Borates for fire retardancy in cellulosic materials

1. Introduction

The burning of cellulosic materials occurs by two alternative mechanisms (References 1 and 2). Temperatures of 300°F (149°C) or above cause thermal degradation of cellulose into gaseous, liquid, tarry, and solid products. The volatile, flammable gases ignite and provide additional heat to further pyrolyze the liquids and tars into more flammable vapors, and also to form residues, mainly carbonaceous char and a gas mixture containing water and carbon dioxide. This process continues until only the carbonaceous residues are left. The second pathway operates at lower temperatures with the carbonaceous char from pyrolysis. The oxidation of the resulting char is a slow and localized process called glowing or smoldering combustion. Smoldering combustion may occur in the charred area or consume the entire specimen, proceeding as a front in the solid state rather than a flame in the gas phase. Fire retardants are broadly classified as either flame retardants or smoldering retardants. Flame retardants refer to chemicals added so that the treated material will not support flaming combustion after the igniting flame is removed. Smoldering retardants refer to chemicals which effectively prevent smoldering combustion, the flameless combustion of materials which occurs after the igniting flame is removed. Smoldering combustion is the heart of the fire hazard problem due to its potential for transition to flaming combustion.

Four different theories have been developed for describing the action of fire retardants. They are identified as the chemical, thermal, coating, and gas theories. For the purposes of this report we will be discussing chemical fire retardants. Chemical fire retardants commonly used are *Optibor*® boric acid, *Neobor*® borax pentahydrate or borax decahydrate, ammonium sulfate, ammonium phosphates, aluminum sulfate, aluminum trihydrate, and gypsum. These chemicals are generally used in combinations of two or three different chemicals. The most common combination is boric acid, *Neobor* borax pentahydrate or borax, and ammonium sulfate. To better understand the subject of fire retardancy it is necessary to comprehend the various fire retardant mechanisms exhibited by the aforementioned fire retardants. This can apply to most cellulosic applications.

1.1 Fire retardant mechanism

Combustion of cellulosic materials can occur in a primary mode, where visible flames are present, or in a secondary mode, where flames are absent. In the latter case, the combustion is referred to as glowing or smoldering, depending on whether or not light is emitted.

Borate-based compounds

Borates act primarily in the solid phase, where they promote the formation of char and inhibits the release of combustible gases from the burning materials. The release of chemically bonded water in *Optibor* boric acid, *Neobor* borax pentahydrate or borax decahydrate also reduces flame combustion. The formation of protective coating on the char from the melted boric acid is believed to be responsible for reduced air oxidation. This might explain why boric acid is effective in preventing smoldering combustion. Both *Neobor* borax pentahydrate and borax decahydrate are very effective at preventing flaming combustion but relative ineffective in the suppression of smoldering.

Ammonium-based compounds

Ammonium phosphates are believed to act as fire retardants by their ability to increase markedly the conversion of organic matter to char during burning and thus to decrease the formation of flammable carbon containing gases. Combustion is inhibited because the char does not burn readily and the amount of combustible gases is greatly reduced. Both of these compounds contain no chemically bonded water. These chemicals decompose and release ammonia with rapid weight loss beginning in the temperature range of 200 to 300°F (93 to 149°C). Ammonium sulfate (like aluminum sulfate) acting as a fire retardant is probably due to an increase in the production of char. Ammonium sulfate decomposes in the temperature range of 400 to 500°F (204 to 260°C) with an associated odor of released ammonia.

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Aluminum-based compounds

The reason aluminum sulfate act as fire retardants is probably due to the increased production of char. Aluminum sulfate starts to lose its chemically bonded water in the temperature range of 200 to 300°F (93 to 149°C). When heat is applied to materials containing aluminum trihydrate the temperature rise is slowed down because this material absorbs heat and releases water. The water vapor dilutes and cools the combustible gases and retards their burning.

Gypsum compounds

Like aluminum trihydrate, when heat is applied to gypsum, the temperature rise is slowed down as well because this material absorbs heat and releases water. The water vapor dilutes and cools the combustible gases and retards their burring.

