

EFFECTS OF FIRE RETARDANT TREATMENTS ON WOOD STRENGTH: A REVIEW

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ABSTRACT

As evidenced by recent structural problems with fire-retardant-treated plywood, fire retardant chemicals and high temperature environments can degrade the strength properties of wood. We do not know to what extent fire retardant chemicals, thermal environment, and moisture content contribute to wood degradation. We suspect that the combination of acidic fire retardant chemicals and elevated temperatures increases the rate of acid hydrolysis in the wood, thereby causing a loss in strength. This paper presents a review of the pertinent literature on the factors influencing strength reduction in treated wood. These factors are the thermal degradation process of wood, the mechanism by which fire retardant chemicals alter wood degradation, the effect of acids on wood strength, the influence of temperature on strength, and the combined effect of fire retardant chemicals and temperature on strength. We also discuss possible long-term effects of in-service conditions on the strength of treated wood; the effects of treatment on the strength of weaker structural members and on species, size, and grade of lumber; and the application of the relationship between treatment and strength to plywood and lumber.

Keywords: Acid hydrolysis, fire retardants, plywood, strength, thermal degradation

INTRODUCTION

When heated, wood burns by producing flammable volatiles that may ignite. To reduce flammability, wood is treated with fire retardants (FR). Such treatment drastically reduces the rate at which flames travel across the wood surface and reduces the amount of potential heat. However, some FR treatments may produce unwanted secondary side effects, such as increased moisture content, reduced strength, and increased potential to corrode metal connectors. The magnitude of the side effects depends on the particular fire retardant chemicals used, and the relative importance of these side effects depends on the intended application of the product.

Engineered roof systems are a major use of FR-treated plywood for multiple-family dwellings and for light to medium commercial construction. Treated wood is also commonly used for scaffold planking and for reducing flame spread in

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interior finishing material. The use of FR treatments in these situations is required by building codes or insurance companies for safety.

Recently, some FR-treated plywood used for roof decking has exhibited reduced strength. In these cases, the wood has become very brash and brittle, crumbles easily, and has darkened. The length of service time for the roof plywood has varied from 3 to 8 years. The mechanism of degradation in cases such as these is unknown. However, the combination of elevated temperature conditions that exist on roof systems and the acidic nature of the FR may have accelerated the rate of acid hydrolysis of the wood. Thus, the loss of strength and embrittlement of FR-treated wood could be explained by the long-term effect of acids and elevated temperatures on the composition of the wood products. The supporting evidence for this hypothesis can be found in the literature on:

- (1) chemistry of the thermal degradation process of wood,
- (2) mechanisms by which FR treatments alter the thermal degradation process,
- (3) effect of acid treatments on wood strength,
- (4) effects of temperature on wood strength, and
- (5) effect of interaction of FR chemicals and temperature on wood strength.

These five pertinent phenomena are each involved in the degradation process. Moreover, the combined effect of these phenomena may be greater than the sum of the individual effects. The purpose of this paper is to examine the factors that might influence the degradation of FR-treated wood and to expand understanding of these factors to improve design and performance of products made from treated wood.

LITERATURE BACKGROUND

Chemistry of thermal degradation

When wood is heated, chemical bonds begin to break down at about 175 C, and the reactions accelerate as the temperature increases. When heated at 100 C to 200 C in the absence of air, noncombustible products such as carbon dioxide, traces of formic and acetic acids, and water vapor are produced. Above 200 C, the carbohydrates break down and produce tars and flammable volatiles, which diffuse into the surrounding environment (Browne 1958; Shafizadeh 1984). Above 450 C, the production of flammable products is complete. The residue that remains is char (Browne 1958; Shafizadeh 1968, 1971, 1975; Shafizadeh and Chin 1977; Stamm 1955).

Cellulose decomposes in the temperature range from 260 C to 350 C (Shafizadeh 1984), and it is primarily responsible for the production of flammable volatiles. The thermal degradation of cellulose can be accelerated in the presence of water, acids, and oxygen. As the temperature increases, the degree of polymerization of cellulose decreases further, free radicals appear, and carbonyl, carboxyl, and hydroperoxide groups are formed (Broido et al. 1973; Hirata 1979; Shafizadeh 1984). The primary reaction is depolymerization caused by the cleavage of the glycosidic linkage. (The glycosidic linkages are hydrolyzable at room temperatures in the presence of strong acids.)

The hemicelluloses degrade in the approximate range of 200 C to 260 C. Hemicelluloses are less thermally stable than cellulose, and they evolve more noncom-

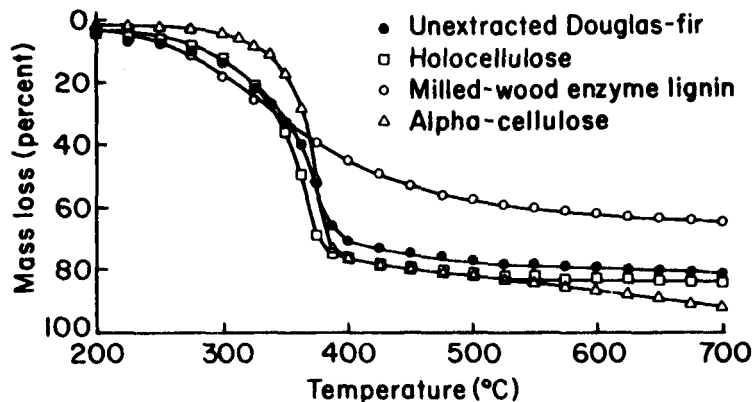


FIG. 1. Thermogravimetric plot of percentage of residual char weight for Douglas-fir and isolated Douglas-fir hemicellulose, lignin, and alpha-cellulose components heated in nitrogen at a rate of 5 C/min. (ML88 5376)

bustible gases and less tar. Much of the acetic acid liberated from wood pyrolysis is attributed to the deacetylation of hemicellulose. Hardwood hemicelluloses are rich in xylan and contain a small amount of glucomannan. Softwood hemicelluloses contain a small amount of xylan and are rich in galactoglucomannan. Xylan is the least thermally stable hemicellulose (Beall 1971) since pentosans are susceptible to dehydration reactions.

Dehydration reactions occurring above 200 C are the primary process of lignin thermal degradation. Between 150 C and 300 C, cleavage of α - and β -aryl-alkyl-ether linkages occurs. Around 300 C, aliphatic side chains start splitting off from the aromatic ring. Finally, the carbon-to-carbon linkage between lignin structural units is cleaved at a temperature range of 370 C to 400 C (McDermott et al. 1986; Obst 1983).

