2.0 TYPES OF CHEMICAL FLAME RETARDANTS

Publicly available scientific literature contains a wealth of information about various mechanisms of flame retardancy and characteristics of flame retardants. This section summarizes the general characteristics associated with flame retardants and associated mechanisms of flame retardancy.

2.1 General Characteristics of Chemical Flame Retardants

Some general characteristics of flame-retardant chemicals mandate how they interact with and flame retard the substrate in which they are used. This section defines some of these important characteristics, including:

- General mechanisms of flame retardancy;
- Additive and reactive flame-retardant chemicals; and
- Flame-retardant synergists.

2.1.1 General Mechanisms of Flame Retardancy

In general, flame retardants act in one of two ways; either by preventing ignition or preventing the spread of a fire. First, the ignition susceptibility of a product lowers when the flame retardant increases the net heat capacity of the product. Second, once a fire has already begun, flame retardants can reduce the tendency of the fire to spread by reacting with the product and forming a less flammable char or noncombustible gaseous layer along the boundary of the fire.

Within these two general flame-retardant mechanisms, Kirk-Othmer's Encyclopedia of Chemical Technology (Kirk-Othmer, 2001) provides a more detailed summary of five specific mechanisms by which flame retardancy may occur: physical dilution, chemical interaction, inert gas dilution, thermal quenching and protective coatings.

- **Physical dilution:** The flame retardant can act as a thermal sink, increasing the heat capacity of the product or reducing the fuel content to a level below the lower limit of flammability. Inert fillers such as glass fibers and microspheres and minerals such as talc act by this mechanism.

- **Chemical interaction:** The flame retardant dissociates into radical species that compete with chain propagating and branching steps in the combustion process. This is the general flame-retarding mechanism by which brominated flame retardants operate.

- **Inert gas dilution:** Flame-retardant additives produce large volumes of noncombustible gases when the product decomposes during combustion. The gases dilute the oxygen supply to the flame or dilute the fuel concentration below the flammability limit. Metal hydroxides, metal carbonates and some nitrogen producing compounds function in this way when used as flame retardants.

- **Thermal quenching:** Endothermic degradation of the flame retardant results in thermal quenching. Metal hydroxides and carbonates act in this way.

- **Protective coatings:** Some flame retardants function by forming a protective liquid or char barrier that acts as an insulating layer to reduce the heat transfer from the flame to the combusting product. Phosphorous compounds that decompose to give phosphoric acid and intumescent systems operate by this mechanism.

BFRs such as pentaBDE react chemically to prevent the spread of a fire. In products without BFRs, combustion is propagated by a series of chemical reactions that occur in the gas phase, where oxygen combines with chemicals in the burning product. BFRs interrupt some of these reactions by introducing the volatilized halogens to react with the product in place of oxygen, slowing combustion.

2.1.2 Additive and Reactive Flame Retardants

Flame retardants are categorized as either additive or reactive. Additive flame-retardant chemicals can be added to a manufactured product without bonding or reacting with the product. They are incorporated and dispersed evenly throughout the product, but are not chemically bound to it. Reactive flame-retardant chemicals may be incorporated into the product during manufacture of the plastic raw materials. They are chemically bound to the raw materials that are used to make the final product.

The basic mechanisms of flame retardancy (discussed earlier) will vary depending on the specific flame retardant and substrate. Additive and reactive flame-retardant chemicals can function in the vapor or condensed phase. Depending on the specific chemical, any of the mechanisms previously discussed may be utilized. Due to specific physical and chemical properties of the flame retardant and its effects on the substrate, most are used exclusively as either reactive or additive.

Additive Flame Retardants

Most flame retardants are used as additive flame retardants. Commercial pentaBDE is added at the time the polymer is formed. In general, additive flame retardants react when heated and either (a) emit substances that displace the oxygen needed for a fire to burn, (b) form a protective coating on the surface of a flammable substrate, thereby limiting access of the fire to fuel sources, or (c) do a combination of both. Halogenated flame retardants act in the gas phase by releasing chlorine- and/or bromine-containing radicals. In contrast, other flame retardants quench the flame by forming an intumescent, resinous char on the surface of the polymer. This char insulates and protects the polymer from further decomposition. The flame retardant in the system then expands, helping to form an insulating barrier that limits further damage to the polymeric material.

Additive flame retardants used in foam and other plastics are typically incorporated after manufacture of the polymer and during the manufacture of the end product (at the final product manufacturing facility). These additives are mixed into the polymer in common processing equipment concurrently with other ingredients such as stabilizers, pigments and processing aids. This is most likely to occur during a very preliminary stage at the end-product manufacturing facility (typically during the compounding step).

Reactive Flame Retardants

Reactive flame retardants are chemically bound to polymer products either by incorporating them into the polymer backbone during the polymerization reaction or by grafting them onto it. This is most likely to occur at the foam manufacturing facility. Therefore, reactive flame retardants are typically already incorporated in the raw materials that are purchased and received by the furniture manufacturers

Note that because they are chemically bound to the substrate, reactive flame retardants tend to exert a much greater effect than additive flame retardants on the properties of the polymer they are incorporated into.

2.1.3 Flame-Retardant Synergists

Many flame-retardant synergists do not have significant flame-retardant properties by themselves; however, their use increases the overall effectiveness of the flame-retardant system.

While char formation in the condensed phase and halogen interference in the vapor phase take place when flame retardants are used alone, the presence of a synergist can dramatically increase the flame retardant's effectiveness, lowering the quantity of the flame retardant needed to meet the required standard. Since high levels of flame retardants often affect product quality, a synergist to reduce the amount of flame retardant is often used. Additionally, the cost of flame retardants can be significant; therefore, any method to decrease the quantity of flame retardants needed is advantageous.

