Chemistry of Fire Retardancy

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Fire retardancy of wood involves a complex series of simultaneous chemical reactions, the products of which take part in subsequent reactions. Most fire retardants used for wood increase the dehydration reactions that occur during thermal degradation so that more char and fewer combustible volatiles are produced. The mechanism by which this happens depends on the particular fire retardant and the thermal-physical environment. This chapter presents a literature review of the investigations into the mechanisms, a discussion of test methods used for determining fire retardancy, the various formulations used to make wood fire retardant, and the research needs in the field of fire retardancy.

WOOD WAS FIRST TREATED FOR FIRE RETARDANCY in the first century A. D. when the Romans used solutions of alum and vinegar to protect their boats against fire. In 1820, Gay-Lussac advocated the use of ammonium phosphates and borax for treating cellulosic material. Many of the promising inorganic chemicals used today were identified between 1800 and 1870. Since then, the development of fire retardants for wood has accelerated. Commercially treated wood became available after the U.S. Navy (1895) specified its use in ship construction, and New York City (1899) required its use in buildings over twelve stories tall *(1)*. production reached over 65 million board feet in 1943, but by 1964 only 32 million hoard feet was treated annually *(1)*.

Increased efforts to expand the use of wood products in institutional and commercial structures may require wood to be treated with fire retardants. Therefore, research on fire-retardant treatments for wood has accelerated.

Early Studies

One of the earliest studies on fire-retardant treatments for wood was conducted between 1930 and 1935 (Forest Products Laboratory).

This study resulted in a series of reports on a comprehensive evaluation of fire-retardant treatments for wood *(2–6)*. One hundred and thirty single chemicals or combinations of chemicals in the form of various salts were evaluated for flame-spread reduction, smoke, and corrosivity. Diammonium phosphate ranked first in reducing flame spread, followed by monoammonium phosphate, ammonium chloride, ammonium sulfate, borax, and zinc chloride. Zinc chloride, although excellent as a flame retardant, promoted smoke and glowing. Ammonium sulfate was the least expensive, but under certain environmental conditions it was corrosive to metals. None of the 130 compositions tested was considered ideal because of the adverse effects on some of the properties of wood. Several reviews of the subject are available and provide additional background material *(1, 7–10)*.

Protection of Wood with Fire Retardants

Fire-retardant treatments for wood can be classified into two general classes: (1) those impregnated into the wood or incorporated into wood composite products, and (2) those applied as paint or surface coatings. Chemical impregnation has the greater use, primarily for new materials, whereas coatings have been limited primarily to materials in existing constructions. There are advantages and disadvantages to each class. Coatings are applied easily and they are economical. Chemical impregnation usually involves full-cell pressure treatment and can be costly. A coating is subject to abrasion or wear that can destroy the effectiveness of the fire retardant. Chemical impregnations deposit the fire retardant within the wood, so that if the surface is abraded, chemicals are still present. On-site application of surface coatings requires strict control of the amount applied to ensure correct loading levels for a particular flame-spread rating *(11)*. Both coating and impregnation systems are based on the same chemical compounds, although the formulations for each vary.

Most of the chemicals used in fire-retardant formulations have a long history of use for this purpose, and most formulations are based on empirical investigations for best overall performance. These chemicals include the phosphates, some nitrogen compounds, some borates, silicates, and more recently, amino-resins. These compounds reduce the flame spread of wood but have diverse effects on strength, hygroscopicity, durability, machinability, toxicity, gluability, and paintability *(1, 12, 13)*.

Test Methods

Knowledge of various test methods used to evaluate the effectiveness of fire retardants is necessary to understand the mechanisms

of fire retardancy and formulations of fire retardants. Some of these tests are used by regulatory agencies to evaluate building materials and some are used for research and development work only. The commonly used test methods applicable to evaluate fire-retardant treatments include thermogravimetric analysis (TG); differential thermal analysis (DTA), and a similar technique, differential scanning calorimetry (DSC); 2-, 8-, and 25-ft tunnel flame-spread tests; and the oxygen index test. Other test methods are used to evaluate the effect of fire-retardant treatments on such related properties as smoke development, heat release rate, and toxicity.

Thermogravimetric Analysis (TG). TG involves weighing a sample while it is exposed to heat. The chief use of this technique has been to study the thermal decomposition of polymeric materials and to accumulate kinetic information about such decomposition. A sample is suspended on a sensitive balance that measures the weight (Figure 1) as it is exposed to a furnace. Air, nitrogen, or another gas flows around the sample to remove the pyrolysis or combustion prod-
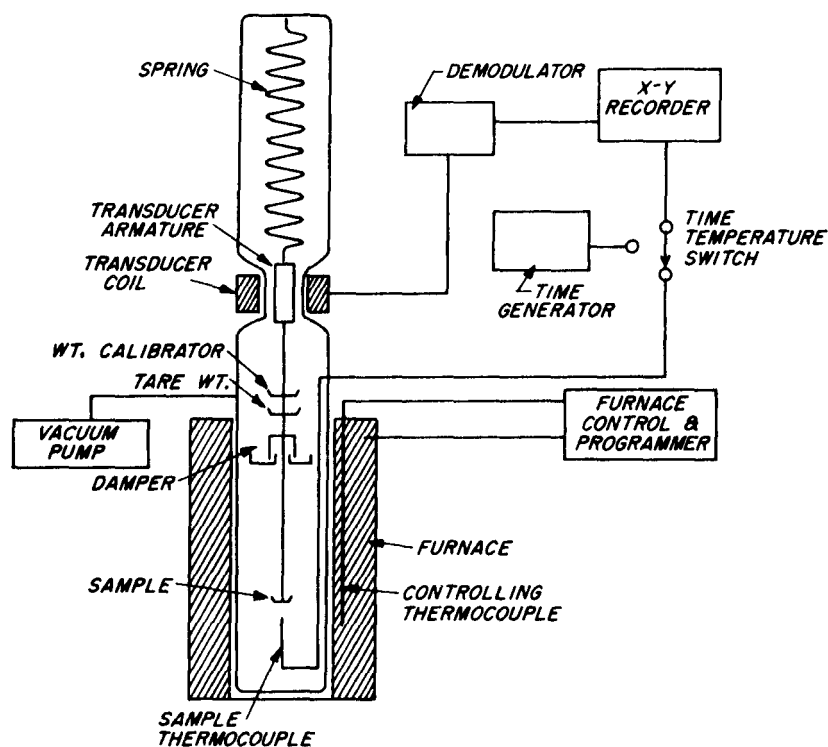

Figure 1. Schematic diagram of an early thermogravimetric analysis

ucts. Weight loss is recorded as a function of time and temperature. In isothermal TG, the change in weight of the sample is recorded as a function of time as the temperature remains constant. In dynamic or nonisothermal thermogravimetry, the change in weight is a function of both temperature and time as the temperature is raised at a given heating rate. With the use of a derivative computer, the rate of weight loss as a function of time and temperature can also be determined. The computer allows a more accurate determination of peak temperature transitions. This is referred to as derivative thermogravimetry *(14)*.

Differential Thermal Analysis and Differential Scanning Calorimetry. DTA measures the amount of heat liberated or absorbed as a material moves from one physical transition state to another (i.e., melting, vaporization) or whenever it undergoes a chemical reaction. This heat is determined by measuring the temperature differences between a sample of the material and an inert reference. DTA can be used to measure heat capacity, to provide kinetic data, and to give information on transition temperatures. The test device consists of sample and reference pans exposed to the same heat source. Temperatures are measured by thermocouples embedded in the sample and reference pan. The ternperature difference between sample and reference is recorded against time as the exposure temperature is increased at a linear rate. For calorimetry, the equipment is calibrated against standards at several temperatures. As in TG, air, nitrogen, or some other atmosphere flows through the sample cell to remove the resulting vapors *(14)*.

DSC is similar to DTA except the actual differential heat flow is measured when the sample and reference temperature are equal. In DSC both the sample and reference are provided with individual heaters. If a temperature difference develops between the sample and reference because of exothermic or endothermic reactions in the sample, the power input is adjusted to remove this difference. Thus, the temperature of the sample holder is always kept the same as the reference.

The small sample size, rapid removal of pyrolysis or combustion products, and availability of huge excesses of reactant oxygen during thermal analysis can lead to erroneous interpretation of the material in terms of its performance in actual thermal situations. However, thermal analysis tests can provide basic information on the pyrolysis and combustion mechanism and can provide data on the relative performance of materials. This information should be supported by larger-scale fire tests.

Tunnel Flame-Spread Tests. The growth of a small fire in a building is influenced by the rate at which flames spread over the

fire-exposed surfaces. Therefore, the combustibility and flame-spread characteristics of furnishings and the interior finish are important safety factors. Building standards designed to control fire growth often require certain flame-spread ratings for various parts of a building. For code regulations, flame-spread ratings are determined by a 25-ft tunnel test (Figure 2) which is an approved standard test method *(15)*. For research and development work there are 2- and 8-ft tunnel tests. The 8-ft tunnel test (Figure 3) is also an approved standard *(16)*. All tunnel tests measure the surface flame spread of a material although each differs in the method of the exposure. A specimen is exposed to an ignition source, and the rate at which the flames travel to the end of the specimen is measured. In the past, red oak flooring was used as a standard and was given a flame spread index of 100. Today, red oak flooring still has an index around 100, but is no longer used in the calculation of the ASTM E 84 flame-spread index.

The severity of the exposure and the time a specimen is exposed to the ignition source are the main differences between the tunnel test methods. The 25-ft tunnel test is the most severe exposure and the specimen is usually exposed for 10 min. An extended test of 30 min is performed on fire-retardant treated products. Materials that pass the extended test (have flame spread less than 25 with no evidence of glowing) qualify for a special "FR-S" rating. Because the 25-ft tunnel test is the most severe exposure it is used as the standard for building materials. The 2-ft tunnel test *(17, 18)* is the least severe. Because of the small specimen size required with this test, it is a valuable tool for development work on fire retardants. The 8-ft tunnel falls between the 2- and 25-ft tunnels in severity. It can he a valuable
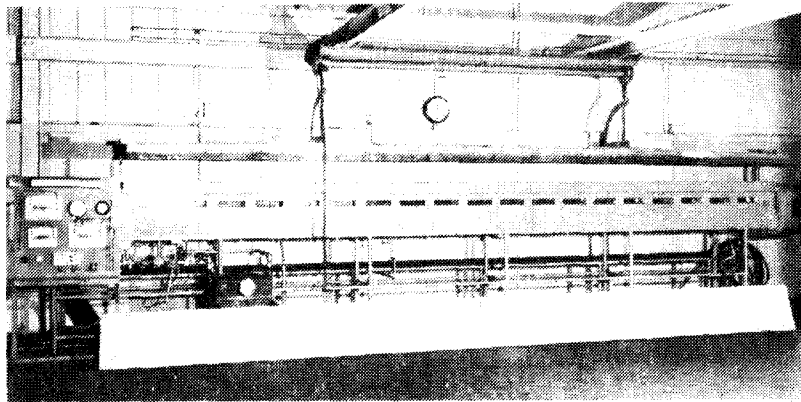

