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Flame Retardants for Plastics and Textiles

Practical Applications

Sample Chapter 3:
Polystyrenes and Thermoplastic Styrene Copolymers

3 Polystyrenes and Thermoplastic Styrene Copolymers

3.1 Introduction

In the present chapter, we will cover each main type of styrenic, including high impact polystyrene and foamed polystyrene. Styrene-butadiene elastomers are discussed in the chapter on polyolefins and diene elastomers. Other reviews on styrenic flame retardancy published in recent years have encompassed the theory as well as mixing and test methods, rather than focusing on the retardant chemicals [1, 2]. The present authors have reviewed this topic with inclusion of theory and academic or non-commercialized industrial work [3].

3.2 General Comments on the Fire Properties of Styrenic Polymers

Polystyrene and its copolymers have the tendency to depolymerize when exposed to fire temperatures, and the volatile products are materials of high fuel value, namely styrene monomer, styrene dimers and related hydrocarbons such as benzene, lower-alkylbenzenes, and a few percent of oxygen-containing related aromatics [2]. Polystyrenes, unless blended with char-formers, by themselves form little or no char [4]. The volatiles burn with copious soot formation. In the vicinity of a polystyrene fire, visibility can be nil. Moreover, while depolymerization is taking place, melt flow and drip are also occurring, and the drips may be capable of igniting other flammable objects. If flaming drips are allowed by the test standard, as in the UL-94 V-2 rating, then the dripping may actually be useful to meet flame retardancy requirements.

It is possible to retard the vapor phase combustion reaction by means of additives which reach the flame zone. These will be discussed in more detail below. For many uses of styrenics, especially electrical equipment, the requirements are to prevent a small source of ignition, such as a hot or sparking wire, from igniting the item, or if ignited, causing it to self-extinguish quickly. The UL 94 test is the dominant one in the US and indeed in much of the world, although other small scale tests are also significant.

Styrenic polymers that will be discussed in this chapter include polystyrene itself, the copolymers with other vinyl monomers such as acrylonitrile and butadiene, and the impact modified (high impact, HIPS) which is generally a grafted blend of a rubbery polymer.

Styrenic polymers fall into several main subclasses: polystyrene itself as molding resin; high impact (rubber modified) styrene copolymers (two main subclasses: HIPS and ABS), and expandable polystyrene (foam). Two other types of styrenic polymers, namely, the blends of HIPS with PPO and the blends of ABS with polycarbonates, have their own combustion characteristics, mainly because of the char-forming PPO or PC components, therefore we are discussing them elsewhere in this book.

Where properties of the additive or formulation are stated without reference, the information was taken from the manufacturers' product literature.

3.3   Crystal Polystyrene

This is nearly pure polystyrene and is primarily used in food containers, compact disk boxes, and miscellaneous housewares where flame retardancy is not required. Where flame retardancy is required, a soluble bromine compound is usually used, typically hexabromocyclododecane. A recent patent [5] also suggests the use of pentabromobenzyl bromide.

3.4   Expandable Polystyrene and Extruded Polystyrene Foam

There are two main technologies used to make polystyrene foams. One, expanded polystyrene (EPS) involves the preparation of polystyrene beads containing a blowing agent, typically a lower alkane, the beads are then placed in a mold or void to be filled, and expanded by heat. Extruded polystyrene foam (XPS) involves the expansion of a melt, containing the blowing agent and any other desired additives such as a flame retardant, through a slotted die from whence it expands. The processing temperature is somewhat higher for XPS than for EPS so that a somewhat higher stability requirement is imposed on the flame retardant system for XPS. It is convenient to add the flame retardant to the styrene before polymerization, but it must not interfere with polymerization and cause a high concentration of residual styrene, or, in the case of XPS, it must have enough thermal stability to survive the extrusion process.

Expanded polystyrene foam is a major material used for insulation of buildings, refrigerators, and the like. The maximum flame-spread and smoke-developed ratings at a maximum 4″ (102 mm) thickness and 4.0 lbs./cu.ft.(64 kg/m^3) density are less than 25 and 450, respectively, as measured by the ASTM E-84 25-ft. tunnel. This and various other standards allow styrenic foam to melt and flow when exposed to fire, provided that the drips are not burning, and melt-flow can be exploited as a mode of flame retardancy. Because some pyrolysis to monomer and dimer takes place, aside from the flow of molten polymer out of the fire zone, a vapor-phase flame retardant is often needed. The patent literature shows that this retardant is almost always a brominated aliphatic compound which can readily release HBr (a vapor-phase flame retardant). At the relatively low processing temperatures for foamable polystyrenes, these aliphatic bromine compounds are generally stable enough. And, with fast enough HBr release, a synergist such as antimony trioxide is not needed and generally not used.

The leading brominated additives actually used are as follows.

3.4.1   Hexabromocyclododecane (HBCD)

HBCD (Albemarle's Saytex HP900 powder or granules, HP900HG granules, and 9006L ground particles or ICL-IP's FR-1206), made by addition of bromine to cyclododecatriene, a product of catalyzed trimerization of butadiene. It is a mixture of three diastereoisomers, with one (the gamma-isomer) comprising 80 % of the technical product. The structures

have been elucidated by nmr and X-ray crystallography [6]. There are some differences in stability of the isomers [7] and presumably the manufacturers have tried to optimize the process to favor stability at processing temperatures. This matter is complicated by the fact that there is a thermal isomerization process which interconverts between diastereoisomers [8] and this conversion occurs during compounding. Generally, HBCD is not used with antimony oxide.

There are many special grades of hexabromocyclododecane. Saytex HP900SG and BC-70HS are blended with stabilizers for use in XPS and injection molded HIPS, and allow better color stability of the resin. BC-70HS appears to be more highly stabilized and is targeted for use in HIPS (see section below on HIPS). Some of the stabilizer systems for HBCD have been disclosed and claimed in patents, for example a combination of a dialkyltin dicarboxylate and a barium or cadmium carboxylate [9]. The use of a zeolite in the range of 0.6–1.2 %, optionally with a zinc salt of a fatty acid, is also patented as a means for stabilizing a HBCD formulation [10]. The systematic development of an optimized stabilized HBCD using two stabilizers is described by ICL Industrial Products (ICL-IP former Dead Sea Bromine Group) [11]. Other stabilizers mentioned [2] are metal hydroxides, metal oxides and hydrotalcite.

