in the degradation patterns of the wood constituents at 180°F (82°C) only.

### Control Group

For the control group, the percentage of the wood constituents remained constant over the various exposure temperatures and the exposure times. For the 180°F (82°C) exposure, the percentage of arabinose appeared to decrease with exposure time. The total sum of the percentages of the wood constituents in the control group ranged between 93 and 103 percent. The sums in Table 8 differ from 100 percent because of the differences in the samples, experimental variability, and components that were not taken into account.

### Treatment Groups

**Phosphoric Acid**—The PA-treated specimens showed the most changes in the percentages of the various wood constituents. Klason lignin and acid-soluble lignin showed an increase, and some sugar residues decreased. With the exception of glucose, all the sugar residues showed a pattern of decreasing percentage with exposure time. The percentage of glucose appeared to remain constant. The sums of the percentages of wood constituents in the PA-treated specimens were lower than that of the controls. The sums ranged from 87 to 93 percent, roughly a 10-percent difference from that of the controls.

Table 8—Effect of temperature and exposure time on chemical composition of treated Southern Pine specimens

Chemical <sup>a</sup>	Temperature (°F (°C))	Exposure time (days)	Composition (percent)							
			Klason lignin	Acid- soluble lignin	Glucose	Xylose	Galactose	Arabinose	Mannose	Sum
Control	80 (27)	3	29.4	0.6	48.1	8.0	3.0	1.3	12.9	103.3
		160	27.6	0.4	44.9	6.1	2.1	1.2	11.2	93.5
	130 (54)	3	29.6	0.5	47.0	7.5	3.4	1.2	12.6	101.8
		7	28.4	0.6	48.0	7.0	2.4	1.3	13.2	100.9
	180 (82)	21	29.6	0.6	47.1	7.1	2.6	1.2	12.4	100.6
		60	29.4	0.6	45.9	6.6	2.5	1.0	12.0	98.0
		160	27.8	0.4	52.9	7.1	2.2	1.3	13.6	105.3
		3	29.2	0.6	46.7	7.3	2.6	1.2	12.4	100.0
		7	29.3	0.6	46.5	6.9	2.5	1.2	12.3	99.3
		21	29.7	0.6	48.0	6.8	2.4	0.9	12.7	101.1
		60	29.1	0.7	46.9	6.8	2.6	0.7	12.7	99.5
		160	27.6	0.8	53.1	6.9	2.3	0.6	13.4	104.7
PA	80 (27)	3	26.7	0.6	40.9	5.9	2.6	0.7	10.8	88.2
		160	24.8	0.5	44.3	5.8	1.8	1.2	11.3	89.7
	130 (54)	3	27.1	0.6	41.5	5.9	2.4	0.8	11.9	90.2
		7	27.0	0.6	41.6	5.9	2.7	1.1	10.7	89.6
	180 (82)	21	26.8	0.6	43.6	6.1	2.7	1.1	12.2	93.1
		60	27.4	0.7	43.2	5.7	2.8	0.8	10.8	91.4
		160	26.7	0.9	44.1	6.4	1.5	0.6	10.3	90.5
		3	28.4	0.9	42.0	5.4	2.5	0.7	10.2	90.1
		7	29.3	1.0	44.2	4.4	1.8	0.6	10.1	91.4
		21	34.0	1.3	41.2	2.6	1.7	0.2	6.2	87.2
		60	37.9	1.4	40.7	2.0	0.8	0.0	4.2	87.0
		160	(b)	(b)	(b)	(b)	(b)	(b)	(b)	
MAP	80 (27)	3	27.3	0.5	43.8	5.9	2.1	0.7	11.3	91.6
		160	23.6	0.4	42.5	6.2	2.1	1.0	11.8	87.6
	130 (54)	3	27.5	0.5	43.6	6.6	2.4	1.2	11.7	93.5
		7	27.2	0.5	41.8	6.4	2.2	0.9	11.0	90.0
	180 (82)	21	26.6	0.5	42.6	6.1	1.7	0.7	11.3	89.5
		60	27.0	0.5	41.5	6.2	2.6	0.9	11.1	89.8
		160	26.3	0.5	44.2	6.4	2.0	0.6	11.6	91.6
		3	27.1	0.5	41.8	6.2	2.1	0.6	10.9	89.2
		7	27.3	0.6	41.1	5.7	2.0	0.5	10.6	87.8
		21	27.7	0.8	42.7	6.0	1.7	0.3	10.5	89.7
		60	30.2	1.2	43.5	4.9	1.2	0.0	9.8	90.8
		160	26.3	1.8	44.7	2.6	0.2	0.0	5.6	87.2
BBA	80 (27)	3	27.8	0.6	42.2	6.7	2.6	1.1	14.8	95.8
		160	26.3	0.4	39.3	5.9	2.4	1.2	10.5	86.0
	130 (54)	3	27.1	0.6	42.8	6.5	2.3	1.0	14.7	95.0
		7	26.8	0.6	44.4	7.0	2.7	1.4	15.5	98.4
	180 (82)	21	26.7	0.6	43.9	6.5	1.9	1.0	15.7	96.3
		60	27.0	0.6	43.5	6.8	1.9	1.2	14.9	95.9
		160	25.7	0.4	44.9	6.5	2.0	1.0	12.4	92.9
		3	27.0	0.6	43.1	6.7	2.7	1.2	15.7	97.0
		7	27.1	0.6	43.5	6.3	1.4	0.6	14.8	94.3
		21	27.0	0.6	46.0	6.8	2.3	0.9	15.4	99.0
		60	27.0	0.7	42.3	6.5	2.5	0.9	14.5	94.4
		160	26.3	0.9	43.8	6.1	2.3	0.7	11.4	91.5