Figure 2. Underwriters Laboratory's 25-ft tunnel flame-spread test.
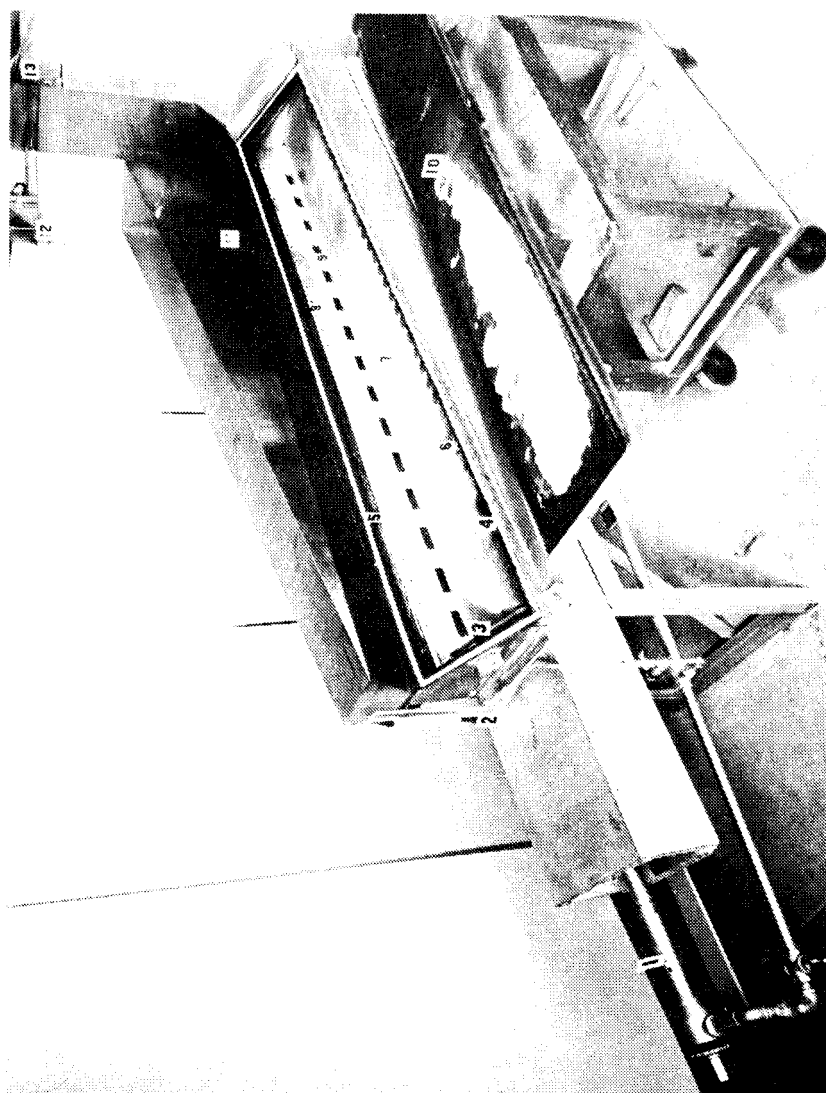
Figure 3. Forest Products Laboratory's 8-ft tunnel flame-spread test.

tool to determine the effectiveness of treatments as shown in Figure 4 *(19)*.

Critical Oxygen Index Test. The oxygen index test measures the minimum concentration of oxygen in an oxygen-nitrogen mixture that will just support flaming combustion of a test specimen. This standard test method *(20)* provides the critical oxygen index required to maintain this flaming combustion under experimental conditions. Highly flammable materials have low oxygen index, less flammable materials have high values. The test was originally developed for plastics but it can be used for wood and, in particular, fire-retardant-treated wood *(21–23)*. Figure 5 shows the effect of chemical retention levels on the oxygen index value for different chemical treatments on Douglas-fir.

One advantage of this test is the very small specimen size *(24)*; another is that this method can be used to study the retardant mechanism in the gas phase which cannot be done with TG, DTA, or DSC because they only measure properties in the solid phase. A specimen treated with a chemical compound that acts as a gas-phase inhibitor should demonstrate the following: (1) show an increase in oxygen
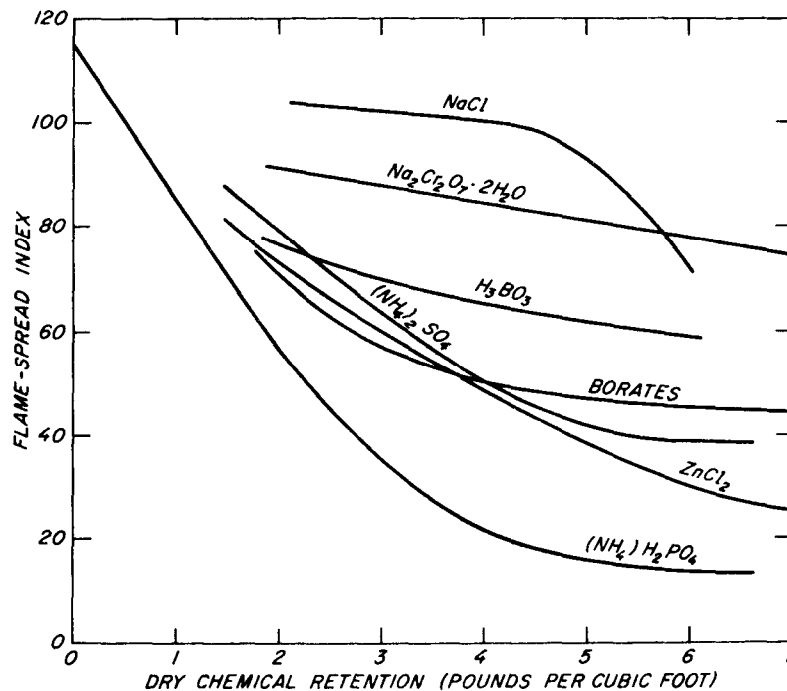

Figure 4. Effect of inorganic additives on flame-spread index, measured in 8-ft tunnel (19).
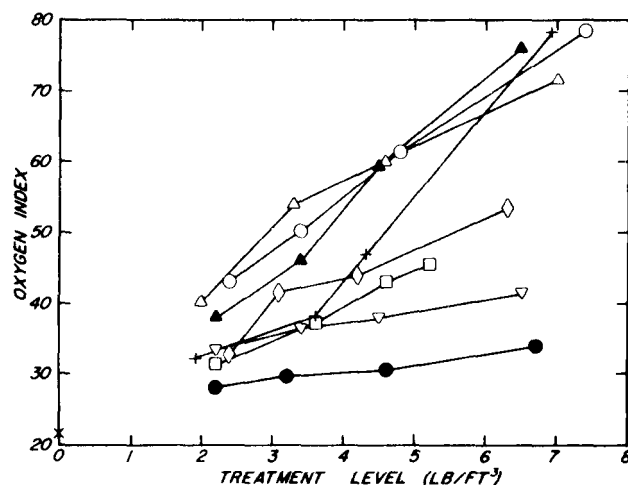
Figure 5. Effect of fire-retardant chemicals on oxygen index (21). Key: ∇, ammonium sulfate; +, sodium tetraborate decahydrate; ○, disodium octaborate tetrahydrate; □, boric acid; △, monoammonium phosphate; ▲, ammonium polyphosphate (11-37-0); ◇, zinc chloride; ●, sodium dichromate; ×, untreated.

index value when the sample is run in a regular oxygen – nitrogen atmosphere, and (2) show no change from the untreated specimen when the sample is run in N_2O_4. However, if the flame retardant acts in the solid phase, its effectiveness should not be affected by a change in oxidant. Therefore, discrimination is possible between vapor- and solid-phase activity *(25, 26)*.

Test Methods for Related Properties. Test methods are available to evaluate such related physical properties of retardants as smoke production, heat release rate, and toxicity.

SMOKE PRODUCTION. Smoke production can be a critical problem in fire-retardant formulations. The 25-ft tunnel test uses a photoelectric cell to measure the amount of smoke evolved. The smoke density is measured continuously and is assigned a value relative to the behavior of red oak. The effect of fire retardants on smoke production varies depending on the chemical. Figure 6 demonstrates this effect as measured in the 8-ft tunnel; however, smoke values measured in various tunnel tests may not agree or correlate.

The National Bureau of Standards smoke density chamber (Figure 7) is a more recent technique used to evaluate smoke. This chamber can be used to measure adequately the smoke produced from untreated and fire-retardant-treated wood *(27, 28)*. This method has three advantages over the tunnel method: (1) application to a variety of room situations, burning areas, and light-path lengths, (2)
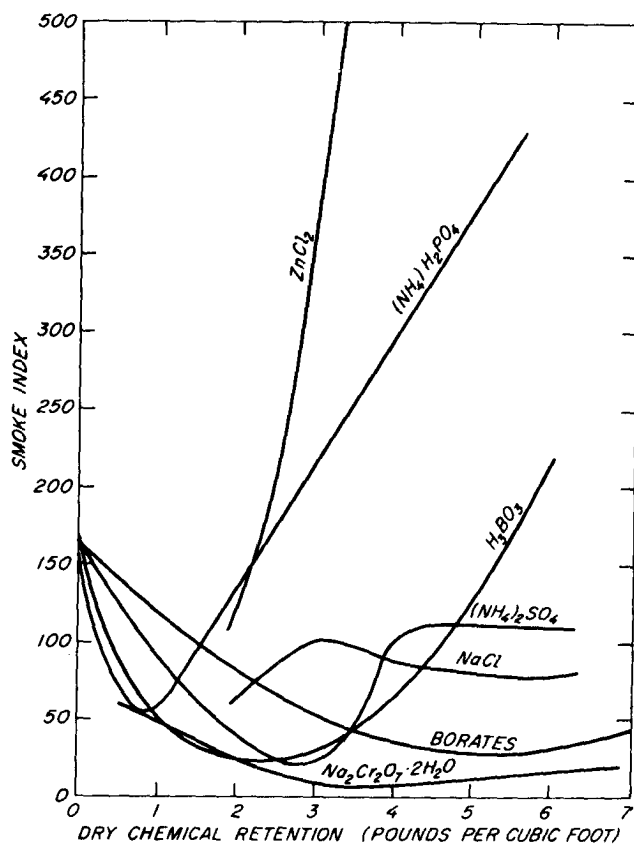
Figure 6. Effect of inorganic additives on smoke index measured in 8-ft tunnel (19).

control over exposure conditions, and (3) measurement of smoke production in flaming and nonflaming modes. This method is now a standard test procedure *(29)*.

HEAT RELEASE RATE.   Another measurement that is gaining acceptance as a tool for evaluation of fire-retardant treatments is the measurement of the heat release rate *(30–35)*, The heat of combustion of wood varies depending on the species, resin content, moisture content, and other factors. The contribution to fire growth from wood depends on the total effect of these factors, along with the fire exposure and degree of combustion. Although the heat of combustion of a material never changes, fire retardants reduce the rate of heat release and extend the time at which the heat release begins to be measurable *(31, 32, 35, 36)*. The rate of heat release for treated and
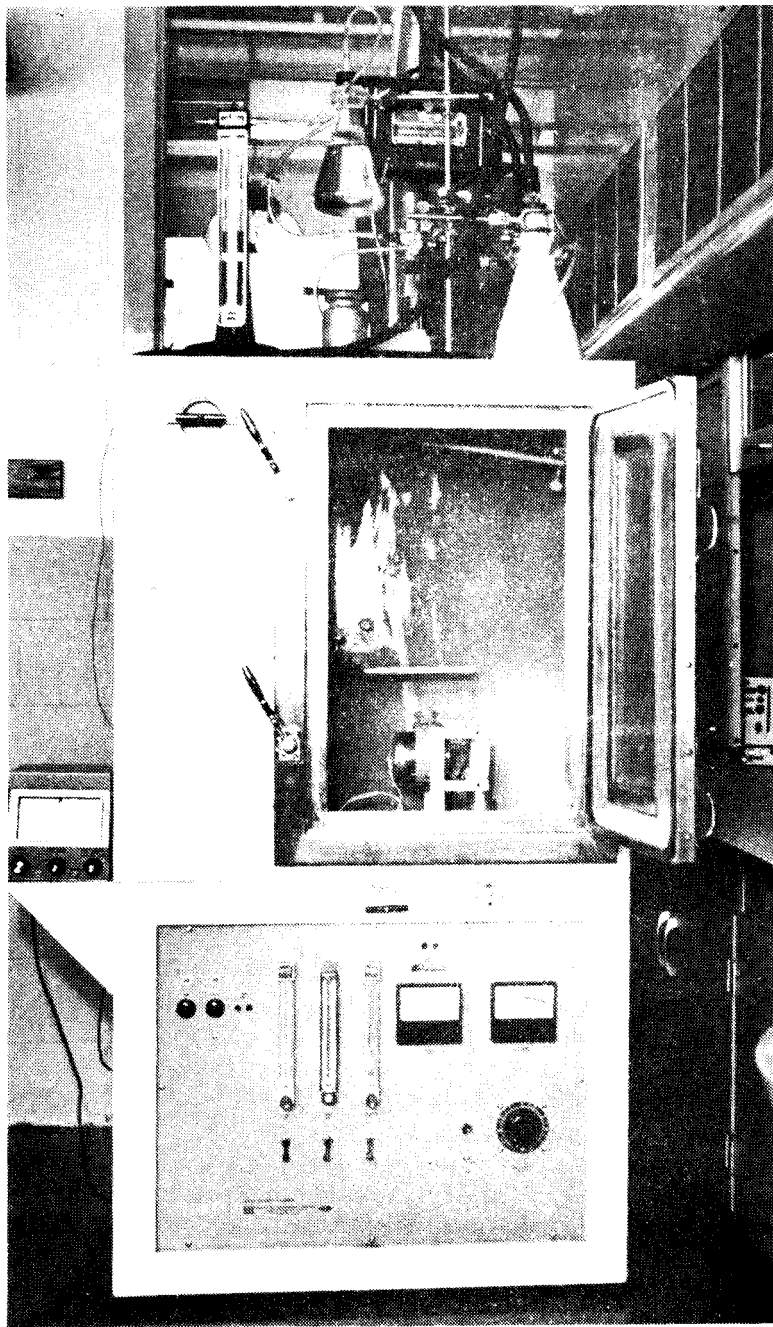
Figure 7. *NBS smoke chamber is used to determine the obscured optical density from various materials.*

untreated materials can be utilized in mathematical models to predict fire growth.