2. Cellulose insulation

During the energy crisis of the 1970s, the public became much more concerned about the energy efficiency of their homes. One of the simplest ways to increase energy efficiency of a house is to lower the heat loss to the surroundings by increasing thermal insulation in the house.

Because of its high insulating value, ease of application, especially for existing homes, and relative low cost, cellulose loose-fill insulation was a frequently utilized insulating material. For example, a layer of cellulose 5 inches deep is used for an approximately R-value of 19, where R-value is a measurement of resistance to heat transfer through the material; the higher the R-value, the better the insulation.

2.1 Manufacturing process

Cellulose insulation is produced by passing shredded newsprint through a hammer mill which converts it to a fibrous consistency with a high thermal insulation value. Loose-fill and spray-on cellulosic insulation are used extensively in the walls and attics of residential and commercial buildings. The oldest and simplest use is loose-fill

cellulose in attics. The insulation is blown or poured into the attic space. Dry-blown cellulose is also installed in walls as a retrofit insulation material. The loose-fill cellulose insulation has an apparent thermal resistance of 3.2 to 3.7 ft^2 hr °F/BTU per inch of thickness at a density of 2.2 to 3.5 lb/ft^3. (Reference 3).

There are two major processes for the preparation of loose fill cellulose: dry process and wet process. The dry process is the more widely used in the industry and it generally follows the scheme shown below. The first mill breaks the paper into approximately 1-2 inch size pieces through the use of swinging hammer or rotary cutters. The flame retardant chemicals are usually introduced simultaneously with the ground paper at the second mill. This is the most critical stage of the manufacturing process to maintain a consistent quality of product. Introduction of chemicals may be by pneumatic means, gravity feed, or auger feed. In many processes, the chemicals are pre-blended, and then ground in a mill to the consistency of fine four. The finely ground material is dispersed more readily and easily blended into cellulosic material. A newly designed mill to produce long cellulose fibers of a lower density and higher R-value was pioneered by several producers.

The wet process involves introduction of an aqueous fire retardant solution which is sprayed onto the shredded paper leaving the first mill and prior to entering the second mill. This method relies on the evaporative ability of the air stream and the sort duration heat buildup in the final milling process to remove excess moisture. Wet processes offer a potentially improved product with better chemical dispersion and fire retardant characteristics with less chemicals. The disadvantage of needing a drying operation with the associated energy requirements should be balanced against the benefits of the process.

2.2 Installation

There are a number of ways to install cellulose insulation. The simplest use is loose-fill cellulose in attics. The insulation is blown or poured into the attic space. Dry-blown cellulose is also installed in walls as a retrofit insulation material.

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Spray-on cellulose has water and/or binder added during installation to make it stick when blown into wall cavities. Spray insulation can provide insulation and sound control of exterior cavity walls in residence, apartments, hotels, and offices.

Adhesive concentrate can be pre-mixed with water and sprayed into the product as a fine mist or added to the product during manufacture which is activated by a water spray at the nozzle during its installation. A major advantage of spray insulation over other types is its ability to provide a completely homogeneous coverage for thermal and/or acoustical treatment that is free of voids or cracks.

Another relatively new formulation of cellulose insulation (stabilized cellulose) is used in attics. This product has a binder (a polyvinyl acetate or an acrylic adhesive) in it and is applied with a small quantity of water. The binder prevents settling, which may otherwise reduce the installed thickness of loose-fill cellulose insulation by as much as 25%. One of several manufacturers producing stabilized cellulose achieves a 1.3 lb/ft^3 density with its stabilized attic insulation. Two other approaches used for walls do not require water. In the dense-pack process, cellulose is blown into closed wall cavities at a relatively high density of 3 to 3.5 lbs/ft^3. Because of the high density, settling does not occur. With the other approach, installers use forms to blow dry cellulose into open wall cavities. The forms, which are propped against the inner side of stud bays, hold the insulation in place as it is installed, and the insulation stays in place after forms are removed and until the inner wall surface is installed.