HBCD has shown bioaccumulation tendencies in the environment [12, 13]. A risk assessment under EU auspices is still underway as of 2008; a preliminary report was rather inconclusive [14]. No risk was identified for manufacturers or users. Brominated flame retardant industry is implementing Voluntary Emissions Control Action Program (VECAP) which helps decreasing further emission of HBCD in the environment [15]. Research by users and flame retardant manufacturers is underway to find substitutes.

Hexabromocyclododecane particles can be coated with a resin to make them insoluble in styrene, and can then be added into the styrene polymerization stage. The coating seems to improve the foam structure, reduces the water content of the foam, and improves dimensional stability [16].

3.4.2   Tetrabromocyclooctane

This compound is Albemarle's Saytex BC-48, made by addition of bromine to cyclooctadiene, a product of catalyzed dimerization of butadiene. This compound is more easily soluble in the polymer than hexabromocyclododecane and lower processing temperatures can be used, in the 150–160 °C range. It has found only minor usage, mainly in styrenic foams, textile coatings, solvent-based paints and hot-melt adhesives.

3.4.3   Dibromoethyldibromocyclohexane

It is Albemarle's Saytex BC-462 made by addition of bromine to vinylcyclohexene, a product of the Diels-Alder dimerization of butadiene. It also is more soluble in the polystyrene, and is used where the expandable polystyrene is processed in the 150–160 °C range. It is somewhat less volatile than tetrabromocyclooctane.

Thermal stabilization of brominated aliphatic or cycloaliphatic flame retardant additives for styrenics, exemplified by tetrabromocyclooctane or dibromoethyldibromocyclohexane

is shown to be accomplished by addition of a thermoplastic acrylate or methacrylate, in the 5–10 % range relative to the bromine compound. Optionally, hydrotalcite is also added [17].

3.4.4   Other Bromine Flame Retardants

Chloropentabromocyclohexane is made by addition of bromine to chlorobenzene (Dow 651).This was at one time a leading additive for expanded polystyrene foam, but appears to have been discontinued.

Certain other brominated compounds were in use for a time but appear to have been discontinued, such as cinnamalacetophenone tetrabromide [18]. A few other bromine compounds have been recommended for this use in patents. and, if the leading additive HBCD is viewed as an unfavorable risk, one or more of these may be revived. At this time, the authors are not aware of the current commercial use of these additives. For instance, hexabromohexene [19], 1,2-dibromoalkyl ketones [20], 1,1,2,3,4,4-hexabromo-2-butene [21], dialkyl tetrabromophthalate [22], bis(2,3-dibromopropyl) tetrabromophthalate [23], 2,4,6-tribromophenyl allyl ether [24] and bis(allyl ether) of tetrabromobisphenol A [25].

A more likely substitute for hexabromocyclododecane, judging from a series of Albemarle patent applications, is N-(2,3-dibromopropyl)-4,5-dibromotetrahydrophthalimide [26–28].

For a time, tris(2,3-dibromopropyl) phosphate was used, but this compound was shown to be a mutagen and was discontinued in the mid-1970s.

More recently, it was shown that non-brominated polystyrene can be blended with a flame retardant amount of a brominated anionic styrene polymer plus a bis(pentabromophenyl) ethane to make extruded flame retarded foam [29]. The use of a polymeric or oligomeric additive is often considered more environmentally benign than the use of migration-capable small molecular weight additives.

A substantial patent literature exists on the use of combinations of brominated additives in expandable polystyrene. Combinations of the usual bromoaliphatic flame retardant with a more thermally stable bromine compound with an aromatic, vinylic or neopentyl structure may permit a lower total loading of flame retardant [30].

3.4.5   The Flammability Effect of the Expanding Agent

The expanding agent is often a flammable hydrocarbon, such as pentane, and there is a problem in the use of ethyl chloride or other halogenated blowing agents. Some combinations of fluoro- or fluorochloroethanes with alkanes have been patented [31].

A patent to Hoechst [32] suggests that there may be need for a storage period of extruded polystyrene foam, depending on dimensions, before it will pass flammability tests, and they claim shortening this period by use of less than 1.9–3 % propane/butane mixture. It is not clear how general these constraints may be.

3.4.6   Synergists with Brominated Additives in Polystyrene Foam

Along with the brominated additive, certain synergists are used. An early example is 0.25–0.75 phr of an allyl ether, said to aid in the decomposition of the bromine compound

during burning [33]. The use of peroxy compounds or other free-radical-forming compounds with labile C—C, O—O or N=N bonds, to enhance the action of the brominated flame retardants has been known and used for a long time, since some early work of Dow [34–38]. An advantage in efficiency was claimed by applying the radical-generating synergist to the outside of the polystyrene particles while having the bromine compound distributed throughout [39]. Peroxides useful in this mode of synergism must not decompose at processing temperatures, but must decompose at the temperatures reached by the molten polymer when exposed to flame: examples are dicumyl peroxide (Hercules' Dicup R), 1,3-bis[2-t-butylperoxy)isopropyl]benzene (Akzo Nobel's Perkadox® 14) or 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (Arkema's Luperox 101). With care to feed the peroxide so as not to decompose it prematurely, combinations of HBCD with di-tert-butyl peroxide (Trigonox® B) or tert-butyl hydroperoxide (Trigonox® A80) can be used [40].

A non-peroxide synergist which can be used is one which undergoes C-C bond cleavage to produce tertiary-alkyl radicals, such as 2,3-dimethyl-2,3-diphenylbutane (Akzo Nobel's Perkadox® 30).

Another type of synergist to be used along with the usual brominated flame retardant is a waxy material such as a chloroparaffin, melting above the foaming temperature of the EPS, at about 0.1–2 % [41].

3.4.7   Phosphorus-Bromine Combinations in Polystyrene Foam

Combinations of HBCD with a wide variety of phosphorus compounds, with examples showing the use of triphenyl phosphate, were claimed by Dow as flame retardants permitting lower levels of bromine [42].

