

## **2. Fundamentals of flammability.**

Fire is the oxidative destruction of a combustible material. This process is accompanied by the release of heat and light energy. There are certain mechanisms of combustion as well as fundamental terms and definitions that must be clearly understood. Some of the relevant terms and definitions are clarified below.

### ***2.1 Terms and Definitions.***

*Inert gas dilution* involves the use of additives to produce large quantities of non-combustible gas when the polymer decomposes thermally. This gas dilutes the oxygen concentration in the air. Insufficient oxygen is then present for complete combustion and the fire extinguishes (Pettigrew, 1993).

*Thermal quenching* refers to the method by which the polymer surface temperature is kept low due to some endothermic degradation reaction, e.g. dehydration of ATH. This reaction acts as a heat sink, causing insufficient energy to be available for the production of flammable decomposition products (Pettigrew, 1993).

*Protective coatings.* Some flame retardants function by producing a protective char or liquid barrier. These minimise the flux or diffusion of the volatile decomposition products from the substrate to the flame front and act as an insulating layer to reduce heat transfer (Pettigrew, 1993).



*Physical dilution.* Inert fillers such as glass fibres and some minerals such as talc act according to this mechanism when added in large quantities. This reduces the amount of flammable polymer available, i.e. the effective heat of combustion of the substrate. Fillers may also increase the heat capacity of the polymer, creating a thermal heat sink (Pettigrew, 1993).

*Chemical interaction.* Halogens and phosphorous flame retardants act by chemical interaction. The flame retardant dissociates into radical species that interfere with the gas-phase combustion process (Pettigrew, 1993).

Terms that are applicable to intumescent flame retardants include (Pettigrew, 1993):

The *carbonific* (e.g. dipentaerythritol) provides the carbon source that produces the char layer.

The (latent acid) *catalyst* (e.g. ammonium polyphosphate) makes the intumescent reaction kinetically feasible; so that the carbonisation reaction takes place fast enough.

The *blowing agent* produces a gas, e.g. ammonia that inflates the char layer by a foaming process.

Polymer flammability can be expressed in terms of a *Limiting Oxygen Index* (LOI). The LOI refers to the minimum amount of oxygen that must be present to just sustain combustion in a vertical burn test. It involves a polymer strip lit from above with the gas streaming upwards. A higher LOI implies that a higher oxygen concentration in the gas stream is required to sustain the combustion of the strip.



## ***2.2 Mechanism of combustion and flame retardancy.***

In order for a solid polymer to burn it must be volatile, or produce volatile products, because combustion usually occurs in the gas phase. An exception is glowing combustion, a type of flameless combustion usually accompanying intumescent flame retardant systems. In the case of polymers, the solid substrate has a high molecular mass, i.e. consists of long chain molecules. Heat causes decomposition (e.g. depolymerisation) and volatilisation of the polymer. Decomposition begins in the solid phase and continues in the melt and gas phases. It produces decomposition products of low molecular mass. These volatile decomposition products enter the gas phase where they burn to produce more heat, driving further polymer decomposition. This provides the feed-back loop that sustains the combustion process. For a compound to function as a flame retardant it must interrupt the burning cycle in some way (Pettigrew, 1993).

The above process can be visualised in terms of the so-called fire triangle shown in Figure 1 (Gilman & Kashiwagi, 1997). It shows the interaction between the three elements essential for a fire:

- Heat generated by the flames.
- Fuel from the thermal decomposition of the polymer.
- Oxygen from the air.

The fire generates heat, part of which is absorbed by the substrate via radiation. The polymer substrate thermally decomposes into combustible gas fractions. These mix with the oxygen in the air to form a combustible mixture that fuels the fire. Once started, this process can sustain itself via the feed-back loop.