TOXICITY. Toxicity testing may become applicable to fire-retardant treatments because the toxicity of combustion products is becoming an important fire-performance characteristic. A large percentage of fire victims are not touched by flames but are overcome as a result of exposure to smoke, to toxic gases, and to depleted oxygen levels. The effect of fire retardants on the combustion products is, therefore, of increasing concern. A critical review by Kaplan et al. *(37)* discusses all the various proposed toxicity test methods and the advantages and disadvantages of each.

Mechanisms of Fire Retardancy

The burning of a solid is essentially a three-stage process consisting of a heating stage, a thermal degradation stage, and an ignition stage. Chapter 13 contains discussion of the chemistry of pyrolysis and combustion. Some of these concepts are reviewed here briefly in order to facilitate the discussion of fire-retardant mechanisms.

Chemistry of Burning. PYROLYSIS. The temperature of wood rises when it is exposed to an outside heat source. This rise in temperature is accompanied by the breaking of chemical bonds, which accelerates as the temperature increases further. In the absence of oxygen, this thermal degradation is called pyrolysis. As the wood undergoes thermal pyrolysis, volatile gases are produced and diffuse into the surrounding air.

VAPOR-PHASE COMBUSTION. If the volatile gases are mixed with air and heated by an external heat source to the ignition temperature, exothermic reactions known as combustion begin. The heat from these exothermic reactions in the vapor phase reradiates to the original material, thereby propagating the pyrolysis reactions in the solid phase. If the burning mixture accumulates enough heat to emit radiation in the visible spectrum, the phenomenon is known as flaming combustion and occurs in the vapor phase.

SMOLDERING AND GLOWING. In many materials, including wood and paper, a solid-phase combustion can also occur. This type of combustion is known as glowing or smoldering combustion. In this condensed phase, the activated char produced by the pyrolysis of the material combusts with oxygen to produce CO_2 and water vapor. Smoldering combustion usually is distinguished h-em glowing combustion in that combustion of the volatile pyrolysis products is not essential to propagate smoldering, and it may proceed in materials that have not undergone prior conversion to a char residue. Smoldering combustion usually is associated with materials that have a high surface-to-weight ratio, such as sawdust, upholstery material,

and coal. The essential ingredient for smoldering combustion is low heat losses. Materials that smolder have good insulating properties and produce abundant char.

Theories of Fire Retardancy.   Several theories have been proposed for the mechanism of fire retardants. Browne *(38)* made a complete literature search on these theories and summarized the research in an effort to understand the mechanisms involved in the inhibition of pyrolysis and combustion of wood. These mechanisms can be categorized under several theories.

1. *Barrier theories.* Fire-retardant chemicals prevent the escape of volatile products by forming a glassy barrier. This barrier also prevents oxygen from reaching the substrate and insulates the wood surface from high temperatures.
2. *Thermal theories.*   Fire-retardant chemicals may increase the thermal conductivity of the wood to dissipate the heat from the surface faster than it is supplied by the igniting source, or they may affect chemical and physical changes so that heat is absorbed by the chemical, preventing the wood surface from igniting.
3. *Dilution by noncombustible gases theories.* Nonflammable gases released by the decomposition of the fire-retardant chemicals dilute the combustion gases formed by the pyrolysis of the wood and form a nonflammable gaseous mixture.
4. *Free radical trap theories.*   Fire-retardant chemicals release free radical inhibitors at pyrolytic temperatures that interrupt the chain propagation mechanism of flammability.
5. *Increased char/reduced volatiles theories.* Fire-retardant chemicals lower the temperature at which pyrolysis occurs, directing the degradation pathway toward more char production and fewer volatiles.
6. *Reduced heat content of volatiles theories.* Fire-retardant chemicals lower the heat content of the combustible volatiles. This reduction in heat content always occurs when the amount of char is increased and the amount of volatiles is reduced. Therefore, Theories 5 and 6 function together, resulting in more char, fewer volatiles, and lower heat content of volatiles.

In most cases, a given fire retardant operates by several of these mechanisms, and much research has been done to determine the magnitude and role of each of these mechanisms in fire retardancy. The influence of the combining effect of several of these mechanisms is illustrated by phosphorus-nitrogen synergism. The theories involved in this synergistic system are discussed to demonstrate this interaction between mechanisms. Some mechanisms apply only to

flaming combustion (vapor phase), some apply to both flaming and smoldering combustion, and others only apply to smoldering. The phase to which each theory pertains will be indicated, as well as a separate section on smoldering inhibition theories.

BARRIER THEORIES.   A physical barrier can retard both smoldering combustion and flaming combustion by preventing the flammable products from escaping and by preventing oxygen from reaching the substrate. These barriers also insulate the combustible substrate from high temperatures. Common barriers include sodium silicates and coatings that *intumesce* (puff and form a cellular structure that remains attached to substrate). Intumescent systems swell and char on exposure to fire to form a carbonaceous foam and consist of several components. These components include a char-producing compound (polyhydric alcohol, carbohydrates, or epoxy resins), a blowing agent, a Lewis-acid dehydrating agent, and other optional components,

In the intumescent systems, the char-producing compound, such as polyol, will normally burn to produce CO_2 and water vapor and leave flammable tars as residues. However, the compound can esterify when it reacts with certain inorganic acids, usually phosphoric acid. The acid acts as a dehydrating agent and leads to increased amounts of char and reduced volatiles. Such char is produced at a lower temperature than the charring temperature of the wood substrate. *Blowing agents* decompose at characteristic temperatures and release gases that expand the char. Common blowing agents are dicyandiamide, melamine, urea, and guanidine *(39, 40);* they are selected on the basis of their decomposition temperature. Many blowing agents also act as the dehydrating agent. Other materials such as binders are added to the formulation to improve the toughness of the carbon foam.

Ingredients used in intumescent systems usually fulfill more than one function, Most compounds release some gas on heating, therefore they can be considered to be blowing agents. Many compounds produce some char.

THERMAL THEORIES.   Researchers at Forest Products Laboratory impregnated wood with a metal alloy to determine whether change in thermal conductivity is a mechanism of fire retardants *(38)*. The alloy was selected to melt at 105 °C. The treatecl and untreated specimens were subjected to a flame on one side and the temperature rise was recorded on the unexposed side. The rise of temperature was slower over the alloy-treated specimen than over the untreated specimen until the melt temperature of the alloy. Above this temperature the treated and untreated specimens then followed the same time–temperature regimes. The untreated specimen burst into

flames and the treated specimens smoked and charred; however, all specimens did so at the same time and temperature. These observations could not be explained on the basis of changes in thermal conductivity alone *(38)*.

Another thermal theory suggests that fire retardants cause chemical and physical changes so that heat is absorbed by the chemical to prevent the wood surface from igniting. This thermal absorption theory is based on chemicals that contain much water of crystallization.

Water will absorb its latent heat of vaporization from the pyrolysis reactions until all the water is vaporized. This serves to remove heat from the pyrolysis zone, thereby slowing down the pyrolysis reactions. This is demonstrated in the increased ignitability of very dry woods and forest fuels compared to woods and fuels with high moisture contents. However, Browne and Tang *(41)* and others *(42–48)* have demonstrated with TG and DTA that, after the water is lost, the pyrolysis of wood occurs and is independent of the past moisture content of the wood.

DILUTION OF NONCOMBUSTIBLE GASES THEORIES. Most of the evidence for this mechanism can be derived by considering the blowing agents in the intumescent systems discussed previously, or agents that release large amounts of water vapor. Agents such as dicyandiamide and urea release noncumbustible gases at temperatures below the temperature at which the active pyrolysis begins. Borax compounds release water vapor in large quantities. The main difficulty with this theory has been that not enough noncombustible gas can be liberated to dilute the volatile gases. However, Browne *(38)* found that flammable gases account for only 23% of the total volume produced. Any reduction in this percentage would be beneficial because it increases the volume of combustible volatiles needed for ignition. Also the movement of gases away from the substrate may dilute the amount of oxygen near the boundary layer between the substrate and the vapor-phase reaction.

FREE RADICAL TRAP THEORIES. Combustion vapor-phase reactions have been studied using premixed gas flames such as methane. Considerable information concerning the mechanism of flame propagation has resulted from this work *(40, 49, 50)*. Basically the process occurs predominantly by branching chain reactions among free radicals. The major chain branching reactions are

$$H \cdot + O_2 \rightarrow HO \cdot + O \cdot \tag{1}$$

$$O \cdot + H_2 \rightarrow HO \cdot + H \cdot \tag{2}$$

These two equations govern the exponential increase in free radical concentration; however, these postulations are based on premixed

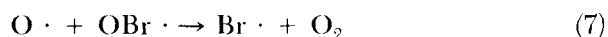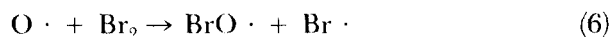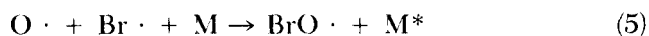gas flames with excess oxygen available. Application of this theory to the combustion of solids must be treated with reservations because the combustion of wood proceeds in oxygen-deficient diffusion flames whose processes are a complex series of simultaneous reactions dependent on the material and the environment. Therefore, the exact role free radicals play in the combustion of wood is not known.

Certain fire retardants affect vapor-phase reactions by inhibiting the chain reactions in Reactions 1 and 2. Halogens such as bromine and chlorine are good free radical inhibitors and have been studied extensively in the plastics industry *(40, 49, 50)*. Generally, large amounts of halogen are required (15–30% by weight) to attain a practical degree of fire retardance. The efficiency of the halogen decreases in the order Br > Cl > F. A mechanism for the inhibition of the chain branching reactions (using HBr as the halogen) is

$$H \cdot + HBr \rightarrow H_2 + Br \cdot \tag{3}$$

$$OH \cdot + HBr \rightarrow H_2O + Br \cdot \tag{4}$$
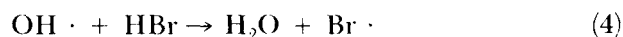
The hydrogen halide consumed in these reactions is regenerated to continue the inhibition. Although this proposed mechanism was based on experiments with premixed hydrocarbon flames, the same order of effectiveness exists with wood.

An alternate mechanism (Reactions 5–7) was suggested for halogen inhibition which involves recombination of oxygen atoms *(50)*.

$$O \cdot + Br \cdot + M \rightarrow BrO \cdot + M^* \tag{5}$$

$$O \cdot + Br_2 \rightarrow BrO \cdot + Br \cdot \tag{6}$$

$$O \cdot + OBr \cdot \rightarrow Br \cdot + O_2 \tag{7}$$

Thus the inhibitive effect results from the removal of active oxygen atoms (O •) from the vapor phase. Additional inhibition can result from removal of OH radicals in the chain-brancning reactions:

$$BrO \cdot + \cdot OH \rightarrow HBr + O_2 \tag{8}$$

$$BrO \cdot + \cdot OH \rightarrow Br \cdot + HO_2 \tag{9}$$
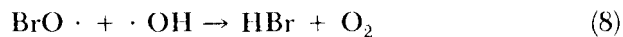
Reactions 5–9 explain the lack of halogen inhibition in hydrocarbon–nitrous oxide flames where the hydrogen–oxygen chain is not required for oxidation *(50)*. Some phosphorus compounds also have been found to inhibit flaming combustion by this mechanism *(51)*.

