4. Inorganic Flame Retardants.

Plastics can be given flame retardant characteristics by introducing elements of organic, inorganic and halogen origin. Such elements include magnesium, aluminium, phosphorous, molybdenum, antimony, tin, chlorine and bromine. Flame retardants are added in either the manufacturing step of the polymer or the compounding step of the polymeric article. Phosphorous bromine and chlorine are usually included as some organic compound. Inorganic flame retardants are usually added together with other flame retardants to provide a more efficient flame retardant action through synergism.

Halogen flame retardants usually need an addition of about 40% in order to be effective, and this affects the properties of the polymer quite negatively. Structural integrity of the polymer article is often very important, and a drastic decrease in strength and other mechanical properties is simply not acceptable. The efficiency of halogen flame retardants is often enhanced by the addition of inorganic flame retardants. A smaller mass percentage halogen flame retardant is now needed, so the adverse effect on the polymer properties is also reduced (Touval, 1993).

4.1 Antimony Compounds

The antimony compounds used for flame retardancy include antimony trioxide, antimony pentoxide and antimony-metal compounds. In 1990 in the United States alone, the use of antimony trioxide amounted to 20 000 metric tons just for the flame retardancy of plastics. Antimony oxide is readily found in nature but in very impure form. This is not suitable for direct use as flame retardant, so antimony oxide is often rather produced from antimony metal. There are therefore many different grades of antimony oxide that can be used for flame retardants. Some of the physical properties of antimony trioxide are listed in Table 7.

Table 7: Physical properties of commercial antimony trioxide (Touval, 1993).

Property	**Grade**		
	Ultra fine	High tint	Low tint
Specific gravity	5.3-5.5	5.3-5.8	5.3-5.8
Particle size (μm)	0.25-0.45	0.8-1.8	1.9-3.2

Antimony oxide with a small particle size will for example give a polymer with a high opacity and white colour whereas the larger particle sizes produce translucent polymers. Although particle size affects pigmentation, it does not appear to affect the flame retardant efficiency. The price for antimony oxide is quite high, depending on the purity (Touval, 1993).

With cotton textiles, antimony oxide is usually applied by impregnating the fabric with a water soluble antimony solution, followed by secondary treatment (such as evaporation) that deposits the oxide on the fibres. When the treated sample is exposed to a flame, the fibres decompose endothermically. The decomposition products, apart from the volatile components, are water and char, and this reduces the combustion temperature of the flame (Touval, 1993).

The second most widely used antimony compound for flame retardancy is antimony pentoxide (See Table 8). Unlike the trioxide, the pentoxide does not cause a pigmenting effect on the treated polymer. Furthermore, the average particle size for a typical commercial pentoxide is 0.03 μm, which causes a more even distribution throughout the polymer. This implies a less drastic change in the polymer properties, and overall better flame retardancy. Antimony pentoxide is however priced two to three times higher than the trioxide.

Table 8: Typical properties of commercial grades of antimony pentoxide and sodium antimonate (Touval, 1993).

Property	**Sb_2O_5**	**Na_2SbO_4**
Particle size (μm)	0.03	2
Surface area (m^2/g)	50	Not available
Specific gravity	4.0	4.8
Surface activity	Weak acid	Base
Refractive index n^{20}_D	1.7	1.75

Another antimony synergist of commercial importance is sodium antimonate (Refer to Table 8). As it only contains 60 percent antimony on a mass basis, it is less effective. than either the trioxide or pentoxide. Sodium antimonate has an average pH of 9-11 when dissolved in water. The bacisity of this antimony form makes it ideal for a polymers that are easily hydrolysible (Touval, 1993). For example, it is used instead of antimony trioxide in PET applications. The sodium antimonate price is in the range of \$3.30 to \$4.40 per kilogram.

It has to be mentioned that antimony compounds are not currently used on their own as flame retardant. Antimony in combination with elements such as chlorine and bromine shows remarkable flame retardant synergism.

Due to the world-wide scarcity of antimony, new products containing antimony-metal synergists have been found. Some of these contain zinc, silicone or phosphorous and were found to be as effective as antimony alone. These antimony compounds are also typically 10 to 20 percent less expensive than antimony trioxide.

4.1.1 Mechanism of Antimony compounds

The antimony flame retardants follow the mechanism of the formation of antimony chloride with an oxychloride as a highly reactive intermediate. The antimony oxide reacts with the halogen containing compound forming highly volatile antimony oxychloride (Touval, 1993).

$$Sb_2O_3 + 2\,HCl \rightarrow 2\,SbOCl + H_2O$$

The antimony oxychloride is a very reactive intermediate that forms antimony trichloride through several reactions (Touval, 1993).

$$5\,SbOCl\,(s) \rightarrow Sb_4O_5Cl_2 + SbCl_3$$

$$4\,Sb_4O_5Cl_2 \rightarrow 5\,Sb_3O_4Cl + SbCl_3$$

$$3\,Sb_3O_4Cl \rightarrow 4\,Sb_2O_3 + SbCl_3$$

$$Sb_2O_3\,(s) \rightarrow Sb_2O_3\,(g)$$

By means of the above reactions, antimony helps to quickly move the halogen into the gas phase, where it acts as an effective flame retardant.

