6. Intumescent Flame Retardants

Intumescence is an interesting phenomenon. The French verb *tumere* means “to swell”. The Latin equivalent *tumescere* can be translated as “to swell up”. Therefore tumid or tumescent means swollen or bulging, and the process of getting to a swollen state is intumescence. In flame retardant terms, exposure to heat initiates a series of chemical and physical processes, leading to a tumescent condition. This state is characterised by a fire-resistant insulating foam. The foam serves to isolate heat and oxygen from the fuel source, extinguishing the fire (Mount, 1992).

6.1 Condensed phase charring

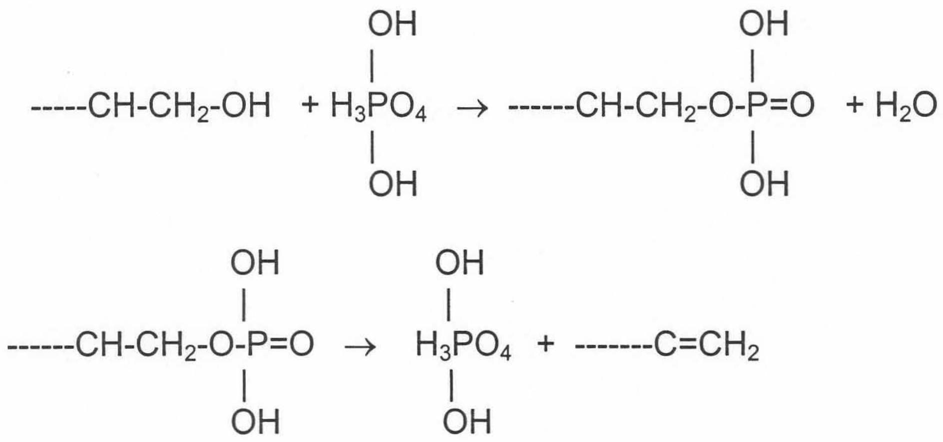
A complete description of intumescence requires analysis of both chemical and physical process.

6.1.1 Chemical mechanism of intumescence

A suggested mechanism for char formation is discussed by Mount (1992). The chemistry is often written in terms of simple acid-catalysed, dehydration reactions. This is shown in the four reactions below.

$$\text{-----CH-CH}_2\text{-OH} + H^+ \rightarrow \text{-----CH-CH}_2\text{-OH}_2^+$$

$$\text{-----CH-CH}_2\text{-OH}_2^+ \rightarrow \text{-------C=CH}_2 + H_2O + H^+$$



The first two reactions show the depolymerisation catalysed by an acid. The second two show the dehydration of the polymer when phosphoric acid is present. Both reactions essentially lead to the same result: producing -----$C=CH_2$ fragments at the polymer chain ends. These fragments condense to form carbon-rich char residues.

Briefly stated, the way the phosphorous compounds work is that they phosphorylate carbonifics such as pentaerythritol to make polyol phosphates. These polyol phosphates can then break down to form char (Weil, 1992).

6.1.2 Physical model of intumescence

Intumescent flame retardants were initially used, in paints and coatings. Typical formulations contained a phosphorous compound such as ammonium polyphosphate, a char forming polyol such as pentaerythritol, along with a blowing agent such as melamine. A binder is also necessary to keep the compounds in contact with each other.

With such intumescent coatings, one can visualise the burning polymer as a block consisting of several separate layers. The top char layer, is followed by the intumescent front where the foaming reactions take place. Below is an unburned polymer coating layer that still contains flame retardant. The bottom layer represents the polymer substrate that is being protected by the intumescent coating. The char-foam provides a physical barrier to heat- and mass transfer, and therefore interferes with the combustion process (Gilman & Kashiwagi, 1997).

For a mixture to be an efficient intumescent system, three ingredients are needed (Mount, 1992; Camino, *et al.*, 1989):

- An inorganic acid (dehydrating agent);
- A carbon rich polyhydric material as char former (carbonific); and
- A blowing agent – called a spumific.

The interaction of these components, to form a foamed char is illustrated in Figure 2.

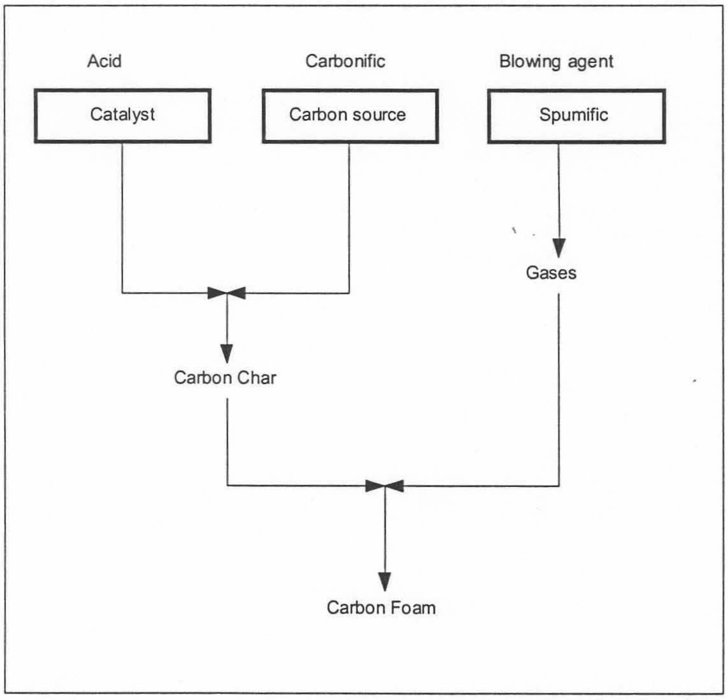


Figure 2: chematic diagram of the formation of char during intumescence (Gilman & Kashiwagi, 1997).