The degradation of wood can be viewed as the sum of the degradation of its components (Fig. 1). The degradation of holocellulose, which consists of the alpha-cellulose plus the hemicelluloses, most closely follows that of wood. Lignin generally pyrolyzes at a slower rate than cellulose and holocellulose (Fig. 1), although the degradation period begins somewhat earlier than that of holocelluloses. The lignin is mostly responsible for increased residual char (Beall and Eickner 1970; Hirata 1979; Shafizadeh 1984; Tang 1967a, b). Wood and alpha-cellulose appear to degrade at similar rates, although the wood begins to degrade at slightly lower temperatures than alpha-cellulose but at higher temperatures than holocellulose. This lower degradation temperature of wood is primarily due to the hemicellulose in the wood and in the holocellulose. The degradation of wood more closely resembles the degradation pattern of alpha-cellulose and holocellulose than that of lignin. This is reasonable because cellulose and holocellulose account for approximately 50 and 75% of the wood, respectively.

Mechanisms by which fire retardants alter thermal degradation

Many different proprietary FR chemical systems exist for imparting fire retardancy to wood. The most common FR chemicals used for wood are the inorganic

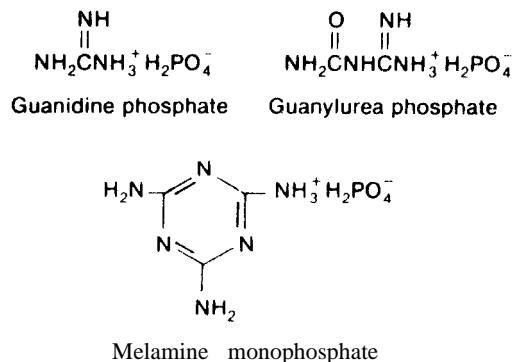


FIG. 2. Chemical structure of three organic P-N compounds that are used as fire retardants. (ML89 5524)

salts, such as diammonium phosphate, monoammonium phosphate, zinc chloride, ammonium sulfate, borax, and boric acid. Some FR systems for wood are based on formation of a phosphate salt of an organic compound (Oberley 1983) and are referred to as organic salts. However, all FR systems for wood rely on the elements of phosphorus, nitrogen, or boron; phosphorus is usually the central element.

All FRs that contain phosphorus are in odd oxidation states (Lyons 1970). The most common phosphorus FR is phosphoric acid and its salts, including diammonium and monoammonium phosphate. These phosphates are among the oldest known FR systems and they are usually included in most proprietary systems used for wood. The newer FR systems, which form a phosphate salt of an organic compound, involve P-N compounds such as in urea-phosphoric acid organic salts. Similar P-N organic salt compounds include guanidine phosphate, guanylurea phosphate, and melamine monophosphate (Fig. 2). Other P-N compounds, such as polyphosphoramides, phosphorylamides, and phosphonitrilic compounds, are not used commercially for wood products. Research on phosphonium salts and organophosphorus compounds has been conducted to evaluate the potential of these compounds as fire retardants for wood (Ellis et al. 1987; LeVan and Holmes 1986), but the compounds currently are not used commercially for wood.

The inorganic salts are fairly inexpensive to use for fire retardancy and are easy to apply. The volatility of the inorganic salts in water is dependent on the particular compound; zinc chloride is the most soluble (2 g/ml) and boric acid, the least (0.056 g/ml) (Merck Index 1968). Because of their volatility and molecular size, the inorganic salts are susceptible to moisture movement and migrate with the movement of water in wood. This paper mainly addresses inorganic salts because most of the available literature is on the performance of such compounds.

Several theories have been proposed for the mechanism of FR chemicals; these theories have been reviewed by Browne (1958) and LeVan (1984). The most widely accepted mechanism is referred to as the chemical theory. This theory suggests that the retardant chemicals directly alter the pyrolysis of wood, increasing the amount of char and reducing the amount of volatile, combustible vapors. The pyrolysis reactions are altered such that thermal decomposition occurs at lower temperatures for FR-treated wood than for untreated wood. Browne and Tang

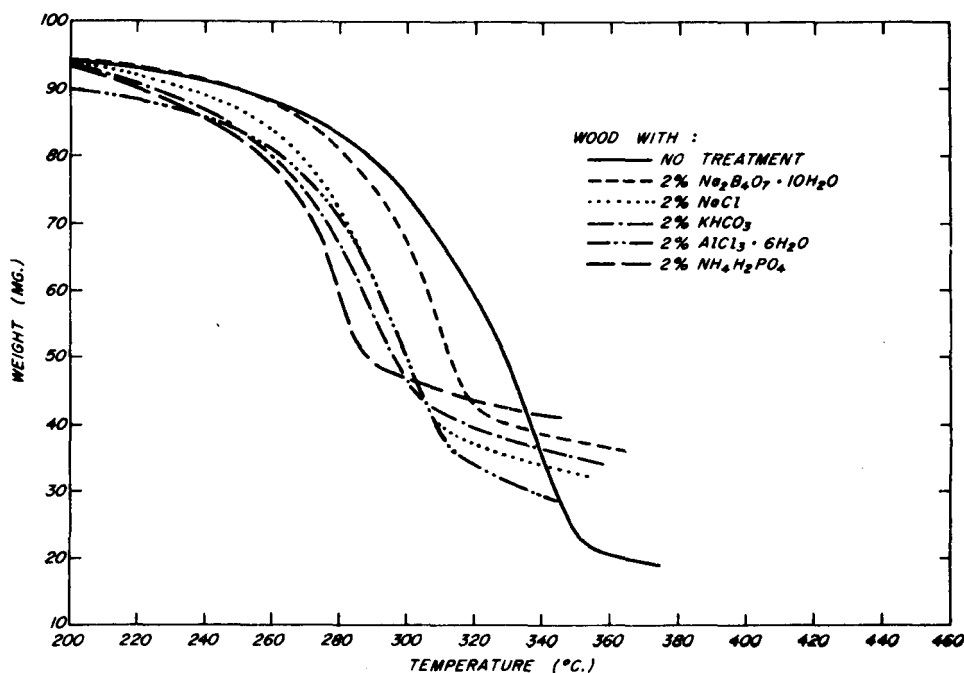


FIG. 3. Effect of fire retardant treatment on residual char weight of cellulose. (M 131815)

(1963) tested sodium borax, sodium chloride, potassium carbonate, aluminum chloride, and monoammonium phosphate. All compounds increased the residual char weight of the material (Fig. 3). Furthermore, Browne and Tang found that the more effective the inorganic salt as a flame retardant, the lower the temperature of active pyrolysis and the greater the amount of char as indicated by monoammonium phosphate. In other experiments, Brenden (1967) found that increased amounts of char correlated with reduced amounts of tar.

