# ASPECTS OF FLAME RETARDANTS AND THEIR ROLE IN SOCIETY

Elena Janina VILCEA[1], Rodica Mariana ION[2]

**Abstracts**. *Flame retardants are extremely important in a lot of industrial application, and their use has expanded greatly. Among the most widespread are brominated flame retardants, low cost due and extremely effective at what they do. Reactive flame retardants - are usually introduced during the polymerization stage and copolymerized, together with other monomers, for example the main reactive retardants for polyesters are brominated retardants which are said to be 70% more efficient than chlorinated retardants. Flame retardants additive can be inorganic (hydrated alumina, antimony trioxide, magnesium hydroxide, phosphorus), halogenated compounds (chlorinated compounds and brominated compounds). This paper aims to make a review of the properties listed flame retardants, of their usefulness in society and the law governing their use.*

**Keywords:** flame retardants, classification of flame retardants, brominated retardants, properties of flame retardants.

## 1. Introduction

Flame Retardants are extremely important in protecting people and property from fire. Flame retardants are additives that can be added to or applied as a treatment to organic materials such as plastics, textiles and timber. Flame retardants additives work by breaking one of the links that produce and support combustion: heat, fuel and air. They may quench a flame by depriving it of oxygen or may absorb heat and produce water, so reducing the temperature. Experience has shown that fire itself is not the real hazard: far more dangerous to people are the toxic by-products generated during combustion, and dense smoke that prevents people from escaping in time. The control of these is becoming the decisive factor in assessing flame retardant additives. Correct selection and utilization of the type of flame retardant dependent on a number of criteria. The process is very complex and regards suitability, performance, health and safety, end of life and of course cost issues require consideration. The flame retardant must be compatible with

[1]Asist., Eng., Faculty of Engineering and Management of Technological Systems, Politehnica University of Bucharest, PhD., Faculty of Materials Engineering, Mechatronics and Robotics, Valahia University, Targoviste, România, elenaj.vilcea@yahoo.com
[2] Prof., Ph.D., M.Sc, Faculty of Materials Engineering, Mechatronics and Robotics, Valahia University, Targoviste, România, rodica_ion2000@yahoo.co.uk

the material it is to protect compromising the desired mechanical properties of the material.

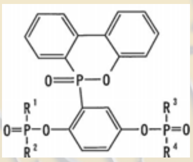
It is also important that the flame retardant resin be stable throughout fabrication and processing and indeed at end of life recycling. Health and safety concerns include industrial safety, handling, consumer safety and environmental impact. Finally and usually most importantly the flame retardant material chosen should be cost effective.

## 2. Classification and properties of flame retardants

There are more than 175 different types of flame retardants. Two basic types of flame retardant chemicals used, together with some representative examples are listed below:

A) **REACTIVE FLAME RETARDANTS** - imparts excellent flame retardancy to resins even when added in a small amount and can be prevented from bleeding out; and a flame-retardant processed resin obtained with the flame retardant.

The reactive flame retardant is, for example, an organophosphorus cyclic compound which is represented by the following general formula (1) and has at least one unsaturated group at ends of R1 to R4. The flame-retardant processed resin is obtained by solidifying a resin composition containing this organophosphorus cyclic compound and then reacting the compound by heating or irradiation with a radiation.



(1)

These are mainly relevant to thermosetting resins, such as unsaturated polyesters and epoxies. For polyesters, the main reactive retardants are HET acid (based on chlorine) or dibromoneopentyl glycol (DBNPG). Brominated flame retardants are said to be 70% more efficient than HET acid (which has also become expensive). With epoxies, the best system (on present evidence) appears to be reactive phosphorus organic compounds, which are toxicologically harmless in fire and are chemically linked to the resin matrix, so that mechanical and chemical properties are not affected.