2.3 Fire retardant treatment

Cellulose insulation is flammable and particularly prone to smoldering combustion so it is necessary to incorporate flame retardants. In 1981, the State of California began requiring all cellulose insulation sold in the state to be flame retardant and smolder resistant. Flame retardant means the material resists the spread of an open flame. Smoldering combustion is a non-flaming combustion; the most common example being a burning cigarette. Cellulose can be treated by a number of different chemicals to achieve flame retardancy and smolder

resistance. Boric acid is the primary chemical applied for smolder resistance and *Neobor* borax pentahydrate the primary chemical for retarding flame spread, although other chemicals such as ammonium sulfate, ammonium phosphates, aluminum sulfate and aluminum phosphate are also used (Reference 4).

The concentrations of chemicals commonly added in commercial cellulosic insulation normally range from 10 to 40% by weight (Reference 5). Chemicals commonly used are *Optibor* boric acid, *Neobor* borax pentahydrate, sodium borate, ammonium sulfate, aluminum sulfate, aluminum trihydrate, mono- or di-ammonium phosphate. These chemicals are generally used in combinations of two or three different chemicals. The most common combination is boric acid mixed with sodium borate such as borax decahydrate or *Neobor* borax pentahydrate. Most effective flame retardants increase the quantity of carbon formed at the expense of flammable tars, lower the decomposition temperature of cellulose, and raise the temperature at which exothermic pyrolysis occurs (Reference 6).

2.4 Common problems associated with fire retardants

Ammonium sulfate is deleterious since it combines with moisture to form acidic byproducts which have been found to cause corrosive damage to electrical wiring. Moisture in the heavily moisture-laden air from a bathroom or range hood tends to condense on the exposed insulation on cold days. This condensation has been found to form the acidic byproducts from ammonium sulfate. There have been anecdotal reports of copper pipes and steel truss fasteners in attics corroding when in contact with cellulose insulation that has gotten wet. With the rising popularity of wet-spray cellulose for wall applications, the issue of corrosion is particularly significant. Many wet-spray cellulose installers specify material treated only with boric acid and borax to eliminate concern about corrosion. Additionally, ammonium sulfate is very soluble in water. Under the effect of moisture, ammonium sulfate will migrate due to the periodic solubilization upon moisture condensation followed by re-crystallization upon subsequent moisture evaporation so that the solubilized compounds are removed from portions of the cellulose. The exposed cellulose is thereby deprived

of its fire-retardant protection with a resulting, potentially dangerous condition. Accordingly, some governmental regulations have required the discontinuance of cellulose insulation products incorporating ammonium sulfate as the fire-retardant material. In addition to becoming very corrosive when getting wet, ammonium sulfate will react with strong oxidizers, decompose under heat or in alkalis. It reacts violently with bases to give off noxious ammonium vapor. Thermal decomposition of ammonium sulfate produces gaseous ammonia and oxides of sulfur. It may also produce toxic oxides of nitrogen.

The acidic monoammonium phosphate exhibits corrosive properties which must be neutralized. Borax constitutes neutralizing agent which inhibit corrosion thereby rendering the insulation non-corrosive. The pH of the agent should be above 7.5, more desirably between about 7.9 and about 8.3. A maximum amount of borax is desired because of its flame retardant properties. Ammonium phosphates as well as ammonium sulfate are effective smoke suppressants.

Aluminum sulfate is rarely used due to corrosion concern. Aluminum trihydrate is also seldom used because it is too abrasive to grind.

Today, most manufacturers use a mixture of borates and ammonium sulfate, and some add small quantities of ammonium phosphates. The *Optibor* boric acid/*Neobor* borax pentahydrate combination yields reliable fire and corrosion test performances. Ammonia-based compounds are cheaper but they are known to give off ammonia (especially in the presence of borax 5 mol). In addition, ammonia-based compounds can cause corrosion problems in the field. There is a trend in the industry to replace some of the borate with ammonium sulfate, because the latter is less expensive.

2.5 Permanency of fire retardants

Fire retardants used in cellulose insulation are expected to be effective not only at the time of manufacture but also for the life of the structure in which they are installed. Thus, the permanency of the fire retardants becomes an important consideration. Unfortunately, an accepted test for determining retardant permanence does not exist and this has caused the cellulose industry to be confronted with a confusing issue.