Acidic compounds have the greatest effect on reducing the amount of flammable volatiles and increasing the amount of char (Shafizadeh 1984). In tests with 21 different compounds, phosphoric acid was the most effective in reducing the amount of volatiles and increasing the amount of residual char, followed by mono- and diammonium phosphate and zinc chloride. (Diammonium phosphate loses ammonia (NH_3) at elevated temperatures to yield monoammonium phosphate.) Acids can catalyze the dehydration of a glucose unit by addition of a proton to the oxygen atom of a hydroxyl group, resulting in formation of the unstable carbonium ion. The carbonium ion rearranges and regenerates the proton, thereby propagating the process (Browne 1958). The glycosidic linkages can also undergo attack from a proton, resulting in depolymerization of polysaccharide chains. The proton forms a conjugate acid with the glycosidic oxygen. The C-O bond is cleaved to form an intermediate cyclic carbonium cation, which initiates addition of a water molecule, resulting in a stable end product and release of the proton (Fengel and Wegener 1984). In degree of polymerization (DP) studies of borax and monoammonium phosphate treatments (Fung et al. 1972), cellulose treated with the acid charred and depolymerized very rapidly. The cellulose DP value decreased

from 1,110 to 650 after only 2 minutes of heating at 150 C. Cellulose treated with borax showed a DP reduction from 1,300 to 700 after 1 hour of heat treatment at 150 C. Both these compounds reduced the quantity of flammable volatiles produced but had different effects on the chain depolymerization reaction. Acidic flame retardants may not only catalyze dehydration and depolymerization of the cellulose to more char and fewer volatiles, but they may also enhance the condensation of the char to form cross-linked and thermally stable polycyclic aromatic structures (Shafizadeh and Sekiguchi 1983).

Effect of acid treatment on strength

In general, wood has demonstrated resistance to acids and alkali in low concentrations. However, wood is severely attacked by strong acidic and caustic solutions (Kass et al. 1970; Stamm 1955; Thompson 1969). As previously mentioned, the primary mechanism of FR chemicals is an acid-catalyzed reaction to reduce flammable volatiles and increase residual char. Thus, the following discussion deals only with the effect of acids. A review of the effect of alkali treatments on strength can be found in Fengel and Wegener (1984). Although different woods behave differently, softwoods are generally more chemically resistant to acids than hardwoods because soft woods have a low pentosan concentration (Wangaard 1966; Kass et al. 1970; Kauman 1962). Conversely, since the primary hemicellulose of hardwoods is a pentosan (xylan), the hardwoods are more susceptible to acid attack. Kass et al. (1970) quantified the relationship between pentosan content and modulus of rupture (MOR). Wangaard (1966) found that both low and high original pentosan content correlated well with resistance to acid degradation as measured by strength retention.

Bublitz and Hull (1983) studied the long-term performance of wood exposed to hydrochloric acid solutions by immersing Douglas-fir specimens in water and acid solutions at different temperatures for different times and then subjecting the specimens to bending and chemical tests. Tanks with Douglas-fir specimens were filled with acid solutions of 2 or 10% strength and maintained at different temperatures for 1 year. This resulted in significant changes in bending strength and chemical composition. High temperatures and high acid concentrations caused the greatest loss of strength.

Wood that is treated with acid is subjected to the catalytic action of the cation as previously discussed. For strong acids, the effect of this cation on the carbohydrates is hydrolysis of the glycosidic linkages within the polysaccharide chains. The effect on the lignin is initiation of condensation reactions. The degree to which wood is affected can be determined by the hemicellulose and pentosan retention values after treatment (Kass et al. 1970). The degradation of the wood with respect to strength is critical when the degree of polymerization of the polysaccharides is lowered.

The kinetic data and overall course of acid hydrolysis degradation are influenced both by the acidic (hydrolyzing) medium and the anatomical and chemical characteristics of the wood species. The hydrolyzing medium is characterized by the kind of acid and acid concentrate ion. Raising the temperature accelerates the rate of hydrolysis. Hydrolysis of glycosidic bonds usually follows a first-order reaction (Springer 1966).

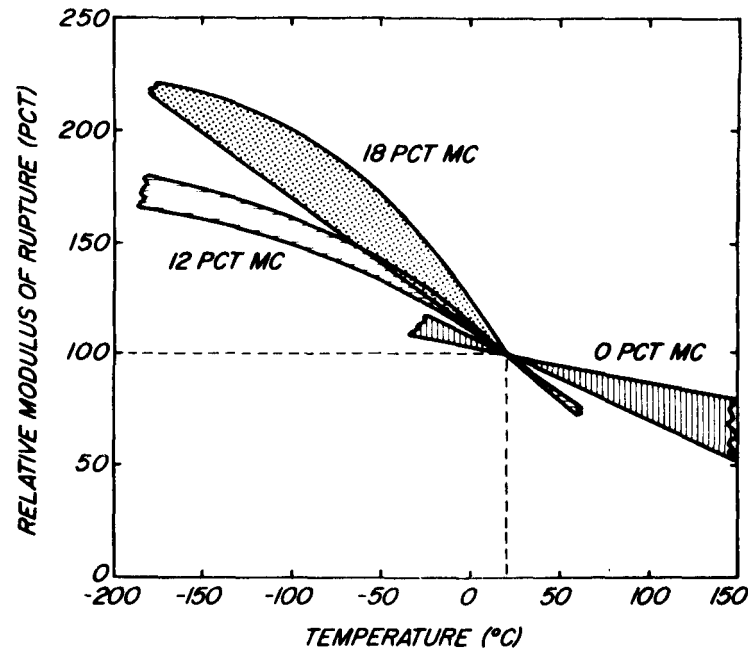


FIG. 4. Immediate effects of heating on modulus of rupture relative to moisture content level at 20 C. Plot is a composite of several studies (USDA 1987). Variability in trends is illustrated by width of bands. (ML84 5720)

Effect of temperature on strength

The strength and stiffness of wood decreases when the wood is heated and increases when the wood is cooled. This effect on mechanical properties is immediate and approximately linear at constant moisture content between temperatures of -50 C and 150 C. At temperatures below 100 C, the immediate effect is essentially reversible. The immediate effects of temperature on the mechanical properties of wood have recently been reviewed (Gerhards 1982). However, the immediate effects of temperature are significantly influenced by the moisture content of the wood (Fig. 4). For example, if a green piece of lumber at 20 C is heated to 90 C, the immediate effect of temperature is a reduction in strength. However, the piece also tends to dry, which tends to increase its strength. For most practical purposes, while the piece is initially losing moisture, the positive moisture effect tends to overwhelm the negative temperature effect and control the magnitude of the combined effect on strength.

If wood is exposed to elevated temperatures for an extended time, strength is permanently reduced (Fig. 5). Similarly, extended exposure to a low temperature (65.5 C) can induce permanent reductions in the mechanical properties of wood (data not shown). The magnitude of permanent strength reduction depends upon moisture content, heating medium, temperature, exposure period, species, and specimen size.