B) **ADDITIVE FLAME RETARDANTS** - are more frequently used and are very numerous, depending on the precise conditions in which the additive is expected to operate (and also the desired cost level). Types of additive flame retardants are presented below:

**a) INORGANICS**

1) Aluminium trihydrate - hydrated alumina $Al(OH)_3$- is the most widely used flame retardant additive in volume terms, representing 43% of all flame retardant chemicals in volume (but only about 29% in value). As well as flame retarding and smoke suppressing, it is an economical filler/extender. In a fire, it undergoes an endothermic dehydration with a two-fold action, simultaneously absorbing the heat energy needed to sustain combustion and releasing water vapour, which dilutes the combustion gases and toxic fumes. It is used mainly in unsaturated polyesters in the building/construction industry, and in cable sheathing compounds. Use is limited by a maximum processing temperature of about 200°C, and the high loading needed to achieve good flame retardant performance can be detrimental to mechanical and electrical properties.

2) Aluminium trihydroxide - this chemical begins to decompose at temperatures above 180°C, with an endothermic reaction that absorbs 1-2 kJ/g of energy. This has the effect of decreasing the rate of heat release from a burning polymer filled with aluminium trihydroxide, also decreasing the time to ignition and surface spread of flame.

3) Antimony trioxide - this material has a synergistic effect with most halogenated, flame retardants. It is also used in plasticized PVC because of its synergy with chlorine. Antimony oxide should not be used if translucency is required. In some cases ferric oxide is used in its place, for similar physical properties but improved electrical properties. It has been shown by extensive research to be non-carcinogenic.

4) Magnesium hydroxide - it is temperature stable to 332°C, allowing processing with a wide variety of thermoplastics and use where aluminium trihydrate is not sufficiently stable. It is used particularly in cable sheathing, polypropylene and polyamides.

5) Phosphorous compounds - influence chemical reactions taking place on the surface and so the degradation pathway of the material. Upon heating they decompose to phosphoric acid which when condensed causes the material to char. Some phosphorous flame retardants can also act in the gas phase as radical traps but it is less common.

**b) HALOGENATED COMPOUNDS** - act chemically in the gas phase during combustion. The halogen component (typically bromine or chlorine) trap the high energy H. and OH. radicals produced on heating of the material. The performance of such halogenated flame retardants, particularly brominated compounds is dependent upon the chemical composition of material.

1) Chlorinated compounds such as chlorinated paraffins

2) Brominated Flame Retardants contain more than 75 different chemicals and that flame retardants can be divided into three distinct classes:

1.1) *Aromatics*, including tetrabromobisphenol-A, (TBBA), polybrominated diphenyl ethers (PBDEs) and Polybrominated biphenyls (PBBs)

1.2) *Aliphatics*, which tend to have limited use

1.3) *Cycloaliphatics*, such as hexabromocyclododecane (HBCD)

The major types used in the Flame Retardant industries are:

• Poly Brominated Diphenyl Ethers (PBDEs) – They are synthesised via the catalytic bromination of diphenyl ether; Most widely known are the commercially marketed members of the PBDE family, penta-BDE and octa-BDE and deca-BDE; They exist in a mixture of isomers with their names being derived from the dominant isomer or the average bromine content. Penta-BDE is usually provided as a mixture of 24-38% tetra-brominated diphenyl ether and 50-60% penta-brominated diphenyl ether. It is used mainly in polyurethane foams such as in furniture and car interiors.

• Hexabromocyclododecane (HBCD) - is produced by the bromination of cyclododecane in a batch process; it is used in polystyrene and the textile industry. Applications include upholstered furniture, automobile interiors, and insulation blocks in building, textile coatings and electrical and electronic equipment.

• Tetrabromobisphenol-A (TBBA) - grades available for use with most resins except polyamides, PVC, rigid and flexible PU foams; can be used as an additive or reactive flame retardant i.e. chemically bound to polymer structure during processing. It is most often used in its reactive form in epoxy resins, unsaturated polyesters and polycarbonates in electronic and electrical applications. In plastics such as ABS, TBBA tends to be additive with loadings of up to 16% 15, which results in a higher potential for losses to the environment

• Polybrominated biphenyls (PBBs) – used with applications predominantly in textiles and fabrics. Research was carried out into the toxicity of PBBs and it was found that they have properties and toxicological effects similar to that of polychlorinated biphenyls (PCBs). (PCBs are recognised as one of the 12 most toxic groups of chemicals worldwide).

• Polybrominated diphenyl oxide (PBDO) compounds: Suitable for most plastics, except PS foam.