A lack of permanence means either that fire retardant has been transported away from the insulation or that redistribution of the chemical has left regions in the insulation with insufficient fire retardant. Several possible loss mechanisms for borates have been identified: Vibration, sublimation, leaching as well as separation during shipping and installation. Studies by researchers at Tennessee Technological University and Allied Signal Corporation provide evidence that the fire-retardant chemicals do not disappear from cellulose insulation except at much higher temperatures than would commonly be found in attics (Reference 7). Enough vibration to simulate 672 years of use in an attic was found to cause no measurable settling of boric acid or borax in test samples. As for evaporation (sublimation) of boric acid from cellulose, the study found that at very high temperature (90°C or 194°F) and 100% relative humidity, the loss of boric acid was significant, but the loss was negligible when the temperature is lower than 70°C (158°F), even at 100% humidity and air exchange rates of 2.0 attic changes per hour. It appears that it would take 300 years or more to lose enough boric acid under these conditions to significantly affect the combustion tests. Separate studies of ammonium sulfate by David Yarbrough and Allied Signal Corporation reached similar conclusions: That loss was not significant except at very high temperatures.

The potential loss of fire-retardant chemicals is believed to be the most significant concern relating to cellulose insulation. Further research on this concern is clearly needed, but the apparent lack of building fires in which cellulose insulation has been implicated gives us confidence that cellulose insulation is safe enough for use.

2.6 National standard for cellulose insulation

As a result of a large increase in sales of insulation sales of all types, especially cellulose insulation, and the appearance of a large number of unsophisticated newcomers in both the manufacturing and

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installation aspects of the business, the Consumer Product Safety Commission of the Federal Government adopted a national standard for cellulose insulation in 1978. The Federal Specification HH-I-515-D, currently in effect, (largely based on the ASTM C-177, -236, -518 and -739), consists of a series of tests such as design density, starch content, thermal resistance, moisture vapor absorption, odor emission.

In addition to corrosiveness, fungi resistance, critical radiant flux, and smoldering combustion are performed. The design density controls how much insulation should be used to achieve the required thermal resistance (R-value) in the attic of a building. Thermal resistance (R-value) is determined by measuring the apparent thermal conductivity of a 4 inch or greater thickness of insulation. The R-value is the reciprocal of thermal conductivity. To get R-value per inch the R-value is divided by the thickness of the test specimen. The fire retardant chemicals used with the wrong ratio of chemical or if not buffered may be corrosive. The Federal Specification calls for tests with the insulation to determine its corrosiveness to steel, aluminum, and copper. Once a mix of fire retardant chemicals is found to be non-corrosive by the tests, the pH of the insulation is determined. As a control of the corrosiveness of the insulation in production the pH is determined. If it falls within proper limits the insulation is considered non-corrosive.

Fire tests: radiant panel, smolder combustion, flame spread

Fire resistance of the insulation is defined by two tests: critical radiant panel and smoldering combustion. The first test shows the resistance of the insulation to fire traveling on the surface of the insulation. The radiant panel test involves a horizontal sample, exposed to the radiation from a ceramic panel at about 1000°F (538°C) as in ASTM E-162 except the panel is tilted forward until it makes an angle of 30° with the horizontal. The sample is ignited with a pilot flame at the end receiving the most intense radiation. The distance the flame front advances front he ignition point (during a five-minute period) is determined. From a previously determined calibration, the incident radiant flux at that point is established and is termed the "critical radiant flux" (CRF). In order to meet the standard, the critical radiant flux must be greater than or equal to 0.12 watts/cm2. The sample of insulation to be tested is contained in a horizontal, stainless steel tray; it has been conditioned at 69.8°F (21°C) and 50% relative humidity for a minimum of 48 hours before testing.

The second shows its resistance to smoldering inside the insulation. The smolder test uses a sample of preconditioned cellulose insulation contained at its "settled density" in a stainless steel box 8" x 8" x 4". A hole is punched in the center of the sample with a sharp rod, and a lighted cigarette dropped into the hole.

The weight loss is determined after two hours, and must not exceed 15% for the sample to meet the standard.

Although it is not part of the Federal Specification, there is a test used by testing laboratories called flame spread. This compares the surface burning of insulation to red oak. Red oak's flame spread is 100. Cellulose insulation's flame spread is 25 or less.

