STATE OF THE ART PAPER: EFFECTS OF FIRE-RETARDANT TREATMENTS ON CHEMISTRY AND ENGINEERING PROPERTIES OF WOOD

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EXECUTIVE SUMMARY

Wood is an environmentally desirable material for fiber and structural use. It is efficient in both economic and environmental costs to the user. Sometimes wood is treated with chemicals to extend its utility into new markets. In North America, fire retardant-treated lumber and plywood are sometimes permitted as alternatives to noncombustible materials in structures that require increased fire safety. The history of the development of fire-retardant chemicals and their adaptation as wood treatments in standards and building codes is beyond the scope of this review, but it has been comprehensively documented (Barnes 1993, 1994). This review focuses on the effects of fire-retardant chemicals and their treatment processes on the physical and mechanical performance of fire retardant-treated wood (FRTW). It also deals with how the conditions of the use environment further affect those performance properties.

Some commercial fire-retardant (FR) treatments made from the early to late 1980s failed to perform as expected when the treated products were used as roof sheathing plywood and roof truss lumber. Elevated roof temperatures caused by solar radiation in combination with FR chemi-

cals and moisture prematurely activated some FRs, often causing the wood to exhibit a dark brown color, become brittle, experience cross-grain checking, and crumble easily. In some cases, this problem required costly roof replacement. Because of the regional nature of building codes in North America at the time, the problem was initially most common in the eastern US on nonresidential commercial and multifamily dwellings built without parapet walls after 1980, but it eventually was experienced from coast to coast. More recently, fire-retardant treatment (FRT) degrade in roof truss lumber has been reported. The FRT degrade problem took longer to occur in truss lumber because of the lower roof system temperatures experienced by truss lumber compared with plywood roof sheathing.

Between 1988 and 2001, extensive research at USDA Forest Service, Forest Products Laboratory (FPL) with many cooperators defined the mechanism of the problem. In addition to understanding the thermal–chemical mechanism of degrade, serviceability assessment methods were developed to evaluate the condition of FR-treated plywood and trusses for estimating residual service life. An intensive literature review was conducted followed by a comprehensive research program in which methods were developed to determine laboratory degradation rates for various FR model compounds.

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As we learned more, this broad research program was expanded to evaluate comparisons among laboratory and field degrade rates, document field exposures (ie thermal loads), and develop methods to evaluate current condition of FR-treated wood used in roof system sheathing and predict its residual serviceability. Two of these experimental laboratory methods that quantified the effects of various FR model compounds that experienced thermal degrade and eventual loss of mechanical properties were the basis for test methods for commercial systems to assess their potential to undergo thermal degradation on extended exposure to elevated temperatures. This work resulted in two ASTM standard test methods (ASTM 2012a, 2012b). Standard practices for using those test data to derive design adjustment factors for FR-treated plywood and lumber were also developed (ASTM 2012c, 2012d). To preclude future serviceability problems with FR-treated wood used in engineered wood systems, results from these four ASTM standards on test methods and design practices have been incorporated as mandatory performance requirements for FR formulations in American Wood Preservers' Association (AWPA) Standards U-1 and T-1 (formerly C20 and C27) for FR-treated wood (AWPA 2012a, 2012b) and in the International Code Council-Evaluation Services' AC-66 (ICC-ES 2012).

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REVIEW OF LITERATURE ON THERMAL
DEGRADATION OF UNTREATED WOOD

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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 and decelerate as temperature decreases. This thermal degradation of cellulose can be accelerated in the presence of water, acids, and oxygen (Le Van and Winandy 1990). As the temperature increases, the degree of cellulose polymerization decreases further, free radicals appear, and carbonyl, carboxyl, and hydroperoxide groups are formed (Beall and Eickner 1970; Hirata 1979; Shafizadeh 1984). The primary

reaction is depolymerization caused by cleavage of the glycosidic linkage (The glycosidic linkages are hydrolyzable at room temperatures in the presence of strong acids.).

Hemicelluloses degrade at lower temperatures than cellulose (Beall 1971) because they are less thermally stable than cellulose. Much of the acetic acid liberated from wood pyrolysis is attributed to the deacetylation of hemicellulose. In summary, wood degradation can be viewed as the sum of the degradation of its components (Lebow and Winandy 1999a) with the following order of most to least susceptible to degradation:

a) side chain of hemicellulose, such as arabinans and galactans;
b) main chain of hemicellulose, such as mannans and xylans;
c) amorphous cellulose, such as some glucans;
d) lignin; and
e) crystalline cellulose, such as some glucans.

Effect of Acid Treatment on Strength of Untreated Wood

In general, wood has demonstrated resistance to acids and alkali in low concentrations. However, wood is severely attacked by strong acidic and caustic solutions (Stamm 1964; Beall and Eickner 1970; Kass et al 1970; Fengel and Wegener 1984). The primary mechanism of FR chemicals is an acid-catalyzed reaction to decrease flammable volatiles and increase residual char. Because most FR chemical systems can be thought of as acids of various strengths, borates are often added to the system to buffer its pH because at higher temperatures, higher acid concentrations cause greater strength loss.

Research has proven that degradation via acid hydrolysis is controlled both by pH of 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. The temperature-controlled (ie kinetic) rates of hydrolysis for various generic

FR systems with varying pH have been defined (Winandy 2001) and empirically modeled (Lebow and Winandy 1999a). The precise thermochemical mechanisms of this degradation have also been defined and modeled (Winandy and Lebow 2001).

Effect of Temperature on Strength of Untreated Wood

Strength and stiffness of wood decrease when heated and increase when cooled. This effect on mechanical properties is immediate and approximately linear at constant moisture content between −50 and 150°C. Below 100°C, the immediate effect is essentially reversible. The immediate effects of temperature on mechanical properties of wood were reviewed by Gerhards (1982). He showed that the immediate effects of temperature were significantly influenced by wood moisture content. For example, if a green piece of lumber at 20°C is heated to 90°C, the immediate effect of temperature is a strength decrease. However, the piece also tends to dry, which tends to increase its strength. For most practical purposes, although 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 short-term strength.

If wood is exposed to elevated temperatures for an extended time, strength is permanently decreased. Similarly, extended exposure to temperatures above 65°C can induce permanent decreases in mechanical properties of wood (FPL 2010). The magnitude of permanent strength decrease depends on moisture content, heating medium, temperature, exposure period, species, and specimen size.

The initial kiln-drying process has a negligible effect on strength at 71°C or below (FPL 2010). At higher temperatures, however, 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 decrease 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 decreases associated with HTD presumably arise from 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.

Some high-temperature drying procedures have only a minimal effect on mechanical properties of softwoods; the difference compared with controls for modulus of rupture (MOR) ranges from 5 to −10% and for modulus of elasticity (MOE) from 2 to −3% (Koch 1976; Yao and Taylor 1979). Hardwoods have a greater amount of thermally sensitive pentosans compared with softwoods, thus hardwoods probably are 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.

Early Research on Effects of Fire-Retardant Treatment on Wood Properties

Most FRTs significantly decrease the strength and stiffness of the treated wood product. This was recognized and documented soon after the initial development of FR chemicals and treatment technology by a series of important studies on effects of FR chemicals on physical and mechanical properties of treated wood.

Luther (1921) showed that ZnCl could cause strength loss and that the loss in strength was directly related to in-service exposure temperatures. Wilson and Bateman (1921) found that initial strength loss increased as ZnCl retention

increased, but in contrast to what has been reported by some, they did not study extended exposures or elevated temperature exposures. Another very interesting point not often appreciated (or acknowledged by some users of this literature) is that any interpretation of strength test results for treated wood must account for the swelling induced by hygroscopic treatments such as many waterborne FR systems (Gardner 1965). McKnight (1962) showed that hygroscopicity (ie equilibrium moisture content [EMC] at any temperature–humidity environment) of FR-treated wood was clearly increased. As a result, King and Matteson (1961) discussed how the change in EMC is a product of the treatment, therefore when comparing treated and untreated data, a moisture content adjustment is not advised. Countryman (1957) and King and Matteson (1961) studied the effects of three commercial FR systems of that time on Douglas-fir plywood and found that two systems had little effect on load-carrying capacity and decreased MOR about 6-8%, whereas the third system decreased both by 18 and 24%, respectively.

