Overview of Flame Retardants

Fire and Fire Safety, Markets and Applications, Mode of Action and Main Families, Role in Fire Gases and Residues

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1. INTRODUCTION

Fire safety is an integral part of fire precautions. Fire precautions have the objective to minimise the number of and damage from fires by measures hindering their initiation, limiting their propagation and if possible excluding flash-over. Preventing fires or delaying them makes escape possible over a longer period of time. As a result, life, health and property are efficiently protected.

One way to better protect combustible materials against initiating fires is the use of flame retardants. They help to enhance the fire safety level of combustible materials like plastics and to fulfil the respective requirements for fire sources of small and higher energies up to 40 kW/m². More information on the topics dealt with in the following is given in [1].

2. FIRES AND FIRE SAFETY

Modern fire precautions guarantee a high level of fire safety and virtually exclude catastrophic fires which, only one century ago, razed entire towns.

The rules and regulations of fire protection are basically set by governmental bodies. In addition, professional societies and industrial, commercial, technical and insurance associations help to create an appropriate and practical "state of the art" system of fire precautions, which is often taken over in governmental regulations.

Today, extensive sets of fire precaution regulations exist for building, transportation (motor and rail vehicles, ships and aircraft), electrical engineering and many other fields.

However, even today, fire statistics show a high death toll and huge losses for the economy.

According to Wilmot [2], in the USA, in 1991, there were 4,860 fire deaths (1989: 5,880 deaths). Losses caused by fires exceed billions (direct losses USA 1989: 9.2 billions; 1991: 10 billions USD). Further details are summarised in Tables I and II.

Table I - Cost of direct losses					
In millions except for Japan – billions Adjusted direct losses					
Country	Curr.	Direct losses			Percentage of GNP
		1989	1990	1991	(1989-1991)
Hungary	Ft				0.12	(1986-88)
Spain	Pta				0.12	(1984)
Japan	Y	450	520	720	0.14	
Finland	FMk	880	880		0.17	(1988-89)
United States	US $	9200	8200	10 000	0.17	
Canada	Can $	1150	1250	1250	0.18	
New Zealand	NZ $	120	150	125	0.18	
Germany-West	DM	4600	4350		0.19	(1989-90)
Germany-unified	DM			6100		
Netherlands	f				0.20	(1987-88)
Austria	Sch				0.21	(1979-80)
United Kingdom	£	1050	1300	1300	0.22	
Switzerland	SwF	675			0.23	(1989)
Denmark	DKr	2400	2100	2350	0.28	
Sweden	SKr	4000	3850	3600	0.28	
France	F				0.29	(1981-82)
Norway	Nkr	2450	1900	1750	0.31	
Belgium	BF	26 000			0.40	(1988-89)
Fire losses include explosion losses following fires but exclude explosion loss where no fire occurs, e.g. some acts of terrorism					

Table II – Fire deaths			
Country	Adjusted figures (fire deaths)		
	1989	1990	1991
Austria	60	40	60
Belgium	140	160	140
Canada	570	510	430
Czechoslovakia	195	220	215
Denmark	80	65	85
Finland	105	110	125
France	770	720	790
Germany-West	660	710	
Germany-unified		985	1040
Hungary	300	320	350
Netherlands	95	80	90
Norway	75	70	65
Spain	325	345	
Sweden	135	135	115
Switzerland	30	25	30
United Kingdom	945	935	910
United States	5880	5640	4860
None-ECE			
Japan	1780	1860	1850
New Zealand	45	35	35

The influence of new legislation is essential for increasing the fire safety level in many fields. One striking example is the introduction of the UK regulations for flame retarded upholstered furniture in 1988: As can be seen from Table III, it shows a dramatic drop of fires and deaths from upholstered furniture (comparison 1988 to 1993: 4,818 to 3,746 fires; 247 to 146 fire deaths) [3].

