FLAME RETARDANTS, HALOGENATED

1. Introduction

The total world market for flame-retardants is estimated to be more than 1.2 million metric tons valued at $\sim$2.3 billion U.S. dollars. Approximately 36% of this revenue is based on bromine organic compounds and $<$10% on chlorinated organic compounds. The rest is made up of nonhalogenated organophosphate esters, halogenated organophosphate esters, alumina trihydrate, antimony oxides (antimony trioxide, pentoxide, sodium antimonate), boron compounds, magnesium hydroxide, ammonium polyphosphate and red phosphorus. Some of these inorganic compounds function as synergists rather than directly as flame-retardants, enhancing the effectiveness. (e.g. antimony or boron based compounds).

Flame retardant use is affected by regulation in two opposing ways. Government regulations (as well as voluntary trade standards and concern of litigation potential due to product failure) for flame retardancy of various products which dictate the use of flame retardants to meet given fire standards and government regulations governing what compounds are deemed to be safe for use in flame retardant applications and not have a negative effect on the environment or human health. Currently halogenated compounds are increasingly facing pressure from the second situation, which has seen a drive to expand the use of non-halogenated flame-retardants. Despite this, halogenated flame-retardants remain the most important group of flame-retardants in use today. Halogenated flame-retardants typically have high levels of either bromine or chlorine that coupled with their high efficiency allows these additives to be used at relatively low loadings. This in turn translates to a greater retention of the physical properties of the base polymer.

Halogenated flame-retardants fall into three general classes, additive, reactive and polymeric. Additives are blended into the polymer using common polymer processing equipment at the same time other ingredients such as synergists, stabilizers, pigments, and processing aids are added. This is typically true of polymeric flame-retardants as well but these materials also have the advantage of low blooming and less environmental concerns due to their polymeric nature. Reactive flame-retardants become part of the polymer by either reacting into the polymer backbone or grafting onto it.

The most important class of brominated flame retardants to date has been the polybrominated diphenyl oxides (diphenyl ethers) of which decabromodiphenyl oxide (Deca) is the largest volume product and whose primarily use is in HIPS (high-impact polystyrene). Octabromodiphenyl oxide was used primarily in ABS resins and pentabromodiphenyl oxide in flexible polyurethane foam. Both octa and penta diphenyl oxide have recently been banned in Europe. The sole producer of Penta and Octa in the U.S. has announced production will cease by the end of 2004 which will effectively remove these products from the market. Other highly brominated aromatic compounds have been developed as possible alternatives to Deca to address the concerns with diphenyl oxide based flame retardants and ethane-1,2-bis(pentabromophenyl) is one such example. Other types of brominated flame retardants have also come into wider use including tetrabromobisphenol-A, which is the largest volume, brominated flame retardant in use today. It can function as either an additive or a reactive flame retardant and is used as a raw material in the manufacture of other flame-retardants. Other newer flame retardants, which exemplify the move to polymeric flame retardants, include brominated polystyrenes, polybromostyrenes and brominated epoxy oligomers (BEOs).

The use of flame retardants came about because of concern over the flammability of synthetic polymers (plastics). A simple method of assessing the potential contribution of polymers to a fire is to examine the heats of combustion, which for common polymers vary by only about a factor of two (1). Heats of combustion correlate with the chemical nature of a polymer whether the polymer is synthetic or natural. Concern over flammability should arise via a proper risk assessment, which takes into account not only the flammability of the material, but also the environment in which it is used.

2. Fundamentals of Flammability

In order for a solid to burn it must be volatilized, because combustion is almost exclusively a gas-phase phenomenon. In the case of a polymer, this means that decomposition must occur. Decomposition begins in the solid phase and may continue in the liquid (melt) and gas phases. It produces low molecular weight chemical compounds that eventually enter the gas phase and act as fuel. Heat from combustion of this fuel causes further decomposition and volatilization and, therefore, further combustion. Thus the burning of a solid is like a cyclic chain reaction. For a compound to function as a flame retardant it must interrupt this cycle in some way. There are several mechanisms by which flame retardants modify flammability by braking this cycle and some flame retardants have more than one mode of action. For example, metal hydroxides such as $Al(OH)_3$ (ATH) decompose endothermically (thermal quenching) to give water (inert gas dilution). In addition, in cases where up to 60 wt% of ATH may be used, such as in polyolefins, there is physical dilution (less fuel) as well as char formation.

