

## Protection from Fire

C R McIntyre, McIntyre Associates, Walls, MS, USA

© 2004, Elsevier Ltd. All Rights Reserved.

### Introduction

Wood has been an excellent building material for many centuries; however, its ability to ignite and burn has limited its use in many applications. Applications of various fire retardant chemicals has expanded the use of wood and provided significant safety to occupants of wooden buildings. The fire-retardant systems used for wood generally contain nitrogen, boron, and phosphorus chemicals. The properties of specific formulations and their advantages and disadvantages are discussed in this article, and the modes of action and testing procedures for fire retardants are also given.

### History of Fire Retardants

Although various chemicals were utilized through history, the modern use of fire retardants for wood stems from 1820 when Gay-Lussac developed treatments with ammonium phosphates and borax. The full impact of this invention can be gauged by the realization that systems similar to this are still in use today. But there have been many other inorganic chemicals investigated as fire retardants in the intervening years. Around 1900, formulations based on silicates, sulfates, borates, phosphates, zinc, tin, and calcium were in vogue and by 1915, ammonium chlorides, phosphates, and sulfates were known to be effective for wood.

From 1930 to 1935, researchers at the US Department of Agriculture Forest Products Laboratory (FPL) reported on investigations of about 130 different inorganic fire retardant formulations. It was found that diammonium phosphate was the most effective for reducing flame spread while mono-ammonium phosphate, ammonium chloride, ammonium sulfate, borax, and zinc chloride were also active. However, many of the chemicals in this test program had associated problems of high cost, corrosion, hygroscopicity, strength reduction, or glow promotion. Therefore, other approaches such as *in situ* polymerizations or reactions of retardants with wood components were investigated.

By the 1950s, there were several formulations in commercial use for pressure treating wood. (Fire retardant coatings were also being investigated but, as discussed later, their acceptance and regulation lagged that of pressure treated products.) The

American Wood-Preservers' Association (AWPA) listed four formulations and the US Navy allowed several others for shipboard use (Table 1). All of these formulations were inorganic combinations blended to achieve a reasonable compromise of cost and acceptable performance. However, in the 1960s, three formulations similar to the four AWPA formulations had supplanted the previous ones and were by far the dominant retardants (Table 2).

In the late 1960s, formulations were introduced in the USA and Canada that protected exterior products such as shingles, shakes, and siding or scaffold planking that are exposed to the elements. These systems typically injected the precursors to a nitrogenous polymer system such as urea-formaldehyde or melamine-formaldehyde along with phosphoric acid into the wood. Then a special kiln cycle was used to effect an *in situ* polymerization that encapsulated the phosphoric acid and rendered it

**Table 1** 1950s formulations for five retardants

AWPA formulation ingredients	Percent
1. Chromated zinc chloride (CZC)	
ZnCl <sub>2</sub>	> 77.5
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	> 17.5
2. Chromated zinc chloride FR	
CZC (above)	80
H <sub>3</sub> BO <sub>3</sub>	10
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	10
3. Minalith	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	60
H <sub>3</sub> BO <sub>3</sub>	20
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	10
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	10
4. Pyresote	
ZnCl <sub>2</sub>	35
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	35
H <sub>3</sub> BO <sub>3</sub>	25
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O	5
Other formulation ingredients	
5.	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	> 78
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> or (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	> 19
6.	
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	60
H <sub>3</sub> BO <sub>3</sub>	40
7.	
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	67–70
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	33–30
8.	
ZnCl <sub>2</sub>	54
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	46

Source: Prepared from AWPA and other documents cited.