Table III – Fires and casualties from all dwelling fires attended by local authority fire brigades, and dwelling fires where the item mainly responsible was upholstery and covers UK, 1983					
	Year	**Fires (000s)**	**Dwellings-total**		**Non-fatal casualties per 100 fires**
			Deaths per 100 fires		
	1988	64.2	11.4		159
	1989	64.5	10.0		161
	1990	63.2	9.9		166
	1991	64.1	9.5		175
	1992	64.6	9.2		174
	1993	65.3	8.2		175

Year	Number of fires	**Upholstered furniture, covers and cushions etc**				
		Percent of dwelling fires	Number of deaths	Deaths per 100 fires	Non-fatal casualties	Non-fatal casualties per 100 fires
1988	4818	7.5	247	51	1896	394
1989	4482	6.9	201	45	1707	381
1990	4327	6.9	180	42	1759	407
1991	4311	6.7	147	34	1803	418
1992	4048	6.3	166	41	1660	410
1993	3746	5.7	146	39	1618	432

3. FLAME RETARDANTS MARKETS

The most important families of flame retardants are those based on bromine, chlorine, phosphorous, nitrogen, antimony and metal salts and hydroxides. They are used for flame retarding polymers, rubber, textiles, and also wood in order to fulfil fire precaution requirements and to give these combustible materials a higher fire safety level.

According to OECD [4], the world demand for flame retardants chemicals was estimated at over 600,000 tons in 1992 and can be broken down as in Table IV.

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Table IV – 1992 world demand for flame retardants	
Base chemicals	**Flame retardants volume (tons)**
Bromine	150,000
Chlorine	60,000
Phosphorous	100,000
Antimony	50,000
Nitrogen	30,000
Aluminium	170,000
Other	50,000

More recent figures show an substantial increase in the use of flame retardants. According to [5], the 1993 world market for FRs was estimated to around 800,000 tons, aluminium hydroxide between 120,000 and 300,000 tons, chlorinated paraffins around 45,000 tons, antimony trioxide around 60,000 tons and phosphorous compounds in the region of 30,000 tons per year.

It is likely that the consumption of flame retardants will continue to rapidly grow as new major markets are emerging particularly in China and other Asian countries.

4. MAJOR FLAME RETARDANTS APPLICATIONS

The most important industry sectors where flame retardants are used are applications in electrical engineering and electronics, wire and cable, building and transportation. Some of the major application areas are summarised in Table V.

Table V – Major applications for flame retardants	
Industry sector	**Application**
Electrical Engineering and Electronics	Wire & cable Consumer electronics housings and backplates Office electronics housings and backplates Printed circuit boards Appliances
Transportation	
Motor vehicles	Wire & cable Seats
Rail vehicles	Compartment linings and coverings Insulation Compartment interior Seats
Aircraft	Panels Carpets, flooring
Building	Thermal insulation for Roofs, facades, walls Sheeting for roofs Floor coverings Ducting & conduit Panels, linings and coverings

5. COURSE OF A FIRE

The course of a fire can basically be split into three phases, the initiating fire, the fully developed fire and the decreasing fire. As can be seen from Figure 1, the time temperature curve describes these three phases which are connected with some basic parameters governing a fire. Plastics, like all other combustible materials, always burn in a fully developed fire. Thus, in estimating the fire hazard of combustible materials, only distinct steps in the early stages of combustion up to the flash-over point need to be considered.

Figure 1: Course of a fire
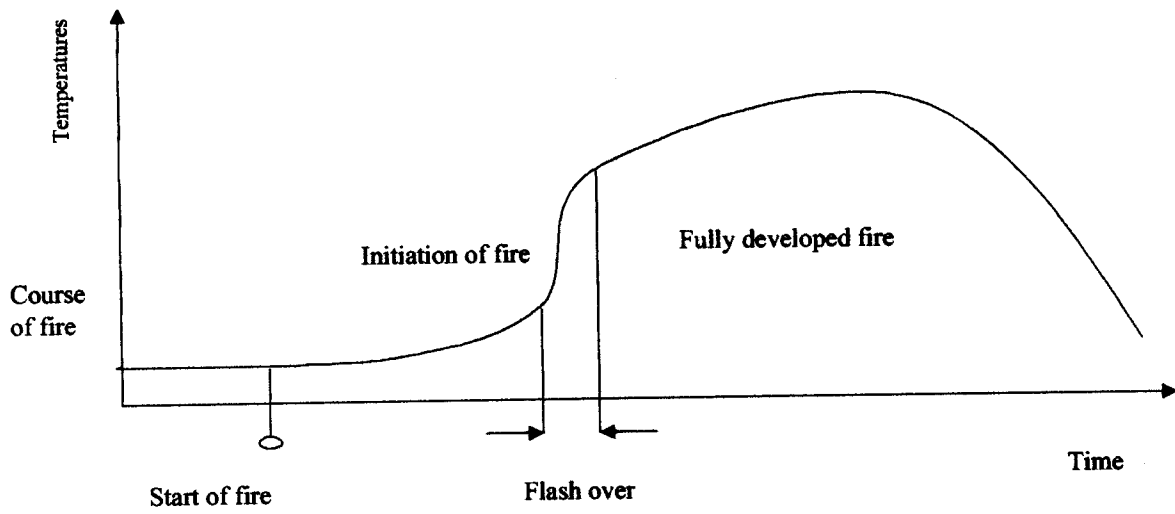
| Risks	Ignition sources Flammability Ignitability	Flame spread Heat release	Fire penetration
	Smoke, irritation, toxicity, corrosivity		