As an example of synergistic mechanisms, some synergists retard fire via two processes. In the condensed phase, a char layer is formed during the reaction with the synergistic compound, the flame retardant and the polymer. As discussed above, this char acts as a shield as it reduces the rate of decomposition of the polymer; therefore, less fuel is available for the flame. In the vapor phase, the chemical reaction is slowed down. This adds to the flame retardant's inhibitory effects on combustion by allowing it to react more completely with free radicals of oxygen and hydrogen, which are necessary for combustion to occur (Kirk-Othmer, 2001).

As an example of how synergists can be used, consider organophosphorous flame retardants. When used alone, organophosphorous flame-retardant concentrations may need to be extremely high. These concentrations of the flame retardant often adversely affect the properties of the product. Testing has shown that adding inorganic synergists can dramatically increase the flame-retardant efficiency. Therefore, a significantly smaller quantity of the flame retardant is required. The synergistic effect on flame retardancy, coupled by the reduction in adverse effects on the product from the flame retardant is attractive to flame-retardant and end-product manufacturers.

2.2 Flame-Retardant Chemicals Currently Used in Foam

A wide variety of flame-retardant chemicals are currently in use throughout the world to meet fire safety standards for various types of foam. Many of these chemicals could theoretically be used to meet U.S. fire safety standards for low-density, flexible polyurethane foam. However, their use will result in trade offs. Some, for example, require high loadings that result in an effect on foam quality. Others are cost prohibitive. Still others will require significant modifications in the handling and process equipment that is currently used in most U.S. foam manufacturing facilities. The environmental assessments presented in this report correspond to 14 specific formulations that chemical companies presented as the most viable large-scale substitutes for pentaBDE. However, other chemicals (besides these 14 formulations) are currently used for other types of foam and in niche markets for low-density polyurethane foam.

PentaBDE is an additive flame retardant that was used as a liquid formulation, typically blended with isopropylphenyl diphenyl phosphate/triphenyl phosphate and other additives. The commercial PentaBDE products have been used to flame retard low-density, flexible polyurethane foam (Weil and Levchik, 2004). Great Lakes Chemical Corporation was the sole manufacturer of pentaBDE in the United States, but Akzo Nobel and Great Lakes produced pentaBDE flame-retardant products prior to its phase-out. PentaBDE composition in products is proprietary.

The remainder of this section briefly discusses three of the most commonly used chemicals that various reports have suggested may be viable alternatives to pentaBDE. The chemicals are used domestically and abroad to flame retard high-density, flexible polyurethane foam. Chemical companies and foam manufacturing facilities have experimented with their use in low-density flexible foams with moderate success. Generally the use of these chemicals either results in scorching of the foam (an aesthetic effect unless severe) or a negative effect on the physical properties of foam. Also, many formulations of these chemicals are available only as solids; making them less desirable as drop in substitutes for pentaBDE.

Melamine

There are numerous international manufacturers of melamine. Melamine and its derivatives are non-halogenated flame retardants, typically used as a crystalline powder. Flame retardants based on melamine are currently used in flexible polyurethane foams, intumescent coatings, polyamides and thermoplastic polyurethanes (Special Chemicals, 2004). They are used effectively in Europe in high-density flexible polyurethane foams but require 30 to 40 percent melamine per weight of the polyol.

Tris (1,3-dichloro-2-propyl) phosphate (TDCPP)

TDCPP is a chlorinated phosphate ester that is often used in polyurethane foam formulations. TDCPP comprises approximately 12 percent of the weight of the polyol in the final foam product (Weil and Levchik, 2004). It is used in high-density foam domestically and abroad and has been used domestically in low-density foams when light scorching (discoloration) is not a primary concern (Akzo Nobel, 2002). Note that TDCPP has been mistakenly referred to as tris (chloropropyl) phosphate (TCPP) in many reports.

Ammonium Polyphosphate (APP)

APP is an additive flame retardant containing nitrogen and phosphorus, typically used in a crystalline form. It is currently used to flame retard flexible and rigid polyurethane foams, as well as in intumescent laminations, molding resins, sealants and glues (Leisewitz et al., 2001). APP formulations comprise approximately 4 to 10 parts per hundred parts polyol in flexible foam, and 20 to 45 parts per hundred parts polyol in rigid foam.

APP is included in this section because it has been listed in multiple sources as a flame retardant for several products, including flexible, polyurethane foam. However, chemical manufactures and foam manufacturing trade groups do not consider it to be an alternative for pentaBDE on a large scale. Reasons for this are that APP is typically incorporated as a solid, it has adverse effects on foam properties and processing and it is not considered to be as effective as a fire retardant compared to other alternatives (U.S. EPA, 2002).

These chemicals have been used in the United States and around the world to flame retard flexible polyurethane foam. However, only pentaBDE is capable of achieving flame retardancy and non-scorching requirements in the low-density foam that is manufactured in the United States. While other flame retardants have historically been used and will continue to be used to flame retard higher-density foams, these flame retardants result in scorching in many low-density foam formulations. These chemicals are potential alternatives for pentaBDE, but scorching and other drawbacks must be addressed before large-scale use is feasible.

Scorching results in foam that has a color gradient but unless severe, it will not adversely affect flame retardancy or foam performance. White foam has become the industry standard for flame-retarded, low-density foam in the mattress and bedding industries, and in many upholstered furniture applications in the United States. The color of the foam, however, is not a determinant of its flame retardancy. Greater acceptance of darkened foams would allow manufacturers to choose from a wider variety of alternative flame retardants.