Fire Retardants – necessary, nuisance or nemesis?

T Richard Hull
Centre for Fire and Hazard Sciences,
University of Central Lancashire, Preston PR1 2HE, UK,
trhull@uclan.ac.uk

Introduction

The huge growth in products based on synthetic polymers has increased the flammability of our built environment. The incorporation of fire retardants into these polymers has been effective in reducing the flammability of many materials. Fire retardants have evolved over the last four decades in order to meet the demands of industry and regulators, from halogen based flame inhibitors to cleaner, char promoters, resulting in less smoke and toxic gas emissions. While halogenated flame retardants continue to be used in a wide range of existing products, very little new work has been published on them. Instead, research has been heavily focussed on finding suitable halogen-free alternative fire retardants, indicating that the industry has indeed recognised the need for change, in the face of increasing pressure, predominantly resulting from environmental concerns.

The benefits of fire retardants in terms of flammability reduction will be reviewed. The chemistry of the current and proposed groups of fire retardants will be discussed in relation to their mode of action, influence on flammability, fire toxicity and smoke production.

Historically, the increased growth in use of synthetic polymers has been accompanied by an increase in the number of fire deaths and injuries, shown in figure 1 and 2 (Stec & Hull 2010). These are now in decline, but whether this results from increased use of fire retardants, the availability of low cost smoke detectors or other factors such as improvements in standard of living is unclear.

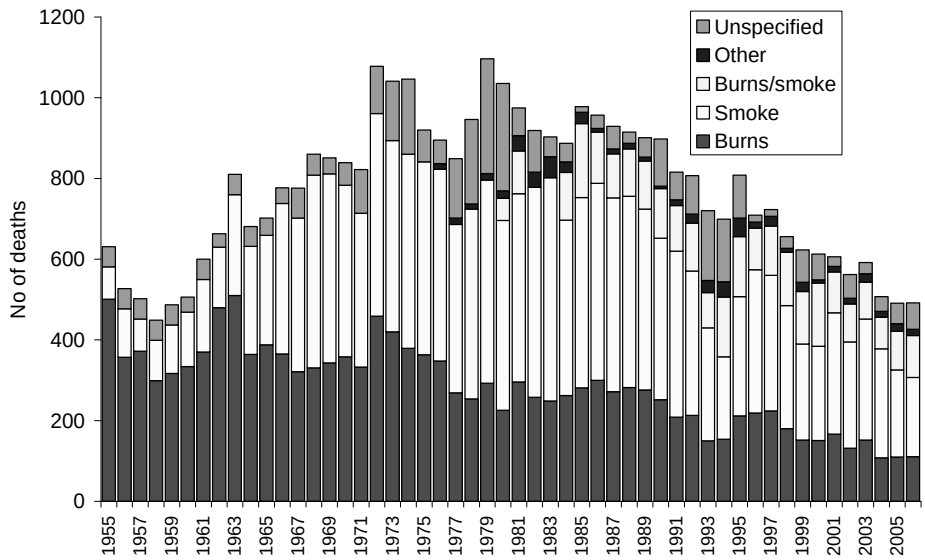

Figure 1 Causes of UK Fire deaths 1955-2006

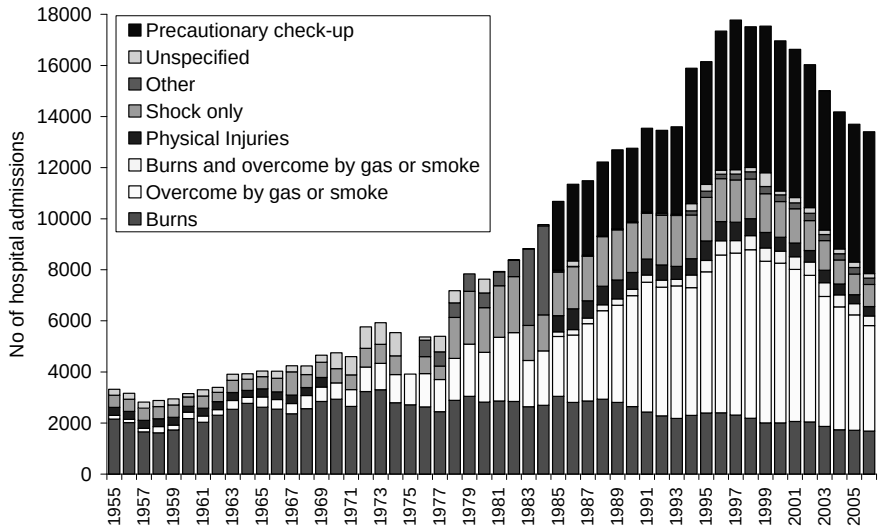

Figure 2 UK non-fatal fire injuries requiring hospital treatment, 1955-2006, excluding precautionary check-up.

Fire retardants

The range of different types of fire retardants provides considerable scope for manufacturers to meet physical property, environmental and other criteria as well as keeping the flammability within prescribed limits. Fire retardants act by interfering with the fire propagation processes, as illustrated by the fire triangle (Figure 3).