Table 8—Effect of temperature and exposure time on chemical composition of treated Southern Pine specimens—concluded

Chemical <sup>a</sup>	Temperature (°F (°C))	Exposure time (days)	Composition (percent)							Sum
			Klason lignin	Acid- soluble lignin	Glucose	Xylose	Galactose	Arabinose	Mannose	
GUP-B	80 (27)	3	28.3	1.5	41.4	5.7	2.3	1.2	11.2	91.6
		160	25.9	2.2	44.1	6.0	2.4	1.1	12.4	94.1
	130 (54)	3	27.9	1.5	43.0	6.2	1.9	1.1	11.4	93.0
		7	27.5	1.6	43.1	5.9	1.8	1.1	11.4	92.4
		21	28.1	1.5	42.6	6.3	2.3	1.2	11.6	93.6
		60	27.9	1.5	42.4	5.8	1.9	1.3	11.3	92.1
		160	25.6	1.7	46.2	6.2	2.3	0.8	12.0	94.8
	180 (82)	3	27.9	1.6	42.2	5.7	2.1	1.5	10.9	91.9
		7	28.1	1.4	42.3	6.2	2.3	1.4	10.9	92.6
		21	29.5	1.2	44.2	6.6	2.4	1.2	11.1	96.2
		60	29.3	1.4	44.2	6.5	2.6	0.9	10.4	95.3
		160	26.9	2.1	48.4	5.3	1.6	0.3	9.8	94.4
DPF	80 (27)	3	27.4	2.6	42.3	6.6	2.1	0.8	11.0	92.8
		160	28.0	3.2	40.3	5.6	2.4	1.4	10.5	91.4
	130 (54)	3	28.4	2.4	41.6	6.1	2.4	1.1	11.1	93.1
		7	27.9	2.5	42.4	6.8	2.2	1.0	11.0	93.8
		21	27.4	2.2	43.6	6.5	2.4	1.0	11.4	94.5
		60	27.7	2.5	40.7	6.5	2.4	0.8	10.4	91.0
		160	28.0	2.9	42.3	5.4	2.3	0.8	10.0	91.7
	180 (82)	3	27.7	2.5	42.1	5.7	1.8	0.7	11.2	91.7
		7	28.4	2.3	42.5	6.0	1.9	0.8	10.9	92.8
		21	27.9	2.3	43.9	6.7	2.0	0.6	10.6	94.0
		60	28.3	2.2	45.5	6.0	2.0	0.4	11.2	95.6
		160	27.8	2.2	40.5	4.1	1.4	0.3	8.8	85.1
OPE	80 (27)	3	27.2	0.6	42.8	6.2	2.4	0.9	10.9	91.0
		160	25.9	0.4	44.6	5.9	1.9	1.2	10.7	90.6
	130 (54)	3	26.6	0.6	44.8	6.7	2.1	1.1	11.8	93.7
		7	26.4	0.6	45.0	6.3	1.8	0.9	11.9	92.9
		21	27.0	0.6	42.0	6.0	2.0	1.4	11.1	90.1
		60	27.2	0.6	43.8	6.6	2.5	1.1	11.4	93.2
		160	25.7	0.5	44.0	5.9	1.5	1.0	10.7	89.3
	180 (82)	3	26.8	0.6	42.5	6.3	2.5	0.9	11.8	91.4
		7	26.4	0.6	43.7	6.2	2.2	1.0	11.7	91.8
		21	26.9	0.6	43.8	6.8	2.1	0.8	11.5	92.5
		60	27.5	0.8	45.0	6.8	2.1	0.5	11.4	94.1
		160	27.9	0.9	46.5	5.7	1.5	0.5	11.0	94.0