Combinations of HBCD (or many other Br additives) with triphenyl phosphate or with encapsulated red phosphorus are disclosed as flame retardants in foamed styrene copolymers with specified olefins [43]. In extruded styrenic foam, combinations of a halogenated flame retardant with a P—N compound (such as APP), various tetrazoles and triazines, boron compounds or phosphoric esters (such as triphenyl phosphate) are disclosed for the production of flame retardant foam with certain cell dimensions [44, 45].

Achievement of improved flame retardancy of a EPS while reducing the amount of HBCD to less than 2.5 % is made possible by the use of 0.1–4 % of a phosphorus co-additive, exemplified by triphenyl phosphate and various other phosphates, phosphonates, phosphinates, phosphines, phosphonium compounds or phosphine oxides [42].

3.4.8   Non-Bromine Systems in Polystyrene Foam

Alternatives to the bromine additives have been disclosed in the patent literature. Very high loadings of ATH, such as 150–250 phr, afford a flame retardant foam and it is surprising that densities lower than 100 g/l can be thus obtained. Further addition of phosphorus or brominated flame retardants is recommended to reach adequate flame retardancy [46].

The use of heat-set flame-resistant carbonaceous fibers derived from polyacrylonitrile or pitch has been claimed as a flame retardant method for foams, including polystyrene foams.

The fibers appear to collect at and protect the surface [47]. The use of carbonaceous particles or platelets is similarly disclosed by the same inventors in a later patent [48].

Graphite particles of 1–50 micron size can also be used, particularly in combination with a high percentage Br additive, such as HBCD, to obtain flame retardant EPS foam with density of equal or less than 35 g/l [49]. Expandable graphite plus a halogenated flame retardant and optionally antimony oxide are disclosed for flame retarding EPS [50].

A combination of 1–12 % expanded graphite and a phosphorus flame retardant (exemplified by red phosphorus and/or triphenyl phosphate) can enable EPS of 20–200 g/l and cross-sectional area of at least 50 cm^2, to be self-extinguishing [51].

A combination of less than 2 % elemental sulfur plus a phosphorus additive (exemplified by triphenyl phosphate, triphenylphosphine oxide or sulfide, or hexaphenoxytriphosphazene) afford higher oxygen indices, up to 26, in polystyrene such as the type used in foam production [52].

A 2008 patent application [53] with many Dow inventors covers a wide range of thiophosphates and dithiophosphates, most examples having neopentylene rings, such as
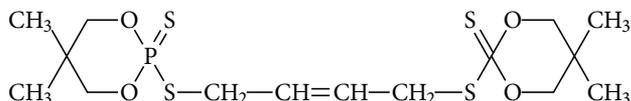
The applications exemplified are in foamed polystyrene.

Extruded polystyrene foam can be made flame retardant by use of a blend with an epoxy resin containing reacted-in DOPO and phosphoric acid [54]. Another way of increasing flame resistance of EPS is to make a board with a flame-resistant barrier, such as a coating, laminate or foil [55].

A novel way of making a flame retardant polystyrene foam is to coat the beads before expansion with a boric acid plus a binder. After expanding, the boric acid forms a vitreous coating when the foam is exposed to flame [56].

A patent application by Owens-Corning inventors [57] claims that nanoclays such as sodium montmorillonite in a carrier such as water are useful to improve fire peformance of a foamed polystyrene.

3.4.9   The Recommended Fire-Safe Use of Extruded Polystyrene Insulation

Ample directions are available from Dow and other manufacturers regarding the safe use of polystyrene foam insulation. Some of the key points are:

Polystyrene foam boards should be separated from the interior of a building by a code-compliant thermal barrier such as ½″ thick (12.7 mm) gypsum wall board applied with code-compliant fasteners. More details as to the various styrene foam insulation boards and their recommended applications are available from Dow and ICC [58].

Expanded polystyrene foam is highly useful for rooftop applications, withstanding foot traffic and weathering. In order to be used directly on steel roof decks, the proposed configuration

must pass UL1256 or FM4450. Large scale tests have been done by Underwriters Laboratories with favorable results [59].

At least one application has had an adverse fire experience and is advised against. The US Coast Guard recommends that foamed polystyrene insulation not be used in commercial fishing vessels for example as engine box covers, since in this high heat location, the foam could ignite and spread fire rapidly with dense smoke [60].

3.5   High Impact Polystyrene

Polystyrene produced by polymerization, with some grafting, in the presence of rubber latex particles, is known as "high impact polystyrene" (HIPS). HIPS is used widely in equipment enclosures such as TV sets, computers, business equipment housings, and other electrical equipments. The TV set use is probably the largest application. In the US, this application requires a UL-94 V-0 rating, whereas in Europe a typical level of flame retardancy is about in the range of a UL-94 HB [61]. Recent publicity about the high rate of fire deaths from TV fires in Europe (contrasting with a low rate in the US, where fire standards for TV sets are more stringent) may stimulate a higher level of flame retardancy in Europe. Flame retardant HIPS has an attractive balance of mechanical properties, processability and cost.

3.5.1   Bromine-Containing Flame Retardants for HIPS

Approximately 10 wt.% Br in combination with antimony oxide is required to pass UL94 V-0 requirements. The exact amount will vary with the rubber content of the HIPS. HIPS is usually processed at 220–230 °C, so thermally stable bromine compounds are favored.

3.5.1.1   *Decabromodiphenyl Oxide (Ether) in HIPS*

DBDPO, Albemarle's Saytex 102, ICL-IP's FR-1210, Chemtura's DE-83 (also available from Chinese manufacturers) is the most widely used flame retardant for HIPS. Its high bromine content (83 %) and low cost make it a favorite choice. It is a stable solid up to its melting point of 305 °C. It is soluble in hot molten HIPS and only partly phase-separates on cooling, thus reduces impact only slightly but lowers HDT somewhat more [62]. It does have a tendency to yellow when exposed to ultraviolet light (such as sunlight) and therefore is mainly used in painted or dark pigmented plastic. DBDPO is typically used at about 12 % with about 4–5 % antimony trioxide as a synergist. A formulation in HIPS with 6 % rubber content with 12 % DBDPO and 5 % antimony trioxide is reported to have a LOI of 25.3 and a UL-94 rating of V-0, notched impact of 43 kJ/m (without fire retardant., 85.9) and Vicat softening point of 91.5 (without fire retardant, 92.5).

