FLAME RETARDANTS

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Flame Retardants

Materials and Applications

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Preface

This book focuses on the chemistry and applications of flame retardants for polymers and other materials. The text focuses mainly on the literature of the last decade.

The book starts with a description of flame retardants. Here various types of flame retardants, their properties, and their chemical structures are detailed. These include chlorine- and bromine-containing flame retardants, phosphorus-based flame retardants, nitrogen-based flame retardants, and silicones. Inorganic materials that serve as flame retardants, such as boron-based additives, graphenes and others, are also discussed. Here, in general, the activity of such flame retardants is also illustrated and the flame retardant effect, mostly on polymers, is illustrated. However, flame retardant polymers as such are discussed in a separate chapter.

In the next chapter, the mechanisms of flame retardants are discussed, such as flame cooling, synergetic effects, degradation of flame retardants, and others.

Besides flame retardants, other compounds are of interest in flame retardant compositions, such as dripping inhibitors and smoke suppressants. These compounds are detailed in two separate chapters. In addition, testing methods for flame retardants and available international standards are of importance. These issues, together with human health hazards, such as smoke toxicity and problems with wastes, are discussed in another chapter.

In still another chapter, synthesis and fabrication methods, as well as recycling methods, are discussed. Besides common chemical synthesis methods, some unconventional methods are available, such as mechano-chemical methods.

Also, the application of flame retardants to the final material is of interest. This can be done using 3D printing, reactive coating, or bulk addition methods.

As mentioned at the beginning, flame retardant polymers as such are discussed in a separate chapter, i.e., *Examples of Polymers*. Besides commonly known flame retardant materials, such as PVC, Teflon, etc., a lot of polymers can be made flame retardant by including non-burning comonomers. Also, issues concerning foams, nanocomposites, and bio-based material are discussed.

The final chapter deals with special uses of flame retardants. These include textiles, wool, and electrical applications such as batteries.

So, a lot of interesting points of view are presented that might be of interest to various professionals in, for example, the car, aircraft and electric industries. So, beyond education, this book will serve the needs of industry engineers and specialists who have only a passing knowledge of the plastics and composites industries but need to know more.

How to Use This Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

The reader should be aware that mostly US patents have been cited where available, but not the corresponding equivalent patents in other countries. For this reason, the author cannot assume responsibility for the completeness, validity or consequences of the use of the material presented herein. Every attempt has been made to identify trademarks; however, there were some that the author was unable to locate.

Index

There are three indices: an index of acronyms, an index of chemicals, and a general index.

In the index of chemicals, compounds that occur extensively, e.g., “acetone,” are not included at every occurrence, but rather when they appear in an important context.

Acknowledgements

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Last, but not least, I want to thank the publisher, Martin Scrivener, for his abiding interest and help in the preparation of the text. In addition, my thanks go to Jean Markovic, who made the final copyedit with utmost care.

Johannes Fink
Leoben, May 6, 2020

1
Types of Flame Retardants

Polymeric materials are generally subject to burn. Therefore, for safety reasons, flame retardants are added. A measure for the flammability is the limiting oxygen index (LOI). The LOI is the percentage of oxygen in the atmosphere that allows burning under standardized conditions (1, 2). Table 1.1 gives an idea about the flammability.

A series of flame retardants with different chemical structures exists and the mechanism of action is dependent on the nature of the particular compounds.

There are monographs dealing with flame retardant materials (3–6).

1.1 History of Organic Flame Retardants

The history of organic flame retardants has been detailed in an article (7) as follows:

Polychlorinated biphenyls were manufactured and used as flame retardants from the late 1920s until the mid-1980s, although polychlorinated biphenyls were also used in a multitude of other applications, particularly in electrical equipment. Other chlorinated compounds came into use as flame retardant, probably from the 1960s onwards, sometimes also including a phosphate group, such as the tris-(2,3-dichloropropyl) phosphate and tris-(1,3-dichloro-iso-propyl) phosphate (8).

Table 1.1 Limiting oxygen index of selected materials (9–11).

Material	**LOI/[% Oxygen]**
Poly(formaldehyde)	15
Poly(ethylene oxide)	15
Styrene-butadiene rubber	16.9
Poly(methyl methacrylate)	17
Poly(acrylonitrile)	18
Poly(ethylene)	18
Poly(propylene)	18
Acrylonitrile-butadiene-styrene	18.0 – 39
Cellulose acetate	18 – 27
Poly(butadiene)	18.5
Poly(styrene)	18.5
Poly(imide)	18.6
Cellulose butyrate	18.8 – 19.9
Cellulose	19
Styrene acrylonitrile copolymer	19.1
Poly(ethylene terephthalate)	21
Poly(vinyl alcohol)	22
Poly(amide) 66	23
Wool	25
Silicone rubber	25
Poly(carbonate)	27
Aramid	28.5
Poly(vinyl chloride)	42
Poly(vinylidene fluoride)	44
Isocyanurate foam	29

Material	LOI/[% Oxygen]
Phenol formaldehyde	35
Poly(benzimidazole)	38.0 – 43.0
Poly(vinylidene chloride)	60
Carbon	60
Poly(tetrafluoroethylene)	>95.0

The brominated analog of the former compound, tris-(2,3-dibromopropyl) phosphate made headlines in the 1970s due to its use in children's pajamas (12).