3. Wood products

Building codes requiring the use of fire-retardant treated wood have been in existence for nearly 50 years.

3.1 Dimensional lumber/plywood

Flame retardant-treated lumber and plywood have been successfully evaluated for structural strength and durability at service temperatures per ASTM D5664 and AWPA Standard U1. The usual method of treatment of dimensional lumber and plywood is by vacuum/pressure impregnation with aqueous solutions of flame retardants. Flame retardant plywood can also be produced by impregnation of individual veneers, often just by soaking, prior to assembly and gluing into plywood. It is necessary to ensure compatibility between the flame retardant additives and the adhesive system to obtain strong bonding.

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Boron compounds by themselves are effective flame retardants in lumber or plywood (Reference 8). They can be used in conjunction with other flame retardant chemicals including ammonium sulfate, diammonium phosphate or zinc chloride (Reference 9). Several theories have been proposed for the mechanism of flame retardant chemicals. The most widely accepted mechanism is referred to as the chemical theory. This theory suggests that the retardant chemicals directly alter the pyrolysis of wood, increasing the amount of char and reducing the amount of volatile, combustible vapors.

Borate-based treatments also inhibit or reduce the rate of thermal degradation in wood exposed to elevated temperatures. It is of particular concern for roof-truss lumber and plywood roof sheathing due to the typical roof temperatures induced by solar radiation (References 10 and 11). The borate-treated wood showed no significant decrease in modulus of rupture values for all temperature exposures. The phosphoric acid treatment had the most deleterious initial and thermal induced effects on module of rupture. Although not as severe as the effects of phosphoric acid treatment, the monoammonium phosphate treatment also had deleterious initial and thermal induced effects on modulus of rupture.

Currently, flame retardant chemicals commonly used for treating lumber and plywood include boron compounds (eg, borax decahydrate, *Optibor* boric acid and *Neobor* borax pentahydrate) and phosphorus compounds (eg, phosphoric acid, monoammonium phosphate, guanylruea phosphate and diethyl-N,N-bis (2-hydroxyethyl) aminomethyl phosphate). Dicyandiamide is also used in the Dricon process for flame retardant treatment of wood products (Reference 12).

Borax-boric acid provides pH control. When used together with other chemicals, borates can neutralize some acidic commercial fire retardant chemicals and maintain a neutral pH. Phosphoric acid is not used as a sole ingredient in commercial formulations. However, it is a good fire retardant.

Monoammonium phosphate and guanylurea phosphate are commonly used in some commercial formulations. Diethyl-N,N-bis aminomethyl phosphate, a phosphate ester, is a good flame retardant because of its neutral pH.

Generally, in commercial practice, flame retardant compositions comprise a mixture of the above-mentioned additives. Four compositions detailed in the American Wood Preservers' Association (AWPA) Specification P10 were commonly used prior to 1975. The concern over hygroscopic properties, corrosion and strength loss in the flame retardant-treated wood resulted in the change from chemical specification to performance standard by the AWPA. Under AWPA Standard C20-96, structural lumber shall be treated for fire-retardance in accordance with the requirements of the AWPA Standard C1. The flame retardant system used shall be listed in AWPA Standard PX. Subsequent to treatment, the lumber shall be air or kiln dried to a maximum moisture content of 19%. When tested in accordance with ASTM E-84 tunnel test (the 25-foot tunnel test: This test method involves the use of 20-inch by 25-foot specimen exposed horizontally to a furnace operating under forced draft conditions). The two results of this test are the flame spread index and smoke developed index.), the lumber shall have a flame spread index of 25 or less. In addition, the lumber shall show no evidence of significant progressive combustion when the test is continued for an additional 20 minute period.

Furthermore, the flame front shall not progress more than 10.5 feet beyond the centerline of the burner at any time during the test.

For both Interior Type A Low Temperature (LT) and High Temperature (HT) lumber, material shall have an equilibrium moisture content of not over 28% when tested in accordance with the ASTM D3201 procedures at 92±2% relative humidity.

However, fire retardant treated lumber which will be used in high temperature applications such as roof trusses and framing shall be tested for strength in accordance with ASTM Standard D-5664 or by

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an equivalent methodology. At least one sample set shall be exposed for a minimum of 105 days.