The effects of standard drying practices upon the mechanical properties of wood are well documented (Koch 1985; Rasmussen 1961; Rietz and Page 1971; USDA

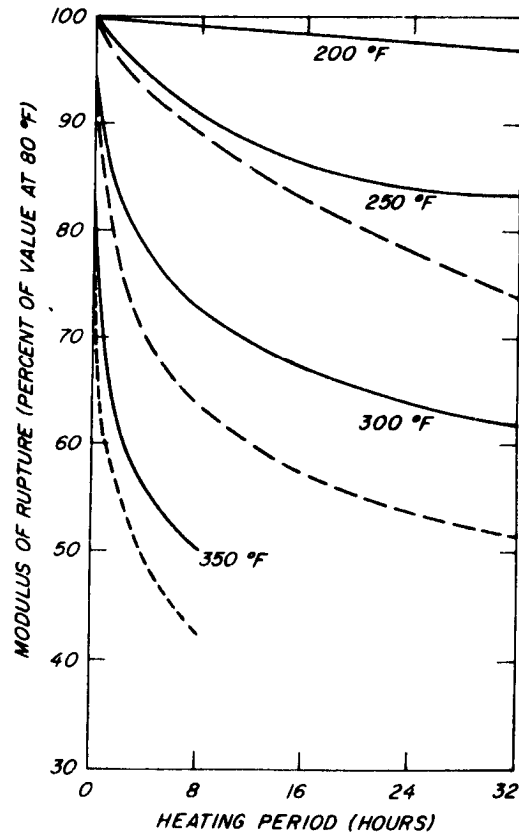


FIG. 5. Permanent effect of heating wood in water (solid lines) and steam (dashed lines). All data based on tests of Douglas-fir and Sitka spruce at room temperature (USDA 1987). (M140 731)

1987). The initial kiln-drying process has a negligible effect on strength at temperatures of 71 C or below. At higher temperatures, however, the initial kiln-drying processes, especially at or above the boiling point of water, can have a considerable effect, depending on the species, size, and process parameters involved.

Kiln-drying is the most common method for seasoning softwood dimension lumber. The significant reduction in mechanical properties attributed to this method of seasoning is generally observed when the drying temperature exceeds the boiling point of water, commonly known as high-temperature drying (HTD). The strength reductions associated with HTD presumably arise from the hydrolysis of the polysaccharides caused by deacetylation of the wood (Hillis 1975). This results in depolymerization, which has been correlated with strength loss (Ifju 1964). Elevated temperature and moisture content have been shown to accelerate the production of acid within the wood (Hillis 1975), increasing the rate of strength loss (Thompson 1969).

Some high-temperature drying procedures have only a minimal effect on the mechanical properties of southern pine; the difference from controls for MOR ranges from + 5 to - 10%, and for modulus of elasticity (MOE), from + 2 to - 3%

(Koch 1971, 1985; Yao and Taylor 1979). However, HTD has a more severe effect on MOR (ranging between – 9 and – 21%) and little differential effect on MOE (ranging between + 3 and – 4%) for other softwoods, notably Douglas-fir, hem-fir, and spruce-pine-fir (Cech and Huffman 1974; Comstock 1976; Gerhards 1979; Kozlik 1968; Salamon 1963, 1969).

The limited data available on the effect of selected HTD procedures on the strength of hardwoods indicate minimal strength reductions (MOR, + 1 to – 10%), with again little differential effect on MOE (+ 4 to – 4%) (Gerhards 1983; Ladell 1956; MacKay 1976). However, because hardwoods have a greater amount of thermally sensitive pentosans compared to softwoods, we would expect hardwoods to be affected by drying temperatures to a similar or greater extent than Douglas-fir, hem-fir, and spruce-pine-fir, which are thermally sensitive softwood species.

Combined effect of treatment and temperature on strength

Most FR treatments significantly reduce the strength and stiffness of the treated wood product. The results of several important studies on the effects of FR chemicals on mechanical properties are summarized in Table 1. In general, the effects of FR treatments and redrying on static mechanical properties of wood can be categorized by the type of FR chemical used and the maximum dry-bulb temperature in the kiln (Winandy et al. 1988). For example, the effects of treatment and redrying are negligible if the wood is air dried after treatment (Johnson 1967). However, if FR-treated wood is kiln dried after treatment (KDAT), its mechanical properties (MOR, MOE, and work to maximum load) are consistently lower than that of untreated wood (Gerhards 1970). Gerhards (1970) concluded that FR treatment and kiln-drying reduce the MOR and MOE of clear wood by an average of 13 and 5%, respectively; for structural lumber, MOR and MOE are reduced by about 14 and 1%, respectively. Consequently, the National Design Specification for Wood Construction (NFPA 1986) requires a 10 to 20% reduction in allowable design stress, depending on the mechanical property under consideration. Recent work supports similar reductions for FR-treated plywood (Winandy et al. 1988).

However, the literature on FR treatment effects is not cohesive. It represents a combination of unrelated studies, none of which is comprehensive. The following questions thus remain unanswered:

1. What are the long-term effects of in-service conditions, such as elevated temperature and moisture content, on the strength of FR-treated wood?
2. What are the effects of FR treatment on the strength of weaker members in the strength distribution?
3. How do FR chemicals affect multiple species-size-grade combinations?
4. Does the relationship between FR treatment and strength apply to both lumber and plywood? Can data from lumber studies be applied to plywood studies and vice versa?

We will speculate on how these four aspects of FR treatment affect the strength of wood using data from the literature on FR treatment and data from research on chromated copper arsenate (CCA), an acidic waterborne preservative. In recent work at the Forest Products Laboratory (Winandy 1989; Winandy and Boone 1988; Winandy et al. 1985, 1989), the effect of CCA on bending strength

TABLE 1. Published information on the effects of fire-retardant treatments on mechanical properties of wood.

Author/manufacturer ^a	Year	Chemical ^b	Species	Redry temperature (C)	Change in mechanical property (%) ^d							
					MOR	MOE	Energy	C-par	T-par			
Adams et al.	1979	Noncom X ^c FRT	SCP	105	+26	—	—	—	—			
				60	-20	—	-30	—	—			
				92	-48	—	-65	—	—			
Countryman	1957	MIN	DF-Ply	—	-8	-5	-57	—	—			
Gerhards	1970	AP APAS	SP	60	-19	-19	-21	—	—			
				Kiln ^e	-17	-3	-44	—	—			
				—	-16	-3	-45	—	—			
		FRT	CMB SP	—	-13	-5	-34	—	—			
				Kiln	-11	-8	-26	—	—			
				—	-17	-13	-33	—	—			
		Noncom X	DF DF SP SP-GL	Kiln	Kiln	-10	-8	-40	—	—		
					Kiln	-16	-5	-32	—	—		
					Kiln	-14	-8	-24	—	—		
					Kiln	-12	-2	—	—	—		
					PYR	SP	Kiln	-10	-8	-28	—	—
						DF DF	Air	-17 -29	-5 -12	-32 -37	—	—
Graham	1964	Borax AS CZC MIN PYR FRT FRT	DF	Air	+20	+19	—	—	—			
				—	-3	+4	—	—	—			
				—	+2	+9	—	—	—			
				—	+6	+9	—	—	—			
				—	-2	+4	—	—	—			
				—	-4	-1	—	—	—			
				—	-5	-1	—	—	—			
Jessome	1962	APAS	RP DF DF-Ply	65.5	-29	-5	-62	—	—			
				Kiln	-23	-5	-55	—	—			
				Kiln	-3	-1	-24	—	—			
				—	-13	-1	-29	—	—			
				Kiln	-15	-9	-6	—	—			
—	—	—	—	-16	-9	-2	—	—				