This photosensitivity not only causes discoloration but interaction of DBDPO (and in the same way, tetrabromobisphenol A) with wavelengths in the 260–280 and 300 nm range can also provoke polymer chain degradation to some degree [63]. Light stabilizers can make some improvement; in one extensive study [64], 0.25 % of a chlorobenzotriazole photostabilizer

plus 0.25 % of a particular hindered phenol radical inhibitor were found most effective in preventing darkening, and could be further boosted by an epoxy cresol novolac or zinc stearate or tin maleate. A hindered amine photostabilizer also was effective in such combinations.

However, the use of dark pigments is the most effective and economical means. If this approach is unsuitable, then it may be necessary to turn to the more expensive more-light-stable brominated additives such as Albemarle's ethylenebis(tetrabromophthalimide) (BT-93), to light-stabilized Saytex® 8010, to ICL-IP's tris (2,4,6 tribromophenoxy) triazine or to tribromophenyl end capped brominated epoxy oligomers discussed further below.

DBDPO has been under attack as a hypothetical environmental problem (to a large extent "guilt by association" with pentabromodiphenyl oxide which does migrate badly). However, a recently issued 10-year study done for the EU concluded that DBDPO does not appear to present a significant risk to humans or to the environment [65]. Further support for this position is based on studies done by the US EPA and by the US National Academy of Science. A further consequence of this recognition is that DBDPO was exempted from the EU Directive 2002/95/EC on the Restriction of Hazardous Substances (RoHS) used in electronic and electrical applications. This conclusion was disputed (2006) by Denmark and various Green organizations. Arguments are presented pointing to some evidence of degradation in the environment to less innocuous lower brominated diphenyl ethers. In 2008, a European court ruling has the effect of banning the electrical and electronic use of DBDPO in the EU after July 1, 2008 [66].

3.5.1.2   1,2-Bis(pentabromophenyl)ethane

It is Albemarle's Saytex® 8010 and Chemtura's Firemaster® 2100. It is a high melting solid (melting point 350 °C) which has a use pattern similar to that of DBDPO. This is useful for customers who wish to have formulations totally free of all brominated diphenyl oxides. It has some other advantages such as superior UV resistance relative to DBDPO and low blooming tendency. It is suitable for HIPS systems where recycling is anticipated. A disadvantage of Saytex 8010 relative to DBDPO is somewhat poorer impact in HIPS, but this can be corrected for by either adding an impact modifier or starting with a higher impact grade of HIPS.

3.5.1.3   2,4,6-Tris(2,4,6-Tribromophenoxy)-1,3,5-Triazine (ICL-IP's FR-245)

This compound is also a high melting (230 °C) but melt-blendable solid with a pattern of utility rather similar to DBDPO but with advantages of better melt flow, impact and light stability [67, 68]. Some comparative data is shown in Table 3.1.
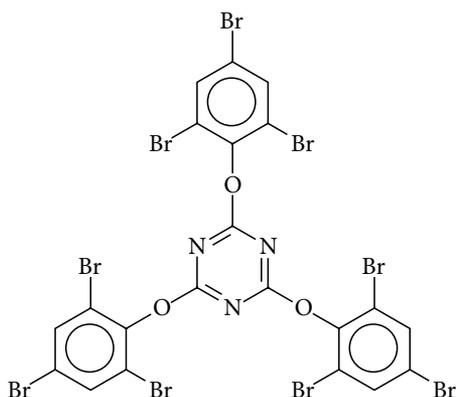
Table 3.1 V-0 and V-2 Formulations of FR-245 in HIPS

Composition (wt. %)	HIPS, no FR	HIPS V2	HIPS V0
HIPS	100	88.4	77.8
FR-245	—	8.9	14.9
Sb_2O_3	—	2.4	4
UV absorber	—	0.3	0.3
TiO_2	—	—	3
Bromine content %	—	6	10
FR UL 94	not rated	V2	V0
GWT 960C	fail	pass	pass
Melt flow, g^{10} min 200 °C 5 kg	5	8	15
Maximum strength, MPa	19	21	22
Elongation at break, %	61	53	47
Modulus, MPa	1600	1700	1800
Izod notched impact, J/m	130	120	115
HDT (1.82 MPa, annealed)	78	76	76
UV stab., ΔE 300 hr xenon	8	10	11

From ref. [66]

A combination of this melt-blendable flame retardant with a filler-like flame retardant such as bis(pentabromodiphenyl)ethane enables molding of large dimension housings of electronic equipment made of HIPS, without the problems of melt flow and poor impact (Table 3.2).

Another advantageous combination of FR-245, as claimed by Dai Ichi, is with tris(2,3-dibro-mopropoxy) cyanurate [69].

Table 3.2 Melt Flow and Impact Properties of FR-245 Based HIPS

Flame retardant	MFI at 200 °C, 5 kg	Gardner Impact kg-cm
FR-245	10	100
1:1 FR-245/Saytex 8010	8	81
Saytex® 8010	5	62

3.5.1.4   Modified Brominated Epoxy Oligomers (MBEO)

These are melt-blendable additives especially suitable for HIPS and ABS They provide excellent flow properties with good light stability. However, for demanding applications with large dimensions, high impact styrenic copolymers flame retarded with MBEO's have rather inadequate impact. Partially replacing MBEO with FR-245 retains the good melt flow but greatly improves the impact.

3.5.1.5   Hexabromocyclododecane

HBCD of the ordinary grade suitable for expandable polystyrene is not quite stable enough for the temperatures commonly encountered in extruding and injection molding, typically up to 220 °C. A stabilized version of HBCD is available from Albemarle as Saytex BC-70HS; it has been targeted for use in injection molded HIPS that must pass the IEC 695-2-1/2 glow wire test from 750 to 960 °C. At 5–7 % loading, without antimony oxide, injection molded HIPS can pass this glow wire test with burning times of less than 10 seconds, and can reach UL-94 V2 rating (1.6 and 3.2 mm). This additive also can be used in crystal polystyrene. Another stabilized version of HBCD is Albemarle's Saytex HP900SG. As mentioned, a risk assessment on hexabromocyclododecane is underway (2005-8) under EU auspices.

