

Protection from Fire

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

Source: Prepared from AWPA and other documents cited.

Table 2 Interior formulations from the 1960s and 1970s

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

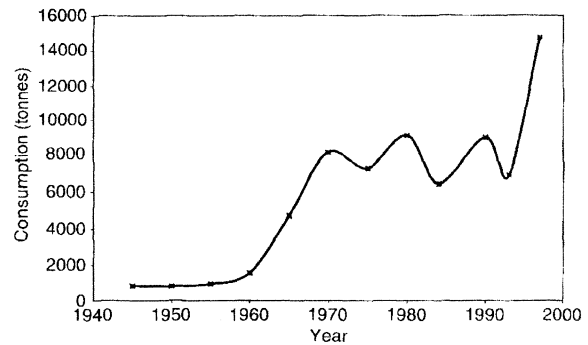


Figure 1 US consumption of fire retardants for wood. Prepared from AWPA publications.

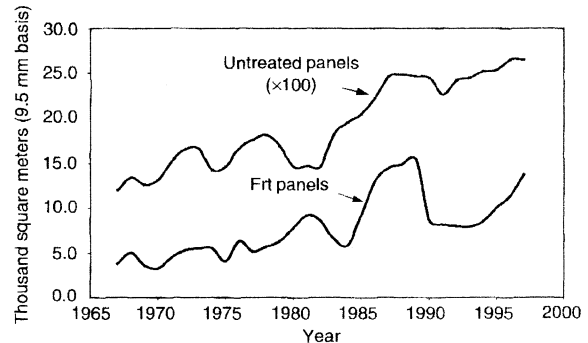


Figure 2 Annual production in the USA of fire retardant treated and untreated panels. Prepared from AWPA and FPL publications.

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.

Table 3 Flame spread indices for untreated wood

	<i>Flame spread index</i>
Lumber	
Western redcedar	70
Douglas-fir	70–100
Maple (flooring)	105
Oak, red	100
Pine, white	75–85
Pine, southern yellow	130–195
Redwood	70
Spruce, Sitka	75
Plywood	
Softwood	
Douglas-fir (10 mm)	110–150
Southern pine (10 mm)	100–105
Hardwood	
Birch (6 mm)	115–185
Lauan (6 mm)	100–140
Oak (6 mm)	125–185

Source: Prepared from American Wood Council *Flame Spread Performance of Wood Products*. Available online at <http://www.awc.org>.

Spray or brush applied fire retardant coatings for wood differ significantly from pressure treated formulations in that they are only tested for 10 min total and then assigned a flame spread rating. Thus, they do not have the additional structural designation. Also, coatings are limited to only one species, Douglas-fir (*Pseudotsuga menziesii*), and are not available for a wide variety of products.

Other important tests for commercial fire retardants include measuring:

- heat release rate
- smoke density
- lateral spread of flame
- smoke toxicity
- ancillary properties: corrosion, hygroscopicity, strength.

There are a number of test procedures used to document the above properties and specific protocols can be found in ASTM, AWPA, Factory Mutual (FM), International Standards Organization (ISO), and ULI documents. It should be noted that in recent years, the fire research community has expended great effort to harmonize the North American and ISO standards on fire testing. However, many differences still exist in the standards and one should not assume interchangeability of the standards from different organizations.

There are also applications where the fire resistance properties of fire retardant wood are more important than the surface spread of flame. For these

tests, the ability of wood to resist burn through is challenged and typically these tests are done on large assemblies such as walls or doors. In these cases, the fire retardant wood contributes a portion of the total assembly properties.

Historically, in Europe, fire resistance properties have been more important than flame spread and the test procedures produce ratings based on measuring resistance. Imparting resistance requires significantly higher retentions of fire retardants wood and this leads to higher costs. Therefore the use of fire retardants in Europe has lagged behind that of North America.

In recent years, there has been an increasing use of fire retardants in Europe for nonstructural products such as wall linings and siding (cladding). There is still only limited use in structural applications. However, there are a number of modified protocols being proposed and/or accepted as part of the European Union process so current affairs in Europe regarding fire retardants for wood are in a state of flux. Presumably these changes will lead to further increases in use.