Since fire retardant treated wood has the potential for further strength loss when exposed to elevated temperatures and humidity in case, users and specifiers should obtain appropriate design modification factors for initial effects on strength or for strength when end use is in extended high temperature and high humidity environments from the chemical supplier. Also, fire retardant treatments may change the corrosion potential of the fire retardant treated product compared to the untreated product. Users and specifiers should obtain fastener recommendations from the chemical supplier.

Flame retardant treated plywood composed of veneers shall be treated in accordance with the requirements of AWPA Standard C1. The performance standard, flame retardant formulations as well as effects of fire retardant treatments are similar for flame retardant treated lumber (see AWPA Standard C27-96). For fire retardant treated plywood which will be used in high temperature applications such as roof sheathing shall be strength tested in accordance with ASTM Standard D-5516 or by an equivalent methodology. At least one sample set shall be exposed for a minimum of 75 days.

It was found that post-treatment redrying at >160°F (71°C) significantly reduced the strength of flame retardant-treated products. Mechanical properties of lumber and plywood were most degraded by chromated zinc chloride treatment. The effect of the other flame retardant treatments are comparable when re-dried at temperature <160°F (Reference 13).

Flame retardant treatment drastically reduced the rate at which flames travel across the wood surface and reduced the amount of potential heat. However, some flame retardant treatments may produce unwanted secondary side effects, such as increased moisture content, reduced strength, and increased potential to corrode metal connectors. The magnitude of the side effects depends on the particular flame retardant chemicals used, and the relative importance

of these side effects depends on the intended application of the product (Reference 14). Borax and boric acid are known to have the least secondary side effects.

The magnitude of wood degradation depends on the flame retardant formulation, exposure temperature and relative humidity. Once degrade has begun at 150°F (66°C), the flame retardant chemicals had a similar rate of strength loss (Reference 15).

The implication of these findings is that once an elevated temperature has imparted sufficient energy to cause a flame retardant chemical to dissociate into its acidic functional form, the strength degrade rate in any flame retardant treated wood is similar.

The essential difference between most flame retardant chemical systems is the time and energy required for each chemical to dissociate at a given temperature into its acidic functional form.

3.2 Wood composites

This covers the various types of resin-bonded composite board where the particles are either wood shavings, flakes, chips, or fibers bonded together with thermosetting adhesives such as urea formaldehyde, melamine formaldehyde, or phenol formaldehyde. Production of wood chipboard has been very substantially greater than the other types of board though, in recent years, world manufacturing capacity for medium density fiberboard has been rapidly increasing.

Currently, only a small fraction of this production is treated with flame retardants and demand for flame retardant versions is very dependent on regulations and hence, localized.

Most particle board production utilize urea-formaldehyde binders and these are acid setting. Sodium borates (borax decahydrate or *Neobor* borax pentahydrate) which are alkaline, can interfere with this setting action and, as a result, boric acid has become the principal boron compound used as the flame retardant in such board (References 16

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and 17). Typically, an *Optibor* boric acid loading of around 15% by weight of dry board is necessary to satisfy required performance levels in most national fire test standards. The most widely used method of incorporation is to feed the boric acid into the flow of particles, usually before the adhesive application stage. If sodium borate is used as the flame retardant, phenol formaldehyde binder is commonly used due to its compatibility with alkaline chemicals.

Fiberboard is made by a process analogous to that of paper making and large quantities of water are involved. Incorporation of soluble flame retardants can pose a problem due to the necessity of recycling this water to avoid loss of the flame retardant in the effluent. The problem was resolved by applying a solution of *Polybor*® disodium octaborate tetrahydrate to the surface of the formed wet-lap on the machine just prior to it passing over the vacuum boxes (Reference 18). In pulling water from the wet-lap, *Polybor* solution is drawn into it.

If necessary, the system can be closed at this point to recycle any of the borate solution which may be pulled through the wet-lap. For adequate flame retardancy in fiberboard, loadings of *Polybor* around 15% by weight of board are required.

There has been a substantial world-wide growth in the production and utilization of a resin-bonded fiberboard, known commercially as medium density fiberboard (MDF).