At the beginning of the 1970s, an increasing number of brominated flame retardants (BFrs), e.g., polybrominated biphenyls and polybrominated diphenyl ethers, came on the market. In 1997, the World Health Organization tried to list all major flame retardants, also including any inorganic chemicals used in that role (13).

The first review of BFrs appeared in 1995 (14), including what was known of their analysis, toxicity and environmental occurrence. Numerous other reviews and/or assessment documents have been published since then (15–19).

Among the most recent documents concerning BFrs are five published opinions from the European Food Safety Authority (EFSA) on polybrominated biphenyls (20), polybrominated diphenyl ethers (21), hexabromocyclododecanes (HBCDDs) (22), tetrabromobisphenol A and its derivatives (23), and also an opinion concerning other phenolic BFrs and their derivatives (24). EFSA is presently also preparing an opinion on emerging and novel BFrs for publication in 2012. In 2011, a book on BFrs was published which covered a multitude of issues relating to BFrs (25).

Other major reviews of BFrs from 2005 onwards are included in (26–29).

A review on phosphorus-containing flame retardants was published (30), while, among the chlorinated flame retardants, only the Dechloranes have been comprehensively reviewed (31).

The scientific literature of bromine-, chlorine- and phosphate-containing flame retardants was reviewed (7). The compounds mentioned are collected therein. Also, the trade names are given. The chemical names of these compounds are given in Table 1.2.

1.2 Commercially Available Flame Retardants

Some commercially available flame retardants are listed in Table 1.3.

Table 1.2 Bromine-, chlorine- and phosphate-containing flame retardants (7).

Compound name
2,4-Dibromophenol
Dibromostyrene
2,4,6-Tribromophenol
1,3,5-Tribromo-2-hydroxybenzene
2,4,6-Tribromophenyl allyl ether
1,2,4,5-Tetrabromo-3,6-dimethylbenzene
1,4-Dimethyltetrabromobenzene
2,3,5,6-Tetrabromo-1,4-dimethylbenzene
2,3,4,5-Tetrabromo-6-chlorotoluene
Tetrabromo-*o*-chlorotoluene
2,3,4,5-Tetrabromo-6-chloromethylbenzene
1,3-Isobenzofurandione
3,4,5,6-Tetrabromophthalic anhydride
4,5,6,7-Tetrabromobenzofuran-1,3-dione
Tetrabromophthalic acid anhydride
Tetrabromophthalic anhydride
1,2,3,4,5-Pentabromo-6-methylbenzene
2,3,4,5,6-Pentabromotoluene
Pentabromomethylbenzene
Pentabromophenol
Pentabromoethylbenzene
Pentabromobenzyl chloride
Pentabromophenol allyl ether
2,4,6-Tribromophenyl 2,3-dibromopropyl ether
2-Ethylhexyl-2,3,4,5-tetrabromobenzoate

Compound name
Hexabromobenzene
2,3,4,5,6-Pentabromobenzyl acrylate
Pentabromobenzyl bromide
Di(2-ethylhexyl) tetrabromophthalate
3-(Tetrabromopentadecyl)-2,4,6-tribromophenol
Tetrabromobisphenol A
2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane
2,2’,6,6’-Tetrabromobisphenol A
3,3’,5,5’-Tetrabromobisphenol A
3,5,3’,5’-Tetrabromobisphenol A
4,4’-(1-Methylethylidene)bis[2,6-dibromophenol]
4,4’-Isopropylidenebis[2,6-dibromophenol]
Tetrabromodiphenylolpropane
Tetrabromobisphenol A
Bis(3,5-dibromo-4-hydroxyphenyl) sulfone
Tetrabromobisphenol A dimethyl ether
Tetrabromobisphenol A methyl ether
(3,5-Dibromo-4-methoxyphenyl) sulfone
2,2-Bis(4-acetoxy-3,5-dibromophenyl)propane
2,2-Bis[3,5-dibromo-4-(2-hydroxyethoxy)phenyl]propane
2,2-Bis(3,5-dibromo-4-allyloxyphenyl)propane
2,2’,6,6’-Tetrabromobisphenol A diacrylate
2,2’,6,6’-Tetrabromobisphenol A diglycidyl ether
Tetrabromobisphenol A bispropanoate
1,2-Bis(2,4,6-tribromophenoxy)ethane
Tetrabromobisphenol A bis(2-hydroxyethyl)ether bisacrylate