**Table 2** Interior formulations from the 1960s and 1970s

Formulation ingredients	Percent
1.	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	50
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	41
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	7
Moldicide	2
2.	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	45
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	45
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	6
H <sub>3</sub> BO <sub>3</sub>	4
3.	
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	65
H <sub>3</sub> BO <sub>3</sub>	35

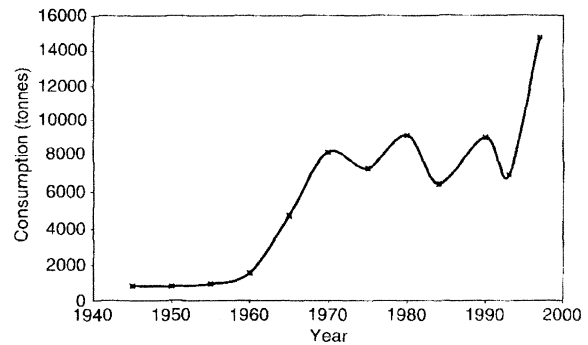
Source: Prepared from AWPA and other documents cited.

leach resistant. The kiln cycle called for moderate temperatures (70°C) for 2–3 days or until the wood was below 25% moisture content and then elevation of the kiln temperature to 100°C for up to 24 h to complete the reaction.

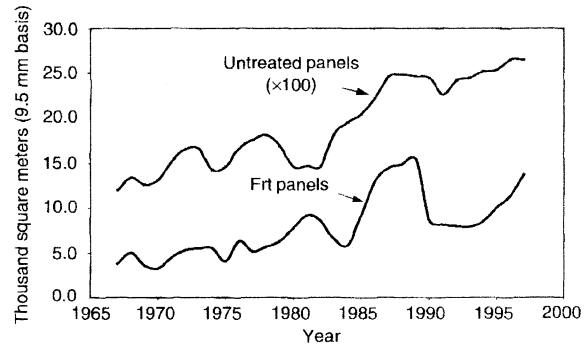
The use of fire retardants climbed very slowly in the USA until the 1960s (Figure 1). Then from 1960 to 1970, the use quadrupled as new formulations became available that expanded the useful applications for fire retardants. There was also an increased awareness of the considerable safety benefits of fire retardants. However, the emergence of corrosion, hygroscopicity, and strength problems began to plague the industry and the market grew only slightly until 1980. Building code changes were implemented in the late 1970s that opened up a major new end use for roof framing and sheathing (predominately plywood) in buildings that otherwise were required to be constructed from noncombustible materials. At about that time, replacements for the above first-generation retardant systems were also being developed.

In the early 1980s, second-generation fire retardants were introduced to address the corrosion and hygroscopicity problems of the first-generation inorganic formulations. One new product was an 'organic' that was a blend of guanidureaphosphate (GUP, formed by the reaction of dicyandiamide with phosphoric acid) with boric acid. There were several other second-generation formulations that were based on ammonium polyphosphates with or without various additives in small quantities. The additives included boric acid, borax, moldicides, and the like.

However, in the late 1980s, reports began to surface that some of the second-generation formulations were experiencing strength loss in high temperature applications such as roof sheathing. After



**Figure 1** US consumption of fire retardants for wood. Prepared from AWPA publications.



**Figure 2** Annual production in the USA of fire retardant treated and untreated panels. Prepared from AWPA and FPL publications.

the initial concern that all second-generation products were involved, it was found that problems were occurring with only some formulations. Multiple lawsuits occurred and further investigations revealed that high humidity conditions frequently existed in problem installations. Numerous causes were alleged for the strength problems and the end result was that the overall market for fire retardants was severely impacted.

Prior to these problems, the market had accepted the second-generation products and growth in treated panels had matched that of untreated panels (Figure 2), but the threat of litigation soon caused a steep decline in volume in the early 1990s. Most of the ammonium polyphosphate containing products were removed from the market as well.

At the onset of the heat degradation problem, researchers at the FPL and elsewhere began investigating the issue. During the next several years a series of publications delineated that certain combinations of fire retardant ingredients with elevated temperatures and humidities would cause liberation of acidic moieties that in turn attacked certain components of the wood. Without these components, the wood quickly lost its strength. Throughout this work,

various laboratory tests were performed for exposure periods of up to 5 years at elevated temperatures and strength testing was done on the aged wood. These results led to development of test protocols for evaluating strength properties of fire retardant wood.