<sup>a</sup>See Table 5 (footnote a) for definitions of treatment abbreviations.

<sup>b</sup>These specimens could not be analyzed for chemical composition because of excessive degradation.

**Monoammonium Phosphate**—Like the PA-treated specimens, the MAP-treated specimens exhibited changes in the percentages of the various wood constituents, although not to the same extent. As with the PA treatment group, the acid-soluble lignin fractions of the MAP treatment group increased significantly. However, the Klason lignin fraction did not appear to increase in the MAP treatment group as it did in the PA treatment group. The percentages of xylose, galactose, arabinose, and mannose showed a decreasing pattern like that of the PA treatment group but to a lesser extent. The sum of percentages for the MAP treatment group was roughly the same as that of the PA treatment group, ranging between 87 and 93 percent.

**Borax-Boric Acid**—Within the wide variability of the data, the BBA treatment group showed almost no change in the percentage of wood constituents. Both lignin fractions as well as the sugar residues appeared to be constant with exposure time. The sum of the percentages of constituents was between 91.5 and 98.4, which is in close agreement with that of the controls.

**Guanylurea Phosphate-Boric Acid**—The GUP-B treatment group showed minor reductions in some sugar residues and no apparent increases in the lignin fractions. Only the percentages of galactose and arabinose appeared to decrease with exposure time. Mannose may have been slightly decreased, but given the wide variability of the data, it would be difficult to quantify this decrease. The sum of the percentages ranged from 91.6 to 96.2 percent, just slightly below that of controls and the BBA treatment group.

**Dicyandiamide Phosphoric Acid Formaldehyde**—The DPF treatment group showed the same pattern in change of the percentages of wood constituents as that shown by the GUP-B treatment group. This is reasonable because these treatments are very similar chemically. The sum of the percentages ranged from 85.1 to 95.6 percent.

**Diethyl-N, N-bis (2-Hydroxyethyl) Aminomethyl Phosphate**—A degradation pattern in wood constituents was difficult to discern in the OPE treatment group. The percentages of galactose and arabinose apparently decreased, but to a lesser extent than that which occurred in the GUP-B and DPF systems. The sum of the percentages ranged from 89.3 to 94 percent.

**Overall Patterns**—Similarities exist between the wood constituents affected and the chemical treatment. For example, only with the strongest acid did we see apparent increases in the Klason lignin. Given the effect of PA acidity on the carbohydrates, we believe this increase resulted solely from the drastic

reductions in the other sugar residues, leaving a larger percentage of Klason lignin. We also observed an increase in the acid-soluble lignin fraction and cannot explain this increase. However, there appeared to be a direct correlation between the observed changes in the percentage of arabinose and the acid-soluble lignin. If the arabinose percentage showed a decreasing trend for a given treatment group, the acid-soluble lignin showed an increasing trend. Since acid-soluble lignin was determined by ultra-violet absorbance at a wavelength of 205 nm, degradation byproducts of arabinose were possibly measured. We are cautious on this speculation, however, because carbohydrate degradation products from the hydrolytic procedure are known to not interfere with the 205-nm measurement (Pearl and Busche 1960). Further research is necessary to positively identify the products that cause the increase in acid-soluble lignin.

Other significant similarities are the reductions in arabinose and galactose. These sugar residues appeared to be the most sensitive to chemical treatment. The percentage of arabinose decreased in all treatment groups and controls. Galactose residues decreased in all treatment groups, except the BBA treatment, but not in controls. Mannose and xylose residues primarily decreased with only the highly acidic treatments, namely PA and MAP. The other treatments may have caused some reduction in these sugar residues, as indicated by the data for the 180°F (82°C) exposure after 160 days (Table 8). However, quantitative evaluation is difficult because of the wide variability in the data and limited number of replicates.