INCREASED CHAR/REDUCED VOLATILES THEORIES. Most of the evidence relating to the mechanism of fire retardancy in the burning of wood indicates that retardants alter fuel production by increasing the amount of char and reducing the amount of volatile, combustible

vapors. Many fire retardants for wood also lower the temperature at which active pyrolysis occurs.

Early studies involved treatment of wood specimens with fire-retardant chemicals, then subjecting the treated specimens to thermal analysis by TG. Browne and Tang *(41)* tested eight compounds, some of which were known to be effective fire retardants, and some of which were not. The TG results (Figures 8–10) indicate that all compounds increased the residual char weight of the material. Except for sodium tetraborate, the more effective the salt as a flame retardant the lower the temperature of active pyrolysis and the greater the amount of char. These results were confirmed through repeated experiments *(45, 46)*.

Experiments were conducted on the pyrolysis products of wood samples to affirm that the increased amounts of char involved a decrease in the amount of combustible tars *(52)*. The chemicals increased the yield of char, water, and noncondensable gases at the expense of the flammable tar fraction. These results confirmed that the increased amount of residual char in TG results was associated with the reduction of the combustible volatiles.

A possible chemical mechanism for the reduction of these combustible volatiles is that fire-retardant chemicals somehow inhibited the formation of levoglucosan (1,6-anhydroglucopyranose), a major volatile fraction obtained from the thermal degradation of cellulose *(see* Chapter 13). The results obtained from TG prompted many researchers to investigate this possible mechanism. The amount of levoglucosan produced by treated and untreated specimens of cellulose was analyzed and the results can be found in Table I *(53)*. All the chemicals in Table I reduced the percentage of levoglucosan regardless of the relative effectiveness of the fire retardant as determined by the oxygen index test. Their findings include the effect of acidic, neutral, and basic additives on the levoglucosan yield (Table II). The acid treatment had the most pronounced effect on the breakdown. These results and the oxygen index results suggest that alkali and acid treatments impart flame retardancy to cellulose through different chemical mechanisms.

In degree of polymerization (DP) studies of borax treatments and ammonium dihydrogen orthophosphate *(53)*, cellulose treated with the acid charred and depolymerized very rapidly. Its DP value decreased from 1110 to 650 after only 2 min of heating at 150 °C. Cellulose treated with borax showed a DP reduction from 1300 to 700 after 1 h of heat treatment at 150 °C. Both these compounds catalyzed the suppression of levoglucosan formation but they had different effects on the chain depolymerization reaction *(53)*.

Figure 8. Thermogravimetric analysis of cellulose treated with various additives (46).

WOOD WITH :

NO TREATMENT
2% $Na_2B_4O_7 \cdot 10H_2O$
2% $NaCl$
2% $KHCO_3$
2% $AlCl_3 \cdot 6H_2O$
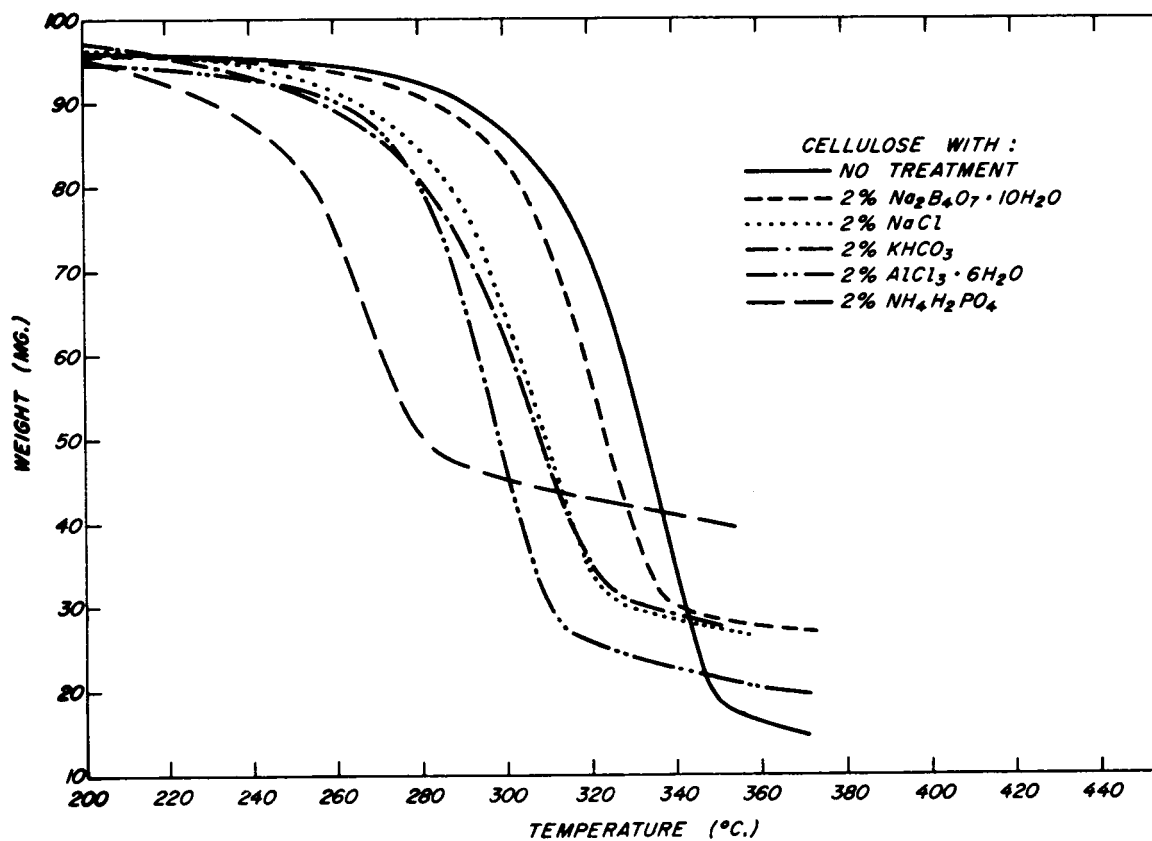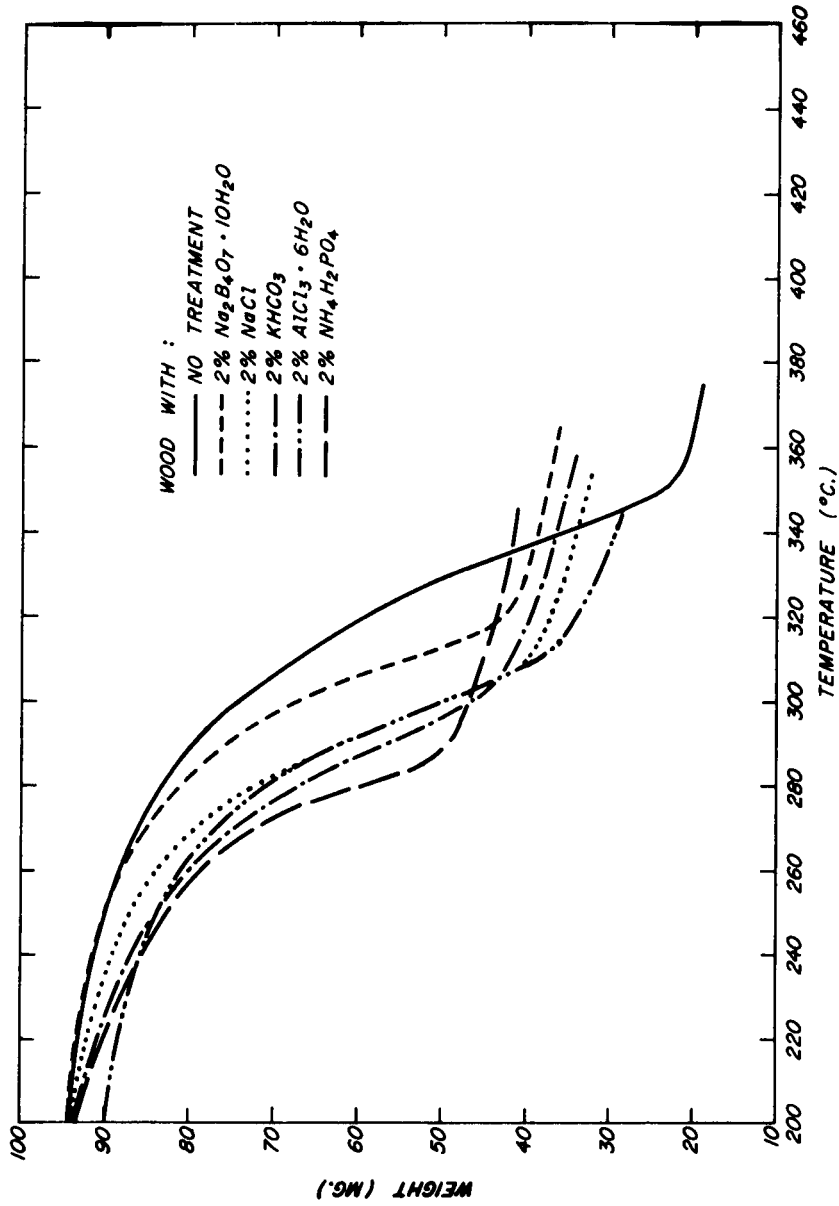2% $NH_4H_2PO_4$

TEMPERATURE (°C.)

WEIGHT (MG.)

Figure 9. Thermogravimetric analysis of wood treated with various additives (46).
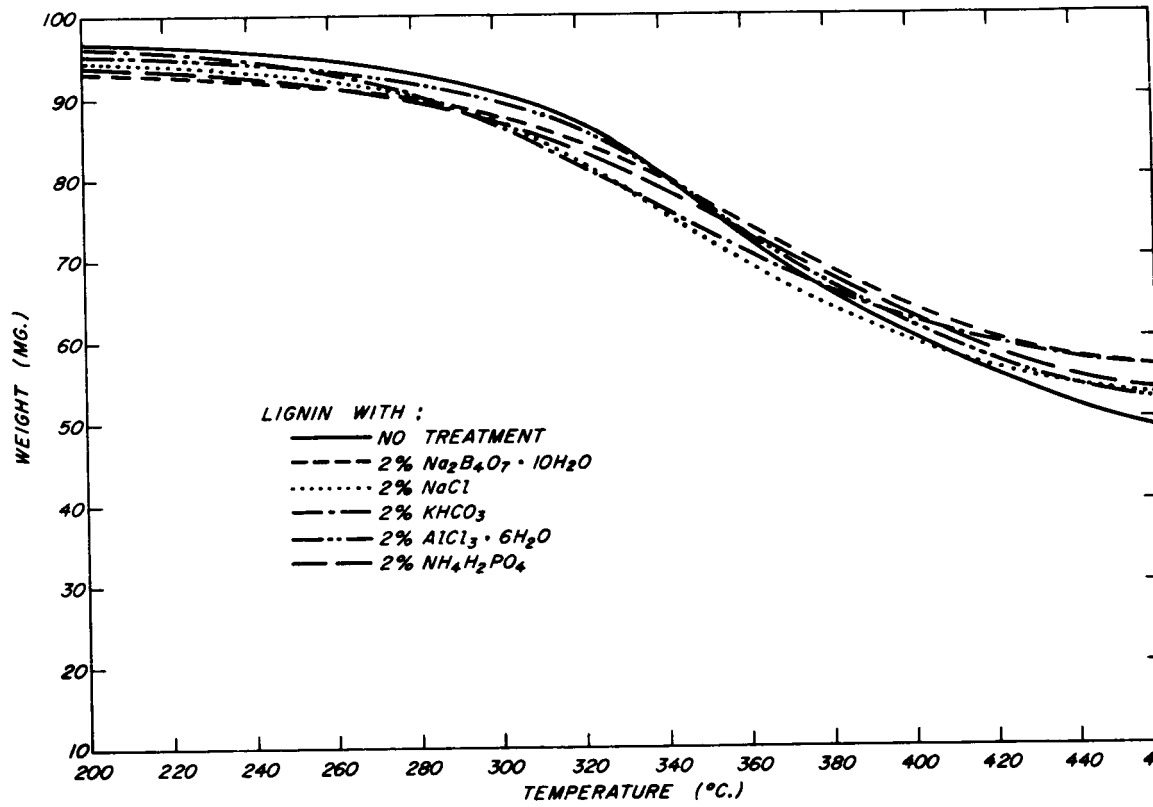
Figure 10. Thermogravimetric analysis of lignin treated with various additives (46).