The ratios in which the different compounds are present are also of utmost importance. The optimum ratio must be determined experimentally. One or more of these substances could be replaced with others of the same class or group. Further studies showed that more effective intumescent systems are obtained when two or more of the elements required for intumescence are incorporated in the same molecular complex (Camino, *et al.*, 1989).

Intumescent flame retardants also work well in bulk polymers, such as polypropylene (PP) (Montaudo & Puglisi, *s.a.*).

The effectiveness of the intumescent flame retardants is due to the foamed char formed on the surface of the burning material (Camino, *et al.*, 1989). The char acts as a physical barrier against heat transfer to the surface of the combustible material. Char formation lowers the rate of temperature increase of the surface beneath the char. (See Figure 1)

The layer of char furthermore hinders the diffusion of oxygen to the site of combustion. Dripping of the molten plastic is also reduced by char formation, thereby eliminating a possible source of further flame propagation.

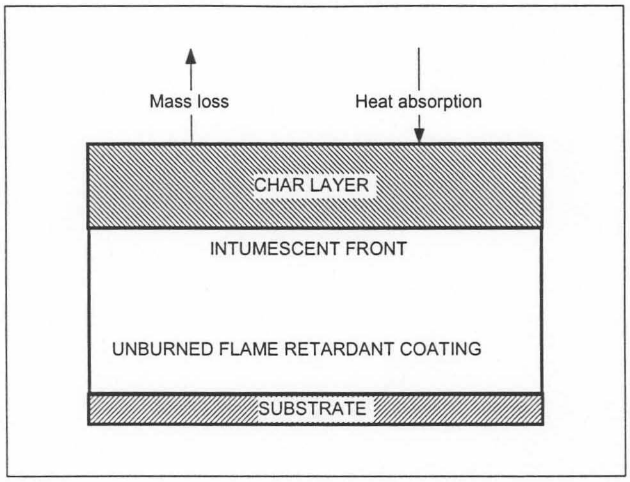


Figure 1: Schematic diagram of the different layers during the burning process (Gilman & Kashiwagi, 1997).

Halogenated compounds such as chlorinated paraffin are commonly used in intumescent coatings as carbonifics. However, they are not widely used in intumescent flame retardants for plastics. Nitrogen based compounds are widely used owing to their environmental soundness. This is true for almost all char forming flame retardant systems (Zaikov & Lomakin, 1996). Nitrogen based flame retardants have many advantages over other systems because they produce less smoke and fewer toxic gases. The smoke is also less corrosive and polymer scrap more readily disposable after use (Horacek & Grabner, 1996). The shift to such environmentally friendly flame retardants, is of high interest world wide. The market is trying to move away from halogenated flame retardants, but alternative systems are usually less effective or more expensive (Mount, 1992).

6.2 Mineral filler synergism

It was believed that the addition of inorganic fillers to the compounds used as flame retardants can improve their efficiency. This is due to the plate-like microstructure of certain fillers and the consequent stabilising effect they might have on the cell-structure of the char foam. The addition of fillers may reduce the amount of intumescent char, but should give the char a better strength and cell-structure. In the late 1980's a study on the then common and frequently used inorganic fillers proved to be a revelation. It was found that the fillers did modify the char structure but reduced the efficiency of the flame retardant system (Bertelli et al., 1989). The chars formed with the added filler were harder and more solid than those without the fillers, but were of lesser volume. The mechanism used to explain the modifications in the chemical and physical characteristics of the char was based on the possibility of the reaction between the acid phosphorus moieties and the fillers.

Recently, a careful study was made by Hoechst-Celanese comparing the effect of titanium dioxide (TiO_2) and stannous oxide (SnO_2) on the flame retardant char forming effect of ammonium polyphosphate in polypropylene. An intumescent nitrogen containing resin was also used. Titanium dioxide increased the flame retardancy by giving a stronger and more cohesive char with higher yield. Stannous oxide on the other hand was antagonistic, made the char flakier and more porous and did not enhance the char yield. Titanium dioxide probably functions by a physical bridging effect in the char, and the negative effect of the stannous oxide is probably due to some chemical interaction with the phosphorous compounds (Weil, 1992).

6.3 Other intumescent systems

Recent research showed that combinations of silica gel and pentaerythritol with potassium carbonate are effective char forming flame retardants (Gilman *et al.,* 1997; Miller, 1996). Unfortunately, these systems are water-soluble, making them unsuitable for outdoor use. It should be possible to convert these systems to intumescent ones.

Other new intumescent systems include the use of expandable graphite flakes in a special intumescent carrier resin (Miller, 1996). These flakes expand their initial thickness by up to a hundred times when exposed to heat. This material is based on natural occurring graphite and is therefore environmentally friendly. The implementation of nanocomposite clays as flame retardants in polymers is also being investigated (Gilman & Kashiwagi, 1997).