2.1. Inert Gas Dilution. Inert gas dilution involves the use of additives that produce large volumes of noncombustible gases when the polymer is decomposed. These gases dilute the oxygen supply to the flame or dilute the fuel concentration below the flammability limit. Metal hydroxides, metal carbonates, and some nitrogen-producing compounds function in this way as flame retardants.

2.2. Thermal Quenching. Endothermic degradation of the flame retardant results in heat removal and the polymers surface temperature is lowered and the rate of pyrolysis is decreased. Metal hydroxides and carbonates act in this way.

2.3. Protective Coating. Some flame retardants function by forming a protective glassy surface or char barrier. These minimize transportation of polymer degradation products (fuel) to the flame front and/or act as an insulating layer to reduce the heat transfer from the flame to the polymer. Phosphorus compounds that decompose to give phosphoric acid and intumescent systems are examples of this category (see FLAME RETARDANTS, PHOSPHORUS).

2.4. Physical Dilution. The flame retardant can also act as a thermal sink, increasing the heat capacity of the polymer or reducing the fuel content to a level below the lower limit of flammability. Inert fillers such as glass fibers and micro spheres and minerals such as talc act by this mechanism.

2.5. Flame Poisoning. Halogens and some phosphorus flame retardants act by chemical interaction. The flame retardant dissociates into radical species that compete with chain propagating and branching steps in the combustion process.

3. Flammability Testing

One problem associated with discussing flame retardants is the lack of a clear, uniform definition of flammability. Hence, no clear, uniform definition of decreased flammability exists. The latest American Society for Testing and Materials (ASTM) compilation of fire tests lists over one hundred methods for assessing the flammability of materials (2). These range in severity from small-scale measures of the ignitability of a material to actual testing in a full-scale fire. Several of the most common tests used on plastics are summarized in Table 1.

Table 1. **Flammability Tests**

Designation[a,b]	Description or application[c]	Characteristic measured
ASTM E162-02a	radiant panel	flame spread
ASTM E119-00a	building materials	fire endurance
MVSS 302	materials for automotive interiors	burning rate
ASTM D2863-00	Limiting Oxygen Index (LOI)	ease of extinction
ASTM E662-03	NBS smoke chamber	smoke
ASTM E84-03B, UL 723, UL 910	Steiner tunnel	flame spread and smoke
UL 94	vertical burn	ignition resistance
UL 790, ASTM E108-00	roof burn	flame spread
UL 1715	room burn	flashover potential and smoke
CAL 133	furniture	flashover potential and smoke
CAL 117 ASTM E1353-02	cigarette ignition for furniture	ignitability
ASTM E1354-03	cone calorimeter	heat release and smoke
ASTM E906-99	OSU heat release rate calorimeter	heat release and smoke
FMRC 4910	contraction	heat, smoke, toxic and corrosive products release, ignition and flame spread

[a] Designations listed together are not meant to imply equivalency.

[b] CAL = California; MVSS = Motor Vehicle Safety Standard; UL = Underwriter's Laboratory.

[c] NBS = National Bureau of Standards; OSU = Ohio State University; FMRC = Factory Mutual Research Corp.

3.1. Material Tests. Material tests measure some property of the polymer or plastic as opposed to measuring the flammability of the final product, which contains the plastic.

3.2. LOI. The minimum concentration of oxygen in an O_2/N_2 mixture that supports combustion of a vertically mounted test specimen is called the limiting oxygen index (3,4). Test specimens are 0.65 × 0.3 m × 12.5 cm. The principal advantage of this test is its reproducibility, which makes it useful for quality control. The main disadvantage is that the results rarely correlate with the results of other fire tests.

3.3. Specific Tests. Federal (United States) Motor Vehicle Safety Standard (MVSS) 302 is used to measure the burning behavior of materials used in automobile interiors. A specimen is mounted horizontally and ignited for 15 seconds. The burning rate should be below 10 cm/min. The test specimen is 35.5 × 10.1 cm by the actual thickness (up to 1.3 cm). Automakers typically impose more severe criteria than the 10 cm/min in the standard.