## Relationship of Chemical Properties to Mechanical Properties of Fire-Retardant-Treated Wood

### Effect of Treatment on Strength

There is a direct relationship between the effect of chemical treatment and the effect of treatment pH on mechanical properties. The PA treatment has the lowest pH, and it had the greatest effect on mechanical properties. It is the strongest acid of the selected chemicals; the hydrogen ion concentration of PA is approximately 100 times greater than that of MAP. This difference in pH at the same loading concentration accounts for the severe effect of PA on mechanical properties.

Three fire retardant chemicals—MAP, GUP-B, and DPF—have the same pH. Monoammonium phosphate is considered an inorganic salt whereas GUP-B and DPF are considered organic phosphate salts. Monoammonium phosphate dissociates more readily at higher temperatures than does GUP-B or

DPF, thereby increasing the acid concentration and decreasing the strength properties more than does GUP-B or DPF.

The BBA and OPE treatments have pH levels that are close to neutrality. These treatments exhibited the least effect on strength properties. However, BBA and OPE reduce flame propagation only slightly. To determine whether these chemicals are acceptable commercial fire retardant treatments, the relationship between loading level and reduced flame propagation needs to be examined.

We believe that mixtures of the fire retardant chemicals used in this study would have intermediate effects. For example, if MAP and BBA were mixed, BBA could reduce the acidity of MAP, thereby reducing strength loss. Thus, a MAP-BBA mixture might produce effects similar to those produced by GUP-B and DPF. On the other hand, we speculate that if MAP and PA were mixed, the effects of temperature over time on mechanical properties of the treated material would be less than the effects of these factors on material treated with PA alone but greater than those exerted on material treated with MAP alone. These intermediate effects would be generally based on the relative proportions of the chemicals in a mixture.

#### Effect of Treatment on Wood Chemical Components

Hemicelluloses are the major wood components affected by chemical type, exposure conditions, and exposure time. However, the side-chain constituents are more susceptible to chemical degradation than is the linear backbone chain. As previously indicated, arabinose showed the greatest decrease, depending on fire retardant chemical and exposure temperature. In softwoods, arabinose is a constituent of arabinoglucuronoxylan, whose complete structure consists of a linear xylan backbone with side chains of 4-O-methyl- $\alpha$ -D-glucuronic acid (2 glucuronic groups per 10 xylose groups) and  $\alpha$ -L-arabinofuranose (1.3 arabinose groups per 10 xylose groups) (Sjostrom 1981). Because of their furanosidic structure, the arabinose side-chains are easily hydrolyzed by acids and temperature. The  $\alpha$ -L-arabinofuranose is also believed to bond with lignin (Sjostrom 1981). It is noteworthy that the only sugar residue affected in the untreated control group at 180°F (82°C) was the arabinose residue and that WML was also considerably reduced. As the percentage of arabinose dropped, so did WML.

Following arabinose, galactose appeared to be the next sugar residue most sensitive to the effects of chemical type and exposure temperature. In softwoods, galactose is associated with the hemicellulose galactoglucomannan, which consists of a glucose-mannose backbone

with side chains of acetyl and galactose. Galactose is easily cleaved from the main chain by acids. Galactose is also believed to bond with lignin (Sjostrom 1981).

Mannose and xylose were affected similarly, but not to the same extent as arabinose and galactose. Mannose and xylose were primarily degraded by PA and MAP at 180°F (82°C), although they may have been degraded slightly by some of the other treatments, as indicated previously. Mannose and xylose are the linear backbone chains of the hemicellulose. Because these sugars are present in higher percentages than are arabinose and galactose, small decreases in these constituents could have a large impact on strength.

Of note is the fact that the side groups of two major hemicelluloses were most affected by treatment; these side groups are both suspected of bonding with lignin (Sjostrom 1981). We speculate that the cleavage of these side groups between the lignin and hemicelluloses releases the linkage by which one microfibril of a wood fiber shares the load with another microfibril. Disruption of such load-sharing would result in increased brittleness. This loss in load sharing in combination with disruption in the hemicellulose backbone chains would also cause a gradual reduction in strength (Winandy and Rowell 1984), and it would support the increased attenuation of a stress wave induced on the wood member (Ross and others 1989).