Gottschalk (1944) studied the relationships of three commercial FR systems of the World War II era and reported on minimum FR retentions required for fire resistance and biological decay resistance and their influence on physical and mechanical properties. This work clearly showed that in all respects, any FR effects were a complex function of wood species and size/thickness of wood being evaluated. Other investigators found that some FR chemicals may decrease wood strength and adhesive bond strength after extended exposure to high humidity (Blew 1946; Blew and Olson 1950). Werren (1962) tested a series of nine matched NonCom-treated and untreated Southern Pine glulam beams and found MOE was on average unchanged but that strength was decreased on average about 11% with the greatest loss being 22%.

Bateman (1929) showed that waterborne FR systems such as the ZnCl he studied will desiccate on extended exposure to high RH environments, but no strength testing was done. This desiccation of FR chemicals from the interior to the surface of treated wood when exposed to high humidity or liquid moisture is today commonly termed "blooming."

Johnson (1976) noted that fastener corrosion was occurring after extended exposure to warm, damp environments (32°C, 90% RH) causing decreased joint strength, but this was more prevalent in some systems, such as pyrosote, than in others, such as NonCom or untreated.

McFarland and Angell (1946) noted that free ammonia can be liberated when wood containing ammonia salts is heated and that this ammonia can then react with wood to cause discoloration (ie browning). Similar discoloration was also noted by Luther (1921) for ZnCl-treated wood exposed to heat.

Combined Effect of Fire-Retardant Treatment and Temperature on Strength

In general, effects of FRTs and redrying on static mechanical properties of wood can be categorized by type of FR chemical used and maximum dry-bulb temperature in the kiln (Winandy et al 1988). For example, the effects of treatment and redrying are negligible if wood is air-dried after treatment (Johnson 1967). However, if FR-treated wood is kiln-dried after treatment, its mechanical properties (MOR, MOE, and work to maximum load) are consistently lower than those of untreated wood (Gerhards 1970; Chung et al 1999). Gerhards (1970) concluded that FRT and kiln-drying decreased MOR and MOE of clear wood by an average of 13 and 5%, respectively; for structural lumber, MOR and MOE were decreased by about 14 and 1%, respectively. Consequently, the National Design Specification (NDS) for Wood Construction (NFPA 1986) required a 10-20% decrease in allowable design stress, depending on the mechanical property under consideration. Prior to that, the NDS (NFPA 1974) had recommended a uniform decrease of 10% for all design properties. Other past work supported similar decreases for FR-treated plywood (Winandy et al 1988; Wang and Rao 1999).

However, prior to the mid-1980s, the literature on FRT effects was not cohesive. It represented a combination of unrelated studies, none of which was comprehensive. The following questions thus remained unanswered:

1. What were the long-term effects of in-service conditions, such as elevated temperature and moisture content, on the strength of FR-treated wood?
2. What were the effects of FRT on the strength of weaker members in the strength distribution?
3. How did FR chemicals affect multiple species–size–grade combinations?
4. Did the relationship between FRT and strength apply to both lumber and plywood? Can data from lumber studies be applied to plywood studies and vice versa?
5. What were the comparative relationships during thermal degradation between FRTW and untreated wood?

LITERATURE ON THERMAL DEGRADATION OF FIRE RETARDANT-TREATED WOOD

Mechanisms by which Fire Retardant Alters Thermal Degradation

Many different proprietary FR chemical systems exist for imparting fire retardancy to wood. The most common FR chemicals used for wood are inorganic salts, such as diammonium phosphate, monoammonium phosphate, ammonium polyphosphates, 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; Alexiou et al 1986) and are referred to as organic salts. However, all FR systems for wood rely on 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. Another similar analogous ammonium phosphate system is ammonium polyphosphates, which have two or more phosphates per ammonium polyphosphate molecule (Eickner et al 1969). 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 (GUP), and melamine monophosphate. 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 (Le Van and Holmes 1986; Ellis et al 1987), but the compounds are not currently used commercially for wood.

Inorganic salts are fairly inexpensive to use for fire retardancy and are easy to apply. The solubility of inorganic salts in water is dependent on the particular compound; for example, zinc chloride is quite soluble (2 g/mL), whereas boric acid is much less so (0.056 g/mL) (O'Neil 2006). Because of their solubility and molecular size, inorganic salts are susceptible to moisture movement and migrate with the movement of water in wood. This review mainly addresses inorganic salts because most of the available literature is about 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 Le Van (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 decreasing the amount of volatile, combustible vapors. Pyrolysis reactions are altered such that thermal decomposition occurs at lower temperatures for FR-treated wood than for untreated wood. Browne and Tang (1963) tested sodium borax, sodium chloride, potassium carbonate, aluminum chloride, and monoammonium phosphate. All compounds

increased the residual char weight of the material. Furthermore, Browne and Tang found that the more effective the inorganic salt was as a flame retardant, the lower the temperature was of active pyrolysis and the greater the amount of char was as indicated by monoammonium phosphate. In other experiments, Brenden (1967) found that increased amounts of char correlated with decreased amounts of tar.

Acidic compounds have the greatest effect on decreasing 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 at decreasing 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 adding 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 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 1110 to 650 after only 2 min of heating at 150°C. Cellulose treated with borax showed a DP decrease from 1300 to 700 after 1 h of heat treatment at 150°C. Both of these compounds decreased the amount 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 condensation of the char to form crosslinked and thermally stable polycyclic aromatic structures (Shafizadeh 1984).

Several groups have developed hybrid FR combinations of phosphates and borates. The strong FR synergism between boric acid and GUP is caused by the different FR mechanisms of boric acid and GUP and the different activation temperatures of these chemicals (Wang et al 2004). Wang et al (2004) showed that boric acid catalyzes the dehydration and other oxygen-eliminating reactions of wood at a relatively low temperature (100-300°C) and postulated that it might catalyze the isomerization of the newly formed polymeric materials to form aromatic structures. This contributed partly to the ability of boric acid to promote charring and fire retardation of wood.

Effects of Fire-Retardant Treatment on Properties of Fire Retardant-Treated Wood

Researchers have long recognized that FR treatments decrease initial strength properties (King and Matteson 1961; Jessome 1962; Graham 1964; Gerhards 1970). Posttreatment redrying has been shown to accelerate this initial strength loss (Johnson 1967; Winandy et al 1988). This initial decrease in strength from FR treatment and redrying was supposedly accounted for through a uniform single modification to allowable stress design values. However, Lyon et al (1988) studied an array of wood properties using a newly proposed protocol for evaluating commercial FR systems and clearly showed that a single uniform design adjustment to any and all design properties was not adequate. However, prior to the mid-1980s, it was not entirely understood by engineers, scientists, and treaters that additional in-service decreases in strength might occur when some FR-treated products were exposed to moderate elevated temperatures, such as those induced by solar loads on roof systems.

About that time, preliminary investigations indicated that field problems of FR-treated plywood

roof sheathing resulted from thermal-induced acid degradation of wood carbohydrates by the acidic FR chemicals (Le Van and Winandy 1990). Subsequent work for the next decade confirmed the relationship between changes in treated wood pH and the proposed acid degradation mechanism (Winandy 1995, 1997; Lebow and Winandy 1999b). The effects of FR treatments on mechanical properties of the treated wood and the mechanisms of this thermal degradation were described in detail by Winandy et al (1991a).

This research confirmed the initial hypothesis of several wood scientists and engineers that the relative effects of many FR treatments could be classified by the type of FR chemical used and the time–temperature combination required for conversion of the FR formulation into its acidic-functional form (Le Van et al 1990). Critical to fully understanding what is happening is recognizing that other factors are also important. Much misunderstanding continues to exist among supposed experts, such as that related to relationships among steady-state laboratory, cyclic laboratory, and diurnal field exposures. Much misunderstanding also exists on the dozens of phosphate system chemistries used commercially and as FR model compounds and their effects on wood. Finally, there is an imperfect understanding of the relationships between pure, technical-grade FR model compounds and commercial FR formulations, including a general lack of appreciation for details of chemical mixtures and buffering. These are critical concepts because virtually all commercial FR formulations are buffered chemical mixtures; and much laboratory FRT research has involved pure FR model compounds.