Antimony oxide was found not to be a carcinogenic nor to pose a risk to the environment. Some antimony products do however contain trace amounts of arsenic, so caution should nevertheless be taken during handling (Touval, 1993).

4.2 Boron Compounds

In the United States the consumption of boron flame retardants for plastics amounts to approximately 4500 metric tons per annum. The most widely used is zinc borate, prepared from water-soluble zinc and boron compounds. Zinc borate can be used on its own or in combination with other flame retardants such as antimony oxide, to form a glass-like substance that prevents further polymer decomposition. Borates, like all other flame retardants, vary in grade and effectiveness, depending on the composition, varying from $2ZnO \bullet 3B_2O_3 \bullet 5H_2O$ to $4ZnO \bullet 6B_2O_3 \bullet 7H_2O$ (Green, 1997).

The ratio of zinc, boron and water in the borate flame retardants determines the performance properties of the compound such as the temperature at which the flame-inhibiting powers are activated. Some of the other boron flame retardants used are barium metaborate ($Ba(BO_2)_2$), boric acid, sodium borate and ammonium fluoroborate (NH_4BF_4) (Touval, 1993).

4.2.1 Mechanism of Boron compounds

Boron functions as a flame retardant in both the condensed and the vapour phases, forming the corresponding trihalide as shown in the reaction below. The boron trihalides are volatile and vaporise to produce halogens in the gas phase, which act as a flame inhibitor. Boron trihalides are Lewis acids so they promote cross-linking of the polymer, producing a minimum of polymer vapour during decomposition (Touval, 1993). Borates are also known to be after-glow inhibitors (Green, 1997).

$$6\,NH_4BF_4 + Sb_2O_3 \rightarrow 6\,NH_3 + 6\,BF_3 + 2\,SbF_3 + 3\,H_2O$$

Zinc borate is used in polyvinyl chloride to replace, in part, antimony oxide. The hydrogen chloride generated from PVC reacts with the zinc borate (Green, 1997). The cost of borates varies from \$2.00 – 2.50 per kilogram (Touval, 1993).

Mixtures of boric acid and borax are used as flame retardants for cellulose. Boric acid decomposes endothermically releasing water in two stages. The first stage is at 130-200°C to form HBO_2 and again at about 265°C. When heated the mixture dissolves in its own water of hydration, froths, and fuses to form a surface coating. Similar to the phosphoric acids resulting from phosphate esters, boric acid dehydrates oxygen-containing polymers, yielding char. The glassy coating and the char protect the substrate from oxygen and heat.

4.3 Aluminium Compounds

The most commonly used aluminium flame retardant compound is alumina trihydrate, $Al(OH)_3$. Alumina trihydrate is the most widely used flame retardant for plastics at low temperatures. In 1991, the use of alumina trihydrate was approximately 113 400 metric tons. Alumina trihydrate is available in many different particle size distributions from 1 – 100 μm. The low refractive index of the particles gives it only slight pigmentation properties, making it ideal for wide-spread polymer applications. Mixtures of up to 50% alumina trihydrate are therefore translucent. A typical commercial alumina trihydrate composition is given in Table 9.

Table 9: Typical composition of commercial alumina trihydrate (Touval, 1993).

Component	**Quantity (wt %)**
Al_2O_3	64.9
SiO_2	0.005
Fe_2O_3	0.007
Na_2O	0.3
Water solubles	0.04
Water loss on ignition	34.6

Alumina trihydrate is relatively cheap, in the order of \$0.25 – \$1.35 per kilogram. Unfortunately, it is the least effective of all flame retardants. It is only about one fourth to one half as effective as the halogen flame retardants. The physical properties of alumina trihydrate are shown in Table 10.

Table 10: Typical physical properties of commercial alumina trihydrate (Touval, 1993).

Property	**Value**
Density (g/ml)	2.42
Refractive index n^{20}_D	1.579
Average particle size μm	1-100
Colour	White
Water solubility	Insoluble

Usually about 50 – 60 % alumina trihydrate must be added to provide some acceptable level of flame retardancy, and the plastic processing temperature must usually not exceed 220 °C.

Alumina trihydrate is also used as a secondary flame retardant and smoke suppressant for flexible poly(vinyl chloride) plastics. It is also used in combination with antimony and halogen flame retardants. The addition of small amounts of zinc borate or phosphorous results in the formation of glasses and protects the polymer surface from the flame (Touval, 1993).

4.3.1 Mechanism of Aluminium compounds

Alumina trihydrate functions as a flame retardant in both the vapour and the condensed phases. When activated it decomposes thermally to alumina trioxide and water as shown by the reaction below.

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$

In the flame phase, the water vapour forms an envelope around the flame, excluding oxygen from the flame. It also decomposes endothermically; thereby lowering the effective flame temperature (Touval, 1993).