The effect of fire retardant chemicals on wood constituents can be related to the pH of the treatment solution. The PA treatment is strongly acidic, and it had the most deleterious effect on strength properties and chemical composition. The MAP treatment is also acidic, but much less so than PA; the relative acidity of MAP is 100 times lower than that of PA. The organic phosphate salts are also acidic, but they require higher temperatures to dissociate to the same extent as does MAP. The BBA and OPE treatments are basically neutral and do not tend to degrade wood chemical components. The decreasing pattern in the hemicellulose residues followed the same decline in MOR and WML with chemical treatment and exposure temperature. Therefore, there is a definite relationship between strength properties and hemicellulose content. This finding supports the wood strength-wood chemical model suggested by Winandy and Rowell (1984).

Except for BBA, all fire retardant chemicals tested include phosphate. The fire retardancy mechanism of BBA is not clearly understood, but Lyons (1970) indicated it may be a barrier mechanism instead of a chemical mechanism. This is probably the primary reason why BBA-treated specimens did not exhibit significant degradation in our study. However, as previously mentioned, we believe that the BBA

complexed with some carbohydrates, possibly resulting in crosslinking, which enhances strength and stiffness but greatly increases brittleness. The fire retardancy mechanism of BBA needs further research.

### Effect of Temperature on Strength

Besides the initial reduction on mechanical properties caused by treating and redrying, all treatments had in general little effect on MOE or MOR over time at 80°F (27°C) and 130°F (54°C). This was also true for WML, except for the MAP treatment at 130°F (54°C).

The lack of a reduction in MOE, MOR, or WML in the untreated controls at 80°F (27°C) and 130°F (54°C) suggests that no permanent thermal degradation in strength occurs in exposures at 130°F (54°C) for up to 6 months. Although the National Design Specification for Wood Construction (Section 2.2.2 and Appendix C, NFPA 1986) allows intermittent exposure to up to 150°F (66°C), our findings support the idea that thermal effects are immediate and recoverable in nature for exposures at 130°F (54°C) for up to 6 months.

At the higher temperature of 180°F (82°C), we noticed reductions in strength properties of all specimens over time, including the untreated controls. The MOR values and, to a greater extent, the WML values, were reduced in the controls after 160 days of exposure. Reduction in WML occurred almost immediately. Also, once the reduction of MOR and WML was initiated and stabilized, the rate of degradation was generally similar for all chemical treatments after 21 to 60 days of exposure at 180°F (82°C), as shown by the similar slopes of MOR curves in Figure 5b and WML curves in Figure 7b. This reveals that once the fire retardant chemical is changed into the acidic chemical form used to reduce flammability, the rate of wood degradation remains the same. Therefore, the fire retardant chemicals tested differ in a practical sense in the temperature-time combination needed for each chemical to dissociate into its acidic chemical form. For example, PA was in the acidic chemical form initially, and therefore, it began to degrade wood strength immediately at 180°F (82°C). Conversely, MAP required approximately 21 days at 180°F (82°C) to dissociate into the acidic chemical form and to initiate strength reduction. Most other chemicals required an even longer time at 180°F (82°C) before they dissociated into their acidic chemical form. Only the BBA treatment did not appear to follow this pattern, indicating another chemical mechanism was operative.

The WML values were reduced earlier than were comparable MOR values. The loss in WML was a direct consequence of the cleavage of bonds between

the constituents. We speculate that bond cleavage decreases the ability of the material to distribute strain energy between constituents. As a consequence, embrittlement occurs.

Embrittlement supports the idea that treatment effects on WML can be used as a tool to predict future trends in MOR. We believe that prudent considerations of treatment effects on WML or other energy-related mechanical properties, such as toughness and impact bending strength, can provide some assurance of future performance of the treated material. This is especially relevant when long-term performance data for traditional engineering design properties are incomplete. Although reduction in WML cannot be used to precisely predict the relative percentage of reduction in MOR, the decrease in WML can be used to indicate future trends in MOR. Hence, we believe that any material that shows a significant loss in WML over time will eventually exhibit lower MOR.