6. COMBUSTION PROCESS

The combustion of plastics is a process comprising a multitude of single steps and basically initiated by endothermic heating and decomposition. The flammable gases formed mix with atmospheric oxygen and ignite, leading to the exothermic processes of flame propagation and heat release.

During heating and pyrolysis, endothermic processes take place for overcoming the high bond binding energies between individual atoms (200 to 400 kJ/mole).

Ignition initiates the exothermic part of the processes which override the endothermic pyrolytic reaction. Pyrolysis of the polymer is reinforced by thermal feedback (heat release) which fuels the flame at an increasing level. The flame spreads over the decomposed polymer surface. The diffusion flame is supported by extremely high energy H and OH radicals which confer a high ' velocity on the flame front. The schematic of the combustion process is shown in Figure 2.

Figure 2: Combustion process
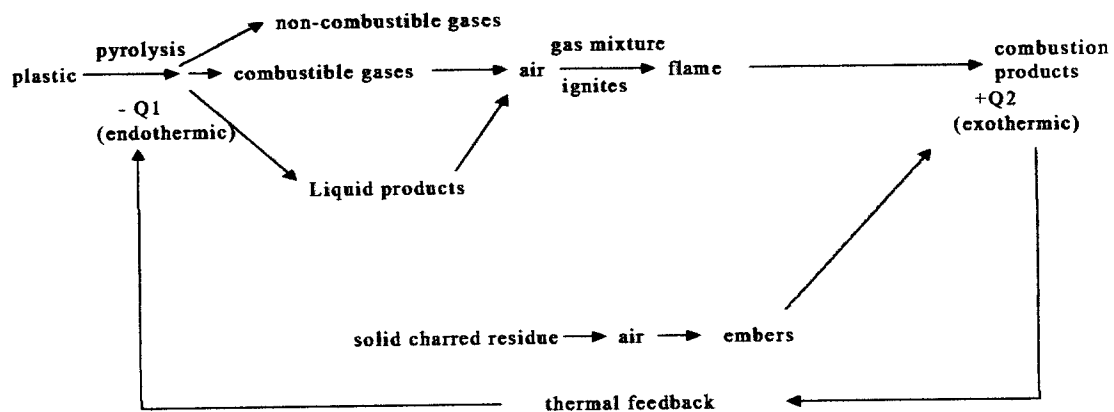
7. MODE OF ACTION OF FLAME RETARDANTS

A flame 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.

A. Physical action

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

a) By cooling. Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process.
Example: Aluminium hydroxide.

b) By formation of a protective layer (coating). The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous 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.
Example: Phosphorous and boron compounds

c) 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.
Example: Aluminium hydroxide.

B. Chemical action

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

a) Reaction in the gas phase. The free radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant. The exothermic processes are thus stopped, the system cools down, and the supply of flammable gases is reduced and eventually completely suppressed.
Example: Halogenated flame retardants.

b) Reaction in the solid phase. The flame retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the flame retardant generating double bonds in the polymer. These form the carbonaceous layer by cyclizing and cross-linking.
Example: Phosphorus compounds.

8. THE MOST IMPORTANT FLAME RETARDANTS

A distinction is made between reactive and additive flame retardants. Combinations of flame retardants may produce a synergistic effect of great importance for practical use.
General surveys on the mode of action of flame retardants are given in [6-14].

a) Reactive flame retardants serving as reactive components are built chemically into the polymer molecule, together with the other starting components. This prevents them from bleeding out of the polymer and volatilisation and their flame 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 easily be incorporated.

b) Additive flame retardants are incorporated in the plastic either prior to, during, or, more frequently, following polymerisation. They are used especially in thermoplastics, but also in thermosets. If they are compatible with the plastic they act as plasticisers, otherwise they are considered as fillers.

c) Combinations of additive or reactive flame retardants can produce an additive, synergistic or antagonistic effect. While the additive effect is the sum of the individual actions, the effects of synergism and antagonism are higher and lower, respectively, than this sum. When used alone, synergists show no or only negligible effectiveness. The synergistic effect occurs when they are used together with specific flame retardants. The flame retardants/synergist systems have achieved great importance in practical use because they are usually less expensive than flame retardants used alone.