Compound name
Octabromotrimethylphenyl indane
4,5,6,7-Tetrabromo-1,1,3-trimethyl-3-(2,3,4,5-tetrabromophenyl)-2,3-dihydro-1H-indene
Tetrabromobisphenol A bis(2,3-dibromopropyl) ether
N,N'-Ethylenebis(tetrabromophthalimide)
4,4’-Bis(2,3-dibromopropoxy)-3,3’,5,5’-tetrabromodiphenyl sulfone
Decabromodiphenyl ethane
Decabromodibenzyl ether
Bis(pentabromophenoxy)benzene
5-(Tetrabromophenyl)-1,2,3,4,7,7-hexachloro-2-norbornene
1,2,5,6-Tetrabromocyclooctane
Hexabromocyclodecane
1,2,5,6,9,10-Hexabromocyclododecane
1,3-Bis(2,3-dibromopropyl)-5-allyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione
1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione
1,3,5-Tris(2,3-dibromopropyl) isocyanurate
1,3,5-Tris(2,3-dibromopropyl)-2,4,6-trioxohexahydrotriazine
Tris(2,4,6-tribromophenoxy)-s-triazine
Tris(tribromoneopentyl) phosphate
Tris(2,3-dibromopropyl) phosphate
Dibromoneopentyl glycol
Tribromoneopentyl alcohol

Table 1.3 Commercially available flame retardants (32).

Trade name	**Supplier**	**Composition**
Apyral 60CD	Nabaltec	Aluminum hydroxide
Sidistar T 120	Elkem	Amorphous silicon dioxide
UltraCarb LH15	LKAB Minerals	Huntite + hydromagnesite
Exolit AP 422	Clariant	Ammonium poly(phosphate)
Exolit OP 1230	Clariant	Aluminum diethylphosphinate
Exolit AP 750	Clariant	APP-based intumescent system
Aflammit PPN 978	Thor	APP-based multicomponent intumescent system, unmeltable
Aflammit PPN 923	Thor	APP-based intumescent multicomponent system, meltable
Aflammit PPN 903	Thor	P/N-based intumescent system
Masteret 15460 B2XF	Italmatch Chemicals	60% red phosphorus in PP
NORD-MIN 503	NRC	Expandable graphite
Safire 400	Floridienne Chimie	Melamine poly(zinc phosphate)
Uniplex FRX 44-94	Lanxess	Ethylenediamine-*o*-phosphate + melamine

Trade name	Supplier	Composition
Charex 44PSS	Nanops	Quaternary ammonium/siloxane treated montmorillonite
LS-8980	Shin-Etsu Silicone	Silicone
Charmax LS-MOM		Melamine octamolybdate

1.3 Chlorine-Containing Materials

1.3.1 HET Acid

HET acid is also known as chlorendic anhydride. In particular, chlorendic anhydride is the Diels-Alder adduct of hexachlorocyclopentadiene and maleic anhydride. HET acid is shown in Figure 1.1.

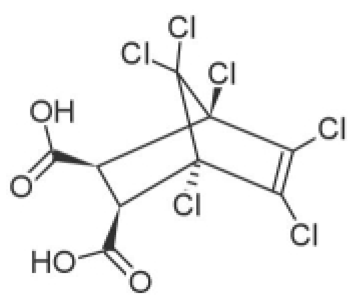

Figure 1.1 HET acid.

Chlorendic acid and chlorendic anhydride are used as reactive flame retardants, i.e., are built into the polymeric backbone, in polyester resins and as plasticizers for electrical systems and paints. Chlorendic acid is fairly persistent in soil. It has been found in landfill leachate in amounts up to 455 mgl^{-1}.

After oral and intravenous administration of radioactive labeled chlorendic acid to rats, the substance is rapidly distributed throughout the body and rapidly metabolized. Chlorendic acid has been reported to exert toxic effects on algae in concentrations of 250 mgl^{-1}.

In summary, these chemicals seem to have a low acute and subacute oral toxicity, although they are dermal, eye and respiratory irritants. From the results of long-term toxicity and carcinogenicity studies on rats and mice, it has been concluded that chlorendic acid induces tumors in rats and mice. Therefore, a carcinogenic potential is suspected. However, a full hazard assessment for humans and the environment cannot be made in view of the lack of data (33).

1.3.2 Dechlorane Plus

Dechlorane Plus is a highly chlorinated flame retardant (34). Dechlorane Plus is shown in Figure 1.2.

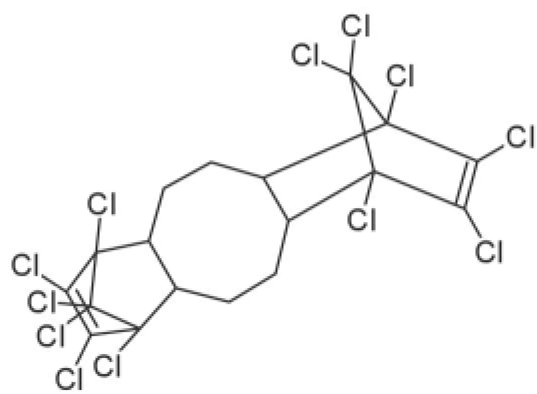

Figure 1.2 Dechlorane Plus.

Dechlorane Plus is a high production volume, chlorinated flame retardant (31). Despite its long production history, it has only recently been found in the environment. Although Dechlorane Plus has been used as a polychlorinated flame retardant for almost half a century, its detection in the environment was not reported until 2006 (35).