3.5.1.6   Tetrabromobisphenol A

TBBA (Albemarle Saytex RB-100 or CP-2000 or ICL-IP's FR-1524) is a lower melting solid, often used as a reactant in epoxies or polycarbonates, but also used as an additive to a limited extent in HIPS and mostly in ABS. Because of its lower melting point, it melts into the polymer, aiding melt flow considerably, and allowing impact to be maintained. Another advantage is low cost. On the negative side, it is poor on color stability and tends to be used only in dark formulations.

3.5.1.7   Tetrabromobisphenol A Bis(2,3-Dibromopropyl Ether)

This product (Albemarle Saytex HP800A or the granular version HP800AG, and ICL-IP's FR-720) is a relatively low melting solid, melting point 108–120 °C, rather soluble in HIPS and suitable for reaching UL-94 V-2 ratings. It has minimal effect on impact strength. Probably, its larger uses are in polypropylene.

Another stable aliphatic bromine compound (actually a blend) with 56 % Br and melt range of 187–240 °C is available as Albemarle's BC-56HS. This has good UV resistance and good

thermal stability, a favorable feature if recycling is anticipated. A recent Albemarle patent application gives a clue that the blend may be a brominated cycloalkane with an acrylate polymer which acts as a stabilizer [17].

3.5.1.8   1,2-Ethylenebis(tetrabromophthalimide)

This additive, Albemarle BT-93, is used when discoloration must be minimized. UV stability is its outstanding feature, but it has a slight yellow color to begin with. A colorless version is a purified grade, BT-93W. BT-93 has a melting point above the processing temperature of HIPS and is quite insoluble in HIPS. It acts like an inert filler, and therefore tends not to lower HDT, but on the other hand, is somewhat detrimental to impact strength [6262]. An alternative way to achieve good UV stability in a flame retardant styrenic is to use FR-245 or Saytex® 8010 with a good UV stabilizer system.

3.5.1.9   Comparison of Typical Formulations of Brominated Flame Retardants in HIPS

Table 3.3 shows a comparison of several of the above-discussed bromine-based flame retardants for HIPS.

Table 3.3   Performance of Some Brominated Flame Retardants in HIPS

Additive	Control	BT-93 ethylenebis (tetra-bromo-phthalimide)	8010 bis(pentabromo-phenyl)ethane	CP-2000 tetrabromo-bisphenol A
Flame Retardant:	0.0	18.0	14.6	20.4
% Antimony trioxide	0.0	4.0	4.0	4.0
% Bromine	0.0	12.1	12.0	12.1
Physical properties				
Izod Impact 3.2 mm, ft-lb/in	3.3	0.6	2.0	1.7
Izod Impact 3.2 mm, J/cm	176.	32	107	91
DTUL 3.2 mm °C	79	82	80	68
MFI 230 °C/3800 g	5.8	3.3	2.6	14.0
UV Stability				
100 hr Xenon arc	7.9	7.3	21.1	nd (bad)
300 hr Xenon arc	9.2	9.4	25.3	34.3

(from Albemarle)

Various other polybrominated additives are shown in recent patents to be useful in HIPS, bis(pentabromobenzyl) ether for example [70].

3.5.1.10   The Dripping Problem and Antidripping Additives

Many thermoplastics, and HIPS is no exception, can have flaming drips. In some end-products, it is acceptable to have drips if they are non-flaming, but flaming drips can be tolerated only in those products allowed to pass UL-94 with a V-2 rating. The contribution to fire safety of V-2 standards is controversial. Where the stricter V-1 or V-0 standards are required, means must usually be found to prevent drip. The addition of very small amounts of polytetrafluoroethylene (PTFE) powder, at loadings generally in the 0.01–0.1 % range, are often effective, probably because of a rheological effect. Uniform and continuous mixing of such small quantities of a powder is challenging.

As a means to reduce dripping, where it cannot be allowed, flame retardant systems involving modified grades of brominated epoxy polymer with built-in antidripping properties ICL-IP's SaFRon 5500 series may be used. Incorporating the antidrip additive allows higher fire retardant efficiency so that lower loadings can be used, allowing adequate impact strength and also good light stability. A typical non-dripping V-0 formulation is 82 % HIPS, 13.8 % SaFRon 5526, 2.5 % Sb_2O_3, 2.5 % TiO_2 and 1 % UV stabilizer [71]. ICL-IP discontinued SaFRon 5526 and replaced it by SaFRon 5531 which is similar.

3.5.1.11   The Effect of Brominated Flame Retardants and Antimony Oxide on Mechanical Properties of HIPS

An academic study [72] showed that the impact strength of HIPS declined gradually and approximately linearly as the loading of DBDPO was increased. Antimony oxide, used as a synergist, did likewise, but it was found that Sb_2O_3 particles at 0.08 micron size did not reduce impact strength, but in the range of 0.5–1.2 microns, severe impact strength loss occurred. However, at 4–10 microns, once again, no impact strength loss occurred. It was postulated that these larger particles served as craze terminators.

A study of the effect of particle size, using representative solid additives showed that impact strength of a polystyrene can even be increased by particles several microns in diameter because of formation of voids, peeling layers and extension of crazes [73]. However, some compounders believe it best to have smaller particles, and in the case of antimony oxide, often the flame retardant effect is improved by using smaller particles. The detrimental effect of powdered additives on impact strength can also be at least partially overcome by starting with a "superhigh" impact plastic, or adding an impact modifier, such as a chlorinated polyethylene (which also contributes to flame retardancy), a thermoplastic styrene-butadiene-styrene block polymer, or ethylene-vinyl acetate. Where the use of very fine particles adversely influences processing characteristics, a surface-modifying agent ("coupling agent") may help.

Liquid flame retardants generally do not lessen the impact strength and may, in fact, often improve it.

A useful study was done at Monsanto addressing the quantitative relationship of solubility of decabromodiphenyl oxide in HIPS to the impact and processing characteristics [74].

Regarding electrical properties, usually the bromine-antimony systems have somewhat decreased loss factor, and may be prone to leakage currents and diminished arc resistance, particularly on aging [2].