TABLE 1. *Continued.*

Author/manufacturer ^a	Year	Chemical ^b	Species	Redry temperature (C)	Change in mechanical property (%) ^c					
					MOR	MOE	Energy	C-par	T-par	
Johnson	1967	ZAB	RP	65.5	-10	+2	-42	-	-	
			DF	Kiln	-2	+2	-12	-	-	
			DF-Ply	Kiln	-13	-10	-8	-	-	
		FRT	DF	Air	-11	-5	-55	-	-	
				Air	-5	0	-	-	-	
				60	-15	-3	-	-	-	
Lyon et al.	1988	Flameproof ^c	DF	71	-8	-5	-18	+2	-23	
			SP		-19	-3	-28	-1	-14	
			SPR		-5	-5	-28	0	-20	
			DF-Ply		-14	-1	-	-	-	
King & Matteson	1961	FRT	DF-Ply	-	-6	-6	-2	-	-	
					-24	-11	-31	-	-	
Hoover	1984	Pro-Tex ^c	CMB	71.1	-10	-1	-21	-5	-9	
Koppers Co.	1985	Dricon ^c	SP	71.1	-10	0	-26	-2	-7	
			DF		-9	0	-11	-5	-12	
			SPR		0	0	-10	0	0	
			SP-Ply		-2	-3	0	0	-	
			DF-Ply		0	-5	0	0	-	
Osrose Inc.	1984	Flameproof	CMB	71.1	-10	0	-	-	-25	
Winandy et al.	1988	Borax	ASP-Ply	60	0		-40	-	-	
			MIN		-1		-20	-	-	
			PYR		-12		-27	-	-	
			FRT		-20		-39	-	-	
		CZC				-37		-56	-	-
			Borax	ASP-Ply	110	-33		-73	-	-
			MIN			-32		-56	-	-
			PYR			-37		-70	-	-
			FRT			-36		-68	-	-
			CZC			-59		-83	-	-

TABLE 1. *Continued.*

Author/manufacturer ^a	Year	Chemical ^b	Species ^c	Redry temperature (C)	Change in mechanical property (%) ^d				
					MOR	MOE	Energy	C-par	T-par
	1988	Borax	DF-Ply	60	-23		-34	--	--
		MIN			-27		-25	--	--
		PYR			-14		-30	--	--
		FRT			-24		-36	--	--
		CZC			-21		-41	--	--
		Borax	DF-Ply	110	-34		-68	--	--
		MIN			-25		-50	--	--
		PYR			-30		-57	--	--
		FRT			-36		-64	--	--
		CZC			-41		-64	--	--

^a The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

^b AP, ammonium phosphate; AS, ammonium sulfate; APAS, AP + AS; Borax, boric acid + sodium tetraborate; CZC, chromated zinc chloride; FRT, unidentified; MIN, minalith; PYR, pyresote; ZAB, zinc ammonium borate.

^c ASP, aspen; CMB, combined species; DF, Douglas-fir; GL, Glulam; Ply, plywood; RP, red pine; SP, southern pine; SCP, scots pine; SPR, spruce.

^d Percentage of change from untreated controls. Energy, properties related to energy, such as work and toughness. C-par, compression parallel to grain. T-par, tension parallel to grain.

^e Proprietary commercial formulation.

^f Kiln schedule not specified. Assumed to be dry-kiln AWPA schedule.

was studied at retentions of up to 40 kg/m³. The CCA results are germane because fire retardants are typically used at retention levels between 32 and 80 kg/m³.

Effects of in-service conditions on strength of treated wood

Although some data exist on FR treatment effects on static strength of wood at room temperature and at elevated redrying temperatures, no data exist on the strength of FR-treated materials continuously or periodically exposed to elevated in-service temperatures. We speculate that the effects of in-service temperature and moisture conditions on the strength of FR-treated wood increase as the temperature and moisture content levels increase. Our speculation is based on data on the effects of temperature and moisture content from the CCA study. As CCA retention levels approach the level required for marine exposures (40 kg/m³), the effect of redrying temperature on strength becomes more detrimental than at lower retention levels. Figures 6 and 7 show the reduction for MOR and work to maximum load, respectively, for clear southern pine exposed to increasing CCA retentions and redrying temperatures (Winandy 1988; Winandy et al. 1985). At its highest level, the retention of acidic CCA approximates that of the usual FR treatment. Therefore, we speculate that in-service temperature conditions will have a somewhat greater effect on FR-treated wood than on the CCA-treated wood illustrated here. We say this because the retention levels of FR chemicals are greater than those of CCA and because processing temperature effects may not be as ongoing as in-service temperature effects.

Effect of FR treatment on strength of weaker members

We speculate that FR treatments will probably cause strength reduction over the entire property distribution as the temperature increases. This hypothesis is based on similar trends that exist for CCA. For example, kiln drying after CCA treatment can play a major role in reducing strength. For CCA-treated lumber, post-treatment air-drying or kiln-drying at temperatures of 88 C or below caused no apparent reduction in strength properties below the 20th to 40th percentile of the bending strength distribution. This is significant since the design strength properties for structural lumber are based upon the lower 5th percentile of strength distribution. However, strength values above this percentile range were reduced by approximately 5 to 10% (Barnes and Mitchell 1984; Bendtsen et al. 1983). Conversely, post-treatment kiln-drying above the 88 C range was shown to result in significant strength reductions throughout the strength distribution, depending on species, size, and grade (Barnes and Mitchell 1984; Winandy in press; Winandy and Boone 1988).

Effect of FR treatment on species, grade, and size

We speculate that no differential FR treatment effects occur between various species, grades, and sizes.

Species. – Lyon et al. (1988) recently reported no difference between the effects of a proprietary FR treatment on the clear-wood properties of southern pine, Douglas-fir, and white spruce. Similarly, Winandy et al. (1988) reported no difference between the magnitude of the effect of various inorganic FR treatments for Douglas-fir and aspen plywood. In the CCA literature, further evidence exists