The effect of the 180°F (82°C) exposure and targeted MC of 6 percent compared to that of 130°F (54°C) and targeted MC of 12 percent clearly demonstrates the dominance of the role of elevated temperature. Using the 180°F (82°C) exposure, we were able to distinguish between the various chemicals and to induce degradation in the untreated controls. However, untreated plywood has long been used as roof sheathing, and, to our knowledge, it has not exhibited significant degradation in the field. The question that arises then is whether the static exposure of 180°F (82°C) is representative of the problem that exists in the field.

The surprising result was the lack of an effect at 130°F (54°C). Specimens treated with MAP (a chemical cited to cause degradation in the field) showed no significant loss in MOR after 160 days at 130°F (54°C). Based on the report by Heyer (1963), 130°F (54°C) exposures on roof sheathing at Athens, Georgia, were achieved for approximately 127 hours per year. Assuming a correlation exists between Heyer's real exposures and our static exposures, the 160-day exposure at 130°F (54°C) in our study could be translated to represent a real 130°F (54°C) exposure for approximately 30 years. Because MAP-treated material has been reported to fail in as few as 1 to 2 years, we expected MAP to show a greater effect at 130°F (54°C).

The discrepancy between our research results at 130°F (54°C) and the field problems raises the question whether another temperature variable is also a factor. Either the plywood roof sheathing is reaching temperatures greater than 130°F (54°C) for considerably longer times, or another exposure of the material to elevated temperature, such as redrying

temperature, was not accounted for in our study. We redried all the material at  $\leq 120^{\circ}\text{F}$  ( $49^{\circ}\text{C}$ ); the AWPAs C20 and C27 Standards (AWPA 1989) stipulate that redrying temperature should not exceed  $160^{\circ}\text{F}$  ( $71^{\circ}\text{C}$ ) until the MC is  $<25$  percent. Further research is necessary to determine the effects of redrying under the AWPAs standard, followed by subsequent exposure at elevated temperatures. Based on our results, we believe this difference in redrying temperature may contribute to the general lack of effect we observed at  $130^{\circ}\text{F}$  ( $54^{\circ}\text{C}$ ) for MAP and may also explain the problems reported in the field.

## Conclusions

The effect of fire retardant chemicals on the strength properties of wood depends on the type of chemical and the exposure temperature. Of the properties tested, work to maximum load was the most sensitive to the influence of chemical type, exposure conditions, and exposure time. The PA treatment had the most deleterious effect, followed by MAP. Wood treated with the other chemicals as well as the untreated controls did not experience such severe effects, although temperature-induced reductions in MOR of approximately 20 to 30 percent were observed after 160 days at  $180^{\circ}\text{F}$  ( $82^{\circ}\text{C}$ ). We suspect that mixtures of the test chemicals would have intermediate effects on wood exposed to elevated temperatures.

Once degradation was initiated and stabilized, the rate of strength loss caused by high-temperature exposure was similar for the various fire retardant chemicals. This indicates that similar chemical reactions are occurring in the wood. The chemicals differ in the temperature and time needed to begin the degradation process. Thus, the influence of treatment on strength properties is highly dependent on the thermal stability of the fire retardant formulation. No effect was observed at  $130^{\circ}\text{F}$  ( $54^{\circ}\text{C}$ ) other than the initial treatment effect. We expected more strength reductions for the MAP treatment based on known field failures (APA 1989a). Therefore, we also suspect that some other previous exposure to elevated temperature, such as redrying temperature, may be important.

Hemicellulose content was significantly reduced depending on the type of chemical, the exposure temperature, and the specific hemicellulose residue examined. Treatment and exposure conditions had the greatest effect on the percentage of arabinose, followed by galactose, then mannose, and finally xylose. Trends in the reduction of hemicellulose residues followed the same trends as the reduction of MOR and WML. The ranking of the effect of chemical treatments on strength properties followed the same ranking as that of the

effect of chemical treatment on wood constituents. We conclude that the degradation of hemicelluloses plays an important role in the reduction of strength properties, especially the increased brittleness of the treated material.