All wood products are prone to varying amounts of strength loss from extended exposure to elevated temperatures above 65°C. The higher the temperature, the less time required to produce a given decrease in strength. Field problems have occurred in the US with FR-treated plywood roof sheathing and roof truss lumber when exposed to elevated temperatures or excessive moisture. The general problem of roof sheathing

failures in FR-treated plywood has been discussed by the American Plywood Association (APA 1989), Le Van and Collet (1989), and the National Association of Home Builders (NAHB 1990). Interim guidelines for design were given by NAHB (1990) and Winandy (1990). The various factors involved in the problem and a proposed thermochemical mechanism were presented by Le Van and Winandy (1990). The historical precedence for redrying temperature limits and the effects of those temperatures used in kiln-drying FR-treated lumber and plywood after treatment was based in part on work by numerous researchers (King and Matteson 1961; Johnson 1967; Gerhards 1970; Winandy et al 1988; Winandy 1997). These studies consistently showed that the temperatures used in the posttreatment redrying process were one factor that was critical to the magnitude of initial FR treatment-induced strength loss. These studies now provide the basis for the redrying temperature limit of 71°C for FR material intended for use at or near room temperature in AWPA (2012a).

From a review of existing literature, it became apparent that the effect of redrying temperature on in-service performance of FR-treated wood subjected to subsequent elevated in-service temperatures was not entirely independent of other factors such as FR chemistries, building design and construction, and building maintenance.

Moisture content is known to exaggerate the immediate effects of elevated temperature on strength of untreated wood, whereas the permanent effect of temperature on untreated wood strength is similar but less documented (Gerhards 1982). It is reasonable to assume that higher moisture contents could also magnify thermal degradation of FR-treated material. However, the literature conflicts itself regarding the magnitude of the effects of moisture content (<25%) on in-service performance of FR-treated wood (APA 1989; Winandy et al 1991b; Le Van et al 1996) and much is still unknown, especially for wood kept from drying or for wood repeatedly rewetted (wood MC > 25%) and subsequently dried. Specific information of this type is vital

to develop a fuller understanding, and it may explain the differential performance between laboratory results and some field experience.

Commercial FR formulations are mixtures of chemicals that provide varying degrees of fire resistance to wood. This FR technology developed gradually for decades (Angell 1951; Catchpole 1976). For example, during World War II, the US Navy created a military specification including three FR systems (US Navy 1944; AWPA 1946). The three systems each had a target retention of 96 kg/m^3 and were defined as 1) 80% ammonium sulfate and 20% ammonium phosphate; 2) 60% borax and 40% boric acid; and 3) 60% ammonium sulfate, 10% ammonium phosphate, 10% borax, and 20% boric acid. Later, other FR systems evolved into four other nonproprietary commercial systems (AWPA 1969). This evolution was reported in a series of AWPA committee reports (AWPA 1959, 1963, 1974) and AWPA Standards (AWPA 2002a, 2002b, 2002c).

The potential of several pure, reagent-grade FR chemicals studied and used as FR model compounds to accelerate thermal degrade has by now clearly been documented by many studies. However, potential chemical interactions between commercial mixtures of FR chemicals and their influence on thermal degradation of treated plywood has not been studied, and the best indication of this relationship is a series of studies using FR model compounds that was conducted by Winandy et al from 1985-2000, the results of which were reviewed by Winandy (2001).

Field Problems with Fire Retardant-Treated Wood

In-service degradation of FR-treated roof sheathing is caused by thermal-induced acid degradation of wood carbohydrates (Le Van et al 1990; Winandy 1995). Previously, predictive models for thermal degrade of untreated and FR-treated wood showed that thermal degrade follows a first-order kinetic relationship (Stamm 1964; Millett and Gerhards 1972; Woo 1981; Pasek

and McIntyre 1990; Winandy et al 1991a). Accordingly, it is clear that recently reported issues of FR degrade with truss lumber took longer to develop and be problematic because truss lumber experiences lower thermal loads than does roof sheathing (Winandy et al 2000).

The extent of degradation in mechanical properties and chemical composition of the wood induced by steady-state laboratory exposures of plywood at 77°C and 79% RH and solid-sawn wood at 82°C and 50% RH was sometimes far less than the magnitude of the degradation often experienced in-service in the field and at other times was fairly representative. It has been suggested that these differences between field- and laboratory-induced property degradation rates are related to

1) severity of the treatment processing factors used in treating,
2) preconstruction storage and handling procedures of FR material prior to field installation (Winandy 1990), or
3) poor design or maintenance resulting in repeated wetting and drying, especially when the drying phase was under load as in most in-service roof systems.

Winandy (1997) evaluated the relative influence of several FR chemical, treatment processing, and exposure factors on the structural performance of FR-treated plywood when subsequently exposed to a long-term steady-state temperature of 65°C and 75% RH. The factors studied included:

1) varying the mixtures of FR components often used in commercial formulations,
2) varying the redrying temperatures used in post-FR treatment kiln-drying, and
3) defining moisture-related leaching of phosphate from FR-treated material during subsequent rewetting in-service.

Some of these experimental factors studied were identified in previous experiments using dynamic mechanical analysis of small veneers (Le Van 1993). The Winandy (1997) study produced three important conclusions; first, that

variation in redrying temperatures from 49-88°C had little effect on the magnitude or rate of subsequent thermal degradation when the treated plywood was exposed at 65°C for up to 290 da. Then, it showed that adding borate-based buffers to FRT chemicals did somewhat mitigate thermal degrade. Finally, the results implied that the combined effects of phosphate retention and accumulated thermal exposure (from both redrying and in-service high temperatures) are additive and cumulative.

The recent development of best-fit kinetics-based models has clearly shown that the application of simple first-order kinetic models is not entirely justified (Winandy and Lebow 1996; Lebow and Winandy 1999a). These other processing factors may account for the differences between first-order kinetics- and best-fit kinetics-based models. These processing factors may include the influence of acidity and/or buffering capacities of various FR chemical components used in commercial FR formulation, the temperatures used in kiln-drying FR-treated material after treatment, and/or rewetting of FR-treated plywood during construction and use. Each factor appears to contribute to the differential performance of laboratory and field materials; however, the relative effect of each factor, and their interactions, is unknown.

Relationship between Thermal Degradation of Fire Retardant-Treated Wood and Untreated Wood

A critical lesson learned during a number of studies conducted at FPL proved that FRTW, waterborne preservative-treated wood, and untreated wood each could experience progressive thermal degradation and the extent of that degradation was directly related to the cumulative exposure temperatures, cumulative duration of those exposures, and initial pH of the wood and/or the molar mass of the treatment salt with treated wood (Lebow and Winandy 1999a; Winandy 2001; Green and Evans 2003). With similar thermal exposures, the results of the thermal degradation models created by Green and Evans

(2003) for untreated lumber-sized wood products predicted within a few percentage points of those created by Lebow and Winandy (1999a) for untreated small clear wood specimens. This implies that thermal degradation in steady-state exposures is independent of wood product size. This is reasonable because, although small specimens would come to steady-state conditions faster than larger lumber specimens, when exposed for weeks and months, that initial difference in duration of thermal exposure is negligible. Furthermore, results of the Lebow and Winandy (1999a) models indicated that untreated and six various FRTW systems each followed similar degradation rates differing mainly by their initial effect on strength. Finally, the initial differences in strength were related to posttreatment pH of the wood and/or molar mass of the nonphosphate moiety associated with the phosphate salt in treated wood. More complete details of these relationships are described by Winandy and Rowell (2013).

Understanding and Modeling Mechanisms of Thermal Degradation

Figures 1-3 show the overall effect of extended high-temperature exposure (up to 4 yr at 66°C at 75% RH) on bending strength of untreated wood or wood treated with several FR model formulations; data were compiled from Le Van et al (1990), Winandy (1995), and Lebow and Winandy (1999a). These three reports summarized data at 27, 54, 66, and 82°C for up to 4 yr. They clearly showed that thermal effects on strength at any temperature within that range were additive and could be predicted using a cumulative damage model based on performance at any other temperature within that range.

