Flame Retardants

Frequently Asked Questions

The European Flame Retardants Association

EFRA - The European Flame Retardants Association

Chemistry making a world of difference

Compiled and edited by Adrian Beard, Clariant, fire test photos by Ralf Baumgarten taken at Siemens Brandversuchshaus in Frankfurt-Hoechst and BayerIndustryServices Fire Test Laboratory in Leverkusen. We thank the teams of Knut Bauer and Michael Halfmann for their help and technical assistance.

Cover photos:
Candles are a common cause of ignition for domestic fires. The stereo shown on the front cover is engulfed in flames after 7 minutes when ignited with a small flame - see the photo on the back cover.

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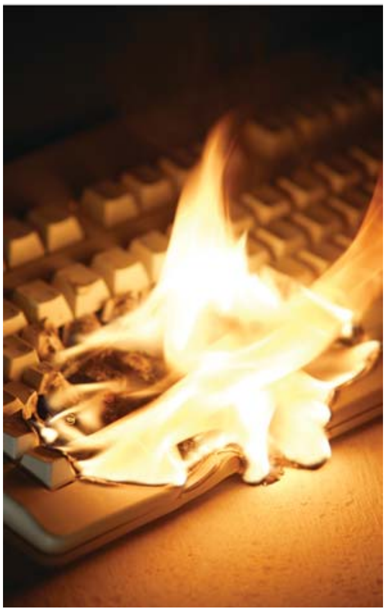
What are flame retardants?

Flame retardants are chemicals which are added to combustible materials to render them more resistant to ignition. They are designed to minimise the risk of a fire starting in case of contact with a small heat source such as a cigarette, candle or an electrical fault. If the flame retarded material or an adjacent material has ignited, the flame retardant will slow down combustion and often prevent the fire from spreading to other items. Since the term "flame retardant" describes a function and not a chemical class, there is a wide range of different chemicals which are used for this purpose. Often they are applied in combinations. This variety of products is necessary, because the materials and products which are to be rendered fire safe are very different in nature and composition. For example, plastics have a wide range of mechanical and chemical properties and differ in combustion behaviour. Therefore, they need to be matched to the appropriate flame retardants in order to retain key material functionalities. Flame retardants are thus necessary to ensure the fire safety of a wide range of materials including plastics, foam and fibre insulation materials, foams in furniture, mattresses, wood products, natural and man-made textiles. These materials are e.g. used in parts of electrical equipment, cars, airplanes and building components.



Why do we need flame retardants?

Both our homes and offices contain an increasing potential "fire load" of flammable materials because of the development of electrical and electronic equipment, and of rising levels of comfort (furniture, carpets, toys, magazines and papers ...). The potential causes of fires also tend to increase, especially in electronic equipment where the accelerating processor power, electronic sophistication but at the same time miniaturisation, result in a concentration of energy and an increase in risks of local overheating or other electrical fire risks. Flame retardants can prevent an increase in fire risk from the growing number of consumer and electronic goods in homes and offices. Flame retardants protect modern materials such as technical plastics, building insulation, circuit boards and cables from igniting and from spreading a fire.

Once a fire starts in a room of a house, it can develop rapidly, if it spreads to items other than that first ignited. Once a number of items are burning, the temperature in the room will rise, and may reach "flash over" point, when hot burning gases cause effectively the whole room to catch light, often violently. Once this occurs, escape from the room is impossible, and spread of the fire to other rooms is very likely. Flame retardants act both by preventing the initial start of a fire by impeding ignition and by delaying the spread of the fire, thus increasing escape time, and perhaps preventing "flash over".

What are the benefits of flame retardants?

Most people do not realise that their television set, sofa, mattress and computer are all made essentially from plastics (originally made from crude oil), and without the inclusion of flame retardants many of these products can be set alight by just a short circuit or cigarette and become a burning mass in just a few minutes. Did you know for example, that a regular TV set contains in its combustible plastics an energy content which is equivalent to several litres of petrol? Flame retardants can be applied to many different flammable materials to prevent a fire or to delay its start and propagation by interrupting or hindering the combustion process. They thus protect lives, property and the environment. Flame retardants contribute to meeting high fire safety requirements for combustible materials and finished products prescribed in regulations and tests. Although fire safety can be achieved by using non-combustible materials in some cases or by design and engineering approaches, the use of flame retarded materials often meets the functionality and aesthetic requirements of the consumer as well as offering the most economical approach.

Examples:

- Metal casings for electrical equipment afford fire safety, but pose electrical risks, as well as being heavier, more expensive and less design flexible than modern plastics.
- An increasing use of plastics in cars, trains and aeroplanes offers lower weight and so improved fuel economy, but necessitates flame retardants to ensure fire safety.
- Mineral fibres for building insulation are not flammable, but may not offer the same energy performance, structural characteristics or flexibility of application as polymer foams.

Even where non-flammable materials such as steel are used, flame retardant intumescent coatings can provide valuable heat protection for these to limit or delay mechanical deterioration in the case of fire.

General Fire Safety

How large is the number of victims from fires?

Statistics show that generally between 10 and 20 fire deaths per 1 000 000 inhabitants are reported in the major industrial countries of the world. The number of severely injured people is estimated at ten times this figure, i.e. 100 to 200 per 1 000 000 inhabitants per year. Every day in Europe there are about 12 fire victims and 120 people severely injured. About 80 % of all fire deaths occur in residential buildings. The people most at risk are the very young and the elderly because they are least able to escape in the event of a fire.

www.flameretardants.eu/pdf/0602/fire_stat0602.pdf
and World Fire Statistics www.genevaassociation.org

What is the economic damage caused by fire?

The total economic damage is estimated at about 25 billion € per year in Europe. In Germany alone, compensation costs covered by insurance companies amount to 1.5 billion € per year and there are about 200 major fire incidents with damages in excess of 0.5 million €.

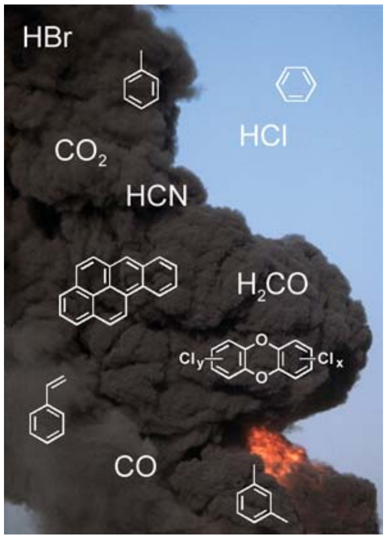
www.gdv.de, www.nfpa.org (USA)

What is the most common cause of death in fires?

The most common cause of death in fires is to be overcome by gas or smoke: In the UK, around 50 % of people die this way, while 25 % of deaths are due to burns and 20 % are attributed to both burns and being overcome by gas or smoke. 5 % of fire deaths cannot be specified. Accidental fires in the home have far higher casualty levels than any other location.

Why are fire gases toxic?

Fires gases are toxic, because in all fires toxic products are formed from the incomplete combustion of organic materials like plastics, wood, textiles and paper. The component which usually dominates the toxicity of fire effluents is carbon monoxide (CO), which is responsible for over 80 % of all people killed by fire gases. One striking example is the Düsseldorf Airport fire in 1996: here, all 17 fire deaths were due to CO poisoning. By delaying the combustion of treated materials and the spread of the fire, flame retardants significantly reduce the emissions of toxic gases.
Besides CO, many other toxic components can be formed in a fire: Hydrogen cyanide (HCN) may be formed from plastics like polyurethane and polyamide as well as from natural products which contain nitrogen like wool and leather. Irritant fire gas components are hydrogen chloride (HCl) evolving from plastics like PVC and acrolein released from natural products like wood. However, compared to the toxic potential of CO, which is present in large quantities in all fires, the other fire gas components usually only play a minor role.



Besides these volatile gases, some more complex products are formed like polycyclic aromatic hydrocarbons (PAHs) or halogenated dioxins and furans (PXDD/F). These products are formed in much lower quantities and are not relevant for acute toxic effects but they can have long term health effects. However, because they are higher molecular weight substances, they are mostly adsorbed to soot which reduces their toxic potential. The polycyclic aromatic hydrocarbons are typical products from incomplete combustion of organic materials and they dominate the long-term toxicity of soot. The conclusion from many studies carried out on this subject is that although the substances emitted from fires are very variable, depending on fire conditions, the toxicity is above all a function of the quantity of material burned.

www.flameretardants.eu/pdf/babrauskas_summary.pdf

www.flameretardants.eu/pdf/prison_mattress.pdf

www.sp.se/fire/Eng/Research/Fire_LCA_study_TV.pdf

Does the presence of flame retardants increase the toxicity of smoke?