The bulk of MDF production employs formaldehyde-based adhesives and where flame retardant grades are required, it is necessary to use boric acid for compatibility reasons. However, there has been some compatible with such adhesives and, hence can be utilized as the flame retardant.

4. Mattresses/futons

In December 1973, the U.S. Department of Commerce Flammability Standard FF4-72 was adopted. This act, which requires all mattresses to pass a cigarette test for smoldering combustion, inspired a frantic search for materials which would pass the test. It was found that boric acid addition to cotton batting was the most effective chemical treatment. This conclusion is still valid.

However, a large percentage of mattress suppliers now produce polyurethane foam-filled mattresses which also pass the current standard but are significantly more expensive than boric acid-treated cotton. Mixed polyester-cotton mattresses have also captured part of this market.

The reason that *Optibor* boric acid-treated cotton is now only a poor third in total usage, even though it is less expensive and also more flame retardant than the synthetics, is apparently the resistance of the manufacturers to adapt their processes to allow chemical addition. Most boric acid is applied dry, although wet applications have been developed by USDA and commercialized by Virginia Chemical. Laboratory work has confirmed that boric acid is the most effective chemical additive in cotton mattresses. It has also been shown previously that crude boric acid produced by simply adding sulfuric acid to sodium borates is as effective as technical grade boric acid.

4.1 Cotton batting/garnetting applications

Optibor boric acid may be added at various points along the cotton batting line at the discretion of the user. Some add powder immediately after garnetting directly on the web and in this fashion each layer of the batting will contain boric acid. Others add boric acid to a second stage willow.

Since dry additions may cause some loss through dusting, add-on requirements up to about 12% by weight may be necessary to assure that the treated product will contain the minimum boric acid necessary to assure the cigarette test.

Boric acid dusting can be minimized and better adhesion to the fiber can be achieved by first spraying the cotton with a suitable dust control oil. The amount of oil will vary from 1%, or more, depending on the setup and operation of the individual plant.

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4.2 Regulatory requirements

Futons or soft furnishings used in automobiles and airplanes must be flame retardant treated according to current U.S. Department of Transportation codes, but there is no federal law in the U.S. which requires cotton used in furniture to be flame retardant treated.

However, the State of California has adopted a standard in March 1977 which requires furniture to pass both a cigarette ignition test, similar to that used for mattresses and a vertical flame test (on the filling only). In addition, synthetic filling also must pass a vertical flame test after heat aging at 150°F (66°C). Treated cotton is excluded from this requirement apparently because the state believes that it could not pass the test. Boric acid-treated cotton may also pass the heat aging test due to vapor phase diffusion.

The law requires that anyone who manufactures, wholesales, or retails upholstered furniture or bedding products that are offered for sales in individual state must hold a valid license. Approximately 40 states have some licensing or registration requirements for certain home furnishing products including mattresses and futons. The Bureau of Home Furnishings and Thermal Insulation is an agency within the state Department of Consumer Affairs with responsibility by law to license or regulate businesses involved in the home furnishings industry as well as thermal insulation in California. Every article of upholstered furniture must have one of four possible types of flammability labels attached. The International Sleep Products Association (ISPA) publishes the home furnishings requirements in all 50 states. They also provide the name, address, and telephone number of the person or agency to contact in each state.

Under the California Administrative Code Title 4, Chapter 3, Section 1371 or Federal Standard 16 CFR 1632 (FF -72), flame retardant properties shall be retained by the mattresses under all normal conditions of temperature, humidity and use and shall be able to meet the test requirements of these regulations at any time during their useful life. The mattresses should pass the cigarette test described in the Technical Service Bulletin 106 - Cigarette Test of Mattresses and Mattress Pads. The upholstered furniture such as futons should pass the cigarette test described in the Technical Service Bulletin 116 - Cigarette Test of Upholstered Furniture.

The filling materials used in upholstered furniture can also be subjected to the flame retardancy test under Technical Bulletin 117 - Flame and Smolder Resistance Test of Furniture Components.