Two FR model formulations (phosphoric acid and monoammonium phosphate) caused a significant decrease in initial bending strength of the treated wood as well as a relatively consistent decrease in bending strength relative to time of exposure at high temperature. Untreated
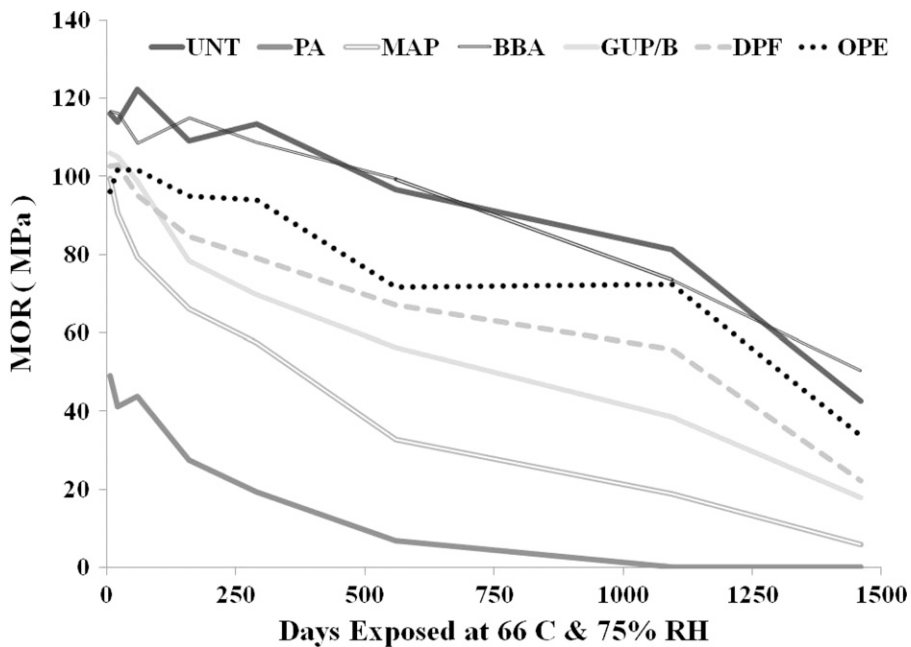
Figure 1.   Change in bending strength with steady-state exposure of up to 4 yr at 66°C for untreated (UNT) wood and wood treated with phosphoric acid (PA), monoammonium phosphate (MAP), guanylurea phosphate/boric acid (GUP/B), dicyandiamide-phosphoric acid–formaldehyde (DPF), organophosphonate ester (OPE), or borax/boric acid (BBA) (Winandy 2001).

wood and wood treated with borax/boric acid exhibited little to no decrease in initial bending strength and then appeared to experience a finite period (<60 da) of resistance to thermal degrade. Comparison of other FRT, for example guanylurea phosphate/boric acid, dicyandiamide/ phosphoric acid/formaldehyde, and organophosphonate ester), showed that treated wood experienced a measurable initial strength loss and may have experienced a brief period (<7 da) of resistance to thermal degrade. This was the basis for our hypothesis that these brief periods of resistance to thermal degradation of strength were related to posttreatment pH of the wood and/or molar mass of the nonphosphate moiety associated with the phosphate salt in treated wood. Thereafter, for each FR model compound, treated wood experienced a relatively consistent decrease in bending strength with time of exposure at high temperature (Fig 1). Initially, MOE was relatively less affected than bending strength, but eventually, the effects

of treatment and temperature were just as apparent (Fig 2).

By contrast, the effect of treatment on work to maximum load (WML) was initially more noticeable than the effects on bending strength and MOE (Fig 3). Because WML is a measure of energy to failure, it is a good indicator of embrittlement. Users have long recognized that many wood treatments result in a less ductile product. Some acid systems lead to a product that is brash in its failure mechanism. Judging by the significant loss in WML for untreated and all treated wood products at 66°C, it is obvious that given a long enough duration of exposure to elevated temperatures, all wood products, treated or untreated, will eventually undergo critical levels of degrade.

The strength loss mechanism in untreated wood and for wood treated with six various FR systems when exposed for extended durations to elevated temperature has been shown
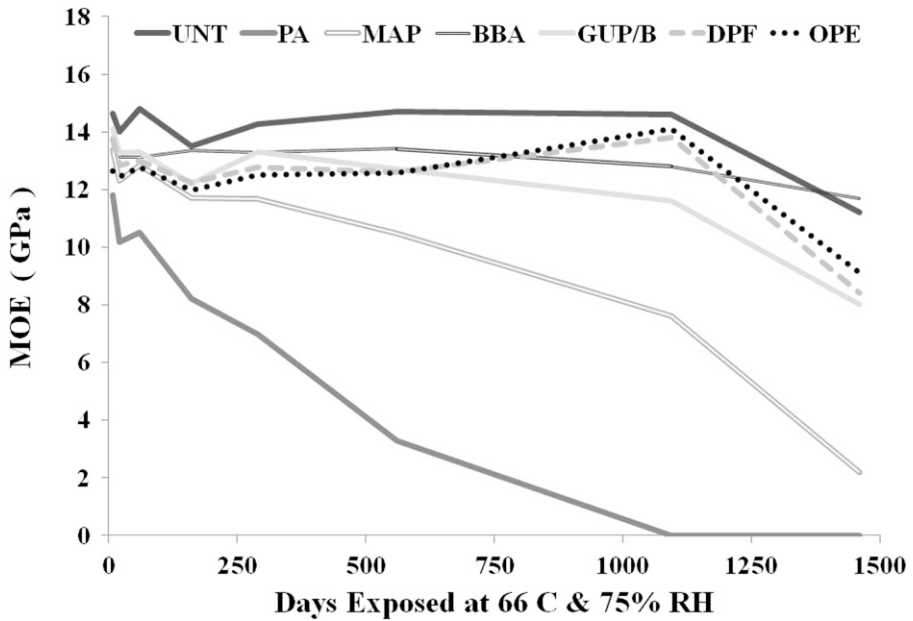
Figure 2.   Predicted change in modulus of elasticity (MOE) with steady-state exposure of up to 4 yr at 66°C for untreated (UNT) and treated wood. PA, phosphoric acid; MAP, monoammonium phosphate; GUP/B, guanylurea phosphate/boric acid; DPF, dicyandiamide-phosphoric acid–formaldehyde; OPE, organophosphonate ester; BBA, borax/boric acid (Winandy 2001).
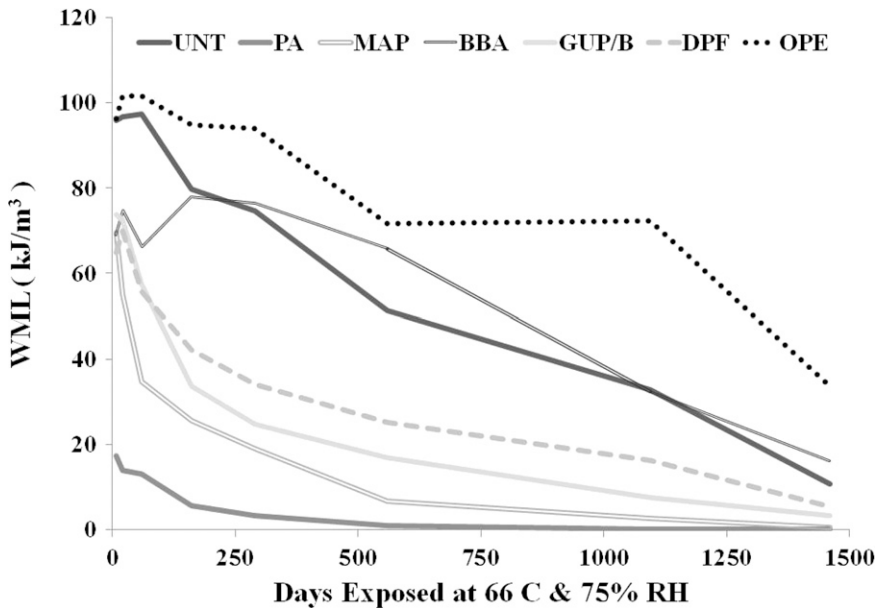