• Dibromoneopentyl glycol (DBNPG): Reactive flame retardant containing 60% aliphatic bromine. Thermosetting polyester resins can be formulated with this over a wide range of compositions to provide a broader selection of resin properties than are available with anhydride flame retardants. Resins formulated with types of DBNPG have high chemical and flame resistance, minimal thermal discolouration and excellent light stability. It can also be used with polyurethane rigid foams.

• Dibromostyrene and derivatives: includes graft copolymers with polypropylene; recommended with ABS and styrenes, most engineering thermoplastics, unsaturated polyester resins and polyurethane foams; not recommended for PVC, PS foam and rigid PU foam.

• Hexabromocyclododecane: high impact polystyrene and polyolefins, PS foam.

• Pentabromobenzyl acrylate (developed for engineering thermoplastics and now in full production by Dead Sea Bromine Group): can be polymerized or copolymerized in the extruder, giving UL 94 V-0 ratings without loss of physical or mechanical properties in host resins such as nylon 6 and 66, PBT and polycarbonate.

• Tetrabromobisphenol A: grades available for use with most resins, except polyamides, PVC, rigid and flexible PU foams.

• Tetrabromophthallic anhydride and derivatives: used mainly with thermosetting resins and PUs; also PVC and thermoplastic elastomers.

• Tribromoneopentyl alcohol (TBNPA): is reactive flame retardant containing more than 70% aliphatic bromine. It is exceptionally stable and is particularly suitable where thermal, hydrolytic and light stability are required. It is highly soluble
in polyether polyols, making it particularly suitable for use in polyurethane polymers.

• Tribromophenol and derivatives: used with ABS and styrenes, polycarbonate, polyamide, PS and PU foams and thermosetting resins; not suitable with polyolefins and PVC.

• Intumescent flame retardants: producing a thick insulating layer with good resistance to erosion by fire and hot gases. Some low-toxicity alternatives to antimony trioxide in halogenated polymer systems work synergistically to form a char in conjunction with halogenated polymers. During combustion the vapour phase changes the flame chemistry to inhibit fire growth by removing free radicals which support combustion. Additional effects in the condensed phase produce carbonaceous char is formed which further retards flame propagation and reduces the amount of smoke and carbon monoxide during combustion. Grades are thermally stable up. to 200°C (392°F), suitable for brominated polyesters, PVC and halogenated polyethylene, or thermally stable in all polymer systems.

• Zinc borate: In ultrafine grades with surface areas from 10 to 15 m2/g and thermally stable up to 290°C (554°F), functions mainly in the condensed phase, promoting the formation of a char, which can be enhanced by the finer particle size. Grades are also suitable for use in translucent halogenated polyester resin systems, to improve fire performance while retaining clarity, and/or with a refractive index of 1.59 (similar to that of glass and many polyester resins).

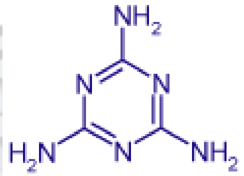
**c) ORGANIC PHOSPHOROUS COMPOUNDS**

• Phosphate esters such as triphenyl phosphate, others combined with halogen compounds.

**d) NITROGEN BASED COMPOUNDS**

• Melamines:

i) Pure melamine - 2,4,6-triamino-1,3,5 triazine

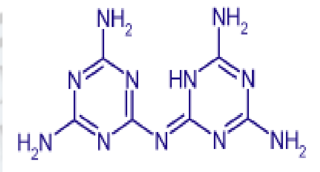
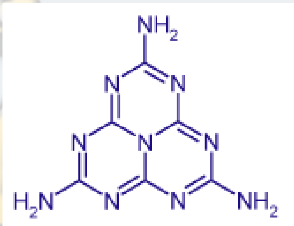
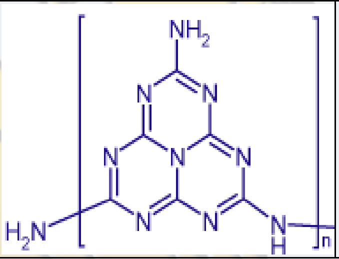



ii) Melamine derivatives such as:

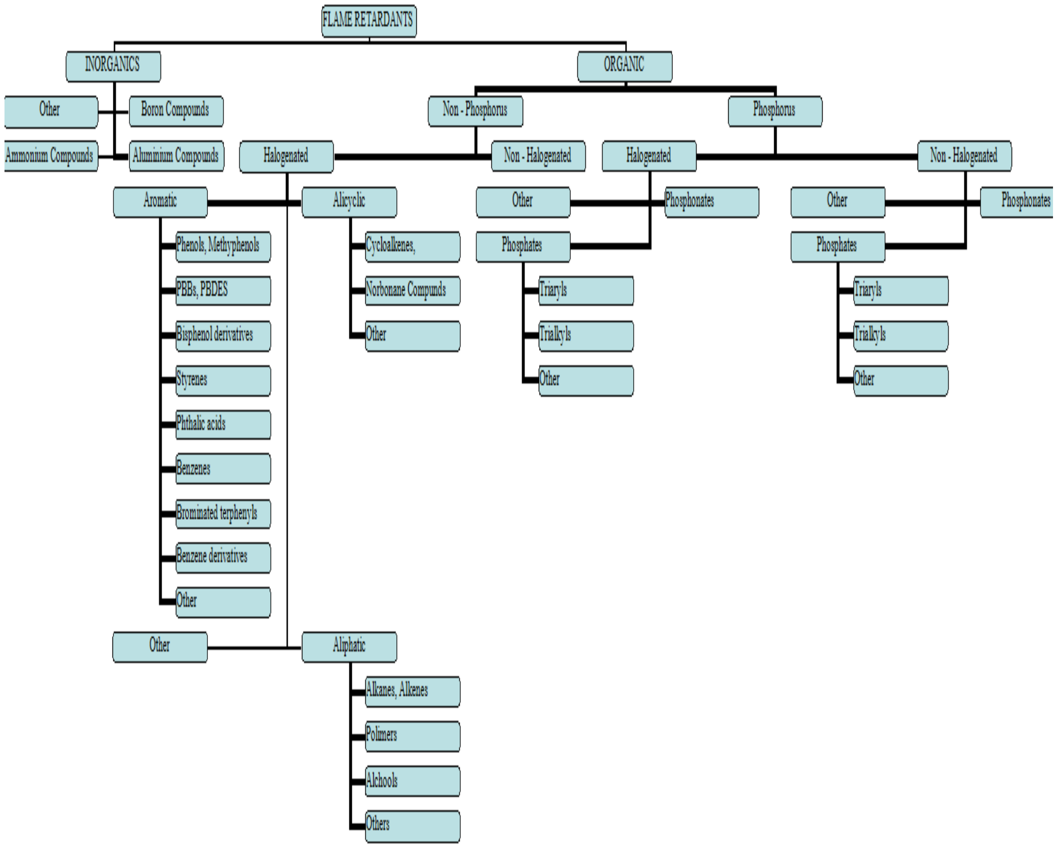
- Melamine borate (MB) - melapur® MB
- Melamine phosphate (MP) - Melapur® MP
- melamine polyphosphate(MpolyP)- melapur® 200
- melamine cyanurate (MC) (eg: Melapur ® MC XL, MC 50, MC 25, MC 15)

| Product | Chemical structure | Application |
|---|---|---|
| melapur® MC | melamine cyanurate | Polyamide, Thermoplastic Polyurethane, Polyester, Epoxy |
| melapur® 200 | melamine polyphosphate | Glass filled Polyamide, Polypropylene, Intumescent paints (epoxy) |
| melapur® MP | melamine phosphate | Polyolefins, Intumescent paints, Textiles |
| melapur® MB | melamine borate | Textiles (backcoating), Polyolefins, Cellulose |
| melapur® P46 | intumescent mixture | Polypropylene, Polyethylene, Elastomers |

iii) Melamine homologues (melam, melem, melon) have higher thermal stability compared to pure melamine and melamine cyanurate; Melam, melem and melon are believed to act in general in the same way as melamine only at higher temperature.

