

## 5. Phosphorous Flame Retardants

Various phosphorous based flame retardants have been shown to produce some action in the condensed phase (polymer melt) and the vapour phase (flame zone). Physical and chemical actions have been proven in both phases. Flame inhibition, heat loss due to melt flow, surface obstructions with char formation, acid-catalysed char formation, and char enhancement have all been noticed in polymer systems with phosphorous based flame retardants. It is therefore quite possible that more than one mechanism is involved in any given case (Weil, 1992).

### 5.1 *Condensed phase mechanisms*

#### 5.1.1 Charring mechanisms

There is convincing evidence, that in oxygen-containing polymers, such as cellulose and rigid polyurethane foam, phosphorous containing flame retardants can increase the char yield. Char formation implies that less of the molten polymer substrate is converted to combustible gases, so the mass loss is reduced. Secondly, char formation is often accompanied by water release, which dilutes the combustible vapours, making the vapours less combustible. Char formation is also sometimes an endothermic process.

The pyrolysis behaviour of cellulose such as cotton paper and wool has been extensively studied. When cellulose is heated to its pyrolysis temperature it normally depolymerises to a tarry carbohydrate product

which further breaks down to smaller combustible organic compounds (Weil, 1992).

Upon fire exposure, phosphorous containing flame retardants decompose to phosphorous acids or anhydrides. These active phosphorous species phosphorylate the cellulose. Phosphorylated cellulose then breaks down to form char. The presence of phosphorous also improves fire resistance by preventing further oxidation of the char by a glowing combustion (Weil, 1992).

It is also known that certain nitrogen compounds such as melamine, urea or dicyandiamide will synergise the action of phosphorous in cellulose. This is not a general phenomenon, and depends on which nitrogen compound is used with which polymer system (Weil, 1992).

Another case in which the char enhancement by phosphorous is important is in rigid polyurethane foams. The analytical evidence shows that phosphorous appears to be largely retained in the char, to make the char more coherent and provide a better protective barrier. In contrast to the situation in rigid foams, char formation is probably not the basis of the action of phosphorous retardants in flexible foams. On the other hand char formation can lessen the flame retardancy in flexible foams (Weil, 1992).

In PET (polyethylene terephthalate) and PMMA (polymethyl methacrylate), phosphorous flame retardants cause an increase in the amount of char residue, reducing the release of volatile fuel. This is probably the result of acid catalysed cross-linking of the system that increases the molecular mass and melt viscosity. In oxygen-free hydrocarbon polymers that don't char very easily, e.g. polyolefins and styrenics, phosphorous flame

retardants are usually not very effective. They can be made more effective by addition of char-forming additives. In the absence of such a char-forming additive the main mechanism of flame retardancy seems to be increased dripping by reducing melt viscosity. Other mechanisms such as vapour phase reactions are not excluded (Weil, 1992).

Phosphorous can also reduce smouldering, as mentioned before. Glowing combustion of the char formed often occurs. The addition of phosphorous flame retardants can prevent this oxidative process. The mechanism is still unclear, but involves the deactivation of the active centres on the carbon atoms (Weil, 1992).

Phosphorous is also important as a char-promoting compound in intumescent flame retardants for paints and plastics.

### 5.1.2 Coating mechanisms

Besides its effect in enhancing the amount of char, the phosphorous flame retardant may provide a protective surface coating that inhibits further burning and smouldering. Phosphorous reduces the permeability of the char, improving its barrier properties. While this may be due to coating, a chemical connection is also possible (Weil, 1992).

Condensed phase mechanisms based on phosphorous acids coating the burning surface have often been proposed (Weil, 1992). Some researchers postulate that phosphorous acid acts as a physical barrier to prevent the vaporisation of fuel from a hydrocarbon polymer. In this case the polymer is flame retarded with ammonium polyphosphate or triphenyl phosphate.

Some infrared evidence supports the proposal regarding the polyphosphoric acid coating (Weil, 1992).

### 5.1.3 Melt viscosity

Phosphorous compounds can generate acids under fire conditions. In some cases, these acids catalyse the thermal degradation of the polymer melt, reducing the molecular mass and reducing the melt viscosity. This causes the melt to flow or drip away from the flame zone, reducing the material that is exposed to flame. Poly(ethylene terephthalate) provides a very impressive example. Addition of as little as 0.15% of a phosphorous flame retardant permitted a polyester fabric to pass a vertical burn test (Weil, 1992).