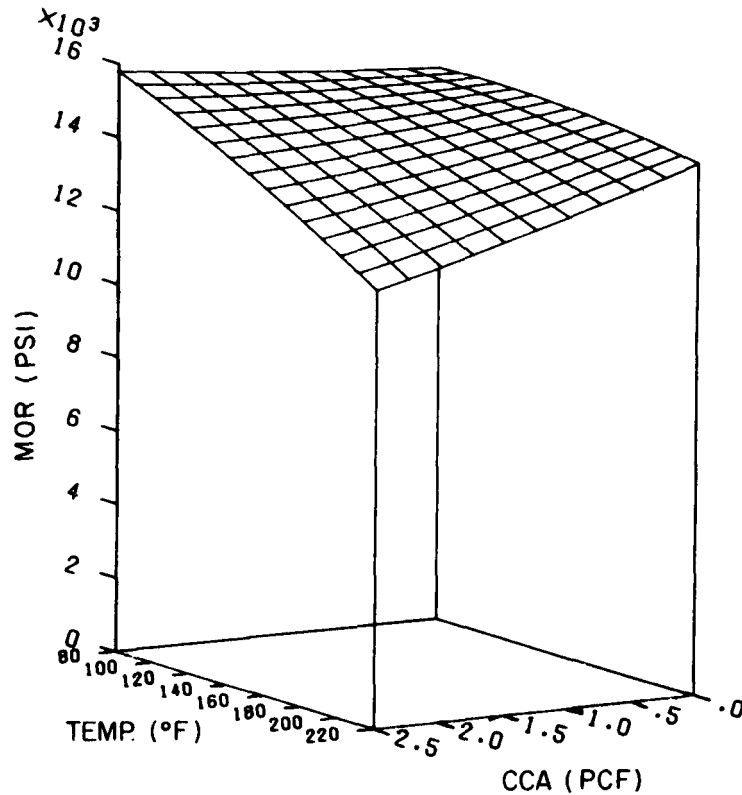


FIG. 6. Predicted response of modulus of rupture (MOR) of southern pine at an assumed moisture content of 15% and specific gravity of 0.59 to CCA treatment and redrying using an empirical model developed by Winandy et al. (1985). (ML84 5767)

for the lack of a differential species effect. Few differences are apparent in the magnitude of reported CCA effects for Douglas-fir (Winandy et al. 1989), southern pine (Winandy et al. 1985), and South African pine (Knuffel 1985).

Grade. – For differences related to grade, we speculate that FR treatments do not exhibit a differential grade effect. For example, Johnson (1967) found no apparent difference in the magnitude of the effect of FR treatment on four grades of Douglas-fir 2 by 6 lumber (average reductions ranged from 9 to 20%). Yet, although the CCA literature documents an effect for grade (Winandy in press; Winandy and Boone 1988), this difference may be more attributable to the five- to ten-fold difference in chemical loading levels that exists between the CCA retentions reported in those studies and common FR retentions. We believe that the differential grade effect of CCA would resolve itself into a consistent negative effect at chemical retentions comparable to those used for FR treatment.

Size. – For differences related to size, little technical guidance is found in the literature on FR-treated wood. We again turned to the CCA data; few differences were found between the effects of CCA on 2 by 4 or 2 by 6 lumber (Winandy 1989; Winandy and Boone 1988). Thus, we anticipate little differential size effect from FR treatments.

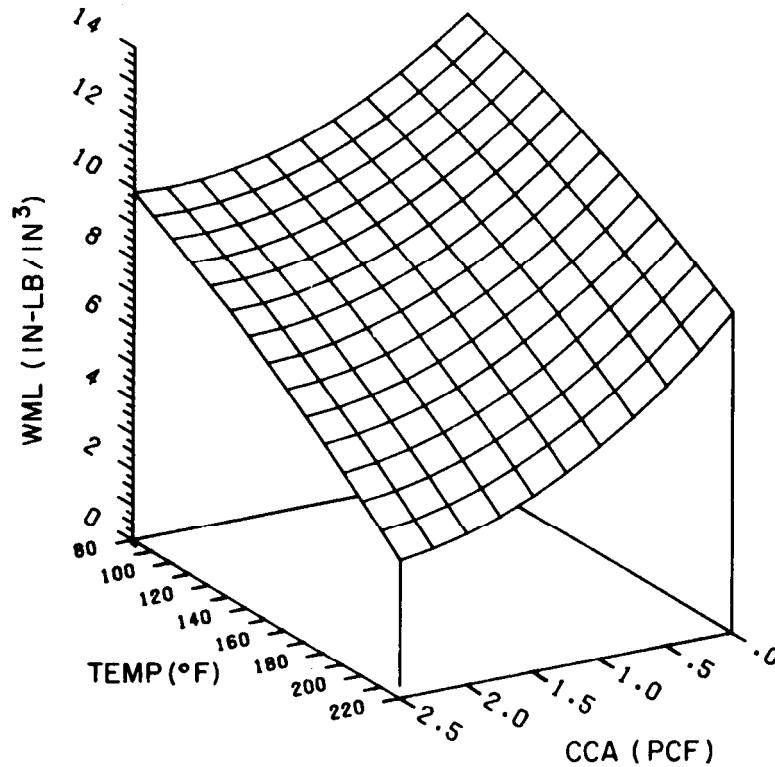


FIG. 7. Predicted response of work to maximum load (WML) of southern pine at an assumed moisture content of 15% and specific gravity of 0.59 to CCA treatment and redrying using an empirical model developed by Winandy et al. (1985). (ML84 5768)

Application of FR-treatment/wood-strength relationship to plywood and lumber

We speculate that FR treatment has the same effect on plywood and lumber. Jessome (1962) evaluated Douglas-fir plywood and clear wood. For such a study, however, the plywood and clear wood specimens must be closely matched for source, pretreatment conditions, and thermal exposure. We do not know whether or not Jessome matched the specimens. Jessome's results for plywood were similar to the results for clear wood, and these results agree with the results for plywood by King and Matteson (1961) and Winandy et al. (1988), and for clear wood by Lyon et al. (1988) and Gerhards (1970).

CONCLUDING REMARKS

We have attempted to highlight those parameters that significantly affect strength degradation of FR-treated wood. From the literature review, we have developed several hypotheses of why strength reductions occur.

First, fire retardants reduce the flammability of wood by an acid-catalyzed reaction that decreases the temperature at which wood begins to decompose and increases the residual char weight. However, the presence of acids in the wood can significantly reduce strength.

Second, the rate at which the acids degrade the strength of wood is influenced by temperature. A 10 C increase in temperature can double or triple the rate of degradation. Thus, the combined effect of acidic FR and the increased sensitivity of treated wood to elevated temperature conditions for extended periods probably causes accelerated acid hydrolysis reactions, which reduce the strength and stiffness of the lumber and plywood.

Third, the particular kind of FR used also affects the extent of wood degradation. Some types of FR are more acidic than others. We know that chromated zinc chloride and aluminum sulfate are highly acidic salts, which cause significant reductions in strength properties. The FR systems may be buffered to reduce acidity as long as the buffer systems do not affect the performance of the wood under fire conditions, but more research is necessary.

Fourth, we think the combined effect of FR chemicals and temperature is probably greater than would be expected from the sum of the individual effects. However, the existence of the problem and its extent depend on several other considerations, such as the differing susceptibility of various species to acid hydrolysis reactions. For example, if hardwoods are used, the expected effect of acid hydrolysis is greater than that for softwood.