A. HALOGEN-CONTAINING FLAME RETARDANTS

The effectiveness of halogen-containing flame retardants increases in the order $F < Cl < Br < I$.

Fluorine- and iodine-based flame retardants are not used in practice because neither type interferes with the combustion process: Fluorine because of its too strong bond and iodine because its too loose bond to carbon.

Bromine is most effective since its bonding to carbon enables it to interfere at a more favourable point in the combustion process. It is assumed, moreover, that the effective agent, HBr, is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone.

Chlorine-containing flame retardants release HCl over a wider temperature range. Thus, the latter is present at lower concentrations and therefore less effective.

i. Mode of action

Halogen-containing flame retardants act by interfering with the radical chain mechanism taking place in the gas phase. The high-energy OH and H radicals formed by chain branching:
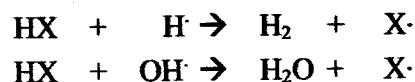
$$H\cdot + O_2 \rightarrow OH\cdot + O$$
$$O + H_2 \rightarrow OH\cdot + H\cdot$$
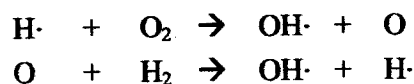
are removed by the halogen-containing flame retardant. At first the flame retardant breaks down to

$$RX \rightarrow R\cdot + X\cdot$$

where X is either Cl or Br. The halogen radical reacts to form the hydrogen halide:

$$X\cdot + RH \rightarrow R\cdot + HX$$

which in turn interferes with the radical chain mechanism:

$$HX + H\cdot \rightarrow H_2 + X\cdot$$
$$HX + OH\cdot \rightarrow H_2O + X\cdot$$

The high-energy H· and OH· radicals are removed by reaction with HX and replaced with low-energy X· radicals. The actual flame retardant effect is thus produced by HX.

The hydrogen halide consumed is regenerated by reaction with hydrocarbon:

$$X\cdot + RH \rightarrow R\cdot + HX$$

Thus HX ultimately acts as a catalyst.

ii. Brominated flame retardants

Halogen atoms can be bound aliphatically or aromatically in flame retardants. The more effective aliphatic halogen compounds are easier to break down and, hence, are less temperature resistant than aromatic flame retardants. Their suitability depends on the plastic and the method of incorporation. Because of their very good technical properties, brominated flame retardants are used in virtually all polymers. In most cases, antimony trioxide is added as a synergist.

Flame retardants with aromatically bound bromine have the highest market-share. They can be subdivided into several classes based on the following types of chemical structure (Table VI).

Aliphatically bound brominated flame retardants can be of aliphatic or cycloaliphatic structure. Examples are dibromoneopentyl glycol and hexabromocyclododecane.

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Table VI	
Type of chemical structure	**Example**
• Several benzene rings	Polybrominated diphenyl ethers Decabromobiphenyl 1,2-bis-(Pentabromophenyl) ethane
• Tetrabromobisphenol acid	Tetrabromophthalate diols and Polyethers
• Tetrabromobisphenol A (TBBPA)	TBBPA-derivatives
• Oligomeric and polymeric compounds	TBBPA-carbonate oligomer TBBPA-based epoxy resin Poly-di and tribromostyrene

iii. Chlorinated flame retardants

In plastics, they are mainly used as chlorinated hydrocarbons or chlorinated cycloaliphatics. They offer good light stability. Compared to brominated flame retardants, higher quantities are needed for achieving comparable flame retardancy.

Aliphatic chlorinated hydrocarbons, mostly chloroparaffins, are liquid or solid, depending on their chlorine contents varying from 30 to 70 %. They have partial plasticising properties and are thermally stable up to 220°C.

Cycloaliphatic chlorinated compounds have a higher thermostability and are used as additive flame retardants in engineering plastics.