3.5.2   Non-Halogen Flame Retardants for HIPS

This is a challenge because of the need to avoid spoiling impact strength, heat distortion temperature and cost. Noting that UL94 V0 can be obtained for PPO-HIPS, researchers have studied the use of smaller loadings of PPO plus the char-forming phosphates. This system can also be aided by adding char-forming phenolic novolacs [75] or by adding small amounts of "nanoclay" (an exfoliated layered montmorillonite). For example, a formulation of 80 parts by weight of HIPS, 20 parts PPO, 20 parts of tetraphenyl resorcinol diphosphate and 3 parts of quaternary amine-treated montmorillonite can give a V-0 rating [76].

A patent shows the use of expandable graphite plus a phosphorus flame retardant, such as resorcinol bis(diphenyl phosphate) or triphenyl phosphate, plus a co-additive, such as 12 wt. % of a polycarbonate, to prevent migration of the phosphorus compound to the surface of HIPS [77].

A US patent application [78] by Israeli inventors shows HIPS flame retarded to V-0 by 15 % expandable graphite and 15 % melamine.

A US patent application [79] by Cheil (Korea) shows HIPS flame retarded by a combination of an aryl phosphate such as PX200 and a phosphonate such as Amgard 1045.

3.6   Flame Retarded Acrylonitrile-Butadiene-Styrene Copolymers (ABS)

Compared to HIPS, ABS is more costly, has somewhat higher heat distortion temperature, substantially greater impact strength and more solvent resistance. It is easily molded, has high gloss, and combines high toughness with flexibility. ABS is available in a wide range of properties. It is used in automotive parts, electrical apparatus and various consumer disposable products.

Non-flame-retarded ABS pipe (Schedule 40 pipe), can be used in many building construction applications, such as in "non-rated construction" (single family dwellings), and, if properly installed, even in some fire-rated construction. Producers of ABS pipe point out that it starts to melt and collapse long before it ignites. In fire-rated construction, NBS tests show that it will not spread fire or smoke where it penetrates a non-combustible wall if properly installed. Firestop caulks, sealants collars and the like with an adequate F rating in accordance with ASTM E-814 must be used. It is pointed out, also by the ABS pipe manufacturers, that in the installation of the competing metallic piping, the plumbers' torch and lead pot actually pose a serious hazard.

However, the use of non-flame-retardant ABS pipe in construction is not without controversy, particularly where codes require materials with a E-84 tunnel rating of less than 25. Favorable conclusions regarding this application have been published in the US [80] but unfavorable conclusions in Canada [81].

Where flame retardancy is required, namely in electronic equipment enclosures, brominated additives are most commonly used. It is important to find a suitable balance of impact strength, heat distortion temperature, melt-flow index, color stability, and cost. Usually tensile strength and flex properties are not much affected by the additives.

3.6.1   Brominated Flame Retardants Used in ABS

The leading flame retardant is tetrabromobisphenol A (TBBA, Albemarle RB-100 or CP-2000, Chemtura BA-59P, ICL-IP's FR-1524). This is the largest volume bromine flame retardant, but a major part of it is used in epoxy resins as a reactive. Its use as an additive in ABS, often synergized by Sb_2O_3, is favored by low price and processing ease. It can be processed in ABS up to about 220 °C. It is not recommended where high impact or high heat distortion temperature are needed. About 4 % of the plastics in automobiles (2003 information) is ABS, used in dashboard and light fixtures [82].

The use of tetrabromobisphenol A has been the subject of an eight year evaluation under the EU Risk Assessment procedure which reviewed over 460 studies. The human health report was finalized in May 2005 and concluded that no health effects have been identified. Some environmenal risk was noted with free TBBA (*i. e.,* TBBA not bound in epoxy resin) in sludge applied to agricultural soil, an unlikely occurrence [83].

Tetrabromobisphenol A can only be used in darker shades of ABS or in painted products because of its photoinstability. A study of it in polystyrene showed that wavelengths of 260–280 and 300 nm were most active and caused not only color change but some polymer main chain cleavage [84].

Some synergism has recently been claimed to occur in ABS flame retarded by tetrabromobisphenol A and antimony oxide by the further addition of a styrene-maleic anhydride copolymer grafted with a titanate coupling agent LICA 44 (Kenrich Chemical Co.) [85].

Another highly effective and commercially-used flame retardant for ABS is bis(tribromophenoxy)ethane (more precisely, 1,2-bis(2,4,6-tribromophenoxy)ethane) (Chemtura's Firemaster FF-680). This solid, melting point 223–228 °C, provides a good balance of impact strength and heat deflection temperature, and low cost. However, it does have some tendency to bloom.

Another ether made from 2,4,6-tribromophenol is the tris(tribromophenoxy)cyanurate (2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine)(ICL-IP's (former Dead Sea Bromine Group) FR-245), discussed above in connection with HIPS. This solid, melting point 230 °C, with 67 % Br, has high melt flow during injection molding, very low vapor pressure and therefore it is free of any tendency to bloom and has good UV stability, good impact and heat distortion temperature in ABS. Formulations using FR-245 in ABS are shown in Table 3.4.

FR-245 has a very favorable impact strength rating, over twice as high, *vs.* bis(pentabromophenyl)ethane (Albemarle 8010) by the falling ball test.

A family of oligomeric polyethers made from tetrabromobisphenol-A and epichlorohydrin has been developed by ICL-IP. The preferred one for use in ABS is F-2016, which is a solid melting at 105–115 °C. Being rather high in molecular weight and having negligible volatility, it is non-blooming. It also has good UV stability. Some of these oligomers have a problem with metal adhesion, which can be overcome by use of a tribromophenol-end-capped version,

Table 3.4 V-0 and V-2 Formulation of FR-245 in ABS

Composition (wt.%)	ABS, no FR	ABS V2	ABS V0
ABS	100	87.5	79.4
FR-245	—	8.6	14,3
Sb_2O_3	—	3.6	6
UV absorber	—	0.3	0.3
TiO_2	—	—	3
Bromine content %	—	6	10
FR UL 94	not rated	V2	V0
GWT 960 °C	fail	pass	pass
Melt flow g^{10} min 220 °C 10 kg	10	19	21
Maximum strength, MPa	44	44	43
Elongation at break, %	19	13	6.3
Modulus, MPa	2100	2300	2200
Izod notched impact, J/m	211	163	131
HDT (1.82 MPa, annealed)	93	93	93
UV stab., ΔE 300 hr xenon	4	7	9

From ref. [66]

F-3020, which also has improved UV stability. On the other hand, F-3020 does cause some loss of Gardner impact.