This is a concern which is often raised. It is based on the fact that some flame retardants act by impeding the combustion reactions in the gas phase and therefore lead to incomplete combustion which in turn means a smoky fire. However, large scale studies have demonstrated that the toxic hazards from a fire are more dependant on how much is burning under which conditions of temperature and ventilation rather than what is burning. Two cases can be considered:

1. The flame retarded (FR) material is subject to the primary ignition source: if this is a small flame or other low energy source like a cigarette butt, the presence of flame retardants in the material may cause it to smoulder and smoke somewhat, but will severely impede ignition and in most cases no fire will develop. If burning is sustained, the release of heat and the spread of flames will be severely hindered by flame retardants allowing people more time to escape from the fire. The most significant reduction in toxic gases from fires is achieved by actually preventing the fire, or preventing it from spreading from one item to a whole room.

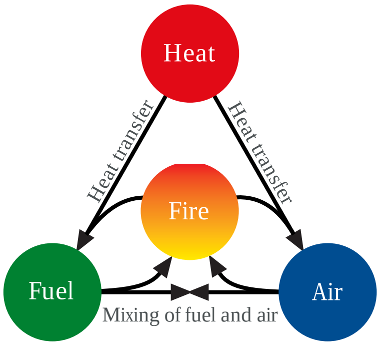
2. The flame retarded material is not the first item ignited but is involved in a fire that is already developing: In this case flame retardants cannot prevent the ignition of the material and it will eventually be thermally degraded or burn. However, flame retardants will reduce the rate of flame spread and heat release. The impact of flame retardants on smoke or fire gases also depends on the proportion of flame retarded material to the total fire load. Room fire tests which compared a room with non flame retarded materials to a room with flame retarded items (TV cabinet, business machine housing, upholstered chair, electrical cables, electrical circuit board) revealed:

- The total quantities of toxic gases released by the FR products was one third that for the non FR.
- Total smoke production was not significantly different.
- "Because the total quantities of material consumed in the full-room tests with FR products are much lower than with non FR products, the total carbon monoxide [the dominant toxic fire gas] emissions are thus around half with the flame retarded products, significantly reducing the fire hazard."
  (Source: Babrauskas V. et al. (1988) Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products. NBS special publication SP 749. NIST, USA)

Therefore, it is clear that because flame retardants reduce the number and extent of fires, they can significantly reduce both the total levels of such toxic gases in a given fire and the total emissions from all fires. This has been investigated and proven for television sets and upholstered furniture in life cycle assessment studies (www.sp.se/fire). Please see the EFRA website for detailed information and references.

How does a fire develop?

A fire can basically be split into three phases, the initiating fire, the fully developed fire and the decreasing fire. The fire starts with an ignition source (for example a match) setting combustible material (for example an upholstered armchair) on fire. The fire spreads, heats up the surroundings and once the materials in the room have formed enough flammable gases and are sufficiently hot, flashover takes place and the whole room is engulfed in the fire. This is the start of the fully developed fire, where temperatures up to 1 200 °C can be reached. The fire will later decrease as the available fire load is consumed by the fire or if the fire occurs in a totally closed room the fire can die because of oxygen deficiency.



Fire Triangle (according to Emmons)

What are the parameters governing a fire?

The fire triangle indicates where flame retardants can interfere in the combustion process.

The fundamental parameters governing a fire are:

- Combustibility: Will a material burn?
- Ignitability: If it is combustible, how and when will it ignite?
- Spread of flame: Once ignited, how quickly will the flames spread?
- Heat release: What will be the rate and total amount of heat released?

On the one hand, there are materials that are easily ignitable but have a relatively small energy content like paper - on the other hand, there are materials which are difficult to ignite but once ignited will release a large amount of energy like diesel fuel or many plastics. In addition, in all fires secondary effects occur. These do not primarily determine the course of the fire, but cause most of the fire deaths or damage to materials. These effects are:

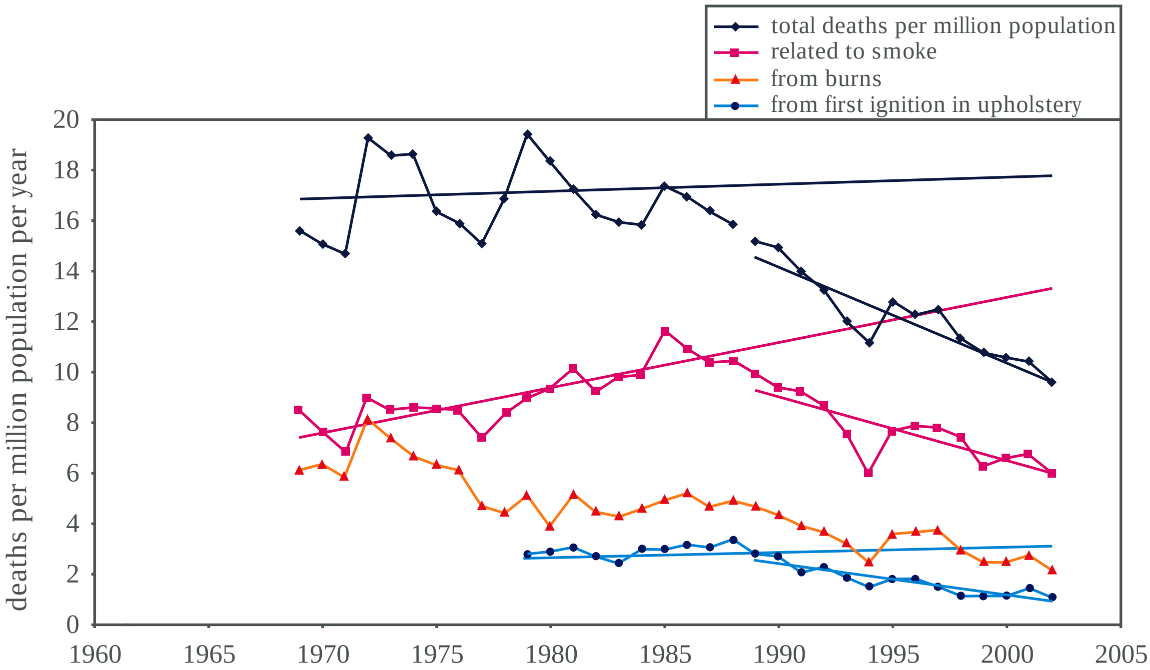
- Smoke development
- Fire gas toxicity
- Corrosivity and contamination by soot (more relevant to materials than to humans and particularly sensitive for electronic equipment)

Fire Safety Standards and Regulations

What is the role of fire safety regulations?

Fire safety regulations aim at preventing fires and saving lives and property. Fire safety regulations exist for building, transportation (road and rail vehicles, aircraft and ships), electrical engineering & electronics as well as for furnishings and textiles. One example for the benefits of fire safety regulations is the introduction of the United Kingdom Furniture and Furnishings (Fire Safety) Regulations in 1988. The strict requirements on the fire performance of upholstered furniture which these regulations stipulated were often met by using flame retardants.
Taking into account changes in smoking habits and increased installation of smoke alarms, these regulations were estimated to be saving more than 230 lives and 4 200 injuries per year by 2002 (see graph on opposite page). A study carried out for the French association of Burns Victims (ABF) indicates that a fire safety requirement for furniture would save, in the long term, 210 lives/year and result in net economic benefits of over 700 million €/year

“Preliminary Legal and Socio-Economic Study for the Projected Decree on Fire Safety Standards for Upholstered Furniture”, C. Chevalier for Association des Brûlés de France, July 2005
www.acfse.org/research2.htm



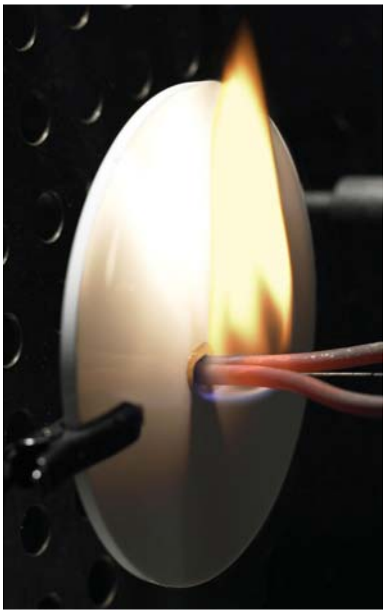
Source: "International Fire Statistics and the Potential Benefits of Fire Counter-Measures", A. Emsley et al., University of Surrey, UK, 2005. Available at www.cefic-efra.org

What are fire safety requirements?