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## References

- APA.** 1989a. Fire-retardant-treated plywood roof sheathing: Field failures. American Plywood Association, Tacoma, WA.
- APA.** 1989b. Fire-retardant-treated plywood roof sheathing: General information. American Plywood Association, Tacoma, WA.
- AWPA.** 1989. C20: Fire-retardant treated lumber; C27: Fire-retardant treated plywood. Annual Book of Standards. American Wood-Preservers' Association, Stevensville, MD.
- Bendtsen, B.A.** 1966. Sorption and swelling characteristics of salt-treated wood. Res. Pap. FPL-60. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Bendtsen, B.A.; Gjovik, L.R.; Verrill, S.** 1983. Mechanical properties of salt-treated longleaf pine. Res. Pap. FPL-434. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Effland, Marilyn J.** 1977. Modified procedure to determine acid-insoluble lignin in wood and pulp. Tappi. 60(10): 143-144.
- Gerhards, C.C.** 1970. Effect of fire-retardant treatment on bending strength of wood. Res. Pap. FPL-145. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Heyer, O.C.** 1963. Study of temperature in wood parts of houses throughout the United States. Res.

Note. FPL-012. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

**Jessome, A.P.** 1962. Strength properties of wood treated with fire retardants. Report No. 193. Canadian Dept. of Forestry, Ottawa, Canada.

**Johnson, J.W.** 1967. Bending strength for small joists of Douglas Fir treated with fire retardants. Report T-23. Forest Research Laboratory, Oregon State University, Corvallis, OR.

**King, Edward G., Jr.; Matteson, DeForest A., Jr.** 1961. Effect of fire-retardant treatment on the mechanical properties of Douglas-fir plywood. Douglas-fir Plywood Association Lab Report 90, May 12.

**LeVan, S.L.** 1984. Chemistry of fire retardancy. In: Rowell, R., ed. The chemistry of solid wood. Advances in chemistry series 207. American Chemistry Society, Washington, DC. Chapter 14.

**LeVan, S.L.; Collet, M.P.** 1989. Choosing and applying fire-retardant-treated plywood and lumber for roof designs. Gen. Tech. Rep. GTR-62. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

**LeVan, S.L.; Winandy, J.E.** 1990. Effects of fire retardant treatments on wood strength: A review. Wood and Fiber Science. 22(1): 113-131.

**Lyons, John W.** 1970. The chemistry and uses of fire retardants. Wiley-Interscience, John Wiley and Sons, Inc., New York. 462 p.

**NFPA.** 1986. National design specification for wood construction. National Forest Products Association, Washington, DC.

**Pearl, Irwin A.; Busche, Louis, R.** 1960. Studies on the chemistry of aspenwood. XI. The Klason lignin determination as applied to aspenwood with special reference to acid-soluble lignin. Tappi. 43(12): 961-970.

**Pettersen, Roger C.; Schwandt, Virgil H.** [In preparation.] Improved method for wood sugar analysis. (Submitted to the Journal of Chromatographic Science.)

**Ross, R.J.; LeVan, S.L.; Winandy, J.E.** 1990. Non-destructive evaluation of fire-retardant treatment effects at elevated temperatures. Proceedings 7th international symposium on nondestructive testing of wood; Washington State University, Pullman, WA. 1989 September 27-29; Madison, WI.

**Sjostrom, E.** 1981. Wood chemistry: fundamentals and applications. Academic Press, New York. 223 p.

**Skaar, Christen.** 1972. Water in wood. Syracuse University Press, Syracuse, NY.

**TAPPI.** 1982. TAPPI standards useful method 250, acid-soluble lignin in wood and Pulp. Technical Association of the Pulp and Paper Industry, Atlanta, GA.

**USDA.** 1987. Wood handbook: Wood as an engineering material. Agric. Handb. 72. Washington, DC: U.S. Department of Agriculture. 466 p.

**Winandy, J.E.** 1988. Effects of treatment and redrying on the mechanical properties of wood. In: Wood protection techniques and the use of treated wood in construction. Hamel, M., ed. Madison, WI: Forest Products Research Society: 54-62.

**Winandy, J.E.; Rowell, R.M.** 1984. The chemistry of strength. Chapter 5: in the Chemistry of Solid Wood. R. Rowell, ed. Amer. Chem. Soc, Advances in Chemistry Series No. 207. Washington, DC: 211-255.

**Winandy, J.E.; Boone, R.S.; Bendtsen, B.A.** 1985. Interaction of CCA preservative treatment and redrying: Effects on mechanical properties of southern pine. Forest Products Journal. 35(10): 62-68.

**Winandy, J.E.; LeVan, S.L.; Schaffer, E.L.; Lee, P.W.** 1988. Effect of fire-retardant treatment and redrying on the mechanical properties of Douglas-fir and aspen plywood. Res. Pap. FPL-485. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.