Some proprietary modified grades of these tribromophenol-end-capped polyethers marketed under the SaFRon 5500 series trade name, have built-in antidripping properties, better Gardner impact, and even some enhancement of flame retardant properties allowing lower bromine and antimony loadings. A typical V-0 formulation in ABS would be 75.7 % ABS, 17,45 SaFRon 5526, 3.4 % Sb_2O_3, 2.5 % TiO_2 and 1 % UV stabilizer [86]. Another variety is SaFRon 5520 which is recommended for UV stable ABS and enables more than a five-fold increase in Gardner impact compared to F-3020 [87]. Recently ICL-IP discontinued SaFRon 5520 and 5526, but it is offering SaFRon 5531 with similar properties.

A patent application by Korean inventors [88] suggest that with a variety of brominated flame retardants (exemplified by decabromodiphenylethane) with antimony oxide in ABS, the use of a small amount in the 1 phr range of a stearate or ethylenebisstearamide is beneficial to flame retardancy by drip enhancement.

Where high light stability (color stability) is needed, the additive of preference is ethylenebis(tetrabromophthalimide), Albemarle's BT-93, or even better, BT-93W.which is a purified version of BT-93. Besides good light stability, these additives resist bloom and plate-out. They do tend to reduce impact, and may be compensated for by impact modifiers. They are also more costly than most other ABS flame retardant additives.

A comparison of some of the principal brominated flame retardants used in ABS is shown in Table 3.5.

Table 3.5 Performance of Some Brominated Flame Retardants in ABS

Component	Tetrabromo-bisphenol A	Brominated epoxy oligomer F-2016	End capped brominated epoxy oligomer F-3020	Tris (tribromophenyl) cyanurate FR-245
ABS	76.8	73.7	75.9	79.4
Flame retardant	17.2	20	17.8	14.3
Antimony trioxide	6	6	6	6
UV absorber	—	0.3	0.3	0.3
Properties:				
UL-94 class (1.6 mm)	V-0	V-0	V-0	V-0
MFI (220, 10 kg) g^{10}min	52	39	28	21
Tensile max., MPa	39	41	41	43
Elongation at break, %	6.7	2.5	3.5	6.3
Modulus, MPa	2 400	2 400	2 300	2 300
HDT, °C	86	91	91	93
Notched Izod, J/m 23 °C	100	65	92	131
UV stability, ΔE 300 hrs	— (poor)	3	8	9

Data from [82]

3.6.2   Chlorinated Additives for ABS or HIPS

A unique chloroparaffin with a high softening point, 160 °C, Dover's Chlorez 760, can be used in styrenics, such as ABS and HIPS, but processing temperature should be 220 °C or less. A small amount of chlorinated polyethylene can also be helpful as a processing aid and flame retardant adjuvant in many styrenic systems flame retarded with bromine additives.

A high melting cyclic chlorohydrocarbon, Oxychem's Dechlorane Plus, melting point 350 °C (with decomposition) and a chlorine content of 65 %, is useful in HIPS and ABS to meet a UL94 V-0 rating, and has its advantage in respect to low smoke and better photochemical stability than decabromodiphenyl ether. It can be synergized with antimony oxide but for lowest smoke, ferric oxide or zinc oxide are preferred [89]. Also, Dechlorane Plus can be used in a moderately synergistic combination with a bromine additive plus antimony oxide. A V-0 rating at 1.6 mm in HIPS uses 78 % HIPS, 9 % Dechlorane Plus, 10 % of a brominated epoxy additive, 3 % of antimony trioxide; the formulation gives a Notched Izod impact of 89 J/m; interestingly, the addition of 1 % of a silicone-silicate such as GE's SFR-100 raises the impact to 106 J/m [90–92]. Dechlorane Plus formulations tend to produce some char which may show afterglow; this can be overcome by including some ammonium polyphosphate or ATH in the formulation.

A significant commercial use for Dechlorane Plus is in light-colored HIPS television enclosures, used with antimony oxide. An improved formulation, in respect to impact and afterglow, uses a combination of 90 % Dechlorane Plus and 10 % chlorowax (70 % Cl). An advantageous

formulation uses 70.9 % HIPS, 18 % of a 90 % Dechlorane Plus-10 % chlorowax mix, 4 % Sb_2O_3, 5 % SBS impact modifier, and 2 % SFR-100 silicone and 0.1 % Teflon gives a V-0 at 1.6 mm and a notched Izod of 134 J/m [89].

Formulations of ABS designed to optimize particular product properties can be achieved by combinations of the various halogenated flame retardant additives; in summary, tetra-bromobisphenol A is favorable for flowability, but inferior for impact, HDT and stability), Dechlorane Plus is favorable for HDT and stability but inferior for impact and flowability, Fire-master FF-680 is favorable for impact strength but inferior for HDT, and brominated epoxy is favorable for HDT and stability but inferior for impact [91]. Acceptable compromises may be attainable by use of combinations.

3.6.3   Non-Halogen Flame Retardants for ABS

ABS-polycarbonate blends are an important family of engineering thermoplastics, which can be flame retarded very well with aromatic diphosphates. They are discussed in Chapter 7.

ABS-poly(ethylene terephthalate) (PET) blends can be flame retarded to a V-1 level by includ-ing a char-forming phenolic novolac. For example, a formulation of 65 parts ABS, 35 parts PET, 3 parts phenolic novolac and 20 parts tetraphenyl resorcinol diphosphate (Fyrolflex RDP) can reach V-1 according to Cheil (Korea) workers [93].

A US patent application [78] by Israeli inventors shows ABS flame retarded to V-0 by 15 % expandable graphite and 15 % melamine cyanurate.