Fire safety requirements are contained in regulations, technical guidelines, safety standards and approval procedures. Today, they cover finished products rather than single materials and allow their classification by the use of specific fire tests. Fire safety requirements are becoming more and more international:

In Europe, the two fields where national requirements are still used, building and railways, are being harmonised in the framework of the European Union. However in the field of upholstered furniture, the national regulations of the UK and Ireland provide the highest levels of fire safety.
In continental Europe efforts to introduce such strict requirements on a European level still continue.

Requirement	Examples	
General safety regulations	EU General Product Safety Directive 2001/95/EC	Construction Products Directive 89/106/EC
Product standards	IEC 60065 for television sets and other audio / video	EN 13162 ... 13171 for thermal insulation products for buildings
Fire test standard	UL 94 flammability standard	Single Burning Item Test, EN 13823


What is the role of fire tests?

The role of fire tests is to determine the fire risk of materials and finished products used in applications like building, transportation, electrical engineering and furniture. They are the basis upon which a material's flammability or a product's fire performance is determined. Fire tests were developed to simulate the ignition behaviour of materials or even real fire events, which are thought to be particularly harmful to humans and property. The products have to meet fire safety requirements defined in the tests. The sample size can vary from a small strip of material (e.g. 12.7 cm x 1.27 cm; for the UL 94 test) up to boards of 1.5 x 1.5 m^2 (SBI-Test), individual furniture items or even complete furnished rooms.

Recent improvements in fire safety standards

In 2006, the United States adopted a federal regulation requiring strict mattress fire safety for all mattresses sold in the USA from July 2007 (flame resistance and limited heat emission). The US Consumer Product Safety Commission estimates that 240-270 lives and 1 150 - 1 330 injuries per year will be saved, and calculate a net benefit to society of US$ 820 million/year. The USA has also issued advance notice of proposed rulemaking for fire safety of upholstered furniture and for bedclothes.

In Europe, the companies Philips, Panasonic, Finlux and Sony voluntarily announced in 2004 that all their TV sets sold in Europe will in future be ignition resistant (www.acfse.org). Unlike generally in Europe, TV sets sold on the US market are already ignition resistant.

Improved standards for furniture and mattresses have recently been developed: in Sweden, 2002, fire requirements for mattresses for high risk health institutions and prisons (standard SS 876 00 10); in France, 2006, revised fire safety standards for seats in public places (Article AM 18, Norme NF D 60013).

What are the most important fire tests for the main application areas of flame retardants?

The most important fire tests for combustible materials used in building, motor vehicles, railways, aircraft, ships, electrical engineering, furniture, mattresses and textiles mainly cover the parameters flammability, spread of flame, heat release and smoke development. Some of the major fire tests are:

- Building
  - National tests:
    - French Epiradiateur test (NF P 92-501 ... 507)
    - German Brandschacht and small flame test (DIN 4102)
    - British Surface spread of flame test (BS 476 part 7)
  - Harmonised European tests:
    - Single Burning Item test (SBI, EN 13823)
    - Small flame test (EN ISO 11925-2)
- Transportation
  - Automotive: FMVSS 302 (Federal Motor Vehicle Safety Standard, USA)
  - Railways: Different national tests and pending new harmonised European tests (EN TS 45545)
  - Aircraft: Various Bunsen burner tests, OSU (Ohio State University) heat release and kerosene burner seat tests
- Electrical Engineering & Electronics
  - Flammability tests according to UL (Underwriters Laboratories) 94: Horizontal burning HB, Vertical burning with classes V2, V1, V0, 5V
  - Glow wire test (IEC 60335)
- Upholstered furniture and textiles
  - BS 5852: tests for assessment of the ignitability of upholstered seating by smouldering and flaming ignition sources
  - EN 1021: Cigarette and match tests for furniture filling and cover (part 1 and 2)
  - ISO 6940/41: Flammability tests for textiles
  - 16 CFR Part 1633: US federal mattress flammability standard (USA 2006)

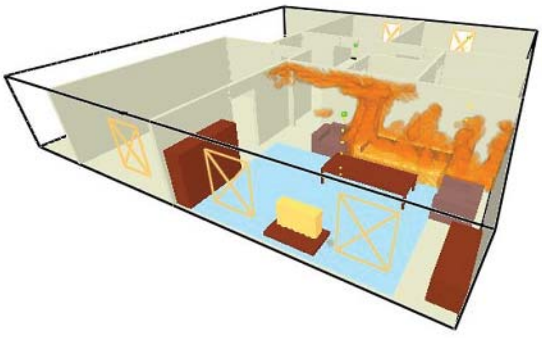
For further information on fire tests please refer to: Troitzsch, Jurgen (2004): Plastics Flammability Handbook. Hanser Publishers and Oxford University Press, Munich. 3rd edition.

Are there ways to meet fire safety levels without using flame retardants?

Yes, there are: safety standards and fire tests do not prescribe how to reach the necessary fire performance. For example, a manufacturer can choose a non-combustible material like steel for an equipment housing, or engineering design approaches are stipulated in some standards which waive the need for fire proof materials if certain safety distances are kept from potential ignition sources. Plastic materials are often favoured because of their low price and ease of processing which allows mass manufacture even of sophisticated designs and shapes. The different types of plastics also differ widely in ignitability. However, with the exception of chlorinated polymers like PVC most "naturally" flame resistant plastics are also very expensive and more difficult to process. In textiles the situation is similar: inherently less flammable materials are available, but often at a considerably higher price and usually with different material properties - the "look and feel" of a fabric is very important if it is used for clothing, furniture items or curtains for example. Flame retardants are only one element of fire safety, however, a very significant one. Other elements are e.g. a good education of the public on fire safety, smoke alarms in public buildings and private homes and a well functioning fire service. Only by combining all measures can we minimise fire damages and fatalities. Just think of your car - do you dispose of the safety belt, now that you have an airbag?

Flame Retardants and other Safety Technologies

Is it not sufficient to have smoke alarms in homes?
Do we need chemicals for fire protection, if everybody had a smoke alarm in his home? To answer this question, EFRA commissioned a study at the German Federal Institute for Materials Testing and Research, BAM (www.bam.de), in Berlin. Their task was to evaluate the contributions to fire safety from smoke alarms and flame retarded items in a home, like TV sets or upholstered furniture.



Previous investigations e.g. of NIST [1] revealed that smoke detectors do have a positive effect on fire safety, but they also show that escape times can be very short in residential fires, even down to less than 4 minutes. This reduction in escape times over the last 30 years is attributed to the widespread use of flammable plastics and textiles. Therefore, the researchers at BAM modelled several fire scenarios in residential buildings by computational fluid dynamics (CFD) which they validated against a number of experimental data sets like the NIST. study. In these scenarios selected furniture and electrical devices were compared with such items with reduced flammability which is typically achieved by the application of flame retardants. Although smoke alarms quickly respond to a developing fire and can alert the inhabitants, especially if they are asleep, a clear safety benefit for the scenarios with flame retarded items could be demonstrated: the times to dangerous smoke densities and flashover are significantly reduced which results in longer escape times. Depending on the ignition source and the fire safety requirements, a fire might not even develop in the flame retarded case. Numerical predictions are in good agreement with the results of experimental studies in which flame retarded furniture or electrical devices were tested in full scale tests. In addition, two large scale fire tests representing a living room and a children's room were carried out together with the Berlin fire service. In these tests, the fires developed very rapidly after igniting either a TV or a bed mattress with a candle.

"From our point of view, a combination of both fire safety measures is necessary to fundamentally improve the fire safety in homes: the installation of smoke detectors as well as the equipment of high risk items of furniture or electrical devices like upholstery or TV sets with flame retardants" says Dr. Anja Hofmann, lead researcher at BAM.

For further information see:

www.bam.de/

www.bam.de/de/kompetenzen/fachabteilungen/abteilung_7/fg73/index.htm

1. Bukowski, R.W., Peacock, R.D., Averill, J.D., Cleary, T.G., Bryner, N.P., Walton, W.D., Reneke, P.A., Kuligowski, E.D. Performance of Home Smoke Alarms, Analysis of the Response od Several Available Technologies in Residential Fire Settings.
NIST Technical Note 1455, July 2004

Flame Retardant types and applications

What is the mode of action of flame retardants?