Table I. Effect of Inorganic Additives on Oxygen Index and Levoglucosan Production

Treatment	Oxygen Index (%)	Levoglucosan Yield (%)
Untreated	17.3	10.1
KH_2PO_4	18.5	0.9
K_2HPO_4	18.6	0.2
$Na_2B_4O_7 \cdot 10H_2O$	19.3	<0.1
$ZnCl_2$	19.6	0.3
$NH_4H_2PO_4$	19.6	0.8
H_3PO_4	20.5	<0.1

(Adapted from Reference 53.)

The nature of uncatalyzed, acid-catalyzed, and alkali-catalyzed thermal decomposition of levoglucosan was studied (54–56). The data in Table III demonstrate that the same products are obtained from uncatalyzed and acid- or alkali-catalyzed reactions, although the quantities produced vary. The acid-catalyzed reaction produced the greatest amount of char. This agrees with the findings of Fung et al. (53).

Fung (57) and Halpern et al. (58) identified the pyrolysis product from cellulose treated with phosphoric acid as 1,6-anhydro-3,4-di-deoxy- D^3- β -D-pyranosen-2-one (levoglucosenone). Halpern et al. (58) found the same compound when the cellulose was treated with mo-noammonium phosphate ($NH_4H_2PO_4$), sodium dihydrogen phosphate (NaH_2PO_4), or sodium hydrogen sulfate ($NaHSO_4$). They proposed the mechanism in Figure 11 for the acid-catalyzed reaction of 1,6-anhydro-ß-D-glucopyranose (I) to 1,6-anhydro-3,4-dideoxy- Δ^3-β -D-pyranosen-2-one (IV), a combustible product. Work with the model compound glucovanillin revealed that Compound IV was produced

Table II. Effect of Acid, Alkaline, and Neutral Additives on Levoglucosan Production

Products	Levoglucosan (wt %)	Levoglucosan + 1% KBr	Levoglucosan + 1% K_2CO_3	Levoglucosan + 1% H_3PO_4
CO_2	0.12	—	0.21	4.05
CO	—	—	—	1.9
Levoglucosan (undecomposed)	86.05	73.30	63.90	2.28
Char residue	3.16	—	—	35.15
Total	97.38	95.55	80.41	80.58

(Adapted from Reference 53.)

**Table III. Effect of Additives on Production of Various
Pyrolysis Products**

Compound	Untreated (%)	$ZnCl_2$ (%)	NaOH (%)
Acetaldehyde	1.1	0.3	7.3
Furan	1.0	1.3	1.6
Acrolein	1.7	<0.1	2.6
Methanol	0.3	0.4	0.7
2,3-Butanedione	0.5	0.8	1.6
2-Butenal	0.7	0.2	2.2
1-Hydroxy-2-propanone	0.8	<0.1	1.1
Glyoxal	1.4	<0.1	4.9
Acetic acid	1.7	0.7	1.5
2-Furaldehyde	0.9	3.0	0.4
5-Methyl-2-furaldehyde	0.1	0.3	—
CO_2	2.9	6.8	5.7
Water	8.7	20.1	14.1
Char	3.9	29.0	16.0
Balance	74.3	36.8	40.3

(Adapted from Reference 55.)

with phosphoric acid treatment *(59)*. Compound I was found to decompose almost completely in the presence of phosphoric acid to give char, water, CO, CO_2, and just a small amount of Compound IV. The acid is believed to react with the cellulose to give Compound IV directly without going through the intermediate Compound I (Figure 11) *(58)*. This mechanism of inhibiting formation of levoglucosan may only exist with phosphorus-type compounds. Some other mechanism may exist for nonphosphorus fire retardants.

Flame retardants may not only catalyze dehydration of the cellulose to more char and fewer volatiles but also enhance the condensation of the char to form cross-linked and thermally stable polycyclic aromatic structures *(60)*. Cellulose was treated with various additives and then charred at 400 °C. The chars were then oxidized with permanganate *(see* Chapter 13) and the results are in Table IV. The char yield was slightly higher for the sodium chloride-treated sample (17.5%) and substantially more for the sample containing diammonium phosphate (28.9%), as compared to the yield from the untreated sample (15.3%). Furthermore, the increased char formation was accompanied by increased aromaticity, as measured by the amount of the aromatic carbon obtained from the char and the amount obtained from the original cellulose molecules *(60)*.

The increased char formation is caused by the increased condensation and cross-linking of the carbon skeleton, in addition to any
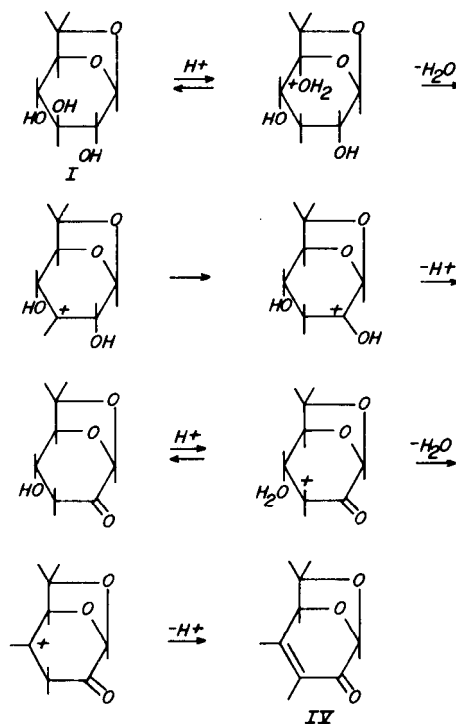
Figure 11. Proposed mechanism of levoglucosan inhibition (from Reference 58).

role that inorganic flame retardants play in dehydration of the glucose units in the cellulose molecule or in lowering the solid-phase combustion rate (60).

Nanassy (61) also examined the effects of fire retardants on the resulting char. He studied the effects of ammonium dihydrogen phosphate on the thermal diffusivity, thermal conductivity, and specific heat of treated and untreated Douglas-fir specimens that had been

Table IV. Effect of Inorganic Additives on Aromatic Char Formation

Additives	Char Yield (wt %)	Aromatic Carbon in Char (wt %)
None	15.3	13.7
NaCl	17.5	16.8
$(NH_4)_2HPO_4$	28.9	18.6

(Adapted from Reference 60.)

charred. The thermal diffusivity of treated specimens decreased from a value of 10.04 to 6.60 mm^2/s at a temperature of 100 °C. At the same temperature the thermal conductivity decreased only slightly, from 6.50 cW/m °C to 6.17 cW/m °C. The specific heat showed a large increase, from 9.1 dJ/g °C for untreated to 11.2 dJ/g °C for treated. The large decrease in diffusivity results in increasing the heat storage capacity of char as evidenced by the large increase in the specific heat.

REDUCED HEAT CONTENT OF VOLATILES THEORIES.   Figure 9 shows that the inorganic additives (except for sodium tetraborate) lower the temperature at which active decomposition begins and this resulting decomposition leads to increased amounts of char and reduced amounts of volatiles. In the previous section, this increased amount of char and reduced amount of volatiles were attributed to the increased dehydration reactions, mainly of the cellulose component of wood. However, other competing reactions are also occurring such as decarbonylation, decomposition of simpler compounds, and condensation reactions. All these reactions compete with each other. As a result, shifts favoring one reaction over another also change the overall heat of reaction. Differential thermal analysis is used to determine these changes in heats of reactions and can help gain understanding about these competing reactions.

DTA of wood in helium (Figure 12) indicates two endothermic reactions followed by a feeble exothermic one. The first endothermic reaction, which peaks around 125 °C, is caused by evaporation of water and desorption of gases; the second, peaking between 200 and 325 °C, indicates depolymerization and volatilization *(47)*. At 375 °C these endothermic reactions are replaced with a small exothermic one. When the wood samples are run in oxygen, these endothermic peaks are replaced with strong exothermic reactions, as evidenced in Figure 13 which has a 10-fold decrease in sensitivity compared to Figure 12. The first exotherm, around 310 °C for wood and 335 °C for cellulose, is attributed to the flaming of volatile products; the second exotherm, at 440 °C for wood and 445 °C for lignin, is attributed to glowing combustion of the residual char *(47)*. These thermograms are (qualitative, but they do indicate the temperatures where oxidation occurs.

DTA of inorganic fire retardants run in oxygen may shift the peak position temperature or the amount of heat released. Sodium tetraborate reduced the volatile products exotherm considerably, increased the glowing exotherm, and stimulated the appearance of a second glowing peak around 510 °C, as seen in Figure 14. Sodium chloride also reduced the first exotherm, increased the size of the second, but did not produce a second glowing exotherm as did the