In particular, two organizations, ASTM International (American Society for Testing and Materials, ASTM) and AWWA, were very active in developing new test procedures and standards to address strength issues. In the late 1980s when the apparent strength problem was first becoming known, ASTM issued an emergency standard that addressed strength losses for plywood exposed at elevated temperatures and humidities. In this emergency standard, which later became ASTM D5516, plywood is exposed for at least 60 days at temperatures of 77°C and 50% relative humidity. The strength reductions from exposure can then be used to develop design adjustment factors for the fire retardant formulation using a computer based modeling approach detailed in ASTM D6305 that considers climatic data. Similar testing procedures and design adjustment methodology for fire retardant lumber are detailed in D5664 and D6841. The AWWA have revised their standards related to fire retardants to require strength testing by the above ASTM procedures and incorporated recommended minimum acceptable levels of strength loss.

These actions have given specifiers the needed confidence to again use fire retardant treated wood without fear of premature strength loss. These tests were quickly adopted by building codes and other regulators with the result that several products are currently available that give excellent strength performance. Corrosion and hygroscopicity concerns that had plagued the first-generation products have also been addressed. Today's products are no more corrosive than untreated wood and do not display any significantly different moisture content up to 92% relative humidity.

The significant commercial formulations now accepted in the US and Canada are the GUP/BA combination, a similar urea-boric acid combination, a nonphosphate containing mixture of nitrogen and borate compounds, and a combination of diammonium phosphate and boric acid where sufficient boric acid is available to buffer any free phosphate acids produced. The market has readily accepted the current formulations and substantial growth has occurred in the last decade (Figure 1).

## Testing of Fire Retardants

### Commercial Testing

For commercial purposes, the dominant test for fire retardant treated wood is the measurement of surface

flame spread by use of ASTM E84. In this test, the treated material forms the roof of a 24-ft long (7.3 m) tunnel and the wind-aided spread of flame is tracked for 10 min. For all structural applications of fire retardant treated wood, building codes require that the test duration be extended an additional 20 min without significant progressive combustion. A standard ignition flame is used and the tunnel is calibrated to have a flame spread rating of 0 using an inert cement board and a rating of 100 using red oak flooring. The flame spread of the test product is determined under these standard conditions and flame spread ratings for fire retardant treated and untreated wood are discussed later. A smoke rating is also obtained during the tunnel test and most uses allowed in the building codes require a smoke level of less than 450.

Typically, a supplier of a fire retardant formulation will contract with a testing laboratory such as Underwriters Laboratory (ULI) to conduct the testing on a number of species of lumber. Various plywood species and grades may also be tested. The testing laboratory monitors all phases of the preparation of the test material. Upon completion of successful testing, the laboratory then lists the materials as acceptable in their publications and issues identification stamps or labels that are used to indicate to others that the material passes recognized testing protocols.

The building codes classify materials in broad ranges of flame spread based on the first 10 min of test: Class I or A has a flame spread of 0–25, Class II or B is 26–75, and Class III or C is 76–200. Class I material can be used in more critical applications such as on the walls of exit corridors while the others are used in less critical applications where there is less risk to human life if a fire occurs. For structural uses of fire retardant treated wood where the E-84 test is extended for an additional 20 min of flame there cannot be any sign of significant progressive combustion as defined in the standard.

When treated with fire retardants, structurally qualified species have a 10-min rating of less than 25 and there is no significant progressive combustion when the test is extended to a 30-min total burning time. All of the commonly available lumber species and plywood sizes are available with this classification. Understandably, the flame spread ratings of untreated wooden commodities lie near 100 since the tunnel is calibrated at that value for red oak. A number of important species and materials have been tested and the flame-spread values for the untreated wood are given in Table 3. Note though that some species such as southern pine (*Pinus*) can have a much higher flame spread than the others when untreated due to their higher resin content.