By chemical and/or physical action, flame retardants will inhibit or even suppress the combustion process. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. The amount of flame retardant one has to add to achieve the desired level of fire safety can range from less than one percent for highly effective flame retardants up to more than 50 percent for inorganic fillers. Typical ranges are 5 to 20 percent by weight.

The most effective chemical action may take place by

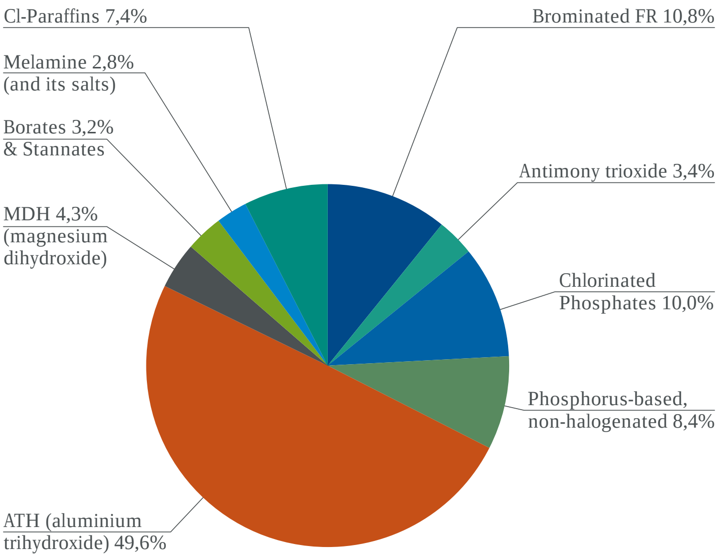
- Reaction in the gas phase: The radical gas phase combustion process is interrupted by the flame retardant, resulting in cooling of the system, reducing and eventually suppressing the supply of flammable gases.
- Reaction in the solid phase: The flame retardant builds up a char layer and shields the material against oxygen and provides a barrier against the heat source (flame).

The less effective physical action may take place by

- Cooling: Energy absorbing (Endothermic) processes triggered by additives and/or the chemical release of water cool the substrate to a temperature below that required for sustaining the combustion process.
- Formation of a protective layer (coating): The material is shielded with a solid or gaseous protective layer and protected from heat and oxygen necessary for the combustion process.
- Dilution: Inert substances (fillers) and additives evolving non-combustible gases dilute the fuel in the solid and gaseous phases.

2005 EUROPEAN FLAME RETARDANT MARKET CONSUMPTION

Data according to EFRA survey and SRI consulting figures, based on tonnages:



What are the main families of flame retardants?

The main families of flame retardants are based on compounds containing:

- Halogens (Bromine and Chlorine)
- Phosphorus
- Nitrogen
- Intumescent Systems
- Minerals (based on aluminium and magnesium)
- Others (like Borax, Sb_2O_3, nanocomposites)

How important is the flame retardants market?

With a global consumption of about 2.9 billion US$, flame retardants are the most important group of plastics additives which have a total market volume of around 11 billion €. According to SRI Consulting, the 2005 global flame retardants consumption amounted to 1.5 million tonnes. EFRA members estimate a consumption of 464 000 tonnes of flame retardants in Europe (EU-25, 2005). Brominated flame retardants have the highest market share by value and aluminium trihydroxide the highest market share by volume. A global growth of around 3 % per year is foreseen for the near future. Inorganic flame retardants like aluminium trihydroxide have experienced the highest growth rates lately, followed by phosphorus and nitrogen based systems. Since a number of flame retardants are high production volume chemicals, they have been scrutinised under current chemical regulations like the European Union risk assessment process.

See chapter on Environmental and Health aspects for further information.

Brominated Flame Retardants (BFRs)

What are the applications of BFRs ?

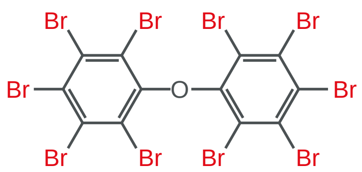
BFRs are commonly used to prevent fires in electronics and electrical equipment. This area accounts for more than 50% of their applications - for example in the outer housings of TV sets and computer monitors. Indeed, the internal circuitry of such devices can heat up and, over time, collect dust. Short circuits and electrical or electronic malfunctions can occur. Printed circuit boards also require flame retardancy properties which are often provided by a crosslinked brominated epoxy resin polymer manufactured from tetrabromobisphenol-A (TBBPA). In addition, BFRs are used in wire and cable compounds, for example for use in buildings and vehicles as well as other building materials, such as insulation foams. They are also used in speciality fabric back-coatings for curtains, seating and furniture in transport and public buildings as well as domestic upholstered furniture conforming to the UK and Ireland Furniture[1] Flammability regulations.

[1] Furniture and Furnishings (Fire) (Safety) Regulations 1988, UK

What does a Brominated FR mean?

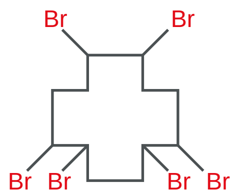
There are about 75 different commercial BFRs, each with specific properties and toxicological behaviour. The only common feature is they contain bromine and act in the vapour phase by a radical trap mechanism. They come in various forms and can be liquids, powders or pellets. The most important BFRs are:

Polybrominated diphenylethers (PBDE)



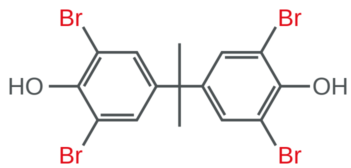
Decabromodiphenylether (Deca-BDE) is the only commercial product currently in use from the PBDE familly. It has 10 bromine atoms attached to the diphenylether molecule, a high molecular weight and high thermal stability. Its major applications are in styrenic polymers, polyolefins polyesters, nylons and textiles. In May 2004, the European risk assessment concluded that no risk was identified for human health or the environment in the use of Deca-BDE. The two other commercial products of the PBDE family -PentaBDE and Octa BDE- may no longer be used in Europe since August 2004.

Hexabromocyclododecane (HBCD)



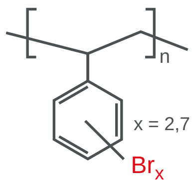
is a cycloaliphatic BFR. It is commonly used in foamed polystyrene for insulation of buildings where it is only necessary at very low loadings. For compact polystyrene (high impact) higher loadings are necessary. Another application is in textiles.

Tetrabromobisphenol-A (TBBPA)



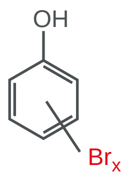
is mainly used in epoxy resins for printed wiring boards, where it is reacted into the polymer backbone and so becomes a tightly bound part of the polymer. It is also used as an additive flame retardant mainly in ABS plastics, as an intermediate in the production of other brominated FR systems, in derivatives, in epoxy oligomers and in engineering plastics for electrical and electronic devices. The human health part of the European Risk Assessment concluded in May 2005 that TBBPA is safe for human health.

Brominated (poly)styrene



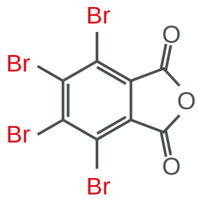
is commonly used in polyester and polyamides, It is a polymer itself and is therefore quite immobile in the matrix.

Brominated phenols



e.g. tribromophenol, are reactive flame retardants most often used as intermediates in the manufacture of polymeric brominated flame retardants. They can be used as end caps in brominated carbonate oligomers and brominated epoxy oligomers, which in turn are used as flame retardants.

Tetrabromophthalic anhydride



is often used as a reactive flame retardant in unsaturated polyesters used to manufacture circuit boards and cellular phones. It also serves as a raw material for the manufacture of other flame retardants.

Flame Retardants based on Phosphorus Compounds (PFRs)

What does a phosphorus based flame retardant mean?
The class of Phosphorus-containing flame retardants covers a wide range of inorganic and organic compounds and include both reactive (chemically bound into the material) and additive (integrated into the material by physical misering only) compounds. They have a broad application field, and a good fire safety performance. The most important phosphorus-containing flame retardants are: • Phosphate esters • Phosphonates and phosphinates • Red phosphorus and ammonium polyphosphate

What are the applications for PFRs?

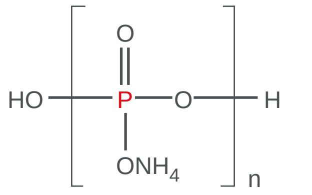
Phosphorus-containing flame retardants are widely used in standard and engineering plastics, polyurethane foams, thermosets, coatings, and textiles.