B. PHOSPHORUS CONTAINING FLAME RETARDANTS

While halogen containing flame retardants act in the gas phase, phosphorus containing flame retardants mainly influence the reactions taking place in the condensed phase. They are particularly effective in materials with high oxygen content, such as cellulose and oxygen containing plastics. The basic flame retardant mechanism is shown here.
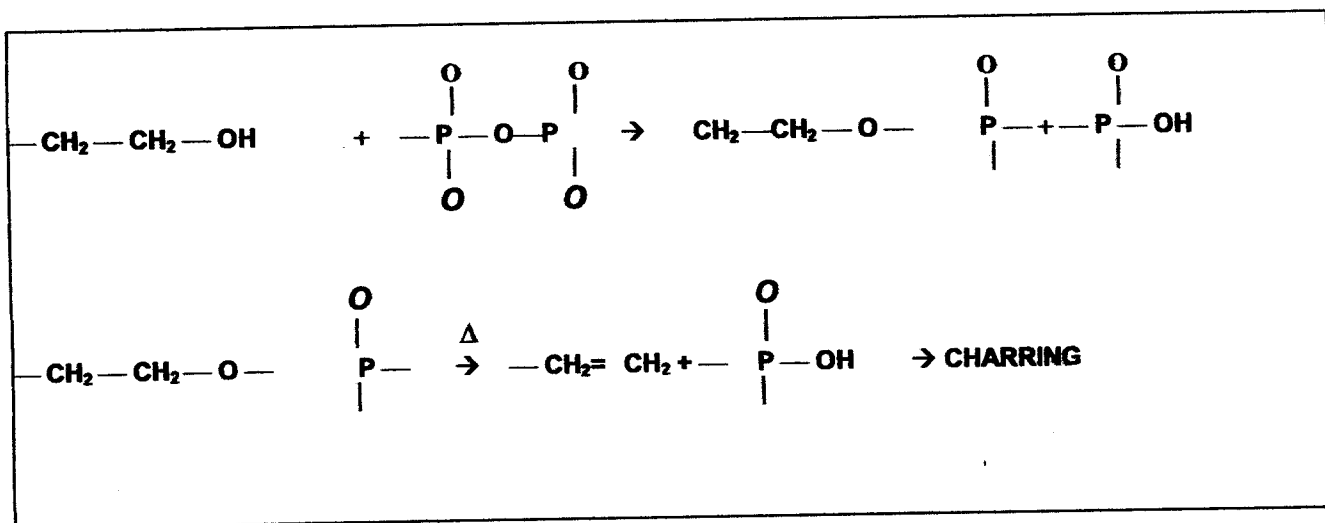
The flame retardant is converted by thermal decomposition to phosphoric acid which in the condensed phase extracts water from the pyrolysing substrate, causing it to char. The individual reaction steps are as follows:

• Thermal decomposition leads to the formation of phosphoric acid:

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$$R-CH_2-CH_2-O-P- \xrightarrow{\Delta} R-CH_2=CH_2 + HO-P-$$

$$2 \; HO-P- \xrightarrow{\Delta} -P-O-P- \; + \; H_2O$$
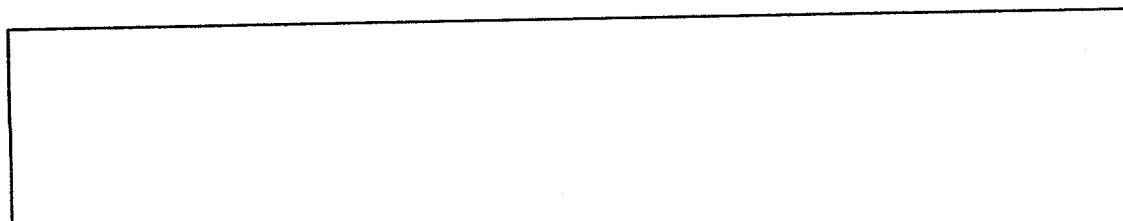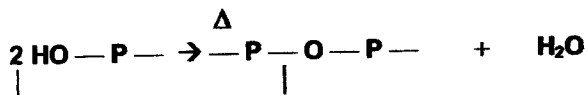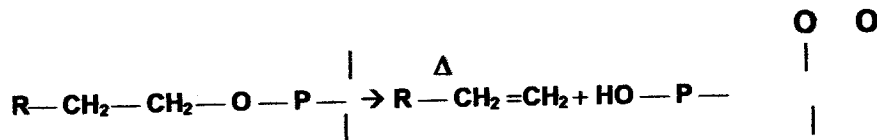
- The phosphoric acid formed esterifies, dehydrates the oxygen-containing polymer and causes charring:

$$-CH_2-CH_2-OH \; + \; -P-O-P- \rightarrow CH_2-CH_2-O- \quad P-+-P-OH$$

$$-CH_2-CH_2-O- \quad P- \xrightarrow{\Delta} -CH_2=CH_2 + -P-OH \quad \rightarrow CHARRING$$