| Type of melamine homologues | The formula | Appearance |
|---|---|---|
| Melam - (1,3,5- triazine-2,4,6-triamine-n - (4,6-diamino-1,3,5-triazine-2-yl) |  | fine, light white-grey powder thermal decomposition at 400ºC |
| Melem (-2,5,8-triamino 1,3,4,6,7,9,9b - Heptaazaphenalene) [1502-47-2] |  | fine, light yellow powder thermal decomposition at 500ºC |
| Melon (poly [8-amino-1,3,4,6,7,9,9b- Heptaazaphenalene-2,5-diyl)imino] |  | fine, yellow powder. Melting Point and thermal decomposition above 500ºC |

Another classification of flame retardants are presented also in table below:




## 3. **Legislation**

Legislation will always play the most important role in influencing industry activities. In Europe, the legislation goes back to the 1990 EC Directive 90/128/EEC - a positive list of authorized monomers. The Commission is now publishing its first list of additives that will require testing for migration in food-contact applications in a Directive due to be ratified during 1999. Dr Luigi Rossi of the EC said that the listed additives would need to be tested to show that the plastic compounds in which they are used comply with EC legislation for materials in contact with food. The process of listing restricted additives will thereafter be continued by means of amendments to the Directive 90/128/EEC.

Summary of relevant environmental legislation is presented in the below table:

| Type | Regulation | Notes |
|---|---|---|
| Food contact | EC Directive 90/128/EEC | Positive list of authorized monomers. The Commission is now publishing its first list of additives which will require testing for migration in food-contact applications in a Directive |
| Flame retardants | EC Directive | Proposed Directive on polybrominated diphenylethers has not progressed |
| | International Programme of Chemical Safety (IPCS) environmental health criteria | Recommends safety levels and handling/disposal for special brominated FRs |
| | German Chemicals Banning (Dioxin) Ordinance | Revised 1994 to include brominated and chlorinated dioxins/furans: limits up to 10ppb to July 1999 and 1ppb afterwards on certain tetra and penta BDDs and BFDs and up to 60ppb to July 1999 and 5ppb after on total levels of specified hexa, penta and tetra BDDs and BDFs. |
| Type | Regulation | Notes |
| Cadmium-based pigments | Directive (91/338/EEC) | Harmonizes regulations on use of cadmium-based pigments, limiting use. Cadmium-based pigments may not be used in plastics materials where there are other satisfactory substitutes. |
| Solvents/ volatile organic compounds | European Union VOC Solvent Emissions Directive | Seeks to reduce VOC emissions from solvent using installations by 657% by 2007, based on 1990 levels. |
| Waste and recycling | Directive on Packaging and Packaging Waste (94/62/EC) | By 2001, to recycle at least 15% of each material in the packaging waste stream and 24-45% of the totality of packaging materials; 50-65% of packaging waste must be recovered. |
| | End of Life Vehicles (ELV) Directive EC 31/7/96 | Restriction of use of heavy metals in car components; Recycling of end-life vehicles to 80% by 2006 and 85% by 2015; Entitles consumers to free take-back of end-of-life vehicles by 2006 |
| | Waste Electrical and Electronic Equipment (WEEE) Directive | Aims to control the use of certain materials and encourage re-use and recycling of all electrical and electronic components. |

The ideal flame retardant does not yet exist. Neither BFRs nor their halogen-free alternatives satisfy all the demand of the ideal flame retardant.
Technical and cost barriers are likely to slow industry progression in the short term. However, as the performance and applicability of alternative flame retardant improve, availability and cost issues will be less of a hindrance.
The available toxicological databases are inadequate to truly understand the risk of many of these chemicals.

## R E F E R E N C E S

[1] Environmental Aspects of Flame Retardants in Textiles - Report for Austrian Standards Institute Consumer Council, April 1999

[2] http://www.specialchem4polymers.com

[3] http://www.ciba.com

[4] http://www.acsh.org

[5] http://www.specialchem.com

[6] Ian Molyneaux, Sina Ebnesajjad, "Environmental Aspects of PTFE Based Laminates in Relation to halogen - free"

[7] Dr. Deborah Rice, John James, "Brominated Flame Retardants", Third annual report to the Maine Legislature, January 2007

[8] Rachel Cahill, "Green chemistry and the producer: flame retardants", MRes Project, 2004