5. Fabrics

Recommendations of fire retardant treatments for fabrics are made basically for cotton or other cellulosic materials, but may be applicable to certain synthetics, particularly rayon. Examples of materials requiring fire retardancy include some clothing, drapes, rugs, ironing board covers, fabric heat deflectors for stoves and fireplaces, canvas fire-smothering blankets, and Christmas tree decorations.

5.1 Typical formulations

The ratio of borax decahydrate and *Optibor* boric acid (5:3 or 3:2), and latterly *Polybor* became recommended materials for imparting so called "temporary" flame retardancy to cotton-based textiles (References 19). The work "temporary" is used in the context that, being water soluble, the borates are removed during laundering and hence the treatment needs to be re-applied. Consequently, the treatment has tended to be restricted to fabrics where laundering is infrequent. Formulations containing borax/boric acid, or boric acid/ ammonium phosphate, or borax/boric acid/sodium phosphate were recommended for such fire-retardant treatments (Reference 20).

One simple formula suggested contains 7 parts of borax decahydrate, 3 parts of *Optibor* boric acid and 60 parts of water. For this composition, approximately 15% solution strength is recommended. Other formulas include 7 parts of borax, 3 parts of boric acid, 5 parts of magnesium chloride hexahydrate (or urea) and 60 parts of water.

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For this composition, approximate 25% solution strength is recommended. In the case of magnesium chloride, water temperature should be lower than 100°F (38°C).

The recommendation of salt solution concentrations is based on the past experience that in treating fabric, on an average, water retention is about 75% of the weight of the fabric. A sample weighed before and after wetting will determine the accuracy of this fact for the material under consideration. If deemed necessary, compensations in salt concentrations may be made based on these findings.

Mixtures containing both urea and magnesium chloride are not recommended because tests show loss of tensile strength of the textile. Formulations using magnesium instead of urea is considered superior with respect to retention of strength of the treated fabric.

5.2 Treatment techniques

Application of the fire retardant to the fabric by direct spraying or by dipping the fabric into warm, fire retardant solution is acceptable. Sprinkling the solution on the fabric is satisfactory but the material must be completely wet. Obviously only water fast colors may be treated. Fabrics containing sizing may be more easily treated by adding small amounts of soap or a wetting agent to the treating solution.

Ironing of treated fabric will not alter the effectiveness of the treatment nor harm materials that may be ironed without a fire retardant treatment. Best results are obtained by allowing the fabric to dry before ironing.

6. Paper

Polybor disodium octaborate tetrahydrate, combinations of borax decahydrate, *Optibor* boric acid, and borates mixed with other chemicals are used to treat paper products where fire retardant properties are required. The high levels of flame retardants necessary (15-20% by weight) for paper do result in a stiffening effect which can be overcome by inclusion of softening agents such as urea in the treated solution. The compositions given below have been tested and found to impart satisfactory fire retardant properties and to minimize embrittlement characteristics.

A mixture of borax, boric acid, and magnesium chloride hexahydrate in a ratio of 7-3-5 has been proven to offer good fire retardancy. A solution strength of 12% is recommended. This concentration may be formulated by dissolving 5.6% borax decahydrate, 2.4% *Optibor* boric acid and 4.0% magnesium chloride hexahydrate in water.

A second composition which offers satisfactory results is borax decahydrate, *Optibor* boric acid and urea in a ratio of 7-3-4. A solution strength of 10% is recommended. This concentration may be prepared by dissolving 5.0% borax, 2.1% boric acid and 2.9% urea in water.

Good fire retardant results are obtained with solutions containing all of the components—borax, boric acid, urea and magnesium chloride. One advantage of the four component mixture over that containing magnesium chloride and not urea, is that solutions have less tendency to precipitate magnesium borate. A solution strength of 12% concentration is recommended. This solution may be obtained by dissolving 5.6% borax, 2.4% boric acid, 2.4% urea, and 1.6% magnesium chloride hexahydrate.

The precipitation of magnesium chloride is very slight in the first three of these formulations, but certain precautions should be taken. *Polybor*, or borax decahydrate/*Optibor* boric acid can be dissolved in the water at any temperature, but magnesium chloride should not be added at a temperature above 100°F (38°C). Likewise, the final fire retardant solution should not be heated continuously above 100°F.

Borates for fire retardancy in cellulosic materials

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