Phosphate esters...
are mainly used as flame retardant plasticizers in polyvinylchloride (PVC, alkyl/aryl phosphates) and engineering plastics, particularly in polyphenylene oxide/high impact polystyrene (PPO/HIPS), polycarbonate/acrylonitrile butadiene styrene (PC/ ABS) blends and polycarbonate (PC, e.g. triphenylphosphate, resocinol- and bisphenol A- bis-(diphenyl) phosphate). The latter are widely used in IT housings requiring high fire safety levels. Other applications include phenolic resins and coatings. Additive chlorinated phosphate esters like tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3-dichloroisopropyl) phosphate (TDCP) are used in flexible polyurethane foams for upholstered furniture and automotive applications. TCPP is also widely used in rigid PU insulation foams.

Phosphates, phosphonates and phosphinates...

are used as reactive phosphorus-containing flame retardants in flexible polyurethane foams for automotive and building applications. Additive organic phosphinates are a new class of flame retardants for use in engineering plastics, particularly in polyamides. Specific reactive phosphorus flame retardants are used in polyester fibres (e.g. Trevira CS) and for wash resi stent flame retardant textile finishes. Other reactive organophosphorus compounds can be used in epoxy resins in printed circuit boards.

Ammonium polyphosphate...



grades are primarily used in intumescent coatings. They are also used in rigid and flexible polyurethane foams and polyolefins (injection moulded), in formulations for unsaturated polyesters, phenolics, epoxies and coatings for textiles.

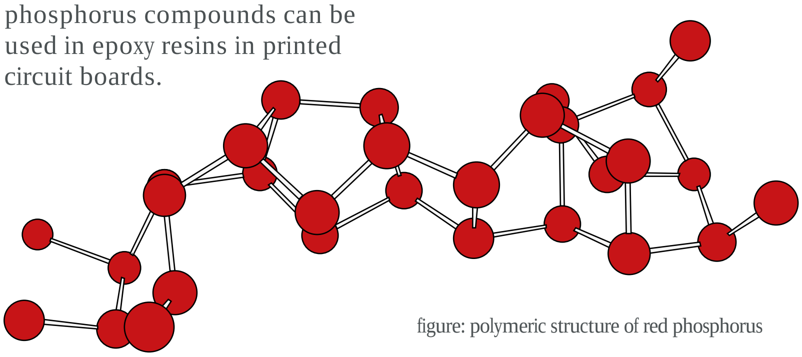
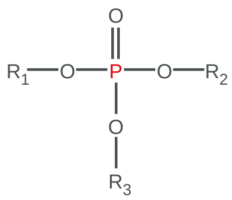


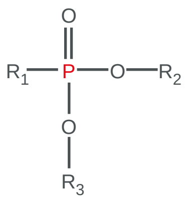
figure: polymeric structure of red phosphorus

Red Phosphorus
Flame retardant grades based on red phosphorus are mainly used in polyamide 6 and 66, meet UL 94 V0 fire safety level at low dosages and are particularly effective in glass fibre reinforced formulations. Further applications are in polyethylene and ethylene vinyl acetate (EVA), polyurethane foam, and thermosettings resins (unsaturated polyesters and epoxies).

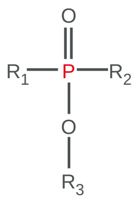
Principal chemical structures:



Phosphate Ester



Phosphonate



Phosphinate

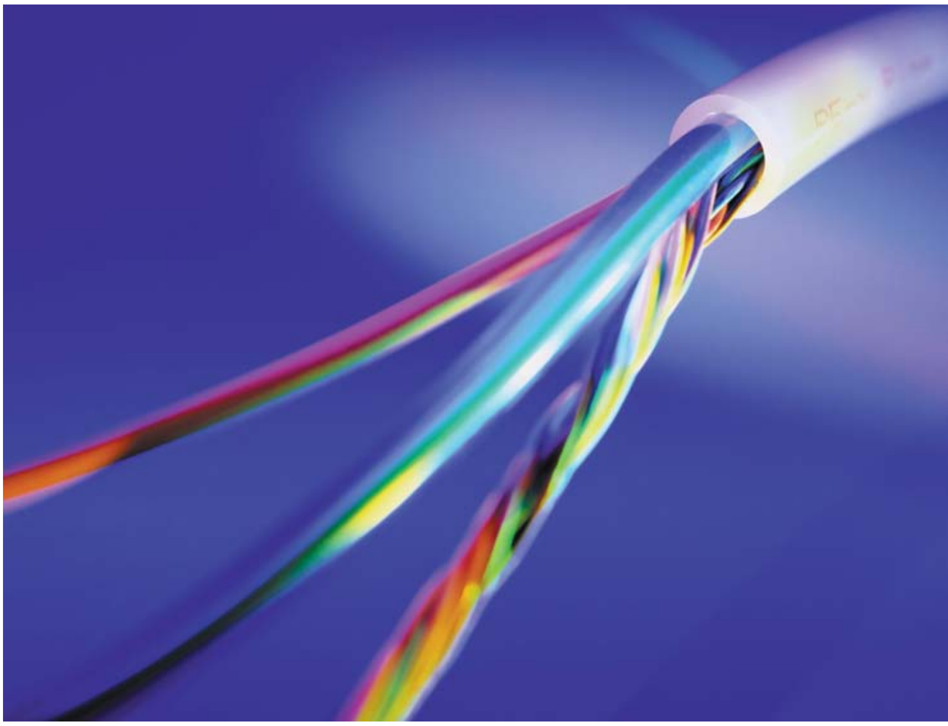
R_1, R_2, R_3 are organic substituents, they can be different or the same

Mineral flame retardants

What does a mineral flame retardant mean?
Aluminium trihydroxide (ATH) is by far the most widely used flame retardant on a tonnage basis. It is inexpensive, but usually requires higher loadings in polymers up to more than 60%, because the flame retardant mechanism is based on the release of water which cools and dilutes the flame zone. Magnesium hydroxide (MDH) is used in polymers which have higher processing temperatures, because it is stable up to temperatures of around 300 ∞C versus ATH which decomposes around 200 °C. Other inorganic fillers like talcum or chalk (calcium carbonate) are not flame retardants in the common sense; however, simply by diluting the combustible polymer they reduce its flammability and fire load.

$$2\,Al(OH)_3 \xrightarrow[+\,1050\ kJ\,/\,kg]{200\ ^\circ C} 3\,H_2O + Al_2O_3$$

$$Mg(OH)_2 \xrightarrow[+\,1300\ kJ\,/\,kg]{300\ ^\circ C} H_2O + MgO$$

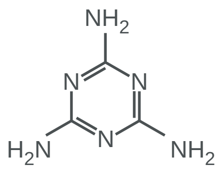


What are the applications for mineral flame retardants?

Fine precipitated ATH and MDH (< 2 µm) are used in melt compounding and extrusion of thermoplastics like cable PVC or polyolefins for cables. For use in cable, ATH and more often MDH are coated with organic materials to improve their compatibility with the polymer. Coarser ground and air separated grades can be used in liquid resin compounding of thermosets for electrical applications, seats, panels and vehicle parts.

Nitrogen-containing Flame Retardants

What does a nitrogen flame retardant mean?
Three chemical groups can be distinguished: pure melamine, melamine derivatives, i.e. salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid, and melamine homologues such as melam, melem and melon, the latter finding only experimental use at this stage. Nitrogen flame retardants are believed to act by several mechanisms: In the condensed phase, melamine is transformed into cross-linked structures which promote char formation. Ammonia is released in these reactions. In conjunction with phosphorus, the nitrogen appears to enhance the attachment of the phosphorus to the polymer. A mechanism in the gas phase may be the release of molecular nitrogen which dilutes the volatile polymer decomposition products.



Melamine

What are the applications for nitrogen flame retardants?

Melamine is mainly used in polyurethane foams, whereas melamine cyanurate is used in nylons or in polypropylene intumescent formulations in conjunction with ammonium polyphosphate. The phosphate, poly- and pyrophosphates of melamine contain both nitrogen and phosphorus and are used in nylons. In some specific formulations, triazines, isocyanurates, urea, guanidine and cyanuric acid derivatives are used as reactive compounds.

Other Flame Retardants - Borates, Stannates, ...

Other Flame Retardants
A number of other substances show flame retarding effects and are used in commercial applications. In this chapter we have compiled information on products which are either synergists, i.e. they enhance the performance of other flame retardants, or which are niche products for special applications, often with a limited market volume.