Halogenated aliphatic phosphates are used in polyurethanes. Phosphorinanes are used for transparent formulations, for example in PMMA. Reactive phosphorus compounds are applied in polyurethanes and thermosets. Red phosphorus and ammonium polyphosphate will be discussed later in the section inorganic flame retardants

C. NITROGEN CONTAINING FLAME RETARDANTS

Nitrogen containing flame retardants only find limited application in polymers, e.g. melamine in polyurethane foams and melamine cyanurate in polyamides. Specifically developed systems based on melamine and derivatives are used in intumescent systems.

The mode of action of nitrogen-containing flame retardants is still not well understood.

D. INORGANIC FLAME RETARDANTS

Few inorganic compounds are suitable for use as flame retardants in plastics, since such compounds must be effective in the range of decomposition temperatures of the plastic, mainly between 150 and 400°C.

Apart from antimony trioxide, which interferes with the combustion process chemically in combination with halogen containing flame retardants, the most widely used inorganic flame retardants such as aluminium and magnesium hydroxide as well as boron containing compounds affect the combustion process via physical means. The effects of red phosphorus and ammonium polyphosphate are based on both modes of action.

Unlike organic compounds, inorganic flame retardants do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, etc., mostly in endothermic reactions. In the gas phase, these act by diluting the mixture of flammable gases and by shielding the surface of the polymer against oxygen attack.

The inorganic flame retardant acts simultaneously on the surface of the solid phase by cooling the polymer via endothermic breakdown process and reducing the formation of pyrolysis products.

In addition, as in the case of inorganic boron compounds, a glassy protective layer can form on the substrate, fending off the effects of oxygen and heat.

i. Aluminium hydroxide

Currently, aluminium hydroxide is the most widely used flame retardant; it is low cost and easy to incorporate into plastics.

Aluminium hydroxide starts to break down in the temperature range from 180 to 200°C, conversion to aluminium oxide taking place in an endothermic reaction with the release of water vapour.

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O - 298\ kJ/mole$$
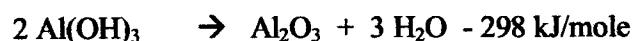
In the combustion zone, this reaction triggers various processes which affect the combustion process:

- As a result of the endothermic breakdown of the aluminium hydroxide, the polymer is cooled, and thus fewer pyrolysis products are formed.
- Together with the charring products, the aluminium oxide formed on the substrate acts as an insulating protective layer.
- The water vapour liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer over the condensed phase.

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Aluminium hydroxide is used in large quantities in PVC and polyolefin (except polypropylene) wire & cable, and in thermosets.

ii. Magnesium hydroxide

Another flame retardant acting in the same way as aluminium hydroxide is magnesium hydroxide, which decomposes at a higher temperature level of 300-330°C. Therefore, it can be used in plastics processed at higher temperatures than aluminium hydroxide, like polypropylene and engineering plastics. For meeting fire performance requirements, extremely high loadings are necessary which can heavily affect the plastics properties.

$$Mg(OH)_2 \rightarrow MgO + H_2O - 200 \text{ kJ/mole}$$

Magnesium hydroxide is used in certain wire & cable applications, in polypropylene and polyamides. For example, about 60-65% magnesium hydroxide in polypropylene is required to meet the UL 94 V0 test.

iii. Boron containing compounds

Boron containing compounds can be effective in the condensed phase, and in some cases, in the gas phase as well. A major application of borates is the use of mixtures of boric acids and borax as flame retardants for cellulose and of zinc borate for PVC and some engineering plastics. Boron containing compounds act by endothermic, stepwise release of water and formation of a glassy coating protecting the substrate. Zinc borate forms zinc chloride during the pyrolysis of PVC. The latter acts as a Lewis acid suppressing smoke formation.