Finally, the influence of cyclic environmental exposures can affect the extent of degrade. Because most FR chemicals used today are inorganic salts, they diffuse throughout the wood with moisture movement. In some situations, such as roofs, elevated temperatures and humidity changes cause shifts in the equilibrium moisture content of the wood. As the moisture moves, so do the inorganic salts. This cycling could cause migration of the salts within the wood. At each new site, the acidic salts can cause further degradation. We know that cyclic moisture contents accelerate creep (Caulfield 1985). In the presence of FR chemicals, creep may be further accelerated and the degradation of other mechanical properties more pronounced.

Therefore, to determine the relative importance of these and other factors, a systematic research program is now underway within the wood industry and at the Forest Products Laboratory to assess the relative importance of each factor and the manner in which these factors contribute to strength reduction of wood treated with fire retardants.

REFERENCES

- ADAMS, E. H., G. L. MOORE, AND J. D. BRAZIER. 1979. The effect of flame-retardant treatments on some mechanical properties of wood. BRE-IP 24/79. Building Research Establishment, Aylesbury, Bucks., U.K.
- BARNES, H. M., AND P. H. MITCHELL. 1984. The effect of post-treatment redry schedule on the strength of CCA-treated southern pine dimension lumber. *Forest Prod. J.* 34(6):29-33.
- BEALL, F. C. 1971. Differential calorimetric analysis of wood and wood components. *Wood Sci. Tech.* 5:159-175.
- , AND H. W. EICKNER. 1970. Thermal degradation of wood components: A review of the literature. Res. Pap. FPL 130. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- BENDTSEN, B. A., L. R. GJOVIK, AND S. VERRIL. 1983. The mechanical properties of salt-treated longleaf pine. Res. Pap. FPL 434. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- BRENDEN, J. J. 1967. Effect of fire-retardant and other inorganic salts on pyrolysis products of

- ponderosa pine at 250° and 350°C. Res. Pap. FPL 80. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- BROIDO, A., A. JAVIERSON, AND E. BARRALL II. 1973. Molecular weight decreases in the early pyrolysis of crystalline and amorphous cellulose. *J. Appl. Polymer Sci.* 17(12):3627–3635.
- BROWNE, F. L. 1958. Theories of the combustion of wood and its control. USDA FPL Rep. 2136. Forest Prod. Lab., Madison, WI (reviewed and reaffirmed in 1963).
- , AND W. K. TANG. 1963. Effect of various chemicals in the thermogravimetric analysis of ponderosa pine. Res. Pap. FPL 6. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- BUBLITZ, W. J., AND J. L. HULL. 1983. Chemical resistance of Douglas-fir for use in storage tanks. *Wood Fiber Sci.* 15(1):59–68.
- CAULFIELD, D. F. 1985. A chemical kinetics approach to the duration-of-load problem in wood. *Wood Fiber Sci.* 15(1):59–68.
- CECH, M. Y., AND D. R. HUFFMAN. 1974. High-temperature drying for mixed spruce, jack pine, and balsam fir. Publ. 1337. Canadian Forest Serv., Eastern Forest Prod. Lab. Ottawa, Ont., Canada.
- COMSTOCK, G. L. 1976. Comparison of mechanical properties of Douglas-fir and southern pine lumber dried by CRT, high temperature, and conventional schedules. In C. C. Gerhards and J. M. McMillan, eds. Proceedings, conference on high temperature drying effects on mechanical properties of softwood lumber. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- COUNTRYMAN, D. 1957. Effect on plywood strength of preservative treatment. Lab. Rep. 74. Douglas Fir Plywood Association, Tacoma, WA.
- ELLIS, W. D., R. M. ROWELL, S. L. LEVAN, AND A. SUSOTT. 1987. Thermal degradation properties of wood reacted with diethylchlorophosphate or phenylphosphonic dichloride as potential flame retardants. *Wood Fiber Sci.* 19(4):439–445.
- FENGEL, D., AND WEGENER, G. 1984. Reactions in acidic medium. Pages 268–292 in *Wood. Chemistry, ultrastructure, reactions.* Walter de Gruyter and Co., Berlin.
- FUNG, D. P. C., Y. TSUCHIYA, AND K. SUMI. 1972. Thermal degradation of cellulose and levoglucosan—The effect of inorganic salts. *Wood Sci.* 5(1):38–43.
- GERHARDS, C. C. 1970. Effect of fire-retardant treatment on bending strength of wood. Res. Pap. FPL 145. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- . 1979. Effect of high-temperature drying on tensile strength of Douglas-fir 2 x 4's. *Forest Prod. J.* 29(3):39–46.
- . 1982. Effect of moisture content and temperature on the mechanical properties of wood: An analysis of immediate effects. *Wood Fiber* 14(1):4–36.
- . 1983. Effect of high-temperature drying on the bending strength of yellow-poplar 2 x 4's. *Forest Prod. J.* 33(2):61–67.
- GRAHAM, R. D. 1964. Strength of small Douglas-fir beams treated with fire retardants. *American Wood-Preservers' Association* 60:172–177.
- HILLIS, W. E. 1975. The role of wood characteristics in high-temperature drying. *J. Inst. Wood Sci.* 7(2):60–67.
- HIRATA, T. 1979. Changes in degree of polymerization and weight of cellulose untreated and treated with inorganic salts during pyrolysis. Forest and Forest Prod. Res. Inst. 304. J. Japan Wood Res. Soc. Bull.:77–124.
- HOOPER TREATED WOOD PRODUCTS. 1984. Personal communication with B. W. Holden, Vice President.
- IFJU, G. 1964. Tensile strength behavior as a function of cellulose in wood. *Forest Prod. J.* 14(8):366–372.
- JESSOME, A. P. 1962. Strength properties of wood treated with fire retardants. Rep. 193. Forest Prod. Res. Branch, Dept. of Forestry, Canada.
- JOHNSON, J. W. 1967. Bending strength for small joists of Douglas-fir treated with fire retardants. Rep. T-23. Oregon State University, Forest Res. Lab., Corvallis, OR.
- KASS, A., F. F. WANGAARD, AND H. A. SCHROEDER. 1970. Chemical degradation of wood: The relationship between strength retention and pentosan content. *Wood Fiber Sci.* 2(1):31–39.
- KAUMAN, W. G. 1962. Kinetics of changes in acidity during thermal degradation of wood from three Australian species. *Forest Prod. J.* 12(6):275–276.