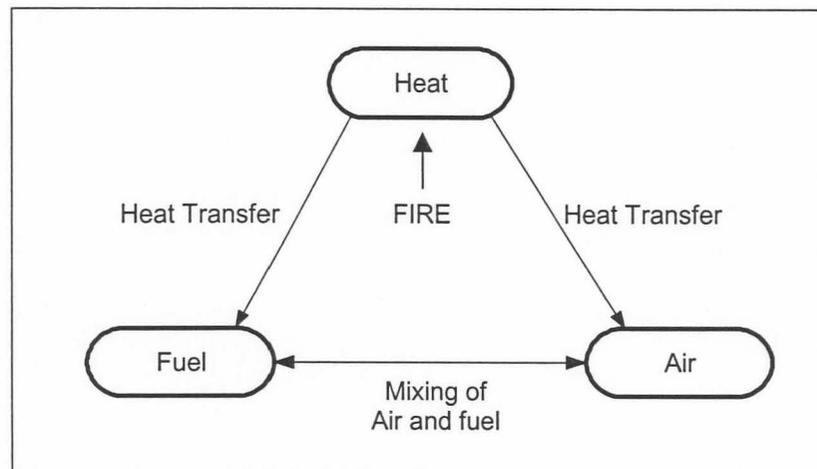


Figure 1: The Fire Triangle (Gilman & Kashiwagi, 1997).

In order to stop the fire, it is necessary to interrupt one or more of the pathways between the three major elements. This can be done in several ways, for example, by preventing the mixing of the polymer decomposition gas with the air. Alternatively, one could prevent the transfer of heat to the polymer substrate. The latter is a more sensible strategy and is easier to achieve (Srinivasan, Gupta & Horsey, 1998).

Flame retardants can modify flammability by several mechanisms. Usually a combination of several separate mechanisms is operative. Endothermic flame retardants such as metal hydroxides absorb heat during decomposition, causing thermal quenching. They also cause inert gas dilution by releasing water in the form of steam. Furthermore, so much of the flame retardant is added that it also causes a physical dilution effect (Srinivasan, *et al.*, 1998). Intumescent and halogenated flame retardants operate according to different mechanisms that are discussed in more detail in later chapters.

### **2.3 Flammability testing.**

One of the problems related to the fire resistance of polymers is the fact that there is no clear, uniform definition of flammability. The American Society for Testing and Materials (ASTM) lists over one hundred methods for the assessment of material flammability (Pettigrew, 1993).

Table 5 shows some of the flammability tests applied to flame retardant polymers to determine their performance and characteristics. As can be seen these tests are primarily from the American Society for Testing and Materials and the vertical burning test is from Underwriters Laboratory (UL) (Pettigrew, 1993).

Table 5: Flammability tests for polymers (Pettigrew, 1993).

<b>Designation</b>	<b>Description</b>	<b>Characteristic measured</b>
ASTM E162-87	Radiant panel	Flame spread
ASTM D2863-87	Limiting oxygen index	Ease of ignition
UL 94	Vertical burn	Ignition resistance
ASTM E1354-90	Cone calorimeter	Heat release and smoke

The most common flame test for flame retarded polymers is the UL 94 vertical burn test. This test uses a vertical burn method to determine the ignitability towards a small flame. Test specimens are mounted vertically and ignited with a Bunsen flame at a 30° angle. A layer of cotton is placed under the sample to test for flaming drips. The flame is applied for 10

seconds and then removed, and a further 10 seconds if the first application has self-extinguished. The flammability classifications include:

- **V-0** if no sample burns for longer than 10 seconds. The sum of the after-flame times, for five samples (i.e. 10 ignitions) must not be greater than 50 seconds, and the cotton must not ignite.
- **V-1** if no sample burns longer than 30 seconds. The sum of the after-flame times, for five samples (i.e. 10 ignitions if necessary) must not exceed 250 seconds, and the cotton must not ignite.
- **V-2** is the same as V-1 but the cotton can be ignited.

Cone calorimeters measure the rate of heat release during the burning of a sample. The specimens are exposed to a radiation flux of up to 100 kW/m<sup>2</sup>. Some of the measured parameters include the heat released, percentage mass loss, ignition time, heat flux and smoke production. The advantage of cone calorimeter testing is that the sample can be subjected to heat fluxes similar to those encountered in real fires (Pettigrew, 1993).

During this literature survey, a modified version of the Underwriters Laboratory vertical burn test (UL94) was used. A vertically mounted unsized polyester fabric sample was ignited twice with a spirit burner flame using an exposure time of 10 seconds. This test is referred to as British Standard 5438 (BS 5438) in accordance with BS 5867 Part 2 (CSIR, 1999).