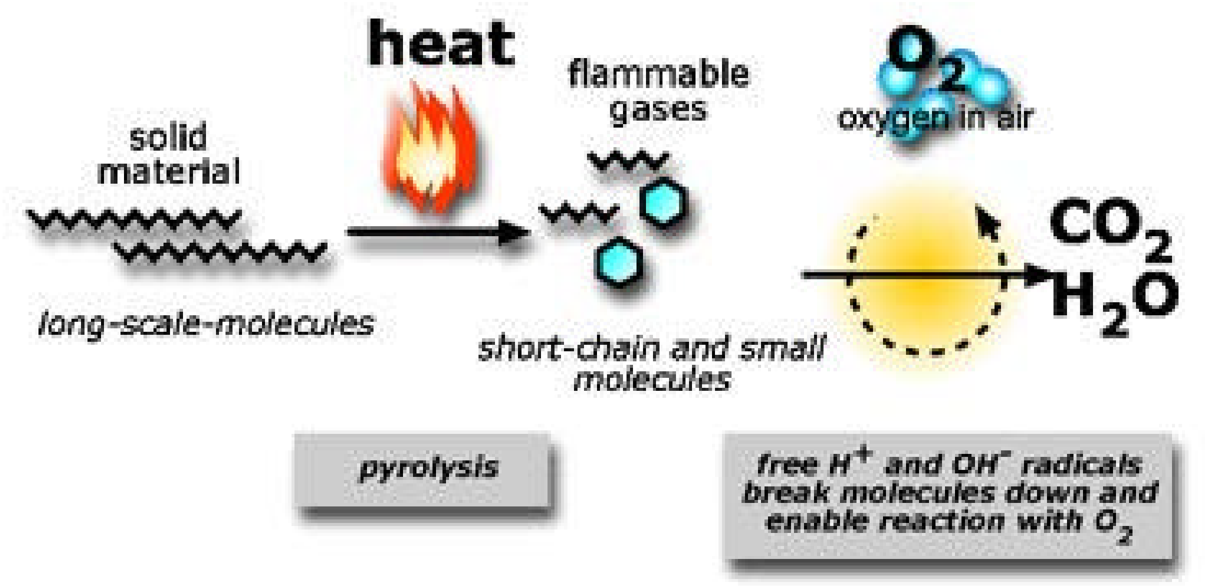
How do flame retardants work ?

There are many different flame retardants, and these work in a number of different ways. Some flame retardants are effective on their own, other products are used mainly or only as “synergists”, acting to increase the effect of other types of flame retardant.
To understand how flame retardants work it is first necessary to see how materials burn. Solid materials do not burn directly, they must be first decomposed by heat (pyrolysis) to release flammable gases. Visible flames appear when these flammable gases burn with the oxygen (O2) in the air. If solid materials do not break down into gases, then they will only smoulder slowly and often self extinguish, particularly if they “char” and form a stable carbonaceous barrier which prevents access of the flame to the underlying material. However, as we all know, even materials such as wood do in fact burn vigorously, because once ignited the heat generated breaks down long-chain solid molecules into smaller molecules which transpire as gases.



The gas flame itself is maintained by the action of high energy “radicals” (that is H_ and OH_ in the gas phase) which decompose molecules to give free carbon which can react with oxygen in air to “burn” to CO2, generating heat energy.

Halogenated flame retardants (containing chlorine or bromine atoms)

These act by effectively removing the H_ and OH_ radicals in the gas flame phase. This considerably slows or prevents the burning process, thus reducing heat generation and so the production of further gaseous flammable material.In fact, the mechanism is as follows. When exposed to high temperatures, the flame retardant molecule releases bromine (Br) or chlorine (Cl), as free radicals (Br_ or Cl_) which react with hydrocarbon molecules (flammable gases) to give HBr or HCl. These then react with the high-energy H_ and OH_ radicals to give water and the much lower energy Br- or Cl- radicals, which are then available to begin a new cycle of H_ and OH_ radical removal.The effectiveness of halogenated flame retardants thus depends on the quantity of the halogen atoms they contain (eg. 10 bromine atoms in one molecule of deca-DBP) and also, very strongly, on the control of the halogen release. Because chlorine is released over a wider range of temperatures than bromine, it is then present in the flame zone at lower concentrations, and so is less effective. Bromine is released over a narrow temperature range, thus resulting in optimal concentrations in the flame zone.Many different bromine containing flame retardants have been developed, with bromine atoms bound into different organic molecules. These offer different properties, in terms of how the bromine is bound into the flame retardant molecule (aliphatically, aromatically), and of how the flame retardant molecule interacts with different plastics. Different specific brominated compounds can thus be added to or chemically bound into different plastics without deteriorating their properties (flexibility, durability, colour ...). The many varying brominated products available thus offer high flame retardancy effectiveness solutions for all plastics currently on the market and for most of their varied applications.Similarly, several chlorinated flame retardants are also available, and are effective flame retardants in standard and technical plastics, thermosets, textiles and rubbers.