3.7   Flammability Requirements and Tests

There are many tests and methods that have been developed to study flammability. A brief summary is given in Chapter 12. For a more complete world-wide overview, the reader is referred to Troitzsch's monograph, recently revised [94]. Only those which are important for flame retardant styrenic polymers are mentioned here, in connection with each flame retardant. Some of these tests are regulatory requirements for specific applications, while others are mainly for research purposes. The flame retarding of styrenic polymers is often done to pass a specific test; the formulation needed to pass one test may be quite different than that required for another test.

Note that those tests which allow passing by melt-flow and dripping favor flame retardants, usually soluble ones, which do not form char. Formulations of this type can often be defeated by solid additives such as mineral fillers or even pigments.

3.8   Mechanistic Considerations as a Guide for Flame Retardation of Styrenics

As mentioned previously, when polystyrene is subjected to temperatures of a flame it py-rolyzes by a depolymerization mechanism to give monomer, oligomers and other aromatic cracking products [95]. Very little char is formed. The burning of these volatile products in

the vapor phase supplies heat back to the solid or molten surface (the "condensed phase"). The aromatic structures of the fuel are able to condense to large polycyclic structures, resulting in a very sooty flame. If the thermal energy from the flame, which is transmitted mainly by radiation, secondarily by convection or conduction, is sufficient to maintain the pyrolysis and vaporization of the pyrolysis products, the flame will sustain itself even after the ignition source is removed. In order to flame-retard a plastic such as a polystyrene, this cycle must be somehow interrupted, either in the vapor phase or condensed phase, or both. Flame retardants may act in either the vapor or solid (condensed) phase, or both.

This cycle may be oversimplified, and two aspects which could be important are often overlooked. First, in burning configurations where oxygen can reach the surface, as in upward burning of a vertical surface, exothermic oxidation in the condensed phase may also be providing energy. Secondly, the radiant energy from the flame must usually pass through the "dark zone" consisting of outflowing pyrosate, and substantial endothermic dissociation may be taking place in that zone. This part of the flaming process has been little investigated.

3.8.1   Vapor Phase Mechanisms in Styrenics and Some Implications

A detailed discussion of flame chemistry and its inhibition is outside the scope of this review, and the reader is referred to a mechanism review by Lewin and Weil [96] as well as to Fristrom's book on flame chemistry [97]. A recent study on aliphatic bromine compounds in polystyrene shows not only the effect of flame poisoning but also the effect of melt flow, and the effect of synergists specifically antimony oxide and talc [98].

3.8.2   The Smoke Problem with Styrenics

Whether or not they are flame retardant, styrenic polymers burn with a very smoky (sooty) flame. The typical flame retardants working in the vapor phase, by inhibiting the combustion chemistry, generally increase the smoke yield. However, it should be kept in mind that to whatever extent the flame retardants prevent the styrenic polymer from igniting and propagating a flame, the net yield of smoke may be lower. Thus, there is some possibility of confusion. It is quite possible the continuous stream of smoke in an apparatus where the combustion is driven by continued application of heat, as in the cone calorimeter, both the continuous smoke and the total smoke will be worse in the presence of the flame retardant, but on the other hand, in a test configuration where the igniting flame is removed and the polymer is allowed to self extinguish, *total* smoke may be less in the presence of the flame retardant because less material is burned.

The decision as to whether the increased rate of smoke production is a problem may hinge on whether the expected ignition source is a small flame, temporarily applied, or whether the styrenic polymer is exposed to an ongoing fire where other materials are burning.

Attempts to reduce the smoke yield have been made by means of additives. Unlike the case of PVC, where good smoke suppressing additives have been found and commercialized, no such smoke suppressant for styrenics has been found.

3.8.3   Condensed Phase Mechanisms in Styrenics

There are a number of flame retarding mechanisms that operate in the solid phase of polymers. One of these depends on additives that absorb some of the heat of combustion by endothermic reactions; this was mentioned in the previous section in connection with metal hydroxides.

Formation of a protective char layer is another important condensed phase mechanism. Unfortunately, polystyrene does not form any appreciable levels of char during burning even in the presence of charring catalysts. There has been some academic progress made in enhancing char formation of polystyrene by the use of Friedel-Crafts chemistry, but this involves building in specific functional groups. Manufacturers have not done this.

Intumescence is the formation of a foamed char, which is a particularly good heat insulator. Intumescent packages generally contain a source of carbon to build up char (carbonific), a compound which generates an acid upon heating in the flame, and a compound that decomposes to generate blowing gases to generate the foamed char [99]. The acid is required to cause charring of the carbonific component. A limitation of this approach is that relatively high levels (30 wt. % or more) of the intumescent package are required to flame retard styrenic polymers.

The formation of a barrier film on the surface during burning is another mode of action, which may in fact be part of the mechanism of action of phosphorus-based flame retardants, which can form polyphosphoric acid on pyrolysis. This action also has not been well studied.

Another mechanism that can be used in the condensed phase is to use an additive that enhances decomposition, and thus dripping, of the polymer during burning. This may be desirable for achieving a UL 94 V-2 rating, but may not be an option for a V-0 requirement. Promoting non-flaming drips is one way to make nylon polymers V-0, but this approach is not used for styrenic polymers other than expandable foams.

3.9   Summary and Future Trends

Flame retardant styrenic polymers find utility in applications such as building insulation (expanded polystyrene foam) and electronic enclosures (flame retardant HIPS, ABS and styrenic blends). The most effective flame retardants are halogen (particularly bromine) containing compounds, these flame retardants act by inhibiting the radical combustion reactions occurring in the vapor phase. The state of flame retardant plastics is in a state of flux, due to influences of regulatory and environmental factors. There are movements to discontinue use of halogen containing flame retardants, but at the present time it is difficult to find cost effective non-halogen alternatives for styrenic polymers other than for their blends containing char-forming components.

The value of having a flame retardant in styrenics, such as in TV enclosures, has been shown by a careful life-cycle study balancing fire risk against environmental risk [100]. European statistics show very substantial life-saving benefits from the use of flame retardants. Moreover, once the environmental risk from fire products such as polycyclic aromatic hydrocarbons is taken into account, the environmental balance also appears favorable for the flame retardants.

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