- KING, E. G., JR., AND D. A. MATTESON, JR. 1961. Effects of fire-retardant treatments on the mechanical properties of Douglas-fir plywood. Lab. Rep. 90. Douglas-fir Plywood Association. 14 pp.
- KNUFFEL, W. E. 1985. The effect of CCA preservative treatment on the compression strength of South African pine structural timber. *Holzforschung und Holzverwertung* 37(5):96-99.
- KOCH, P. 1971. Process for straightening and drying southern pine 2 by 4's in 24 hours. *Forest Prod. J.* 21(5):17-24.
- . 1985. Drying southern pine at high temperature—A summary of research at Pineville, LA from 1963-1982. Pages 1-38 in P. H. Mitchell, ed. Proceedings, North American drying symposium. Mississippi Forest Products Utilization Laboratory, Mississippi State University, Starkville, MS.
- KOPPERS Co. 1985. Strength properties of DRICON treated wood. Product Data Sheet WOL-232. Koppers Co., Inc., Pittsburgh, PA.
- KOZLIK, C. T. 1968. Effect of kiln-drying temperatures on strength of Douglas-fir and hemlock dimension lumber. Oregon State University, Forest Res. Lab., Corvallis, OR.
- LADELL, J. L. 1956. High-temperature drying of yellow birch. *Forest Prod. J.* 6(11):470-475.
- LEVAN, S. L. 1984. Chemistry of fire retardancy. In R. M. Rowell, ed. *The chemistry of solid wood. Advances in Chemistry Series 207.* American Chemical Society, Washington, DC.
- , AND C. A. HOLMES. 1986. Effectiveness of fire-retardant treatments for shingles after 10 years of outdoor weathering. Res. Pap. FPL 474. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- LYON, D. E., K. L. BIGBEE, AND W. S. McNAMARA. 1988. Evaluation of strength properties of fire-retardant treated wood using the 1983 National Forest Products Association protocol. *Forest Prod. J.* 38(6):13-18.
- LYONS, J. W. 1970. *The chemistry and uses of fire retardants.* Wiley-Interscience, New York.
- MACKEY, J. G. G. 1976. Effect of high temperature kiln-drying on lumber properties. Proceedings, research conference on high temperature drying effects on mechanical properties of softwood lumber. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- MCDERMOTT, J. B., M. T. KLEIN, AND J. R. OBST. 1986. Chemical modeling in the deduction of process concepts: A proposed novel process for lignin liquefaction. *I&EC Process Design and Development* 25:885-889.
- MERCK INDEX. 1968. *The Merck index: An encyclopedia of chemicals and drugs*, 8th ed. P. G. Stecher, ed. Merck and Co., Rahway, NJ.
- NATIONAL FOREST PRODUCTS ASSOCIATION. 1986. National design specification for wood construction. National Forest Products Association, Washington, DC.
- OBERLEY, W. J. U.S. Patent 4,373,010. February 8, 1983.
- OBST, J. R. 1983. Analytical pyrolysis of hardwood and softwood lignin and its use in lignin-type determination of hardwood vessel elements. *J. Wood Chem. Tech.* 3(4):377-397.
- OSMOSE COMPANY. 1984. Personal communication with J. C. Gauntt, Director of Codes and Product Acceptance, Osmose Company, Griffin, GA.
- RASMUSSEN, E. F. 1961. Dry kiln operator's manual. Agric. Handb. 188. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- RIETZ, R. C., AND R. H. PAGE. 1971. Air drying lumber: A guide to industry practice. Agric. Handb. 402. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- SALAMON, M. 1963. Quality and strength properties of Douglas-fir dried at high temperatures. *Forest Prod. J.* 13(8):339-344.
- . 1969. High temperature drying and its effect on wood properties. *Forest Prod. J.* 19(3):27-34.
- SHAFIZADEH, F. 1968. Pyrolysis and combustion of cellulosic materials. In M. L. Wolfrom and R. S. Tipson, eds. *Advances in Carbohydrate Chemistry* 23:419-474. Academic Press, New York.
- . 1971. Thermal behavior of carbohydrates. Part C. *J. Polymer Sci.* 36:21-51.
- . 1975. Industrial pyrolysis of cellulosic materials. *Applied Polymer Symposium* 28:153-174.
- . 1984. Pyrolysis and combustion. In R. M. Rowell, ed. *The chemistry of solid wood. Advances in Chemistry Series 207.* Chapter 13. American Chemical Society, Washington, DC.
- , AND P. S. CHIN. 1977. Thermal deterioration of wood. In I. S. Goldstein, ed. *Wood technology: Chemical aspects.* ACS Symposium Series 43:57-81. American Chemical Society, Washington, DC.

- , AND Y. SEKIGUCHI. 1983. Development of aromaticity of cellulosic chars. *Carbon* 21:511-516.
- SPRINGER, E. L. 1966. Hydrolysis of aspenwood with aqueous solutions of hydrochloric acid. *TAPPI* 49(3):102-106.
- STAMM, A. J. 1955. Thermal degradation of wood and cellulose. Presented at the symposium on degradation of cellulose and cellulose derivatives, 127th National Mtg., 1955 April 4-7, Cincinnati, OH. American Chemical Society, Division of Cellulose Chemistry.
- TANG, W. K. 1967a. Effect of inorganic salts on pyrolysis of wood, alpha-cellulose, and lignin determined by dynamic thermogravimetry. Res. Pap. FPL 71. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- . 1967b. Effect of inorganic salts on pyrolysis of wood, cellulose, and lignin determined by differential thermal analysis. Res. Pap. FPL 82. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- THOMPSON, W. S. 1969. Effect of seasoning method on the strength properties of southern pine poles. Part I. Mechanical effects. *Forest Prod. J.* 19(1):21-28.
- USDA. 1987. Wood handbook: Wood as an engineering material. Agric. Handb. 72. U.S. Department of Agriculture, Washington, DC, 1987 rev.
- WANGAARD, F. F. 1966. Resistance of wood to chemical degradation. *Forest Prod. J.* 16(2):53-64.
- WINANDY, J. E. 1988. Effects of treatment and redrying on mechanical properties of wood. Proceedings, FPRS conf. on wood protection and techniques and the use of treated wood in construction, 1987 October 28-30, Memphis, TN. *Forest Prod. Res. Soc.*:54-62.
- . 1989. CCA preservative treatment and redrying effects on the bending properties of southern pine 2 by 4's. *Forest Prod. J.* 39(9):14-21.
- , AND R. S. BOONE. 1988. The effects of CCA preservative treatment and redrying on the bending properties of 2 x 6 southern pine lumber. *Wood Fiber Sci.* 20(3):350-364.
- , ———, AND B. A. BENDTSEN. 1985. The interaction of CCA preservative treatment and redrying: Effects on the mechanical properties of southern pine. *Forest Prod. J.* 35(10):62-68.
- , ———, L. R. GJOVIK, AND P. L. PLANTINGA. 1989. The effects of ACA and CCA preservative treatment and redrying on the mechanical properties of Douglas-fir. Proceedings, Am. Wood Preservers' Assoc. Vol. 8.
- , S. L. LEVAN, E. L. SCHAFFER, AND P. W. LEE. 1988. Effect of fire retardant treatment and redrying on the mechanical properties of Douglas-fir and aspen plywood. Res. Pap. FPL 485. U.S. Department of Agriculture, Forest Serv., Forest Prod. Lab., Madison, WI.
- YAO, J., AND F. TAYLOR. 1979. Effect of high-temperature drying on the strength of southern pine dimension lumber. *Forest Prod. J.* 29(8):49-51.