Laboratory Testing

A number of testing techniques are used for the development of fire retardant formulations. In the past, the fire tube test (ASTM E69), 2-ft (60 cm) tunnel, and other small-scale fire tests were used. However these tests were frequently misleading in that their reproducibility is relatively poor. Consequently, in recent years most researchers have migrated to thermal analysis and other more sophisticated test equipment such as the cone calorimeter.

For fire retardants, the two most important thermal tests are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA measures weight loss as the sample is heated while DTA measures exothermic or endothermic reactions that occur as the sample is heated. Most modern thermal analysis equipment can provide TGA and DTA data simultaneously and the combination can help guide the researcher. The testing can be done in an inert gas atmosphere so that pyrolysis occurs or in oxygen so that combustion occurs. Although the chemical processes for pyrolysis and combustion are similar, the relative degree of formation of various products can greatly differ.

Typical TGA curves are shown in Figure 3 for untreated and wood treated with two different commercial fire retardant formulations. Note that the dominant effect of the fire retardants is to reduce the onset of decomposition to around 200°C and to increase the amount of residue (char) from 1–2% to about 20% when the TGA furnace reached 500°C.

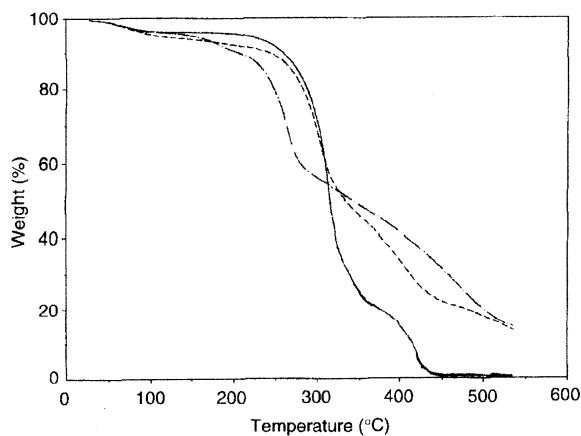


Figure 3 Typical thermogravimetric analyses of fire retardant treated and untreated wood. Solid line, untreated wood; dashed line, commercial formula A; dash-dot line, commercial formula B.

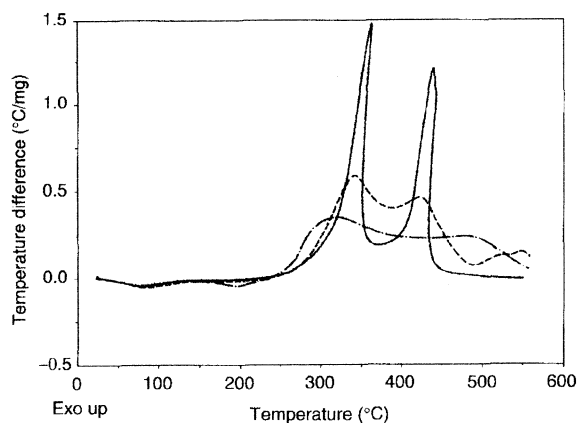


Figure 4 Typical differential thermal analyses of fire retardant treated and untreated wood. Solid line, untreated wood; dashed line, commercial formula A; dash-dot line, commercial formula B.

The DTA curves that correspond to these samples are shown in **Figure 4**. In these cases, most of the samples absorb small amounts of energy (i.e., are slightly endothermic) up to about 250°C and then liberate that energy (i.e., become exothermic) during the later stages of heating. The extent and location of the various thermal events guide the development researcher in the search for fire retardant formulations. Successful laboratory candidates are further tested with the commercial procedures discussed above.