Figure 12. Differential thermal analysis of untreated wood (top), cellulose (middle), and lignin (bottom) run in helium atmosphere (47).
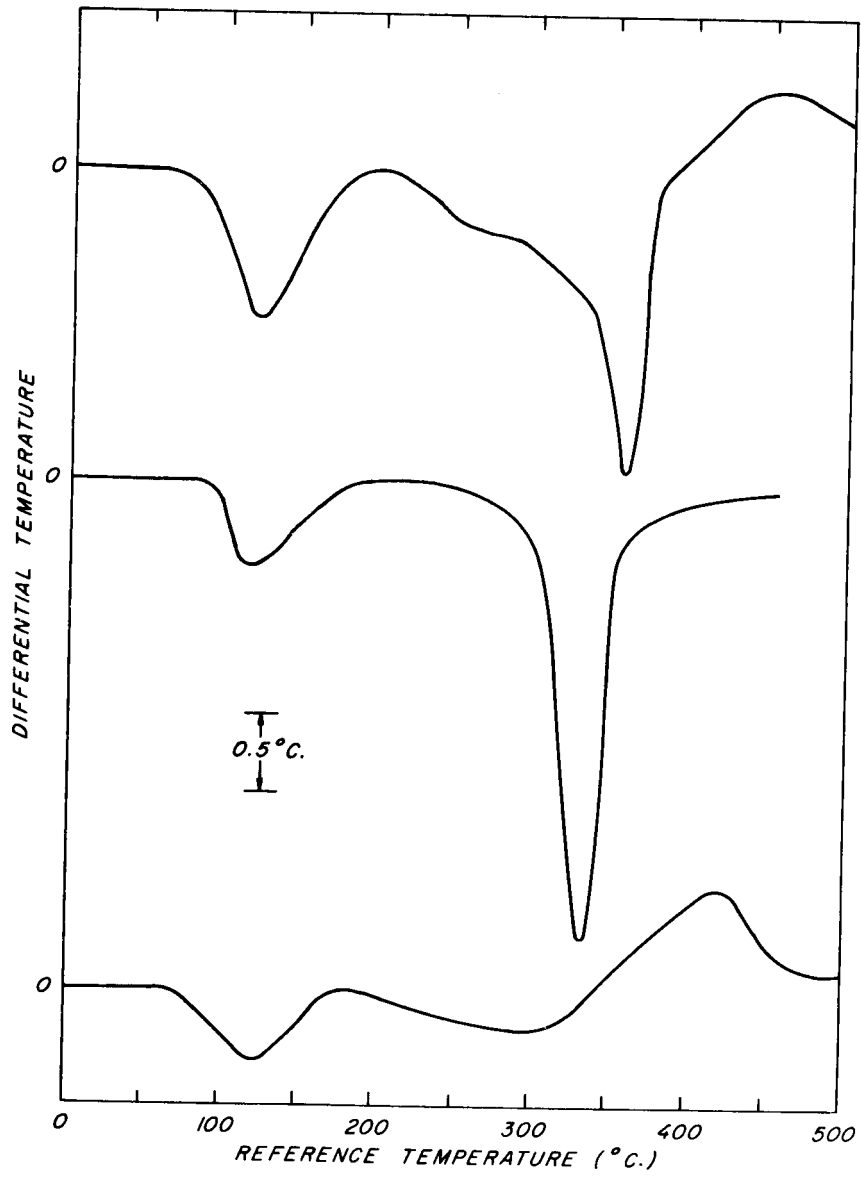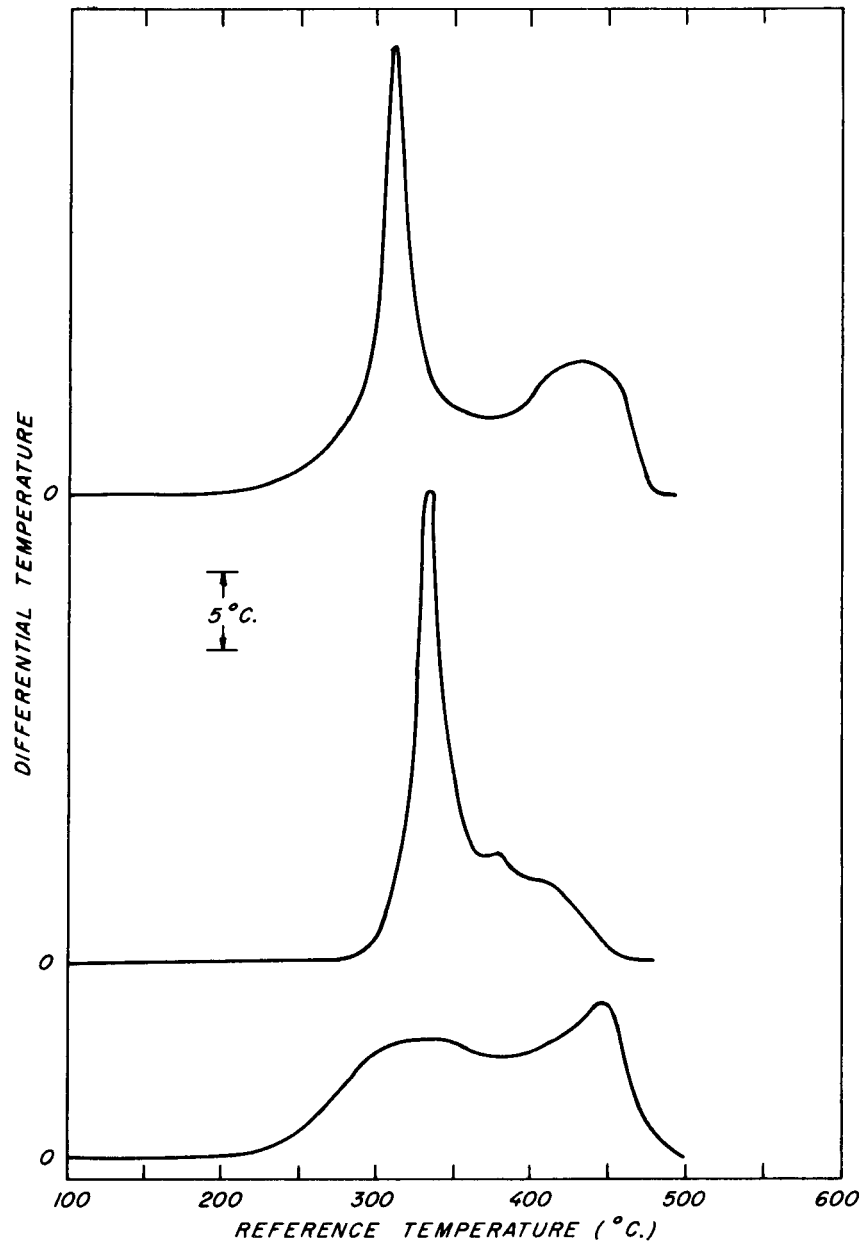
Figure 13. Differential thermal analysis of untreated wood (top), cellulose (middle), and lignin (bottom) run in oxygen atmosphere (47).
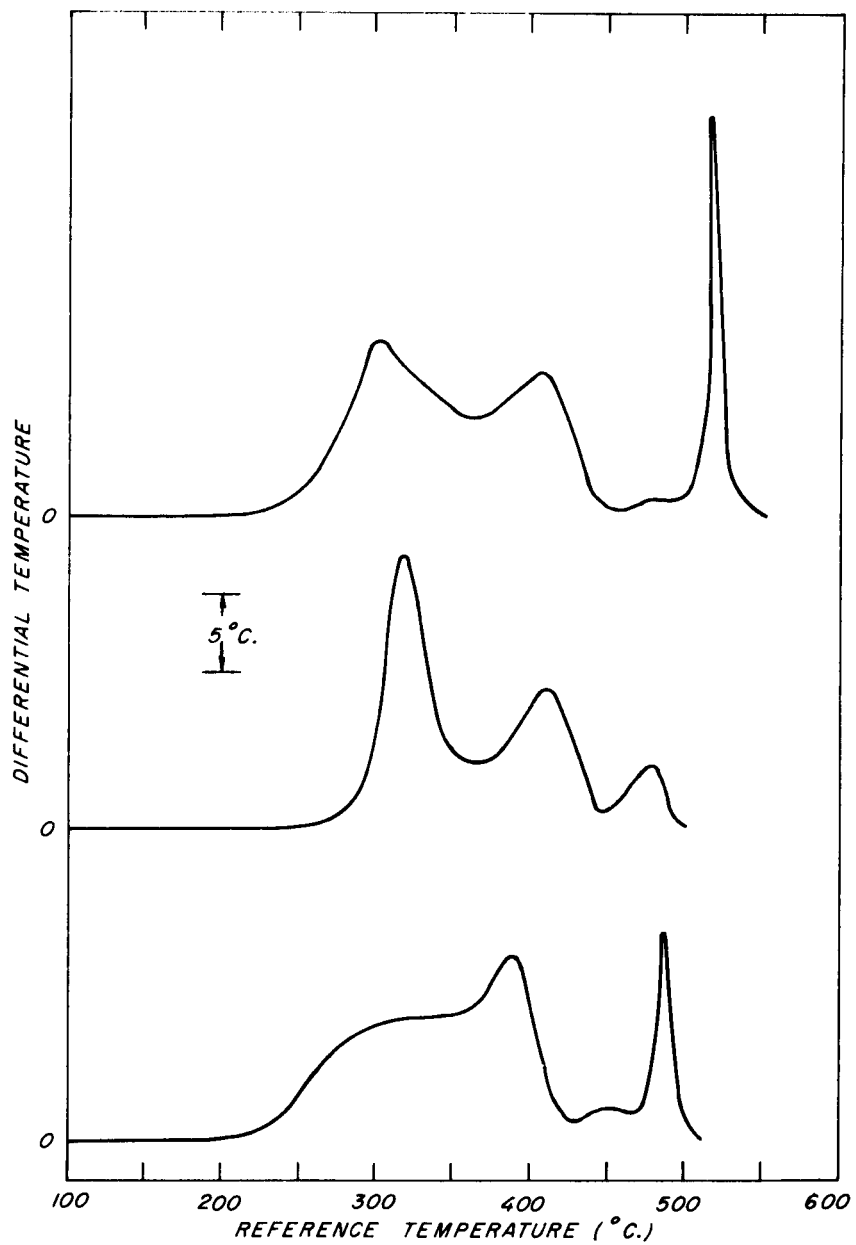
Figure 14. Differential thermal analysis of wood (top), cellulose (middle), and lignin (bottom) treated with 8% sodium tetraborate decahydrate run in oxygen atmosphere (47).

sodium tetraborate. Ammonium phosphate, in Figure 15, caused the most effective reduction in the height of the volatile products peak and also reduced the temperature at which this peak occurs. Also, ammonium phosphate almost eliminated the glowing exotherm. Table V lists the relative maximum heat intensities of the various inorganic and the temperatures at which these peaks occur *(47)*. From this table, we can conclude that effective fire retardants reduced the heights of the volatile products exotherms but had different effects on the glowing peak. (The effect on the glowing peak will be discussed under the section on smoldering combustion.) Further information on the effects of fire-retardant additives on pyrolysis and combustion is contained in References 41, 42, 45–48, 56, 62, and 63.

The heats of combustion of the volatile pyrolysis products released at various stages of volatilization were determined from untreated and chemically treated ponderosa pine *(64)*. Fire-retardant treatments reduced the average heat of combustion for the volatile pyrolysis products released at the early stage of pyrolysis below the value associated with untreated wood at comparable stages of volatilization. At 40% volatilization, untreated wood had released 29% of its volatile products' heat of combustion; treated wood had only released 10–19% of its total heat. Of all the chemicals tested, only NaCl, which is known to be an ineffective fire retardant, did not reduce the heat content. This reduction in heat content of the volatiles was confirmed by using thermal evolution analysis (TEA) *(55)*.

The effectiveness of various compounds by TEA (Table VI) can be compared to the effectiveness determinled by TG (Table VII) *(56)*. Except for a few compounds, such as NaCl, $NaHSO_4$, and Na_2CO_3, the ranking of the effectiveness of various fire retardants by the two different methods agree — high effectiveness numbers by TG correspond to high effectiveness numbers by TEA and vice versa. This is as expected if we assume the mechanism for fire retardancy is to increase the amount of char produced and lower the amount of volatile combustible products.

A reaction coulometer has been used to determine the rate of heat release from these combustible volatiles *(65)*. Table VIII shows these results on the effect of inorganic additives that were obtained by using reaction coulometry. The treated cellulose samples decomposed at lower temperatures and produced less heat than the untreated. Addition of 5% NaOH reduced the heat of combustion of cellulose volatiles at 500 °C to less than one-half of untreated *(65)*.

PHOSPHORUS–NITROGEN SYNERGISM THEORIES.   As mentioned previously, one role of phosphoric acid and phosphate compounds is to catalyze the dehydration reaction of wood to produce more char.
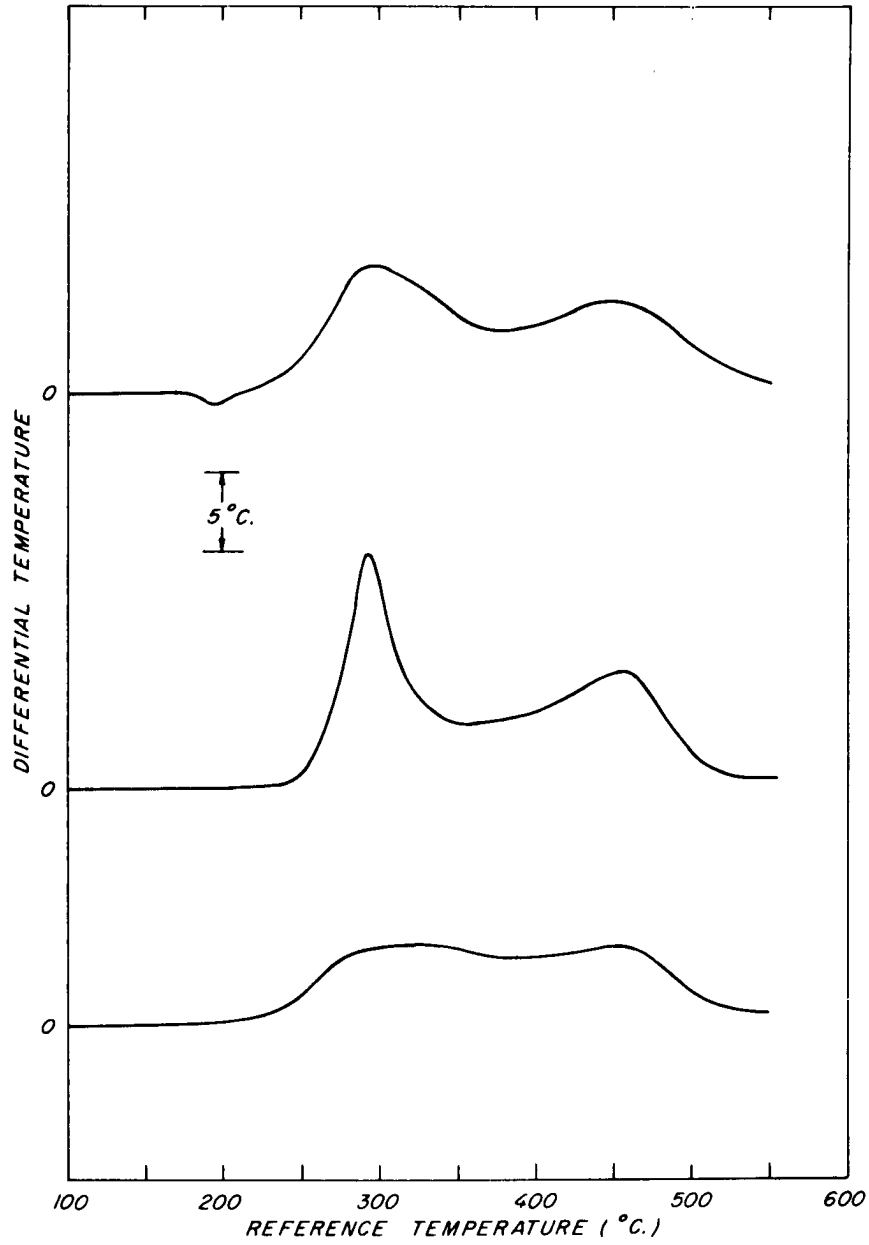
Figure 15. Differential thermal analysis of wood (top), cellulose (middle), and lignin (bottom) treated with 8% monoammonium phosphate run in oxygen atmosphere (47).