This mechanism of changing the melt viscosity can be defeated by adding any non-melting filler or additive that can retard the melt flow. For example, cotton threads in a flame retarded poly(ethylene terephthalate) fabric can have such an effect. A particularly illustrative example is the antagonistic effect of traces of silicone oil on flame retarded polyester fabric. The fabric is rendered flammable probably because the silica, formed during pyrolysis of the silicone oil, reduces the melt flow. Another instance where the melt flow retarding effect occurs, is when phosphorous containing flame retardant polyester (such as Trevira CS™) is pigment-printed with an infusible pigment (Weil, 1992).

### 5.1.4 Free radicals

This idea has been developed by Russian researchers, who offer some evidence in support of free radical inhibition, or at least of an antioxidant

effect. Non-volatile phosphorous flame retardants are usually used for this purpose. By looking at electron spin resonance data, it can be seen that aryl phosphorous flame retardants may scavenge alkylperoxy radicals at the polymer surface (Weil, 1992).

#### 5.1.5 Effects of fillers

Condensed phase mechanisms based on surface effects from fillers are still relatively unexplored. Some phosphorous compounds have characteristics of surfactants and aid the dispersion of the solid flame retardant. Improved binding by the surface-active agent improves the char cohesion. Similar effects are observed with titanate and zirconate coupling agents. They seem to enhance the UL 94 flammability rating of polymers containing various mineral fillers (Weil, 1992). Interestingly, on one filler, barium sulphate, the effect of the titanate seemed to reach maximum at 1% concentration, and the effect was lower at lower and higher concentrations (Weil, 1992).

### ***5.2 Vapour phase mechanisms***

Exactly as in the case of condensed phase mechanisms, there are a number of physical and chemical modes of action for the vapour phase. While the condensed phase reaction products cover the polymer substrate, the vapour phase reaction products may dilute the combustible polymer decomposition products (Weil, 1992).

### 5.2.1 Chemical methods

Volatile phosphorous compounds are also effective flame inhibitors. Mass spectroscopy showed that triphenyl phosphate breaks down in the flame to produce small species such as P<sub>2</sub>, PO, PO<sub>2</sub> and HPO<sub>2</sub>. This reduces the hydrogen atom concentration in the vapour phase, extinguishing the flame. The step in the flame chemistry which is inhibited is the rate-controlling branching step (Weil, 1992):



Vapour phase flame retardant activity appears to be the mechanism whereby triaryl phosphates function. It is used in commercial blends of polyphenylene oxide with high impact polystyrene. The polyphenylene oxide gives a protective char while the triaryl phosphate provides the flame retardancy needed to suppress the combustion of polystyrene (Weil, 1992).

### 5.2.2 Physical methods

Vapour phase flame retardant action does not have to be chemical, but can be physical in nature. It can be based on heat capacities, heat of vaporisation and endothermic dissociation. Studies have shown that the condensed phase mechanisms are significantly more effective than the vapour phase mechanisms, even with polymers that depolymerise thermally to produce volatile monomers (Weil, 1992).

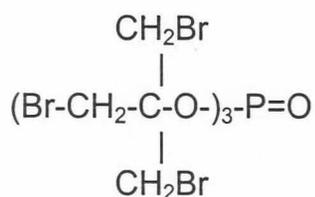
In flexible polyurethane foams, various chloroalkyl phosphates are effective flame retardants, however they don't appear to increase the char

formation or produce a chemical effect on the burning surface of the foam. They do appear to volatilise as the intact molecule, and cause a vapour phase retardant action. Some small degree of condensed phase action is also possible since it was shown that chloroalkyl phosphates become incorporated into the char structure (Weil, 1992).

### **5.3 Phosphorous flame retardant synergism**

#### **5.3.1 Halogen synergism**

Halogen phosphorous synergism is often confused by analogy with the strong and well established halogen antimony synergism. Unlike antimony halogen synergism, phosphorous halogen synergism is not general. The postulated formation of phosphorous oxyhalides completely lacks experimental support. However, good additive results are often obtained with combinations of halogen- and phosphorous-based flame retardants (Weil, 1992). An instance of bromine and phosphorous synergism is found in the structure of the following brominated phosphate ester:



#### **5.3.2 Antimony synergism**

There are a number of published formulations showing the attempted use of antimony oxide in combination with phosphorous and halogen flame retardants. Results sometimes appear favourable, but quantitative studies



show convincing evidence of an antagonism between antimony and phosphorous. In the most severe case the one element cancels out the effect from the other, and in other cases the effect is less than an additive. A detailed study of triaryl phosphate and antimony oxide in polyvinyl chloride (PVC) showed that this antagonism only occurred in a part of the composition range. The antagonistic effect probably is the result of the formation of antimony phosphates, that are very stable and practically inert fillers (Weil, 1992).