Figure 3.   Predicted change in work to maximum load (WML) with steady-state exposure of up to 4 yr at 66°C for untreated (UNT) and treated wood. PA, phosphoric acid; MAP, monoammonium phosphate; GUP/B, guanylurea phosphate/ boric acid; DPF, dicyandiamide-phosphoric acid–formaldehyde; OPE, organophosphonate ester; BBA, borax/boric acid (Winandy 2001).

to be directly related to progressive changes in the chemical composition of wood. Models for predicting strength loss from changes in wood chemical composition have been developed by Winandy and Lebow (2001). These models were based on the strong relationship between loss in strength and loss in hemicelluloses. Monitoring the degradation of the least-protected side chain carbohydrate moieties, such as arabinose, provided the most sensitive predictor of early strength loss. The carbohydrates were followed in sensitivity by galactose, mannose, xylose, and glucose. Sweet and Winandy (1999) further confirmed that FR-related chemical degradation was more related to hemicellulose depolymerization than to cellulose depolymerization. A comprehensive review of these relationships has recently been presented (Winandy and Rowell 2013).

Previous work found that the rate of strength degradation for untreated and FR-treated plywood increased as RH increased; a test method was developed to evaluate commercial FRT (Winandy et al 1991b). Subsequently, three consensus US standards evolved from that test method. To evaluate the data derived from the test method, several kinetics-based models for thermal degradation of FR-treated material were developed (Pasek and McIntyre 1990). Winandy and Lebow (1996) and Lebow and Winandy (1999a) built on that work to develop a single-stage kinetics-based model to predict the magnitude of thermal degradation for a series of FR model treatments. They further demonstrated that their single-stage model could accurately predict strength loss across a wide range of temperatures and exposure conditions. Other work has found that strength loss from cyclic thermal exposure was generally similar to that from steady-state temperature exposure when compared on a cumulative time-at-temperature basis (Le Van et al 1996). More recent work based on field experiments appears to confirm this similarity in steady-state and cyclic exposures (Barnes et al 2010).

The following critical needs were identified before we could develop the procedure(s) to assess current conditions and to eventually develop a predictive residual service life model for FR-treated plywood roof sheathing. We needed to 1) know the influence of processing effects; 2) develop methods to assess current conditions; 3) know thermal loads; and 4) develop an understanding of critical serviceability/durability factors. These projects included extramural cooperative agreements. To the extent possible, the various research components of this program were performed concurrently. Each project is briefly described subsequently.

Effects of Treatment and Processing Factors

The goals of this project were to 1) determine the governing relationships of treatment processing factors, mixtures of chemical components, and posttreatment temperature and moisture factors to in-service performance and to relate these relationships to in-service thermal- induced strength degradation rates; and 2) define the effects of initial plywood quality and its possible interaction with in-service thermal degradation.

Preliminary FPL results indicated that the level of degradation in mechanical properties and wood composition induced by steady-state laboratory exposure was often less than the magnitude of the degradation experienced in the field (Winandy et al 1991b). These differences in property degradation rates appeared to be related to the severity of the processing factors used in commercial treating and drying (Winandy 1994). It was initially suspected that these factors included the influence of the mixture of various FR chemical components used in commercial FR formulations, temperatures used in kiln-drying FR-treated material after treatment, and the presence or absence of posttreatment drying and/or wetting during storage or construction (Le Van et al 1990). Some experts also believe that roof cavity ventilation is a significant factor, and research continues to assess the importance of this. Overall, many product-manufacturing and treatment-processing factors contribute to the differential performance of laboratory and field materials.

Early in this processing factors phase of research, key experimental factors were identified using dynamic mechanical analysis of small plywood veneers about 1 mm thick (Le Van 1993). The key factors that influenced thermal degradation were FR retention and in-service moisture content. The results of that study were used in the larger second phase of this project to define experimental factors using full-sized, 19-mm-thick plywood specimens (Winandy 1997). In Figs 1-3, resistance to thermal degrade was directly related to the initial effect of the FRT on strength and appeared to be related to pH of the treating solution or wood. In the second phase, it was shown that control of the treating solution pH by adding acids or pH buffers, such as borates, could accelerate or mitigate the initial effect of FR on strength and then enhance resistance to subsequent thermal degradation (Fig 4) (Winandy 1997).

Variation in redrying temperatures from 49-88°C was shown to have little differential effect on the subsequent rate of thermal degradation when treated plywood was exposed at 65°C for up to 290 da (Fig 5). Furthermore, effects of thermal exposure during both redrying and in-service solar loading were shown to be cumulative on a time-at-temperature basis (Winandy

Figure 5. Effects of redrying temperatures at 54, 71, or 88°C on bending strength of 12-mm-thick fire retardant-treated plywood subsequently exposed to extended exposure at 66°C. MAP, monoammonium phosphate; KDAT, kiln-drying after treatment (Winandy 1997).

1997). Finally, Winandy and Schmidt (1995) found that remedial borate treatments were useful in mitigating additional thermal degrade.

To address our second goal, the influence of plywood quality on thermal degrade of various grades of FR-treated plywood was studied. At the time, the existing data on thermal effects on FR-treated plywood related to only one very high level of plywood quality. To limit property variability, early data were obtained from tests of high quality plywood, which was especially made from nearly clear veneers with no knots or interior voids and only minimal surface imperfections (Winandy et al 1991b). Additional information was then needed to adapt the thermal-effects data in the database to field applications using commercial quality plywood. Lebow and Winandy (1998) evaluated four grades and two thicknesses of commercial plywood. Results showed that the rate of strength loss in plywood resulting from FR treatment, posttreatment redrying, and subsequent high-temperature exposure was to a great extent independent of plywood quality or grade. Furthermore, although various grades of plywood had large absolute differences in strength, these differences remained relatively constant after treatment and exposure. With respect to the
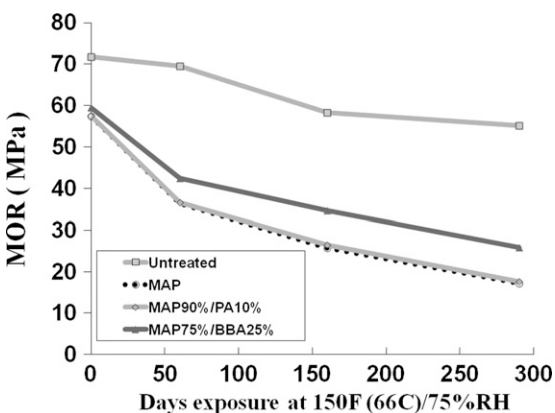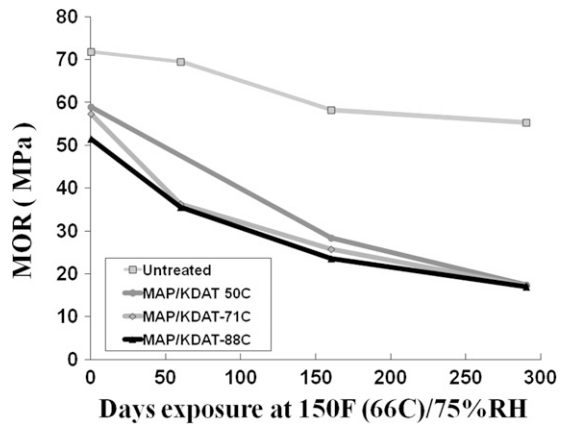

Figure 4. Effects of fire-retardant treatment mixtures on bending strength of 12-mm-thick plywood subsequently exposed to extended exposure at 66°C. MAP, monoammonium phosphate; PA, phosphoric acid; BBA, borax/boric acid (Winandy 1997).

influence of plywood thickness, although the initial treatment effect differed for the two plywood thicknesses tested, the relative loss in strength caused by thermal degrade resulting from exposure at high temperatures was similar for both thickness levels. Thus, thermal degrade results of an earlier study (Winandy et al 1991b) using high-quality N-grade plywood were readily applicable to commercial grades and thicknesses.