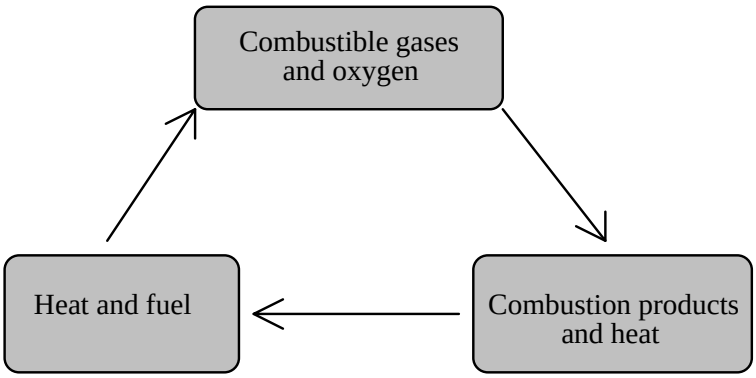

Figure 3 The fire triangle

Mode of action

A fire retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. The various ways in which a fire retardant can act physically or chemically are described below. However, their action should be considered as complex processes with many individual stages.

Physical action

There are several ways in which the combustion process can be retarded by physical action:

- *By cooling*. Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.
- *By formation of a protective layer (coating)*. The condensed combustible layer can be shielded from the gaseous phase with a solid protective layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded.
- *By dilution*. The incorporation of inert substances (e.g. fillers) and additives which evolve inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded.

Metal hydroxides and carbonates, such as aluminium hydroxide (ATH) decompose endothermically with the release of water, leaving a protective residue of alumina. ATH is the world's most widely used fire retardant.

Chemical action

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases :

- *Reaction in the gas phase*. The radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant. The radical concentration falls below a critical value, and the flame goes out. The exothermic processes are thus stopped, the system cools down and the supply of flammable gases is reduced and eventually completely suppressed.

  This is the mode of action of bromine and chlorine based flame retardants, and of some organophosphorus based retardants. Typically they are easiest to formulate into a reduced flammability product, but produce more smoke and toxic gases.

- *Reaction in the solid phase*. The fire retardant can cause a layer of carbonaceous char to form on the polymer surface. This can occur, for example, through the dehydrating action of the additive generating double bonds in the polymer. Ultimately, these form carbonaceous layers by cyclizing and cross-linking.

  The majority of new developments in fire retardancy aim to enhance char formation, sometimes in combination with bowing agents to form a swollen protective layer (intumescence). The effectiveness of a wide range of materials has been demonstrated, including carbon, phosphorus, nitrogen, silicon and iron compounds. Recently, considerable effort has been devoted to investigation of fire retardant effects of nanofillers, particularly nanoclays and carbon nanotubes.

Additive vs Reactive Fire Retardants

An alternative approach to classifying fire retardants uses their attachment to the polymer.

Additive fire retardants are incorporated in the plastic either prior to, during, or, more frequently, following polymerisation. They are used especially in thermoplastics. If they are compatible with the plastic they may act as plasticizers, otherwise they are considered as fillers. They are sometimes volatile or tend to bleed so fire retardance may be gradually lost. The development of high molecular weight products (oligomeric and polymeric flame retardants) may eliminate this problem.

Reactive fire retardants are built into the polymer molecule, for example by attaching a fire retarding group to a monomer group. This prevents bleeding out from the polymer and the fire retardance is thus retained. In addition, they have no plasticising effect and do not affect the thermal stability of the polymer. They are used mainly in thermosets (especially polyesters, epoxy resins and polyurethanes) in which they can be easily incorporated. They are, however, normally more expensive than additive fire retardants since they require custom manufacture. In thermoplastic polymers, where the structural integrity, strength and other physical properties depends on the microcrystalline structure, the presence of foreign groups on the polymer chain is likely to have a detrimental effect on the physical properties, particularly below the glass transition temperature.

Combinations of additive or reactive flame retardants with further additives can produce an *additive*, *synergistic* or *antagonistic* effect. While the *additive* effect is the sum of the individual actions, *synergism* is a greater than additive effect (the combination of antimony with halogen based flame retardants has been shown to be synergistic), and *antagonism* a less than additive effect. When used alone, some additives show no or only negligible effectiveness. The synergistic effect occurs when they are used together with other specific flame retardants. Such synergists have achieved great importance in practical use because they are often more effective or less expensive than the single flame retardants.

Conclusions

Halogen based flame retardants have been widely used because they are easiest to incorporate into a polymer to achieve the necessary fire retardant effect. However, they suffer a number of problems, from greater smoke production and greater fire toxicity to leaching out of the polymer where some have been shown to be persistent ecotoxicants. This has led to decline in their use, particularly in new products, where plenty of alternatives are available. The two major areas where replacement remains problematic are fabrics and foams. However, large quantities of brominated and chlorinated flame retardants are probably still in products currently in use, or in storage, thus their release into the environment will continue. In such circumstances it is essential that waste treatment processes are able to identify, separate and treat materials containing halogenated flame retardants properly, and ensure that they do not end up in halogen free waste streams.

References

Stec A A and Hull T R, (2010) Introduction to Fire Toxicity, Chapter 1 in Fire Toxicity, Edited by Stec A A and Hull T R, Woodhead Publishing, Cambridge, UK (using collected data taken from bulletins of UK fire statistics).