Boron...

containing compounds: A major application of borates is the use of mixtures of boric acids and borax as flame retardants for cellulose (cotton) and of zinc borate for PVC and other plastics like polyolefins, elastomers, polyamides, or epoxy resins. In halogen-containing systems, zinc borate is used in conjunction with antimony oxide, while in halogen-free systems, it is normally used in conjunction with aluminium trihydroxide, magnesium hydroxide, or red phosphorus. In some particular applications zinc borate can be used alone. Boron containing compounds act by stepwise release of water and formation of a glassy coating protecting the surface.

Antimony trioxide...

shows no perceptible flame retardant action on its own. Together with halogen containing compounds like BFRs or PVC it produces a synergistic effect. The most important reactions take place in the gas phase and are the result of enhancing the radical chain mechanism of the halogens. Antimony trioxide is therefore widely used as a synergist in halogen containing systems.

Zinc compounds...

were initially developed as smoke suppressants for PVC (Zinc hydroxystannate). Later it was found that they also act as flame retardants in certain plastics mainly by promoting char formation. Zinc sulphide shows synergistic effects in PVC and can partly substitute antimony trioxide.

Intumescent...

flame retardant systems expand to produce foams. They are used as coatings not only to protect combustible materials such as wood and plastics, but also steel structures in buildings, because steel loses its strength when exposed to high temperatures in a fire. The intumescent effect is achieved by combining an acid source like ammonium polyphosphate, a source of carbon, compounds which release non-combustible gases for blowing the foam on thermal decomposition and resin binders to stabilise the foam.

Expandable graphite...

is manufactured from flake graphite by treatment with strong acids like sulphuric or nitric acid. The acid is trapped in the crystal layers of the graphite ("intercalated"). When it is heated, the graphite starts to expand up to several hundred cm^3 per gram, forming a protective layer for the polymer. Expandable graphite is used in plastics, rubbers (elastomers), coatings, textiles and especially in polymeric foams. To get perfect flame retardancy, the use of synergists like ammonium polyphosphate or zinc borate is necessary. The black colour of graphite limits its applicability in some cases.

Nanocomposites...

have been gaining increasing attention since the late 1990s as potential new flame retardants. Nanocomposites are polymer-layered silicates based on aluminosilicate clay minerals like montmorillonite, composed of layers with gaps (gallery spaces) in between. These silicates have the ability to incorporate polymers. Flame retardancy work with nanocomposites has focused on plastics like polymethyl-methacrylate (PMMA), polypropylene, polystyrene, and polyamides. Nanocomposites particularly prevent dripping and promote char formation. Therefore, they have been used as synergists in some polymer / flame retardant combinations. However, they require special processing and for the time being are not considered to become viable stand-alone flame retardants.

Flame Retardants - Health and the Environment

What are the concerns against using flame retardants?
The main concerns voiced against flame retardants are that they may persist in the environment, accumulate in living organisms and be detrimental to human health or toxic to wildlife. In addition, there are concerns about potential decomposition products in case of fire.

How do we deal with these concerns?

Today, flame retardants are evaluated individually in scientific risk assessments. This factual approach takes into account the different physical, chemical and toxicological properties as well as the environmental fate and exposure of each individual flame retardant. EFRA actively participates in these scientific risk assessments and also sponsors or co-operates in a number of independent studies to address general issues, e.g. on life cycle assessments of flame retarded furniture and TV sets, and on emissions of flame retardants from furniture. Please consult the EFRA website (www.flameretardants.eu) for detailed information on EFRA projects.

What is the difference between hazard, exposure and risk?

Hazard expresses the dangerous property of a substance like corrosive, flammable or having a certain toxicity (e.g. a mean lethal dose of 200 mg per kg body weight for rats). Exposure describes the amount or concentration of a substance that a human or other organism comes into contact with. Only if the level of exposure exceeds the safety level of the hazard of the substance, you may expect negative effects, i.e. there is a significant risk. This in turn means that you can either choose less hazardous substances or reduce the emissions of chemicals from production and processing sites or from finished articles in order to reduce a potential risk. For example, a lion is a very dangerous animal (when hungry), but if it is in a cage, then there is no risk (if you are outside).

What is the status of the EU risk assessments on flame retardants?

Risk assessments are carried out in the European Union as part of the regulations on "existing" substances, i.e. chemicals which were on the market in the European Union before September 1981. Priority lists of high production volume chemicals (> 1 000 tons per year) are defined by the authorities. One or two member states then act as "rapporteurs" and compile a risk assessment on a substance which looks at human health as well as environmental effects. Industry provides data on substance properties and measurements of the substance at the workplace or in the environment. Often, specific studies are commissioned to fill data gaps for a risk assessment.
In the first step the rapporteur looks at the toxicological and ecotoxicological properties of a substance to determine a safe threshold exposure dose. This is then compared to the concentrations which are found in the environment or to which humans are exposed, either real measurements or estimates. The risk is derived both from hazard and exposure. If the exposure is higher than the safety level of a substance (determined in laboratory tests) then a risk is identified. This risk is then subsequently managed by the authorities and companies involved.

The following table provides an overview of the flame retardants covered in risk assessments.

Substance	Abbreviation
Antimony trioxide	ATO
Short-chain Chlorinated Paraffins	SCCP
Medium-chain Chlorinated Paraffins	MCCP
Pentabromodiphenyl ether	PBDE
Octabromodiphenyl ether	OBDE
Decabromodiphenyl ether	DBDE
Hexabromocyclododecane	HBCD
Tris(2-chloroethyl) phosphate	TCEP
Tetrabromobisphenol A	TBBPA
Tris(2-chloroisopropyl) phosphate	TCPP
Tris(1,3-dichloroisopropyl)phosphate	TDCPP
2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate)	V6

The current state of risk assessments as well as published reports are available at: ecb.jrc.it/existing-chemicals . You find a summary for the flame retardants concerned on the EFRA website www.flameretardants.eu. With the introduction of REACH (see below), the system of official risk assessments will cease.

Flame retardants and REACH

The new EU legislation on chemicals, REACH, currently under debate (2006) will be applicable to flame retardants exactly as to all other chemicals sold or used in the European Union. All chemicals used in significant quantities in Europe will have to be registered and subject to evaluation and/or authorisation procedures, according to their properties, involving both chemical suppliers and user industries. Because flame retardants are designed to be stable in polymers or other treated materials over long periods (in order to ensure durable fire protection), they may be subject to the more stringent testing requirements of REACH. For many flame retardants, this will not modify the current situation because EU Risk Assessment studies are already underway or completed.

The costs of registration, however, may mean that it is no longer economic to make some low-volume, specialist application flame retardants, with significant knock-on effects for user industries, e.g. plastic components, electronics, for whom key raw materials may thus cease to be available in Europe. A particular issue is that imported consumer products or parts will not be subject to the same constraints, and may contain chemical additives not registered for use in Europe under REACH. This risks draining manufacturing jobs out of Europe and nullifying the consumer protection which REACH is intended to ensure.

Are flame retardants toxic?

Actually, that question is put wrongly - it should be "how toxic are flame retardants?", because only the dose determines if a substance has a toxic effect or not. The potential toxic effects of FRs are low because they are, in most applications, either chemically reacted into the material they are used to treat, or physically contained within it and so not able to have significant external effects. Furthermore, flame retardants are by no means of particular toxicity compared to other commonly used chemicals. Since there are so many different chemical groups of flame retardants, there are also varying

types and degrees of interactions with living organisms. Even within a chemical group there can be large differences in toxic effects, because depending on the level of molecular interaction with cells, small changes to a molecule can have huge effects. Many flame retardants do not have to be labelled as dangerous substances, which means that they have a very low toxicity or impact on human health or the environment. Others have a certain toxicity as a neat compound, but once they react into a polymer the effect is no longer there. The major flame retardants have been in use for many years now and toxic effects would have shown up at the workplace in production or processing, because there the exposure is generally highest. Only very few flame retardants were withdrawn from the market, phased out or regulated because of suspected or proven toxic properties, often in combination with very high margins of safety and the precautionary principle.

Are any flame retardants banned in the European Union?

The Directive 2003/11/EC bans pentabromodiphenyl ether and octabromodiphenyl ether in the European Union as of 15-August-2004. From then on both chemicals "may not be placed on the market or used as a substance or as a constituent of substances or of preparations in concentrations higher than 0,1 % by mass." And "articles may not be placed on the market if they, or flame-retarded parts thereof, contain this substance in concentrations higher than 0,1 % by mass." Please see also the question on WEEE and RoHS.
In the EU, polybrominated biphenyls (= PBBs, banned by 83/264/EEC), tri-(2,3-dibromopropyl)-phosphate (= TRIS, banned by 79/663/EEC) and tris-(aziridinyl)-phosphineoxide (= TEPA, banned by 83/264/EEC) are also not allowed for clothing and similar products with skin contact. These products are no longer manufactured and used in Europe.