Pricing of Fire Retardant Wood

For most species, the pressure treatment process must leave 32–48 kg m⁻³ retention of the fire retardant formulation in the wood to achieve a Class I flame

spread rating of 2.5 or less. This degree of protection costs about US\$50–60 m⁻³ for the chemicals alone and there is additional cost of about US\$30 m⁻³ for the processing. In addition, building codes require redrying after treatment which generally costs at least US\$40 m⁻³. Thus, most commercial fire retardants add nearly US\$140 m⁻³ to the untreated price of the wood.

Mechanism of Fire Retardant Action

A number of mechanisms through which fire retardants exert their influence on the combustion of wood have been proposed over the years. For combustion to occur, the larger polymeric molecules in wood must be broken down into small, volatile fragments. This breakdown can occur in a variety of ways and it is recognized that combinations of the various mechanisms actually occur during combustion. For convenience though, the various mechanisms can be grouped into six different theories.

Increased Char Formation Theories

In this theory, the fire-retardant chemicals dominant influence is on the various chemical mechanisms that promote char formation while liberating small, highly oxidized fragments of the polymers in wood. Typically, these mechanisms are of the decarboxylation, decarbonylation, and dehydration types where, say, cellulose is transformed into levoglucosan which further degrades to char and small volatiles. (A somewhat simplistic way of thinking of this is to say that the carbon framework of wood is largely charred in place while small fragments such as water, carbon dioxide, and carbon monoxide are liberated.)

Reduced Volatiles Formation Theories

An adjunct to the increased char theory is the reduced volatile theory that in fact means that the heat content of the volatile products is reduced. Since there is less heat generated by the combustion of the volatiles, the propensity for self-sustaining burning is reduced.

Coating or Barrier Theories

It is thought that some fire retardants create physical barriers such as glasses or rigid foams that inhibit oxygen transport necessary to support combustion. The barriers can also provide thermal insulation to prevent heat transfer. Many fire retardant formulations for wood intumesce or swell when heated and this mechanism may be important for these types.

Gas Theories

The gas theories state that fire retardants cause dilution of the combustible gases with noncombustible gases during the early stages of pyrolysis and this inhibits subsequent combustion. In effect, there is a gaseous barrier to combustion.

Free Radical Inhibition Theories

This theory proposes that fire retardants act as traps to inhibit free radical propagations. Thus the various radicals formed by scission mechanisms are not available and subsequent combustion is retarded.

Thermal Theories

The thermal theories predict that fire retardants reduce the capacity of the wood to absorb heat. Consequently, they limit the amount of heat available for pyrolysis reactions.

The first two theories above seem especially important for fire retardants for wood since effective agents demonstrate the two properties of increased char and decreased combustible volatiles over and over again. Many authors have proposed specific chemical mechanisms for the pyrolysis and burning of wood and the interaction of fire retardants with these mechanisms. However these detailed discussions are beyond the scope of this article and the interested reader is directed to the Further Reading section below.

See also: **Solid Wood Processing:** Protection of Wood against Biodeterioration. **Solid Wood Products:** Structural Use of Wood; Wood-based Composites and Panel Products. **Wood Formation and Properties:** Chemical Properties of Wood; Physical Properties of Wood.

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Recycling

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Introduction

Paper has been the mainstay of recycling efforts for many years, but other forest products are making increasingly larger impacts on recycling. This means a growing contribution to environmental benefits from conserving resources and energy as well as reducing the need for landfill space.

Other forest products for recycling include wood in many forms from construction sites to 55-m depths in Lake Superior, from logs with fine-textured growth that are much sought after to much more common products that clutter and are sometimes hazardous, and from spruce milled from the millennium Christmas tree on the White House lawn to live oak from the U.S.S. *Constitution* that was launched in 1797.

Recycled wood is converted into products from fuel to fine furniture, and from carvings and sculpture to composites with plastics and concrete.

Recycling

Problems in Recycling Wood

Major sources of wood for recycling are used pallets from commodity distribution channels and all types of wood from municipal solid waste collection sites. Pallets during their lifetimes could have carried hazardous materials, and there could have been spills of undesirable substances onto pallet frames. However the likelihood of such occurrences is remote.

Similarly municipal solid waste may have unknown constituents that could impact adversely on derived products that find their way into processing