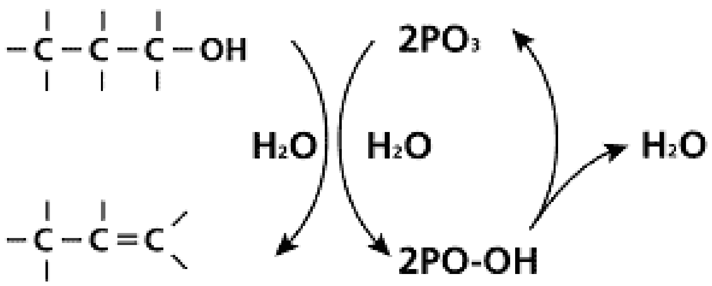
Antimony trioxide SbO3

Antimony trioxide does not have flame retarding properties on its own, but is an effective synergist for halogenated flame retardants. It acts as a catalyst, facilitating the breakdown of halogenated flame retardants to active molecules. It also reacts with the halogens to produce volatile antimony halogen compounds, which are themselves directly effective in removing the high energy H+ and OH- radicals which feed the flame phase of the fire, thus reinforcing the flame suppressing effect of the halogenated flame retardants.

When added to PVC, antimony trioxide acts to suppress flames by activating the chlorine present in the plastic itself.

Phosphorus flame retardants

Phosphorus containing flame retardants usually act in the solid phase of burning materials. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid (PO3). This acid causes the material to char, inhibiting the “pyrolysis” process (break down and release of flammable gases) which is necessary to feed flames [link to how FRs work above].



Different phosphorus containing flame retardants can be either simply mixed into plastics (and then held in the material when the plastic sets) or be reactive, and chemically bind into the plastic molecules at polymerisation. This will depend on the properties required of the plastic in terms of finished product performance, facility of processing (melting, extrusion, moulding) and flame retardancy (temperature of onset of the charring process).
Phosphorus based flame retardants vary from elemental red phosphorus (P), which is oxidised to phosphoric acid with heat, through to complex P-containing organic molecules offering specific performance properties. Certain products contain both phosphorus and chlorine or nitrogen, thus combining the different flame retarding mechanisms of these elements.

Nitrogen flame retardants

The mechanisms of nitrogen containing flame retardants are not fully understood, but it is thought that they have several effects :

formation of cross-linked molecular structures in the treated material. These are relatively stable at high temperatures, thus physically inhibiting the decomposition of materials to flammable gases (needed to feed flames)

release of nitrogen gas which dilutes the flammable gases and thus reduces flames

synergy with phosphorus containing flame retardants by reinforcing their function

To be effective, nitrogen based flame retardants are used at high concentrations, or in conjunction with other flame retardants. They can be either simply added to plastics, or reacted into the plastic molecules.

Melamine-based products are the most widely used type of nitrogen flame retardant today, used in foams, nylons ... but other products are also available or being developed.

Intumescent coatings

Intumescent coatings are fire protection systems which are used to protect materials such as wood or plastic from fire (prevent burning), but also to protect steel and other materials from the high temperatures of fires (thus preventing or retarding structural damage during fires). The coatings are made of a combination of products, applied to the surface like a paint, which are designed to expand to form an insulating and fire-resistant covering when subject to heat.

The products involved contain a number of essential interdependent ingredients :

spumific compounds, which (when heated) release large quantities of non-flammable gas (such as nitrogen, ammonia, CO_2)

a binder, which (when heated) melts to give a thick liquid, thus trapping the released gas in bubbles and producing a thick layer of froth

an acid source and a carbon compound. On heating, the acid source releases phosphoric, boric or sulphuric acid which charrs the carbon compound (mechanism described under phosphorus flame retardants LINK), causing the layer of bubbles to harden and giving it a fire-resistant coating. Often the binder can also serve as this carbon compound.

In a fire, the coating expands to a thick non-flammable layer of bubbles, offering good insulation protection to the material coated.As well as being used to protect flammable materials and structural elements, intumescent systems are now being incorporated into certain plastics, thus providing an inherent fire protection capacity.

Inorganic flame retardants

A number of inorganic compounds are used as flame retardants, interfering by various physical processes with the burning process : release of water or non-flammable gases which dilute the gases feeding flames, absorption of heat energy (in these gas-release reactions) thus cooling the fire, production of a non-flammable and resistant layer on the surface of material. These mechanisms of inorganic compounds are however of a relatively low efficiency and the products have to often be used in relatively large concentrations, or more usually, in combination with other types of flame retardants. Specific application forms of these products (for example, within organic coatings) can enable such high concentrations to be added to plastics without modifying their performance properties.

Inorganic flame retardants include:

-aluminium trihydrate (ATO) : this simple inorganic compound acts with all three of the mechanisms indicated above. At around 200°C, it is decomposed to aluminium oxide (which forms a protective, non-flammable layer on the material surface) and water. The water (as steam) forms a layer of non-flammable gas near the material's surface, inhibiting flames. The reaction is endothermic (absorbs heat energy), thus cooling the material and slowing burning.

-magnesium hydroxide. This acts with the same three mechanisms as aluminium trihydrate, but is only decomposed at somewhat higher temperatures (around 300°C), meaning that it can be used in plastics which are moulded or processed at relatively higher temperatures.

-boron compounds : these also act by releasing water, in a heat absorbing reaction, and forming a protective glassy layer on the material's surface. They can release boric acid, which also acts by causing charring of the material, reducing the release of flammable gases (see the mechanism for phosphate flame retardants LINK).

-zinc borate. This is a multifunctional flame retardant, which can function as a flame retardant (synergist of halogen), smoke suppressant (promote char formation), afterglow suppressant. In some halogen-containing systems, it can display synergy with antimony oxide. In certain halogen-free systems, it can also promote ceramic char formation.

-other zinc and tin compounds also act to reduce smoke emission from PVC, to promote charring, or as synergists to increase the effectiveness of halogenated or nitrogen (melamine) flame retardants.