Similar to the polyphosphoric acid resulting from phosphate esters, boric acid shows dehydrating and charring action with oxygen-containing substrates. The glassy coating and the pronounced tendency to char protect the substrate successfully against oxygen attack and heat.

iv. Antimony oxides

Antimony trioxide and pentoxide are used as synergists for halogenated flame retardants and PVC. They are not active as flame retardants on their own, but enhance the effectiveness of halogenated flame retardants by stepwise releasing the halogenated radical interceptor HX, thus affecting the gas phase radical chain reaction of flame spread.

v. Inorganic phosphorus compounds

Elemental red phosphorus acts as a flame retardant by its oxidation to phosphoric acid or phosphorus pentoxide during the combustion process. The flame retardancy mechanism has already been described above under phosphorus containing flame retardants.
Red phosphorus is commercially used in PA 6 and 6.6, but also suitable for other oxygen-containing polymers.

Ammonium polyphosphate is used for intumescent systems in coatings and in polypropylene formulations. It is also used in polyurethane foams.

vi. Other inorganic flame retardants

Zinc sulphide and zinc oxide are used for partly substituting antimony trioxide in certain formulations. They do not act as flame retardants.

Expandable graphite can be used in flame retardants systems together with ammonium polyphosphate or red phosphorous plus magnesium hydroxide for polyolefins, styrenics and polyamides. At the moment, they are in the introduction phase and will probably only cover smaller market segments.

9. THE ROLE OF FLAME RETARDANTS IN FIRE GASES AND RESIDUES

The role of pollutants like dioxins (means in the following: polyhalogenated dibenzodioxins and -furans) formed in fires has been controversially discussed in recent years, particularly in Germany after catastrophic fires like the Lengerich fire in 1992 and the Düsseldorf Airport fire in 1996. These two fires were extensively investigated and comprehensive reports published [15-16]. The Lengerich fire report contains a series of analytical results which helped to assess the relevance of these contaminants for humans and the environment.

In a fire, the acute and chronic toxicity of fire gases and residues are relevant.

A. Acute toxicity

All gases formed in a fire are deadly toxic irrespective of the products burning. The acute toxicity of fire gases is controlled by carbon monoxide, a highly toxic, non irritating gas, present in significant amounts in virtually all fires. It is responsible for over 90% of fire deaths. Other components of acute toxicity found in fire gases like hydrogen cyanide and irritants like hydrogen chloride and acrolein play a secondary role [17].

Dioxins were not detected as such in fire gases and no fire deaths caused by these compounds were recorded to date. The reason is that, like other pollutants, dioxins are strongly bound to soot particles and thus virtually not biologically available.

B. Chronic toxicity

No chronic toxicity effects from dioxins or other soot-bound pollutants like polycyclic aromatic hydrocarbons (PAHs) were reported to date from persons accidentally involved in a fire (generally one exposure). For professional fire fighters and persons carrying out sanitation measures after a fire and involved in the disposal of fire residues, no chronic toxicity effects were reported either. This is consistent with a German study which showed that professional

fire fighters have no higher dioxin blood levels than the dioxin background levels of the general population [18].

In the Lengerich and Düsseldorf Airport fires, major amounts of halogen-containing products were involved.

In the Lengerich fire, more than 500 tons of PVC and probably also plastics containing brominated flame retardants burnt. The polychlorinated dibenzodioxin/-furan (PCDD/F) levels found in soot in rooms and outside in the vicinity of the fire source were much lower as initially expected and lay significantly under the sanitation value (10 ng 2,3,7,8-TCDD TE/m^2. Polybrominated dibenzodioxins/-furans (PBDD/F) were found in one case at very low levels (60 times less than PCDD/F).

In the Düsseldorf airport fire, PCBs from old fluorescent tubes transformers were the primary source of PCDD/Fs, whereas PVC only played a secondary role. Brominated flame retardants (polybrominated diphenyl ethers) were detected and PBDD/Fs found at very low levels (around 1 ppb).

From these findings, it comes out that flame retardants and particularly brominated flame retardants contained in polymers involved in fires are not a source for environmental pollution.

CONCLUSIONS

Flame retardants are beneficial for protecting flammable materials like plastics against fire sources of small energy, e.g. cigarettes or matches, and of higher energy, e.g. a burning waste basket, and can prevent or delay initiating fires. They therefore enhance the fire safety level of combustible materials in building, furniture, transportation, electrical applications, help to fulfil the requirements of fire precautions and thus to protect life, health and property efficiently.

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