Defining Thermal Loads In-Service

In 1991, test chambers were initially built for both laboratory and outdoor field exposure in Madison, WI (latitude = 43.4° N). Maximum temperatures recorded in the 3-yr study for black-shingled roofs were 76, 58, and 54°C for the top-ply veneer, bottom ply, and internal rafter temperatures, respectively. Maximum temperatures recorded for white-shingled roofs were 64, 53, and 49°C for the top-ply veneer, bottom ply, and internal rafter temperatures, respectively. However, these were 3-yr maximums, and daily maximums were generally 10 to 20°C lower during the summer and 25 to 45°C lower during the winter. Overall, the plywood roof sheathing of black-shingled roofs was exposed to temperatures above 50°C five times more than the sheathing of white-shingled roof systems (364 h/yr for black shingles vs 73 h/yr for white). On sunny days, the temperature of the top ply of plywood roof sheathing under black shingles was generally 5 to 8°C warmer than that of identical white-shingled roof structures. However, after dark, the black-shingled roof temperature quickly cooled and temperatures were similar to those of white-shingled roofs.

These data confirmed that roof sheathing plywood and roof truss lumber temperatures, which are the primary factors influencing thermal degrade of FR-treated materials, are primarily controlled by solar gain. However, the effect of moisture content was not evaluated nor was moisture content controlled by attic ventilation.

Five additional field chambers were constructed in 1994 under a USDA competitive grant and an extramural cooperative project with the Mississippi Forest Products Laboratory near Starkville, MS. These new chambers provided for direct comparisons between northern and southern US climates as well as comparisons between dry and humidified attics. Roof temperature data are now available for 8 yr in Madison, WI (latitude 43.4° N) and 4 yr in Starkville, MS (latitude 33.5° N) (Winandy et al 2000).

Maximum temperatures recorded in the 4-yr Mississippi study for black-shingled roofs in dry unvented buildings were 78, 63, and 58°C for the top-ply veneer, bottom ply, and nominal 2 by 8 (38 × 184 mm) rafters (internal temperatures), respectively. Maximum temperatures recorded for the matched dry unvented Wisconsin roof systems during an 8-yr period were 75, 59, and 54°C, respectively.

Maximum temperatures recorded in the 4-yr Mississippi study for black-shingled roofs in heavily humidified buildings were the coolest at 74, 58, and 54°C for the top-ply veneer, bottom ply, and 2 × 8 (38 × 184 mm) rafters (internal temperatures), respectively. Daily maximums and annualized temperature data for each wood component exhibited similar differences to that of the previously reported 3-yr Madison data (Winandy and Beaumont 1995). These results clearly indicated that the temperatures of wood components used in wood roof systems were dictated more by the influx of radiant solar energy than by ambient outside air temperatures (Winandy et al 2000).

Modeling the Potential for Thermal Degrade

Many of the various data derived by many of the research programs described in this review were then compiled to develop kinetic-based degradation models (Fig 6) (Winandy and Lebow 1996; Lebow and Winandy 1999a). These kinetic models clearly indicated that thermal degradation of wood, treated or untreated, was in an absolute sense occurring, but for all intents and purposes, it was virtually negligible at less than 50°C. At steady-state temperature exposures of 50-60°C and after extended
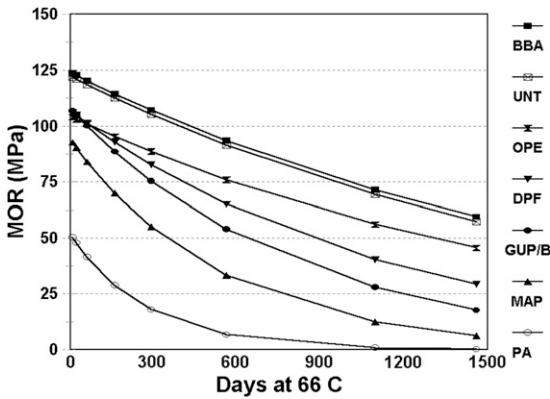
Figure 6. Predicted bending strength using kinetic models for various treated and untreated small clear pine wood specimens after up to 4 yr of steady-state exposure at 66°C. PA, phosphoric acid; MAP, monoammonium phosphate; GUP/B, guanylurea phosphate/boric acid. DPF, dicyandiamide-phosphoric acid–formaldehyde; OPE, organophosphonate ester; UNT, untreated; BBA, borax/boric acid (Lebow and Winandy 1999a).

decades of exposure to typical diurnal moisture/temperature cycling such as in roof systems, the extent of thermal degrade under typical cyclic, diurnal exposures can be important and should be evaluated using appropriate ASTM test methods and the standard practices for evaluating those test data. In this steady-state temperature exposure of 50-60°C and when exposed to long-term cyclic temperatures in this range,
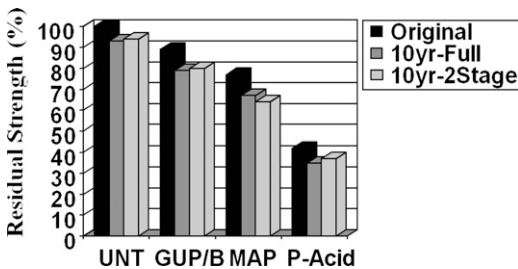

Figure 7. Predicted change in residual strength ratio, defined as ratio of strength of treated to untreated (UNT) wood, comparing two models as defined by Lebow and Winandy (2003) using simulated 10-yr exposure data (from Winandy et al 2000) in north–central US and kinetics-based models of Lebow and Winandy (1999a). GUP/B, guanylurea phosphate/boric acid; MAP, monoammonium phosphate; P, phosphoric acid.

wood has been shown to be a consistent viable material for use in roof systems except when treated with only the more reactive treatment chemicals. When extensive exposures above 60°C are expected, the serviceability of treated and untreated wood must be considered. Many such field serviceability issues have been extensively studied (TenWolde 1997; Winandy et al 2000; Winandy 2001; Barnes et al 2010). Based on both these kinetic models and field serviceability experience and findings, service life models for treated and untreated plywood roof sheathing and roof truss lumber were developed to predict residual serviceability of wood roof systems (Fig 7) (Lebow and Winandy 2003).

SUMMARY

This review provides a fundamental understanding of the factors dictating the effects of FR treatments on wood properties, both initial processing effects and in-service effects, when exposed to elevated temperatures. By reviewing the results of a comprehensive series of research studies, this review has shown that the effects of long-term thermal exposure on wood products (treated, untreated, and/or veneered composites) are a complex function of wood composition, acidity of chemicals used to treat the products, temperatures used in various pre- and posttreatment processing conditions, material size and species, and in-service exposure conditions and durations. To better predict these effects, standards were developed to assess initial and in-service performance. Alternative technologies were also developed, aimed at extending the service life of wood used as structural systems. Also, new analytical tools for providing a more accurate condition assessment and models for predicting residual serviceability were developed. In summary, these developments have increased the utility and serviceability of wood-based structures, increased the reliability and long-term efficiency of such structures, and decreased their environmental footprints by making existing products last longer, thereby decreasing the need for replacement products.

REFERENCES

Alexiou PN, Gardner WD, Lind P, Butler D (1986) Efficacy of an amino resin fire retardant. Forest Prod J 36(11/12):9-15.

Angell HW (1951) The production and use of fire retardant treated lumber. Proc Forest Prod Res Soc 5:107-114.

APA (1989) Fire-retardant-treated plywood roof sheathing: General information. APA-Engineered Wood Association, Tacoma, WA.

ASTM (2012a) D 5516-09. Standard test method for evaluating the flexural properties of fire-retardant treated softwood plywood exposed to elevated temperatures. Annual book of standards. 4.10. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2012b) D 5664-08. Standard test method for evaluating the effects of fire-retardant treatments and elevated temperatures on strength properties of fire-retardant treated lumber. Annual book of standards. Vol. 4.10. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2012c) D 6305-08. Standard practice for deriving allowable stress design adjustments for fire-retardant treated softwood plywood. Annual book of standards. Vol. 4.10. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (2012d) D 6841-08. Standard practice for deriving allowable stress design adjustments for fire-retardant treated lumber. Annual book of standards. Vol. 4.10. American Society for Testing and Materials, West Conshohocken, PA.