Table V. Relative Maximum Heat Intensity of Combustion by DTA for Wood, Cellulose, and Lignin

Sample Treatment[a]	Wood			Cellulose			Lignin		
		Solids			Solids			Solids	
	Volatiles	First Peak	Second Peak	Volatiles	First Peak	Second Peak	Volatiles	First Peak	Second Peak
8% aluminum chlo- ride hexahydrate	310 480	425 235	— —	305 675	420 260	— —	330 465	425 810	— —
2% monoammonium phosphate	300 480	450 235	— —	315 635	450 275	— —	335 370	455 360	—. —
8% monoammonium phosphate	295 340	450 240	— —	290 620	455 300	— —	330 290	455 270	— —
2% boric acid	300 650	440 190	— —	315 830	435 205	— —	310 465	430 540	— —
8% boric acid	315 505	440 240	— —	320 740	445 220	— —	320 415	435 390	— —
8% disodium phosphate	280 580	390 330	440 115	310 755	395 495	— —	295 505	575 600	440 105
8% ammonium sulfate	300 300	445 200	— —	285 460	450 260	— —	315 365	445 390	— —
8% ammonium pen- taborate octa- hydrate	310 545	440 200	— —	324 770	440 215	— —	310 515	425 440	— —

NOTE: Values are for 50 mg wood, 50 mg cellulose, and 30 mg lignin in flowing oxygen. The temperatures at which the peak took place ±3 °C are the top lines for each entry. The heat intensity of combustion, I_c, in calories per gram-minute ±5%, at each peak are the lower lines for each entry.

[a] Chemical percentages

(Reproduced from Ref. 47.)

Table VI. Effect of Inorganic Additives on
Thermal Evolution Analysis

Additive	Percent Carbon at 500 °C	Order of Effectiveness
H_3PO_4	13.9	1
$ZnCl_2$	23.4	2
NaOH	28.1	3
$(NH_4)_2HPO_4$	30.9	4
$NH_4H_2PO_4$	38.6	5
Na_2CO_3	39.5	6
$SbCl_3$ hydrate	45.0	7
H_3BO_3	55.0	8
$NaVO_3$	56.4	9
Na_3PO_4	59.1	10
$CaCl_2$	59.6	11
$SbCl_3$	60.6	12
$NaHCO_3$	63.9	13
NaCl	64.1	14
$Na_2WO_4 \cdot 2H_2O$	66.3	15
$(NH_4)_2SO_4$	66.5	16
$NaHSO_4$	68.7	17
$Na_2B_4O_7 \cdot 10H_2O$	69.9	18
$NaH_2PO_4 \cdot H_2O$	72.5	19
NH_4Cl	73.9	20
Untreated	76.2	21
$(NH_4)_2CO_3$	76.8	22

(Adapted from Reference 56.)

However, this reaction is always in competition with the other reactions that are taking place (i.e., decarbonylation, condensation, decomposition). The mechanism of a particular fire retardant is the summed effect of all simultaneous reactions. This summed effect is especially evident in the synergism of some compounds; the effect of two compounds together is greater than the summed effect of each individual one alone (9, 51, 71–73).

Phosphorus and nitrogen have displayed such a synergistic effect, and much work has been done to understand this. Although most of the work has been done on fabrics, the same synergistic effect between phosphorus and nitrogen appears in wood.

The interaction of phosphorus and nitrogen compounds produces a more effective catalyst for the dehydration because the combination leads to further increases in the char formation and greater phosphorus retention in the char (43, 71–73). This result may be caused by the cross-linking of the cellulose during pyrolysis through

Table VII. Effect of Inorganic Additives on
Thermogravimetric Analysis

Additive	Percent Weight Loss at 500 °C	Order of Effectiveness
H_3PO_4	61	1
$(NH_4)_2HPO_4$	66	2, 3
$NH_4H_2PO_4$	66	2, 3
$ZnCl_2$	74	4
$NaOH$	79	5
H_3BO_3	81	6
$NaCl$	82	7
$CaCl_2$	83	8
$NaHSO_4$	84	9, 10
$SbCl_3$	84	9, 10
$NaVO_3$	85	11
$SbCl_3$ hydrate	86	12, 13
$(NH_4)_2SO_4$	86	12, 13
Na_2CO_3	87	14, 15
$NaH_2PO_4 \cdot H_2O$	87	14, 15
$Na_2B_4O_7 \cdot 10H_2O$	89	16
$Na_2WO_4 \cdot 2H_2O$	90	17
Na_3PO_4	91	18
$NaHCO_3$	92	19
NH_4Cl	93	20, 21, 22
$(NH_4)_2CO_3$	93	20, 21, 22
Untreated	93	20, 21, 22

(Adapted from Reference 56.)

Table VIII. Effect of Inorganic Additives on Heat Release as
Determined by Reaction Coulometry

Additive	ΔH_1 (cal/g)			
	200 °C	300 °C	400 °C	500 °C
Untreated	12	69	3214	3364
$NaHCO_3$	9	175	2384	2565
Na_2CO_3	14	390	1842	2083
$NaOH$	45	543	1180	1441

(Adapted from Reference 65.)

ester formation with the dehydrating agents *(71)*. Also the presence of amino groups causes retention of the phosphorus as a nonvolatile amino salt *(71, 73, 74)*, in contrast to some phosphorus compounds that may decompose thermally and be released into the volatile phase *(51)*. Another possibility is that the nitrogen compounds promote polycondensation of phosphoric acid to polyphosphoric acid *(51)*. Polyphosphoric acid might also serve as a thermal and oxygen barrier because it forms a viscous fluid coating *(75)*. Whatever the particular mechanism is, it is apparent that some other reactions are preceding the dehydration reaction in order to make it more effective.

SMOLDERING INHIBITION THEORIES.   In Chapter 13, Shafizadeh describes the pyrolysis of cellulose by two pathways. The first pathway leads to abundant char that can promote glowing. Flaming is inhibited due to the lack of combustible volatiles. The second pathway leads to combustible levoglucosan and other tars that promote flaming; little char remains for glowing. Oxidation of the carbonaceous char promotes smoldering combustion which is a more localized and slower process than flaming combustion. This type of combustion proceeds as a moving front in the solid phase.

The low-intensity heat flux required for smoldering combustion is provided by the oxidation of the preceding char. Diffusion of oxygen into the char is the rate determining step in this process. The reactions occurring in smoldering compete with each other and, therefore, are influenced by the physical conditions such as material, density, temperature of exposure, radiation losses, and additives present. Shafizadeh in Chapter 13 and elsewhere *(67, 68)* provides a good explanation for smoldering behavior.

The ratio of CO to CO_2 produced in smoldering combustion is influenced by various additives *(68–70)*. Phosphates and berates increase the $CO:CO_2$ ratio. Metal ions such as sodium and potassium reduce this ratio and promote smoldering combustion *(68)*. Smolder promoters tend to be either monovalent metal cations or metals such as iron, lead, or chromium *(70)*. The metal ions aid the dissociation of the adsorbed molecular oxygen, thereby promoting the smoldering process *(60, 67–69)*. Ammonium phosphate and boric acid, which are known to inhibit smoldering or glowing, may interfere with the active sites thereby blocking the process.

Fire-Retardant Formulations

Many chemicals have been evaluated for their effectiveness as fire retardants. Today most fire retardants for wood are based on phosphorus, nitrogen, boron, aluminum trihydrate, and a few other compounds. Phosphorus and nitrogen are frequently used together

because they behave synergistically; amino-resins are an example of such a combination. The chemicals discussed in this section may be either pressure impregnated into the wood or applied to the wood surface, depending on the particular formulation.

Most fire-retardant formulations are not resistant to leaching by water. Therefore, there have been increased efforts to develop leach-resistant chemicals that can he impregnated into wood products for use in exterior or high humidity applications. Some of the proposed leach-resistant systems include chemical combinations that form insoluble complexes, amino-resin systems, and monomers that polymerize in the wood.

Major Chemicals. PHOSPHORUS.   Combination salts of the phosphates have been used for retarding wood since the time of Gay-Lussac. Monoammonium and diammonium phosphates have been the most effective. The efficiency of phosphorus compounds can he increased by the presence of certain nitrogen compounds that produce a synergistic effect. The advantage of such synergism is that increased flame-spread resistance can be achieved with lower chemical loading levels. The amino-resin systems are based cm this synergistic effect.

Organophosphorus and polyphosphate compounds also have been used as fire retardants. In one study, ammonium polyphosphate was used at loading levels of 96 kg/m^3 to achieve a flame-spread index of 15 according to ASTM E 84 *(12)*. This treatment produced low smoke yields; however, this treatment was corrosive to aluminum, slightly corrosive to mild steel, but not corrosive to brass *(77)*. In a patent by Clermont *(78)*, phosphorus pentoxide, dimethylformamide, and urea were used to produce fire-retardant paper or veneer. Other patents *(79, 80)* describe the reaction of ammonia with partial esters of polyphosphoric acid. All patents demonstrated some leach resistance of the phosphorus.

BORON.   Boron compounds have been used to treat wood for fire retardancy. Borax and boric acid, the primary fire-retardant compounds, have low melting points and form glassy films on exposure to high temperature. Borax, also known as sodium tetraborate decahydrate, is available in other hydrated states. Sodium tetraborate pentahydrate can be used in place of the decahydrate at a weight ratio of 74 (pentahydrate) to 100 (decahydrate) *(81)*.

The borax inhibits surface flame spread but also can promote smoldering or glowing. In contrast, boric acid reduces smoldering and glowing combustion but has little effect on flame spread *(82)*. Therefore, these chemicals are used together. This combination of chemicals has some advantages over other inorganic salts. Strength

tests indicate that the alkaline borate solutions produce a smaller reduction on modulus of rupture (MOR) than do the acid treatments *(83)*. The borate solution is also less corrosive and less hygroscopic.

A form of the borax and boric acid solution frequently used to fire-retard wood products is called polybor and has a general formula of $Na_2B_8O_{13} \cdot 4H_2O$. When borax, $Na_2B_4O_7 \cdot 10H_2O$, is added to a saturated boric acid solution, the solubility increases. Polymerization of the polyborates removes boric acid and borate ions from the solution, thus permitting more boric acid or borax to dissolve. This resulting solution (which is near the Na_2O/B_2O_3 ratio of maximum solubility) is polybor. This material dissolves rapidly in water to form a supersaturated solution. The high volubility of this product is an asset for fire-retarding wood products *(84)*.

Boron compounds have been used in several ways to achieve reduced flammability of wood products. Borax and boric acid can be incorporated into particle board chips before addition of a dicyandiamide, phosphoric acid, amino-resin system *(85)*. They can also be used to produce a fire-retardant hardboard. Riem and Dwars *(86)* added water-soluble ammonium borate to wood fibers before the board was formed. A 6–7% boron content produced a hardboard that had a flame spread of 25 or less.

Boron compounds can be added in combination with other chemicals such as nitrogen and phosphorus. A solution containing sodium tripolyphosphate, boric acid, and ammonia provides a ready-to-use treatment on cellulose products such as plywood, fiberboard, and cardboard *(87)*. The resulting products passed the British Standard 476, Section 6 (Fire Propagation test) Class 0 and Class I requirements of the British Standard Section 7 (Surface Spread of Flame).

Aluminum trihydrate also can be used in conjunction with boron compounds, because a synergistic effect between the boron and aluminum trihydrate exists *(88)*. Hardboard, containing 28% aluminum trihydrate and 6% boron, can be produced and has a flame spread of 25 or less. The aluminum trihydrate is added to a slurry of water and wood fiber. The boron solution is added to the surface of the wetlap or as an impregnated solution in a secondary treatment *(88)*.