The Underwriters Laboratory UL 94 Standard for Safety (5) measures the ignitability of plastics by a small flame. The test specimens are mounted vertically and ignited using a Bunsen burner held at a 30° angle. A layer of cotton (qv) is placed under the specimen to test for flaming drips. The specimen dimensions are 12.7 × 1.27 cm by the thickness in the intended application. Typical thicknesses tested are 3.2, 1.6, and 0.8 mm. The flame is applied for 10 seconds, plus a subsequent 10-s application if the specimen self-extinguishes after the first ignition. The flammability is classified as: (*1*) V-0 if no specimen burns longer than 10 seconds after each flame application. The sum of the after-flame times for five specimens (two flame applications per specimen, 10 total flame applications) should not exceed 50 seconds. The cotton cannot be ignited. (*2*) V-1 if no specimen should burn longer than 30 seconds. The sum of the after-flame times for five specimens (two flame applications per specimen, 10 flame applications) should not exceed 250 seconds. The cotton cannot be ignited. (*3*) V-2 if the requirements are the same as for V-1 except that the cotton can be ignited. Most commercial plastics are flame retarded to meet either the V-0 or the V-2 classification.

3.4. Heat Release Calorimeters. There are three principal types of heat release calorimeters. The Cone calorimeter measures the rate of heat release of a burning specimen (6-8). Test specimens 10 × 10 cm by up to 2.5 cm thick are exposed to radiant heat of up to 100 kW/m^2. Many parameters in addition to heat release rate may be measured. These include total heat released, mass loss, time to ignition, critical heat flux, and smoke production. The heat released is calculated based on consumption of oxygen, thus this is also sometimes called oxygen consumption calorimetry. The advantage of this test is that materials can be subjected to heat fluxes similar to those encountered in real fires. The main disadvantage is that the results must correlate with large-scale testing before they are useful. Correlations in the area of wire and cable (9,10) and wall coverings (11) have been developed.

The Ohio State University (OSU) calorimeter (12) differs from the Cone calorimeter in that it is a true adiabatic instrument, which measures heat released during burning of polymers by measurement of the temperature of the exhaust gases. This test has been adopted by the Federal Aeronautics Administration (FAA) to test total and peak heat release of materials used in the interiors of commercial aircraft. The other principal heat release test in use is the Factory Mutual flammability apparatus (13,14). Unlike the Cone or OSU calorimeters this test allows the measurement of flame spread as well as heat release and smoke. A unique feature is that it uses oxygen concentrations higher than ambient to simulate back radiation from the flames of a large-scale fire.

3.5. Product Tests. Tests in which the finished article is subjected to a more or less realistic fire are called product tests. A few examples follow.

Tunnel Test. The tunnel test is widely used to test the flame spread potential of building products such as electrical cable (15) and wall coverings (16). The test apparatus consists of a tunnel 7.62 × 0.445 m × 0.305 m in cross section, one end of which contains two gas burners. The total heat supplied by the burners is 5.3 MJ/min. The test specimen (7.62 m × 50.8 cm), attached to the ceiling, is exposed to the gas flames for 10 minutes while the maximum flame spread, temperature, and smoke evolved are measured. The use of this and other flame spread test methods has been reviewed (17).

Factory Mutual Corner Test. This is a large-scale corner test used to test building products (18-20). The test rig consists of three sides of a cube. The two walls are 15.24 and 11.58 m by 7.62 m tall. The ceiling is 9.14 × 15.24 m. The product to be tested is mounted on the walls and ceilings in a manner consistent with the intended use. The fire source is a 340 kg stack of wood pallets located in the corner. In order to pass the test, no flame can propagate to any extremity of the walls or ceiling. The Factory Mutual flammability apparatus is proposed to replace this test for certain applications (21).

CAL 133. California Technical Bulletin 133 is a test of the fire hazard associated with upholstered furniture (22). The test is carried out by igniting a standard fire source directly on the piece of furniture being tested. In the most recent version of the test, the fire source is a gas flame. Smoke, heat, and toxic gas emissions are measured during the test. A related test, BS 5852, uses various wooden cribs as the fire source (23).