AWPA (1946) Report of special committee on fire retardants. Proc American Wood-Preservers' Association 42:333-359.

AWPA (1959) Report of committee C-20 fire retardant wood. Proc American Wood-Preservers' Association 55:121.

AWPA (1963) Report of committee T-5 lumber and timber. Proc American Wood-Preservers' Association 59:117-121.

AWPA (1969) P 10-68 Fire retardant formulations. Annual book of standards. American Wood-Preservers' Association, Washington, DC.

AWPA (1974) Report of committee T-2 lumber and timber. Proc American Wood Preservers' Association 70:141-143.

AWPA (2002a) C20-98 Structural lumber-fire retardant treatment by pressure processes. Annual book of standards. Treatment. American Wood-Preservers' Association, Birmingham, AL.

AWPA (2002b) C27-98 Plywood: Fire retardant treatment by pressure processes. Annual Book of standards. Treatment. American Wood-Preservers' Association, Birmingham, AL.

AWPA (2002c) P17-98 Fire retardant formulations. Annual book of standards. Treatment. American Wood-Preservers' Association, Birmingham, AL.

AWPA (2012a) T-1-12 Standard for pressure-treated wood. Annual book of standards. Treatment. American Wood Protection Association, Birmingham, AL.

AWPA (2012b) U-1-12 Use category system: User specification for treated wood. Annual book of standards. Treatment. American Wood Protection Association, Birmingham, AL.

Barnes HM (1993) US experience with flame retardants. In Papers of Oxford Fire Conference, Mansfield College, Timber Research and Development Assoc, ed. Oxford, UK, July 1-2, 1993. TRADA, High Wycombe, UK. 33 pp.

Barnes HM (1994) A historical perspective of fire retardant. Proc American Wood Preservers' Assoc 90:413-433.

Barnes HM, Winandy JE, McIntryre CM (2010) Laboratory and field exposures of FRT plywood: Part 2—Mechanical properties. Wood Fiber Sci 42(1):30-45.

Bateman E (1929) Relation of atmospheric humidity to concentration of zinc chloride solution. Proc American Wood Preservers' Assoc 25:120-125.

Beall FC (1971) Differential calometric analysis of wood and its components. Wood Sci Technol 5:159-175.

Beall FC, Eickner HW (1970) Thermal degradation of wood components: A review of the literature. Res Pap FPL-RP-130 USDA For Serv Forest Prod Lab, Madison, WI.

Blew JO (1946) The effect of treatments with wood preservatives and fire-retarding chemicals on glue joints in birch plywood. Proc American Wood Preservers' Assoc 42:364-385.

Blew JO, Olson WZ (1950) The durability of birch plywood treated with wood preservatives and fire-retarding chemicals. Proc American Wood Preservers' Assoc 46:323-338.

Brenden JJ (1967) Effect of fire-retardant and other inorganic salts on pyrolysis products of Ponderosa Pine at 250° and 350°C. Res Pap FPL-RP-80 USDA For Serv Forest Prod Lab, Madison, WI.

Browne FL (1958) Theories of the combustion of wood and its control. Forest Products Laboratory Report No. 2136 USDA For Serv Forest Prod Lab, Madison, WI.

Browne FL, Tang WK (1963) Effect of various chemicals in the thermogravimetric analysis of ponderosa pine. Res Pap FPL-RP-6 USDA For Serv Forest Prod Lab, Madison, WI.

Catchpole RF (1976) A thumbnail history of fire-retardants treated wood and its acceptance by building codes. Proc American Wood Preservers' Assoc 72:152 – 156.

Chung DJ, Jo JS, Yun KE, Kim JJ, Kim GH (1999) Effect of fire-retardant treatment and redrying on mechanical properties of radiate pine. Mokchae Konghak 27(1):37-49.

Countryman D (1957) Effects on plywood strength of preservative treatment. Lab. Rep. 74. Douglas-fir Plywood Assoc., Tacoma, WA. 4 pp.

Eickner HW, Stinson JM, Jordan JE (1969) Ammonium polyphosphate liquid fertilizer as a fire retardant for wood. Proc American Wood Preservers' Assoc 65:260-271.

Ellis WD, Rowell RM, Le Van SL, Susott RA (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, Wegener G (1984) Wood: Chemistry, ultrastructure, reactions. DeGruyter, Berlin, Germany.

FPL (1999) Wood handbook: Wood as an engineering material. Gen Tech Rep FPL-GTR-113 USDA For Serv Forest Prod Lab, Madison, WI. 463 pp.

FPL (2010) Wood handbook: Wood as an engineering material. Gen Tech Rep FPL-GTR-190 USDA For Serv Forest Prod Lab, Madison, WI.

Fung DP, Tsuchiya CY, Sumi K (1972) Thermal degradation of cellulose and levoglucosan—The effect of inorganic salts. Wood Sci 5(1):38-43.

Gardner RE (1965) The auxiliary properties of fire-retardant treated wood. Forest Prod J 15(9):365-368.

Gerhards CC (1970) Effect of fire-retardant treatment on bending strength of wood. Res Pap FPL-RP-145 USDA For Serv Forest Prod Lab, Madison, WI.

Gerhards CG (1982) Effect of moisture content and temperature on the mechanical properties of wood: An analysis of immediate effects. Wood Fiber Sci 14(1):4-36.

Gottschalk FW (1944) Some technical factors in fire-retardant treatment. Proc American Wood Preservers' Assoc 40:368-385.

Graham RD (1964) Strength of small Douglas-fir beams treated with tire retardants. Proc of American Wood Preservers' Assoc. AWPA, Granbury, TX. 60:172-177.

Green DW, Evans JW (2003) Durability of structural lumber products at high temperatures. Part I. 66°C at 75% RH and 82°C at 30% RH. Wood Fiber Sci 34(4):499-523.

Hillis WE (1975) The role of wood characteristics in high-temperature drying. J I Wood Sci 7(2):60-67.

Hirata T (1979) Changes in the degree of polymerization and weight of cellulose untreated and treated with inorganic salts during pyrolysis. Forest and Forest Prod. Res. Inst., Japan Wood Res Soc Bull. Pages 77-124.

ICC-ES (2012) AC-66: Acceptance criteria for fire-retardant-treated wood. International Code Council-Evaluation Services, Whittier, CA. http://www.icc-es.org/criteria/pdf_files/ac66.pdf (16 November 2012).

Ifju G (1964) Tensile strength behavior as a function of cellulose in wood. Forest Prod J 74(8):366-372.

Jessome AP (1962) Strength properties of wood treated with fire retardants. Rep 193. Forest Prod Res Branch, Dept. of Forestry, Ottawa, Ontario, Canada.

Johnson JW (1967) Bending strength of small joists of Douglas-fir treated with fire retardants. Rep T-23. Forest Res Lab, Oregon State Univ., Corvallis, OR. 12 pp.

Johnson JW (1976) Lateral bearing strength of fasteners in lumber-plywood joints treated with fire retardants. Research Paper 28. Forest Res Lab, Oregon State Univ., Corvallis, OR. 28 pp.

Kass A, Wangaard FF, Schroeder HA (1970) Chemical degradation of wood: The relationship between strength and pentosan content. Wood Fiber Sci 2(1):31-39.

King EG Jr., Matteson DA Jr. (1961) Effects of fire-retardant treatments on the mechanical properties of Douglas-fir plywood. Lab Rep 90. Douglas-fir Plywood Assoc., Tacoma, WA. 14 pp.

Koch P (1976) Strength of southern pine lumber dried at high temperature. *In* Proc Res Conf High-Temperature Drying Effects on Mechanical Properties of Softwood Lumber, Feb 25-26, 1976. USDA Forest Serv Forest Prod Lab, Madison, WI.

Lebow PK, Winandy JE (1999a) Verification of a kinetic model for the effects of FR on bending strength at elevated temperatures. Wood Fiber Sci 31(1):49-61.