ALUMINUM TRIHYDRATE.   The utility of aluminum trihydrate as a flame retardant is based on its endothermic dehydration to aluminum oxide and water. In absorbing some of the heat of combustion and lowering the temperature of the substrate near the flame, the hydrate functions as a chemical heat sink. The water vapor provided by such action dilutes the gaseous reactants in the flame until all the water of crystallization is exhausted.

Aluminum trihydrate also can be used as the only fire-retardant

ingredient in the production of fiber-board *(89)*. However, other research indicates that it is more effective when used in combination with other chemicals *(88, 90, 91)*. Hardboard and particle board can be produced by incorporating boron compounds (as mentioned previously) and amino-resin systems.

MISCELLANEOUS CHEMICALS.   The possibilities for various combinations of the chemicals already discussed are endless. There have been some efforts with other chemicals that have not been studied as intensively as the phosphorus, boron, and aluminum compounds. Brominated lignin sulfonate and brominated Kraft lignin *(92)* reduced the char length of paper treated with this solution. Turnbo et al. *(93)* incorporated 1,1,2,4-tetrabromo-2-butene with an organic solvent in order to surface coat wood splints. The splints treated with the solution containing 80% of the 1,1,2,4-tetrabromo-2-butene had a limiting oxygen index of 42 compared to 21 for untreated according to ASTM D 2863 *(93)*.

Oxalates also have been used as fire retardants for wood products *(94)*. They behave like other inorganic salts. Specimens impregnated with potassium oxalate promoted degradation of wood components in the temperature range of 180–320 °C as well as retarding active decomposition during flaming combustion.

Leach-Resistant Chemicals.   INSOLUBLE COMPLEXES. Leach-resistant fire retardants can be formed by reacting soluble salts with metal salts to form insoluble, metallic salt complexes. Sodium silicate reacted with calcium chloride formed an insoluble, hydrated calcium silicate *(95)*. Application of a 20% diammonium phosphate solution, followed by a 20% magnesium sulfate solution, has been proposed as a ready-to-use treatment for wood roofs *(96)*. This combination forms an insoluble magnesium ammonium phosphate and is recommended for roofs that are 5 years old or older. Test results indicate that this treatment provides increased flame-spread protection.

McCarthy et al. *(97)* tested a zinc, copper, chromium, arsenic, phosphor-us preservative on fence posts. The addition of the zinc and phosphorus eliminated the afterglow problem caused by this treatment. However, incorporation of the phosphorus reduced the effectiveness of the decay resistance.

AMINO-RESINS.   The most widely studied leach-resistant systems are the amino-resins. Goldstein and Dreher *(98)* first applied these systems as fire retarants. Basically, the amino-resin systems involve the combination of a nitrogen source (i.e., urea, melamine, guanidine, or dicyandiamide) with formaldehyde to produce a methylolated amine. The new product is then reacted with a phosphorus compound such as phosphoric acid. Because there is a synergistic effect between the phosphorus and the nitrogen. reduced loading

levels can achieve the same level of fire retardancy as each compound alone *(9, 99, 100)*. A composition containing 1.4% phosphorus and 0.4% nitrogen will give the same degree of fire-retardant effectiveness as one with 3.5% phosphorus alone.

In the past, the problems with the amino-resin systems were its limited pot life, leaching of the phosphorus, and excess formaldehyde emission. Recent research has addressed these problems.

Researchers at the Eastern Forest Products Laboratory in Canada have evaluated the urea and melamine amino-resin systems *(9, 57, 99-110)*. Their work demonstrates that both systems show good leach resistance and reduced flame spread. The stability of these resins is controlled by the rate of methylolation of the urea, melamine, and dicyandiamide. The optimum mole ratio for stability of these solutions is 1:3:12:4 for urea or melamine, dicyandiamide, formaldehyde, and orthophosphoric acid. However, even at the optimum mole ratios, the pot life of the melamine system is less than that of the urea system. In both systems the nitrogen is fixed to a greater degree than the phosphorus. However, the degree of fixation of the phosphorus is greater with the melamine than with the urea. The melamine structure may promote formation of compounds with phosphoric acid that are less soluble than those from urea and dicyandiamide.

Another method to increase the stability of the solution, especially for transport purposes, is to use monomethylol dicyandiamide. This eliminates the need for adding formaldehyde and decreases the polymerization rate during transport. Solid monomethylol dicyandiamide was mixed with solid melamine *(111, 112)*. This solid composition can then be shipped to treating facilities where it is mixed with water and then reacted with phosphoric acid. A similar modification allows dicyandiamide to react with formaldehyde at elevated temperatures until no free formaldehyde exists *(111)*. The melamine is then added and the solution can be shipped. Both modifications increase the stability of the solution and eliminate the excess formaldehyde.

Another advantage of the amino-resin systems is their applicability to solid wood and wood-composite products. Cedar shingles were the first products treated with this type of fire-retardant system *(99, 100, 113, 114)*. Commercially treated shingles available in the U.S. are based on these systems. Generally, these systems exhibit good durability to outdoor weathering when tested over extended periods *(115-17)*.

The amino-resins are also suited for use on wood-composite products. In some cases the fire retardant can act as the hinder for particle board *(99, 100)*, the adhesive for plywood *(99, 100)*, or a

flame-retardant finish sealer for decorative plywood *(100, 118, 119)*. In other-cases, the amino resin is added as the fire retardant to the fiber finish used in making particle board *(120)* and hardboard *(121, 122)*. All products demonstrate reduced flame spread. However, the amount of amino-resin incorporated governs the degree of flame-spread reduction. The amount incorporated involves a compromise among the properties of the board such as flame spread, strength, and dimensional stability.

OTHER METHODS.   Other methods used to improve the leach resistance of fire retardants include many different techniques. Most involve incorporating a monomer into the wood, followed by a curing procedure. Most of the investigated monomers are organophosphorus compounds that can be used alone *(123–25)* or with other fire-retardant salts *(126–28)*. Addition of combustible polymers (i.e., polymethyl methacrylate, polystyrene) result in higher values of percent burned than the control due to the additional amount of combustible material. The addition of fire-retardant salts reduces this value considerably, although not to the level of the fire-retardant salt alone. Other monomers investigated include tetrakis(hydroxymethyl)phosphonium chloride (THPC) *(115, 117, 129)*, other salts of the tetrakis(hydroxymethyl)phosphonium group *(130)*, and a cyclic sulfonium zwitterion monomer *(131)*. Although several of these techniques may have possibilities they have not been researched thoroughly.

Of all the proposed leach-resistant formulations, only the amino-resin systems are used commercially. The high costs of many of the other proposed techniques limit their acceptability.

Future Research

Although much research has been done on fire retardants for wood, there are many areas where improvements are needed.

Leach-Resistant Compounds.   Progress for improving the leachability of fire retardants has been made in the past decades. Several commercial treatmcnts are available for exterior use. However, even these demonstrate some leaching of chemicals. Further work needs to he done to increase the leach resistance of these treatments without excessively increasing the cost. Improved leach resistance will be necessary to expand wood products into commercial and institutional buildings.

Improved Fire-Retardant Treatments for Panel Products.   Fire-retardant treatment for panel products is also an area where research efforts need to be concentrated. Currently, there is only one commercially available fire-retardant-treated particle hoard that qualifies for use in commercial and institutional buildings. Ex-

panding the wood products market to such buildings will increase the demand for this product. However, fire-retardant treatments for panel products still suffer from certain disadvantages, primarily reduction of physical properties because of the fire retardant. Further work needs to be done on the development of fire-retardant treatments that minimize these undesirable effects on the properties of treated wood. Alternate treating techniques would expand the range of fire-retardant treatments that could be used and also reduce the cost.

Effective Coating Systems.   Research work in the area of intumescent coatings would benefit both solid and composite wood products. In some instances, the coating system is the more cost-effective treatment, particularly in cases of retrofitting a building. Further work needs to be done on improving the durability and effectiveness of coatings. Also, coatings are needed that are durable to exterior weathering, especially UV degradation. Intumescent coatings incorporated with adhesive binders have been suggested for use in panel products.

Reduced Smoke and Toxicity.   The smoke and toxic products of combustion are a problem of growing concern. Until recently, this problem has been overlooked in developing fire retardants. Future formulations will not only have to limit flame spread, but also limit smoke and toxic combustion products. Addition of smoke suppressants to some formulations may improve some systems. Modification of systems may also be necessary to meet possible code restrictions. More research is necessary in this area to understand the mechanism of smoke production and accumulation.

Basic Mechanisms.   Finally, further work is necessary on fundamental mechanisms of individual fire retardants. These mechanisms are a function of the particular chemicals involved and the environmental conditions of the fire exposure. There is a need to establish common methods and conditions for determining these mechanisms in order to compare different treatments. This would give us a better understanding of how these compounds work in action and would provide a more efficient approach for formulating fire-retardant systems than a trial and error approach. Correlations also need to be established between rapid precise thermal analysis methods and standard combustion tests. Retardant formulations could be evaluated initially on smaller (research and development size) samples. The more promising treatments could be tested for flame-spread index, heat release rate, and toxic smoke production.

Summary

The addition of fire retardants can reduce the flammability of wood; however, this may occur at the expense of related wood prop-

erties such as strength or increased smoke production. Therefore, fire retardants are formulated for best overall performance, including flame spread, smoke reduction, and reduced rates of heat release. The chemicals can he applied to wood products as either an impregnated solution or a coating. The application method depends on the formulation and the end-use of the product.

Mechanism.   No single mechanism explains the action of all fire retardants, so they probably work through a combination of several mechanisms. The mechanisms of fire retardants in wood involve a complex series of simultaneous reactions whose products may affect subsequent reactions. Pyrolysis of cellulose involves dehydration, depolymerization, decarbonylation, decomposition of smaller compounds, condensation, and other reactions. These pyrolysis reactions occur both in the solid phase and vapor phase. Addition of fire retardants will alter the reactions; however, this alteration will depend on the additives, the material, and the thermal–physical environment. The presence of oxygen adds subsequent and competitive oxidation reactions to the above series. These oxidative reactions can take place in both the solid and vapor phases. Evidence indicates that most fire retardants reduce combustible volatiles production and limit combustion to the solid phase. The best retardants also inhibit solid-phase oxidation to effectively remove the fuel from the fire.

Lignin thermally decomposes to char and contributes little to flaming combustion. Most of the flaming combustion from wood is attributed to the hemicellulose and cellulose. However, lignin does support oxidation in the solid phase. Some fire retardants, such as phosphorus and boric acid, inhibit oxidation in the solid phase; other additives, such as sodium compounds, may promote it.

In addition to the chemical mechanisms of fire retardants, thermal or barrier-type mechanisms may be operative. Coatings may prevent oxygen from reaching the wood surface. Dilution of combustible gases by noncombustible gases and inhibition of flaming by free radicals can also be in effect. Therefore, fire retardancy of wood involves many complex reactions. The effectiveness of a particular fire retardant depends on the overall summation of these competitive and sequential reactions and the thermal and physical environment of the material.

Formulations.   Fire-retardant formulations are numerous, although most of them are based on the inorganic salts, such as diammonium phosphates. Increased emphasis on improving the related wood properties associated with fire retardants has led to many interesting and creative formulations and processes.

Phosphorous compounds are the main chemicals used in most formulations. These compounds range from inexpensive ammonium phosphates to the more exotic ones such as phosphorous pentoxide

and polyphosphoric acids. Improving the leach resistance of the phosphorous compounds is a major problem.

The herons are also effective and efficient fire retardants for wood. They are leachable hut they do not reduce the strength or increase the hygroscopicity of the wood as some other compounds do. Little work has been done on the mechanism of action of the borons.

Other compounds such as aluminum trihydrate and silicate compounds have also been tried as fire retardants for wood. These compounds work best in combination with other chemicals, especially those in which the behavior is synergistic.

Future Research.   Improvements in leach-resistant chemicals have been a primary concern over the past decade. Advances have been made in leach-resistant systems such as the amino-resin systems; however improvements still need to he made in leach-resistant compounds without increasing the cost. Other areas where research on fire retardants needs to be conducted are in coating systems, especially those that are durable to weathering and UV degradation; reduction of smoke and toxic products, improvements in fire-retardant treatments for panel products; and fundamental work on the mechanisms of particular formulations.

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