4. Flame Retardants

Bromine and chlorine compounds have the most commercial significance as flame-retardant chemicals with bromine predominating due to its higher efficiency. Efficiency and stability are the two primary factors that determine what halogens compounds can be used as flame retardants, Fluorine compounds are too stable (C-F bond 467 kJ/mol) while chlorine (C-Cl 346 kJ/mol) and bromine (C-Br 290 kJ/mol) show stability in the correct region and iodide is not stable enough to survive processing temperatures (C-I 228 kJ/mol). Halogenated flame retardants can be broken down into three classes: brominated aliphatic, brominated aromatic and chlorinated aliphatic. As a general rule, the thermal stability decreases as brominated aromatic $>$ chlorinated aliphatic $>$ brominated brominated aliphatic. The thermal stability of the aliphatic compounds is such that with few exceptions, thermal stabilizers (eg, organo tins compounds or hydrotacites) must be used to allow the flame retardant to undergo processing. Brominated aromatic compounds are much more stable and may be processed in thermoplastics at fairly high temperatures without the use of stabilizers and at very high temperatures with stabilizers. It is commonly thought that it is desirable for the flame retardant to decompose with the liberation of halogen at a somewhat lower temperature than the decomposition temperature of the polymer. This view is overly simplistic. In fact, in some systems, it is degradation of the polymer that promotes degradation of the flame retardant and not vice versa (24).

Tables 2–4 below have suggested formulations for flame retarding various resins using flame retardants that fall into the three classes mentioned

Table 2. **Formulations for Chlorinated Paraffin**[a,b]

Polymer	UL-94 rating at 3.2 mm	Flame retardant, wt%	Antimony oxide, wt%
polyethylene	V-0	24	10
polypropylene	V-0	22	11
high impact polystyrene (HIPS)	V-0	16	5
unsaturated polyester	V-0	15	5

[a] Ref. (25).

[b] Based on 70% chlorine content. For chlorinated paraffins having lower chlorine content, the use level must be raised accordingly.

Table 3. **Formulations for Hexabromocyclododecane**[a,b]

Polymer	UL-94 rating at 1.6 mm	Flame retardant, wt%	Antimony oxide, wt%
polypropylene, copolymer	V-2	4	1
crystalline polystyrene	V-2	5	0
high impact polystyrene	V-2	7	0
high impact polystyrene	V-2	4	1

[a] Ref. (26).

[b] Acid scavenging stabilizers are typically recommended for use with HBCD in thermoplastic applications. Stabilized grades are available from the manufacturers.

previously: hexabromocyclododecane (brominated aliphatic), chlorinated paraffin (chlorinated aliphatic), and decabromodiphenyl oxide (brominated aromatic). These suggested formulations may not be strictly comparable because of differences in the nature of the base resins. However, the suggestions are specific to a given UL-94 rating for that resin.

In selecting a flame retardant for a given application, the cost contribution of the flame retardant to the final polymer compound must be taken into account. Assessment of cost should be done on a cost per volume basis rather than a simple cost per weight basis.

4.1. Antimony–Halogen Synergism.

Antimony oxide is commonly employed as a fire-retardant supplement for halogen-containing polymer systems as a means of reducing the halogen levels required to obtain a given degree of flame retardancy. This reduction is desirable because the required halogen content may be so high that it affects the physical properties of the final polymer. In many cases, the antimony oxide is used simply to give a more cost-effective system.

Table 4. **Formulations for Decabromodiphenyl Oxide**[a,b]

Polymer	UL-94 rating at 1.6 mm	Flame retardant, wt%	Antimony oxide, wt%
low density polyethylene	V-2	6	2
high density polyethylene	V-2	8	3
cross-linked polyethylene	V-0	20	10
polypropylene with 14% talc	V-0	22	6
high impact polystyrene (HIPS)	V-0	12	4
acrylonitrile butadiene styrene (ABS)	V-0	15	5
polybutylene terephthalate (PBT)[a]	V-0	10	5
polyamide[a]	V-0	14	5
thermoset epoxy resin	V-0	6	3

[a] Ref. (27).

[b] Decabromodiphenyl oxide contains approximately 83% bromine. For flame retardants having a lower bromine content, the use level must be raised accordingly.Glass-reinforced grades may require lower levels of flame retardants.

