3. Halogenated Flame Retardants

A significant application area of halogenated flame retardants is flame retarded plastic used in consumer electronics. The environmental issues concerning brominated flame retardants clouds their future. Consequently, the manufacturers of computers and business machines are re-evaluating the use of halogenated flame retardants.

This is particularly true for the European market place where eco-friendly labels are becoming a major factor in marketing computers and other electronic equipment. To qualify for the label such as the White Swan of Sweden the product must comply with certain environmental ground rules. This includes not using any halogenated flame retardants. Computer manufactures are therefore considering switching from halogenated flame retardant system, to a PC/ABS (polycarbonate/acrylonitrile butadiene styrene) polymers flame retarded with a phosphorous compound (Miller, 1996).

3.1 Mechanism of halogen flame retardants

It is generally accepted that the combustion of gaseous fuel proceeds via a free radical mechanism. A number of propagating and chain branching mechanisms are illustrated below. These are necessary to maintain the combustion process. Methane is used in the example as the fuel or the decomposition gas coming from the polymer (Green, 1986):

$$CH_4 + O_2 \rightarrow {}^{\bullet}CH_3 + H^{\bullet} + O_2$$

$$H^{\bullet} + O_2 \leftrightarrow HO^{\bullet} + O^{\bullet}$$

$$CH_4 + HO^{\bullet} \rightarrow {}^{\bullet}CH_3 + H_2O$$

$${}^{\bullet}CH_3 + O^{\bullet} \rightarrow H_2CO + H^{\bullet}$$

$$H_2CO + HO^{\bullet} \rightarrow CHO^{\bullet} + H_2O$$

$$CHO^{\bullet} + O_2 \rightarrow H^{\bullet} + CO + O_2$$

$$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet}$$

Here $H^{\bullet}$, $HO^{\bullet}$ and $O^{\bullet}$ are radicals and chain carriers. The reaction of the $H^{\bullet}$ radical and the O_2 molecule is an example of chain branching in which the number of carriers is increased. The reaction of the CO molecule with the $HO^{\bullet}$ radical, converting CO to CO_2, is a particularly exothermic reaction (Green, 1986).

3.2 Brominated Flame Retardants

The performance of halogens as flame retardants is rated as follows (Green, 1986):

$$I > Br > Cl > F$$

Iodine compounds, apparently the most effective, are not used in polymers because they do not have adequate thermal stability. Iodine flame retardants decompose thermally at a low temperature and cause brown stains in the polymer. Fluorocarbons are inherently non-burning, but they generally do not impart flame retardancy to other plastics because either the C-F bond is too thermally stable or the highly reactive hydrogen fluoride or fluoride radicals that may form react rapidly in the condensed phase. An exception is that small amounts of Teflon will significantly increase the oxygen index of polycarbonate resins, due to the increase in viscosity that inhibits dripping.

Commercial organohalogen flame retardants include aliphatic, alicyclic and aromatic chlorine and bromine compounds. Aliphatic compounds are the most effective and the aromatic compounds are the least effective with the alicyclic compounds in between (Pettigrew, 1993).

aliphatic > alicyclic > aromatic

The above is true for e.g. polypropylene, but for polyethylene the opposite is observed. This is in the same direction as the thermal stability indicating that the more easily available the halogen the more effective. The actual type of compound used in an application will depend on the processing temperature of the plastic. Bromine compounds are about two thirds more effective than chlorine compounds. The expected relative effectiveness is indicated in Table 6.

Table 6: General effectiveness of halogen compounds for flame retardancy (Pettigrew, 1993).