Can flame retardants be released from consumer products?

This is a very important aspect of assessing a potential health risk from flame retardants for consumers. There have been concerns that flame retardants are emitted from fabrics or plastic materials, or being released as dust particles by migration, wear and tear. They might also be washed out by water from textiles or leached out by children sucking on furniture or toys. One has to distinguish between three cases here:

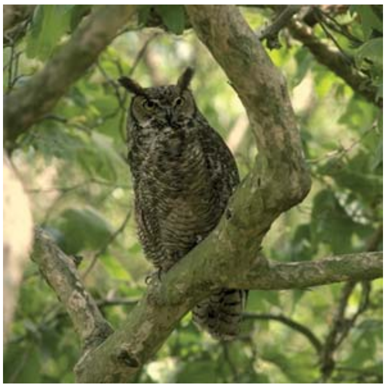
- Firstly, if the flame retardant is a so-called "reactive" one, then it chemically reacts with the polymer material or the fabric so that it is chemically bound in the finished article. Here a release is extremely unlikely.
- Secondly, there are "additive" flame retardants which are physically mixed into polymers and are therefore encapsulated by polymer. To what extent these are released depends on whether they migrate to the surface, their volatility, water solubility and use. Large, heavy molecules or very water insoluble substances will hardly be released.
- Thirdly there are flame retardants which are applied to the surface of a product such as a textile treatment, a backcoating or a paint. In many cases the flame retardant will again be encapsulated within a resin system which reduces the likelihood of release.

A study by the German Federal Material Testing Institute (BAM, Berlin, 2003) looked at emissions of common flame retardants from consumer products to indoor air. The test chambers were operated at realistic temperatures. In many cases they had extreme difficulties in even detecting flame retardants in the air. Certain types of flame retardants were found more often than others, mainly due to differences in volatility. However, the measured concentrations were very low and well below existing workplace exposure limits or threshold concentrations of concern.

A study by the Fraunhofer Institute and TUV Germany looked at concentrations of commonly used flame retardants in car interiors. None were detectable inside a 9-month old car under normal use. Under extreme conditions (car interior closed and heated to 65°C) concentrations were 5 ... 10 times lower than recommended limits.

The Swiss Federal Health Office (BAG, Hartmann 2004) looked at concentrations of flame retardants in indoor air from a variety of buildings, finding low levels, 50 ...1 000 times lower than recommended limits, and concluding ìthe risks are very low and that no additional measures have to be taken to minimise these risksî.

The US National Academy of Sciences commissioned a study on the toxicological risks of 16 commonly used flame retardants for furniture.



It came to the conclusion, that 8 of them were definitely safe to use, whereas the other 8 required more data before a final conclusion could be drawn.

- Kemmlein S, Hahn O (2003): Emission of Flame Retardants from Consumer Products and Building Materials. Project No 299 65 321, Federal Environmental Agency (UBA), Berlin.
- National Research Council (2000): Toxicological Risks of Selected Flame-Retardant Chemicals.
- Salthammer T, Wensing M (2002): Flame retardants in the indoor environment Part IV, Classification of experimental data from house dust, indoor air and chamber tests. Indoor Air 2002 Conference, Monterey, California, Vol. 2, 213-218
- Sagunski H, Roßkamp E (2001): Indoor air orientation values: Tris (2-chlorethyl)-phosphate. Bundesgesundheitsblatt, Vol. 45, 300-306
- Hartmann P, Bürgi D, Giger W. (2004): Organophosphate flame retardants and plasticizers in indoor air. Chemosphere Vol, 57. pp. 781-787

Are flame retardants persistent in the environment?

Flame retardants require a certain chemical stability for their function: most of them are used in polymers which are processed at temperatures of 200 to 350 °C depending on the polymer. If they were not sufficiently stable, they would start to decompose during these processing steps. Furthermore, flame retardants are generally used in long living items like e.g. TV sets, computers, cars, ships, construction products. Therefore, they have to last and provide fire safety for the whole life time of the product. Chemical stability is also an advantage, if you want to recycle polymers, because then the recyclate retains the fire retardant properties. Unfortunately, this necessary chemical stability usually relates to stability in the environment, i.e. persistence against attack by micro organisms, sunlight or water. There are, however, some exceptions to this general rule.

Do flame retardants accumulate in living organisms?

Substances will generally only bioaccumulate if they are well soluble in fats and hardly soluble in water, because water soluble chemicals are easily removed from the body via urine. Furthermore, bioaccumulative chemicals need to be taken up by the body from food, water or air in order to accumulate (resorption). Once taken up, they also need to be sufficiently stable and resistant to biochemical degradation. Only if these conditions are fulfilled, bioaccumulation can occur. From the various flame retardants in commercial use, only very few are likely to accumulate in organisms. However, levels observed are very low compared to potential toxicity. Levels found to date, even for flame retardants which have been in use for many years, are consistently lower than those indicated by Risk Assessments as posing significant risks. As EFRA agrees that these flame retardants like other manmade chemicals do not belong in the environment, we actively support product stewardship programmes to avoid the emissions into the environment.

How are flame retardants treated in European ecolabel schemes?

Ecolabel schemes have been devised to promote environmentally friendly products by granting them special labels. These allow the consumer to identify such products easily. Ecolabel criteria are often defined by environmental agencies together with interested parties. They have no direct legal relevance though, i.e. their criteria are not binding to any product manufacturer. Ecolabels have been most successful in product areas where the consumer sees a direct environmental impact or relevance, e.g. recycled paper or solvent free paints. The most important ecolabels in Europe are the Blue Angel in Germany (one of the oldest schemes) and the TCO-Label in Sweden. The European "EcoFlower" has not gained wide spread acceptance yet, although they have worked out criteria for a number of products. Some ecolabels like the Blue Angel do not allow halogenated flame retardants (with exceptions) in housings of E&E Equipment. The Ecoflower criteria, generally refer to a list of risk phrases which are taken from the European classification of dangerous substances, and which will exclude the use of certain flame-retardants along with various other products. A number of flame retardants however are subject to none of the relevant health and environment risk phrases. Another important ecolabel in the field of electrical and electronic equipment is TCO, run by a Swedish trade union organisation. They also apply some restrictions on halogenated flame retardants, but have recognised the need for fire safety as well.

What is the situation about flame retardants and dioxins?

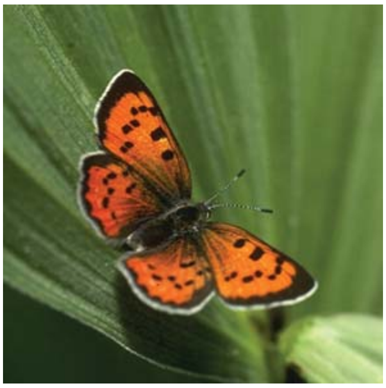
In the 1980ies, it was found that certain halogenated flame retardants could react to form polybrominated dibenzodioxins (PBDDs) and dibenzofurans (PBDFs) during their production, processing like extrusion or injection moulding, and in case of fire or incineration. Comprehensive studies have shown that only very few brominated flame retardants are likely to form amounts

of PBDD/PBDF exceeding the limit values of the German Chemicals Banning Ordinance. Due to their chemical structure, the polybrominated diphenylethers (PBDEs), can be precursors of PBDF formation. However, studies have shown that plastics containing decaBDE produced after 1993 can undergo several recycling loops and still conform to the German Chemicals Banning Ordinance. In general it is recommended to treat historical waste containing PBDEs in thermal processes like feedstock recycling, metal smelters or modern incinerators. Incineration studies done by the Forschungszentrum Karlsruhe in Germany have shown that plastics containing brominated flame retardants can be safely added to state of the art municipal waste incinerators up to 3 % of the total feed without increasing the formation of dioxins or furans.

What is the industry doing to prevent the release of flame retardants to the environment?

The BFR industry has engaged in a voluntary programme with the supply chain -including Small and Medium-sized Enterprises (SMEs)- aiming at controlling and reducing industrial emissions of the main commercial BFRs (deca-BDE, HBCD, TBBPA) into the environment. This programme entitled VECAP (Voluntary Emissions Control Action Programme) represents advance practice of the chemical user chain cooperation which will be required under the new EU chemicals policy of REACH. It is a product stewardship industry initiative that reinforces the reduction of emissions throughout the manufacturing process by fostering a culture of continuous improvement.