Lebow PK, Winandy JE (2003) Using kinetic models to predict thermal degradation of fire-retardant-treated plywood roof sheathing. Proc 31st Annual Conference of North American Thermal Analysis Society, Sept 22-24, 2003, Albuquerque, NM. Paper 048. 10 pp.

Lebow ST, Winandy JE (1998) The role of grade and thickness in the degradation of fire-retardant-treated plywood. Forest Prod J 48(6):88-94.

Lebow ST, Winandy JE (1999b) Effect of fire-retardant treatments on plywood pH and the relationship of pH to strength properties. Wood Sci Technol 33(4):285-298.

Le Van SL (1984) Chemistry of fire retardancy. *In* RM Rowell, ed. The chemistry of solid wood. ACS #207. American Chemical Society, Washington, DC.

Le Van SL (1993) Parametric evaluation of dynamic mechanical analysis of variables influencing strength degradation. MS thesis, Dept. of Chemical Engineering, University of Wisconsin, Madison, WI.

Le Van SL, Collet M (1989) Choosing and applying fire-retardant treated plywood and lumber for roof designs. Gen Tech Rep FPL-GTR-62 USDA For Serv Forest Prod Lab, Madison, WI.

Le Van SL, Holmes CA (1986) Effectiveness of fire-retardant treatments for shingles after 10 years of outdoor weathering. Res Pap FPL-RP-474 USDA For Serv Forest Prod Lab, Madison, WI.

Le Van SL, Kim JM, Nagel RJ, Evans JW (1996) Mechanical properties of fire-retardant-treated plywood after cyclic temperature exposure. Forest Prod J 46(5):64-71.

Le Van SL, Ross RJ, Winandy JE (1990) Effects of fire retardant chemicals on the bending properties of wood at elevated temperatures. Res Pap FPL-RP-498 USDA For Serv Forest Prod Lab, Madison, WI.

Le Van SL, Winandy JE (1990) Effects of fire retardant treatments on wood strength: A review. Wood Fiber Sci 22(1):113-131.

Luther HB (1921) The effect of zinc chloride process of preservation on the strength of structural timber. Proc American Wood Preservers' Assoc 17:89-114.

Lyon DE, Bigbee KL, McNamara WS (1988) Evaluation of strength properties of FRT wood using the 1983 NFPA protocol. Forest Prod J 38(6):13-18.

Lyons JW (1970) The chemistry and uses of fire retardants. Wiley-Interscience, New York, NY. 462 pp.

McFarland WA, Angell HW (1946) Plant control and inspection of fire retardant treatment. Proc American Wood Preservers' Assoc 42:305-317.

McKnight TS (1962) The hygroscopicity of wood treated with fire-retarding compounds. Rep 190. Forest Prod Res Branch, Dept of Forestry, Ottawa, Ontario, Canada.

O'Neil MJ, ed. (2006) Merck index. 14th ed. Merck Publishing. Rahway, NJ.

Millett MA, Gerhards CC (1972) Accelerated aging: Residual weight and flexural properties of wood heated in air at 115 to 175°C. Wood Sci 4(4):193-201.

NAHB (1990) Home builders guide to fire retardant treated plywood: Evaluation, testing and replacement. National Association of Home Builders, National Res Lab, Washington, DC. 65 pp.

NFPA (1974) National design specification for wood construction. National Forest Products Association, Washington, DC.

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

Oberley WJ (1983) Non-resinous, uncured fire retardant and products produced therewith. US Patent 4,373,011.

Pasek EA, McIntyre CR (1990) Heat effects on fire retardant-treated wood. J Fire Sci 8:405-415.

Shafizadeh F (1984) Pyrolysis and combustion. *In* RM Rowell, ed. The chemistry of solid wood. ACS #207. American Chemical Society, Washington, DC.

Stamm AJ (1964) Wood and cellulose science. Roland Press, New York, NY.

Sweet MS, Winandy JE (1999) Influence of degree of polymerization of cellulose and hemicellulose on strength loss in fire-retardant-treated southern pine. Holzforschung 53(3):311-317.

TenWolde A (1997). The FPL roof temperature and moisture model. Res Pap FPL-RP-561 USDA For Serv Forest Prod Lab, Madison, WI.

US Navy (1944) Military Spec M51C38. Chemicals: Fire retardant for lumber and plywood. US Navy, Washington, DC.

Wang Q, Li J, Winandy JE (2004) Chemical mechanism of fire retardance of boric acid on wood. Wood Sci Technol 38:375-389.

Wang SY, Rao YC (1999) Structural performance of fire-retardant treated plywood: effect of elevated temperature. Holzforschung 53:547-552.

Werren F (1962) Effect of a commercial fire-retardant treatment on the bending properties of glued-laminated southern pine beams. FPL Library File L 4-3-2. USDA For Serv Forest Prod Lab, Madison, WI.

Wilson TRC, Bateman E (1921) Results of some testes on the effect of zinc chloride on the strength of wood. Proc American Wood Preservers' Assoc 17:80-88.

Winandy JE (1990) Fire-retardant treated wood: Effects of elevated temperature and guidelines for design. Wood Design Focus 1(2):8-10.

Winandy JE (1994) Serviceability modeling of fire-retardant-treated plywood roof sheathing. Pages 292-297 *in* Proc. Pacific Timber Engineering Conf, Vol. 2, Gold Coast, Queensland, Australia, July 11-15, 1994. Timber Research and Development Council, Fortitude Valley, Queensland, Australia.

Winandy JE (1995) Effects of fire retardant treatments after 18 months of exposure at 150°F (66°C). Res Note FPL-RN-0264 USDA For Serv Forest Prod Lab, Madison, WI.

Winandy JE (1997) Effects of fire retardant retention, borate buffers, and redrying temperature after treatment on thermal-induced degradation. Forest Prod J 47(6):79-86.

Winandy JE (2001) Thermal degradation of fire-retardant-treated wood: Predicting residual service-life. Forest Prod J 51(2):47-54.

Winandy JE, Barnes HM, Hatfield C (2000) Roof temperature histories in matched attics in Mississippi and Wisconsin. Res Pap FPL-RP-589 USDA For Serv Forest Prod Lab, Madison, WI.

Winandy JE, Beaumont R (1995) Roof temperatures in simulated attics. Res Pap FPL-RP-543 USDA For Serv Forest Prod Lab, Madison, WI.

Winandy JE, Lebow PK (1996) Kinetic model of the effects of fire retardants on properties of wood at elevated temperatures. Wood Fiber Sci 28(1):39-52.

Winandy JE, Lebow PK (2001) Modeling wood strength by chemical composition. Part I. An individual component model for southern pine. Wood Fiber Sci 33(2):239-254.

Winandy JE, Le Van SL, Ross RJ (1991a) Fire-retardant-treated wood: Research at the Forest Products Laboratory. Pages 69-74 *in* Proc. 2nd Int Timber Engineering Conf, Vol. 4. TRADA, London, UK.

Winandy JE, Le Van SL, Ross RJ, Hoffman SP, McIntyre CR (1991b) Thermal degradation of fire-retardant treated plywood: Development and evaluation of a test protocol. Res Pap FPL-RP-501 USDA For Serv Forest Prod Lab, Madison, WI.

Winandy JE, Le Van SL, Schaffer EL, Lee PW (1988) Effects of fire retardant treatment and redrying on the mechanical properties of Douglas-fir and aspen plywood. Res Pap FPL-RP-485 USDA For Serv Forest Prod Lab, Madison, WI.

Winandy JE, Rowell RM (2013) Chemistry of wood strength. Pages 413-455 *in* RM Rowell, ed. The handbook of wood chemistry and wood composites. 2nd ed. CRC Press, Taylor & Francis Group, Boca Raton, FL.

Winandy JE, Schmidt EL (1995) Preliminary development of remedial treatments for thermally degraded fire-retardant-treated wood. Forest Prod J 45(2):51-52.

Woo JK (1981) Effect of thermal exposure on strength of wood treated with fire retardants. PhD thesis, Univ. of California, Berkeley, CA. 112 pp.

Yao J, Taylor F (1979) Effect of high-temperature drying on the strength of southern pine dimension lumber. Forest Prod J 19(8):49-51.