Element	**Effectiveness**
Fluorine	1.0
Chlorine	1.9
Bromine	4.2
Iodine	6.7

It takes about 3% bromine of an aliphatic brominated flame retardant plus 1.5% antimony oxide to obtain a polypropylene composition to a UL94 V-2 rating. When burning, profuse dripping is observed. The flaming polymer droplets remove heat from the flame zone. Addition of inert filler to inhibit dripping leads to a burning product. This demonstrates the utility of dripping as a method for passing a small-scale laboratory test. Dripping also allows heat to be removed from the flame zone in large-scale tests, significantly reducing the total heat release. The flame dripping polymer will self-extinguish and the actual amount of polymer burned could be significantly less (Pettigrew, 1993).

3.2.1 Mechanism of Brominated flame retardants

In the radical trap theory of flame inhibition, it is believed that HBr competes for the radical species $HO^{\bullet}$ and $H^{\bullet}$ that are critical for flame propagation (Green, 1986):

$$H^{\bullet} + HBr \rightarrow H_2 + Br^{\bullet}$$

$$^{\bullet}OH + HBr \rightarrow H_2O + Br^{\bullet}$$

The active chain carriers are replaced with the much less active $Br^\bullet$ radical. This slows the rate of energy production resulting in flame extinguishing.

It also has been suggested that halogens simply alter the density and mass heat capacity of the gaseous fuel-oxidant mixture so that flame propagation is effectively prevented. This physical theory is equivalent to the way inert gases such as carbon dioxide and nitrogen may influence combustion (Larsen, 1973).

Suggestions have been made that the flame retardant mechanism of some bromine compounds acts mainly in the condensed phase and also depends on the type of polymer being treated. Reaction of the flame retardant or its decomposition products with the polymer can inhibit the decomposition of the polymer, thereby influencing the flame retardancy (Green, 1986).

3.3 Halogen Synergism

Antimony oxide itself usually renders no flame inhibition properties to polymers, but it is known as a synergist for halogen compounds. Antimony oxide is not volatile but antimony oxyhalide (SbOX) and antimony trihalide (SbX_3) formed in the condensed phase, by reaction with the halogenated flame retardant, are volatile. They facilitate the transfer of halogen and antimony into the gas phase where they function. Antimony oxide flame retardants are therefore usually used indirectly in the form of antimony trichloride ($SbCl_3$) or antimony tribromide ($SbBr_3$). These forms are very effective retardants at typical flame temperatures.

Laboratory flammability tests indicate that the optimum halogen / antimony atom ratio in many polymers is about 2:1 to 3:1. It has been suggested that antimony halides are also highly active radical traps. Although the antimony halides appear to act exclusively in the vapour phase, some effect in the condensed phase can not be ruled out (Pettigrew, 1993).

Historically, impurities such as iron and aluminium, which came from catalyst residues, limited the use of the flame retardants, much like the fouling of a catalyst. The residues tend to bind with the flame retardant, making it less volatile and more prone to condense or precipitate on the surface. The levels of these impurities have since been reduced. Some aromatic bromine compounds, e.g. decabromo diphenyloxide, are thermally stable up to very high temperatures (Pettigrew, 1993).

Interference with the antimony-halogen reaction will affect the flame retardancy of the polymer. For example, metal cations from colour pigments and inert fillers such as calcium carbonate may lead to the formation of stable metal halides. These metal halides can render the halogen unavailable for reaction with the antimony. The result is that neither the halogen nor the antimony is transported into the vapour phase, where they provide flame retardancy. Silicones have also been shown to interfere with the flame retardant mechanism. Consequently, the total plastic composition must be considered in developing a new flame retardant product.

Other members of Group V of the periodic table, such as arsenic and bismuth also function as synergists for halogens. Little work has been done with these compounds for toxicity reasons. The Diels-Alder adduct of hexachlorocyclopentadiene with 1,5-cyclooctadiene (Dechlorane Plus™)

can be used to flame retard nylons, epoxies and polybutylene terephthalate using synergists other than antimony oxide. These compounds include zinc compounds such as the borate, oxide and phosphate as well as iron oxides such as Fe_2O_3 and Fe_3O_4. The use of mixed synergists is also reported to lower the level of the total flame retardant required (Green, 1986).