For more information, see www.vecap.info.



Recycling and Waste Management of Flame Retardants

Can materials containing flame retardants be safely disposed of with municipal wastes? Can they be burnt in household waste incinerators?

Yes, they can. Materials which are treated with flame retardants can be handled in municipal waste incinerators, generating energy. Flame retardants delay and inhibit burning; they do not make materials incombustible. Therefore, waste incineration is no problem per se.

State of the art incinerators will remove any pollutants formed during combustion to the required levels: e.g. acids like hydrogen bromide or hydrochloric acid from halogenated flame retardants will be scrubbed from the flue gasses, phosphorus compounds will primarily remain in the bottom ash as inorganic phosphates together with aluminium oxides from aluminium hydroxide. The very stringent low limit values for dioxins in flue gasses (0.1 ng (TEQ) / m^3) are met for waste usually containing appreciable amounts of halogen, (i.e. 5 - 8 g Cl / kg from PVC and NaCl). This was also shown in studies where plastics waste, containing brominated flame retardants, was used together with municipal waste for energy recovery without exceeding the dioxin/furan limit values required.
Where domestic wastes are sent to landfill, flame retardants will mostly remain within the treated materials, because they are chemically or physically bound to these, so that leaching or loss of significant levels of FRs from landfills is very unlikely.

Flame retardants in plastic wastes are also compatible with valorisation in metal smelters and recovery of the precious metal and copper contents of mixed wastes via this route. The plastics content partly substitutes coke as a reducing agent, and partly provides smelter feed energy. See studies of valorisation of WEEE plastics published by smelter companies Umicore and Boliden.

Tange L, Brusselaers J, Hagelüken C. (2006): Eco-efficient solutions for flame retardant containing, mixed plastics-metals WEEE, in particular resource recovery at an integrated metals smelter. Flame Retardants 2006 Conference. Interscience. pp. 33-46

What do the European Directives on electrical and electronic equipment (WEEE and RoHS) mean for flame retardants?

The Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) says that "Member States shall ensure that, from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE)." Deca-BDE has been exempted from the scope of RoHS by the European Commission decision 2005/717/EC. Penta- and Octa-BDE are already phased out by the marketing and use directive as of 15 August 2004 (2003/11/EC). The Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE) demands a "selective treatment" for plastic materials and components of waste electrical and electronic equipment which contain brominated flame retardants. Member States had to transpose WEEE and RoHS into national legislation by August 2004.

Can plastics containing flame retardants be mechanically recycled?

We need to make a difference between closed loop where the producer is the owner of the plastic like copier machines and open loop like TV and other equipment used in households:

- For open loop where all mixed historical plastics return from the market, mechanical recycling is difficult because of the diverse mixture of plastic materials. It is a demanding task to sort plastics into individual polymer types like PVC, PP, ABS etc. but what makes it really challenging are further differences in pigments and additives used - not only flame retardants but also light stabilizers, compounding aides etc. All plastics containing Penta-, OctaBDE and PBB's must be separated according to the WEEE directive. Therefore, it is extremely difficult to reach a quality comparable to virgin material. Further, the economics are under pressure due to the scale of the process: Mechanical recycling is done in installations up to 15 000 tons per year whereas plastics are produced in processes of up to 300 000 tons per year.
- For closed loop recycling the sorting issue is much less severe, because the origin and composition of the plastics is known. Several practical examples do exist like Technopolymer and Ricoh which mechanically recycle up to 30% into their new products.

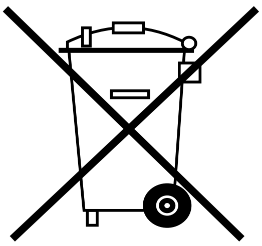
Many plastics coming on the market which contain FRs are very suitable for mechanical recycling. Since flame retardants are generally more expensive than the base polymer, flame retarded plastics have an added value. Therefore flame retarded plastics should be recycled to flame retarded types again so that this economical advantage is not lost. Studies on mechanical recycling of ABS containing brominated flame retardants and polypropylene containing ammonium polyphosphate (APP) based flame retarded systems have shown good recyclability:

- The mechanical recycling of ABS containing a brominated epoxy oligomer flame retardant showed that the main properties like thermal and hydrolysis stability as well as the designed fire safety level were maintained after extruding the material four times.
- Polypropylene flame retarded with ammonium polyphosphate (APP) can be recycled up to eight times and maintains its fire safety level (UL94 V0), melt flow properties and colour stability.

Can flame retardants be chemically recycled?

There are several examples of chemical recycling of plastics containing flame retardants:

- Rigid polyurethane foams containing ammonium polyphosphate (APP) as a flame retardant can be chemically recycled by glycolysis into a polyol, which can be reused as a polyol component. With the exception of a slightly enhanced acid number, no disadvantages occur during glycolysis in the presence of APP.
- A study carried out at ECN Holland showed that E&E plastics can be treated in a pyrolysis/ gasification process safely and the bromine can be recovered as HBr.
- Another pilot trial carried out in Japan by PWMI showed the same results including the bromine recovery option.
- Bromine recovery from waste electrical and electronic equipment incinerated in a pilot plant for waste combustion is possible by quenching the flue gases in water, collecting the hydrogen bromide (HBr) with the option transforming it into elemental bromine as a basis for producing brominated flame retardants.
- Flame retardants have been shown to be fully compatible with recovery of waste electronic and electrical plastics (WEEE) in metal smelters, enabling recycling of precious metals and copper in circuitry, of antimony in flame retardants, and valorisation of the plastics content as a reducing agent replacing use of coke and as an energy source (Umicore Hoboken ñ PlasticsEurope ñ EFRA trials 2005)



What is the industry doing to prevent the release of flame retardants to the environment?

The BFR industry has engaged in a voluntary programme with the supply chain -including Small and Medium-sized Enterprises (SMEs)- aiming at controlling and reducing industrial emissions of the main commercial BFRs (deca-BDE, HBCD, TBBPA) into the environment. This programme entitled VECAP (Voluntary Emissions Control Action Programme) represents advance practice of the chemical user chain cooperation which will be required under the new EU chemicals policy of REACH. It is a product stewardship industry initiative that reinforces the reduction of emissions throughout the manufacturing process by fostering a culture of continuous improvement.

For more information, see www.vecap.info.

Common Abbreviations for Flame Retardants

This table lists common abbreviations for flame retardants which are often used in the technical literature. In addition to these, often trade names are used to denote flame retardants (just as you say "aspirin" when you in fact mean a headache pill containing acetylsalicylic acid). These trade names often also look like chemical abbreviations. However, since these are manufacturer specific and quite numerous, we have not included them here.

Abbr.	Name	CAS RN
AP	Ammonium phosphates	
APP	Ammonium polyphosphate	68333-79-9
ATH	Aluminium trihydroxide	21645-51-2
ATO	Antimonytrioxide	1309-64-4
BDP	Bisphenol-A- bis- diphenylphosphate	5945-33-5, 181028-79-5
DBDE	Decabromodiphenyl ether	1163-19-5
HBCD	Hexabromocyclododecane	25637-99-4
MCPP	Medium-chain chlorinated paraffins	85535-85-8
MDH	Magnesium hydroxide	1309-42-8
OBDE	Octabromodiphenyl ether	32536-52-0
PBDE	Polybrominated diphenyl ethers in general	
RDP	Resorcinol bis-diphenylphosphate	57583-54-7, 125997-21-9
RP	Red Phosphorus	7723-14-0
SCPP	Short-chain chlorinated paraffins	85535-84-8
TBBPA	Tetrabromobisphenol-A	79-94-7
TBP	Tri-n-butyl phosphate	126-73-8
TCEP	Tris (2-chloroethyl) phosphate	115-96-8
TCP	Tricresyl phosphate	1330-78-5
TCPP	Tris (chloroiso-propyl) phosphate	13674-84-5
TDCP	Tris(1,3-dichloro-2-propyl)phosphate	13674-87-8
TPP	Triphenyl phosphate	115-86-6

On www.flameretardants.eu you find fact sheets for the major flame retardants.

Literature and Further Reading

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Websites on flame retardants:
www.flameretardants.eu
www.bsef.com
www.pefrc.org

Websites for fire safety:
www.acfse.org (Europe)
www.nfpa.org (USA)
www.vfdb.de (Germany)
www.gtfi.org (France)

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