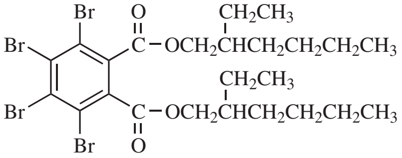
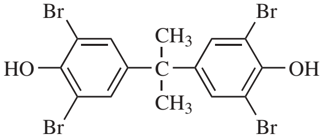
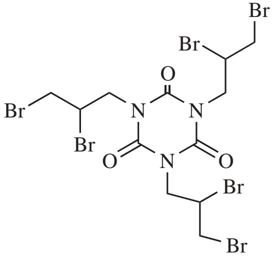
Antimony–halogen systems have been widely studied. The various mechanistic studies of the interaction of brominated flame retardants, antimony oxide, and polymers have been reviewed (28). No completely satisfactory theory to explain the synergistic effects obtained with this combination of elements is available, but it is generally agreed that the active agents, antimony trihalides or antimony oxyhalides, act principally in the gas phase (29-31). The antimony halides are postulated to act as radical traps. Although the antimony halides appear to act principally in the gas phase, some effect on the condensed-phase chemistry cannot be ruled out. Antimony–halogen flame-retardant compositions usually produce a carbonaceous residue, even in polymers such as polypropylene, which produces none in the absence of fire retardants. The production of the carbonaceous residue probably results from the antimony trihalides, strong Lewis acid catalysts, which are capable of promoting the dehydrohalogenation of organic halides as well as coupling and rearrangement reactions in organic systems.

4.2. Brominated and Chlorinated Additive Flame Retardants. Additive flame retardants are those that do not react in the application designated. There are a few compounds that can be used as an additive in one application and as a reactive in another. Tetrabromobisphenol-A [79-94-7] (TBBPA) is the most notable example. Tables 5 and 6 list the properties of most commercially available bromine and chlorine-containing additive flame retardants.

The types of brominated flame retardants has changed over the years because of the risk reduction measures imposed in Europe on the use of certain brominated flame retardants suspected of producing brominated dibenzodioxins or dibenzofurans. Producers have developed new flame retardant technologies as an alternative in order to minimize the formation of brominated dioxins and furans. Albemarle for example offers propriety brominated flame retardants including Saytex BT-93 and Saytex 8010 that do not contain and minimize production of brominated dibenzodioxins or dibenzofurans in normal use. Saytex 8010 (ethane-1,2-bis(pentabromophenyl)) contains no oxygen hetero atom, and its structure precludes the formation of brominated dioxins and furans. Resin samples were prepared by means of extrusion and injection molding for analysis at an outside laboratory. The samples were then recycled and analyzed for brominated dioxins and furans. Results demonstrated that the resin compounds containing this flame retardant conform to the German Dioxin Ordinance regulating dioxin and furan content. Dead Sea Bromine offers FR-1808 (brominated phenyl indane), with 73% bromine content, and FR- 245 (tris [tribromophenyl] iso cyanurate), with 67% bromine content. These flame retardants, used in Styrenics, have undergone extensive toxicological and environmental testing, and have been proven not to produce brominated dibenzodioxins or dibenzofurans in normal use.

Brominated Diphenyl Oxides. Brominated diphenyl oxides are prepared by the bromination of diphenyl oxide and are often referred to as diphenyl ethers. Taken together they used constitute the largest class of brominated flame retardants but due to the phasing out of the Octa and Penta products this is no longer the case. Decabromodiphenyl oxide (Deca or Decabrom) is used, as an additive in virtually every polymer system.

Table 5. **Brominated Additive Flame Retardants**

Name	CAS registry number	Structure	Br, %	Mp, °C	Trade name (Company)
bis(2-ethylhexyl)tetrabromo phthalate	[26040-51-7]		45	liquid	FRP-45 (Unitex) DP45 (Great Lakes)
tetrabromobisphenol-A	[79-94-7] [6386-73-8]		59	180	Saytex CP-2000 (Albemarle) FR-1524 (Dead Sea Bromine) BA-59 (Great Lakes)
tris-dibromopropyl isocyanurate	[52434-90-9]		65.8		FR-930 (Akzo)

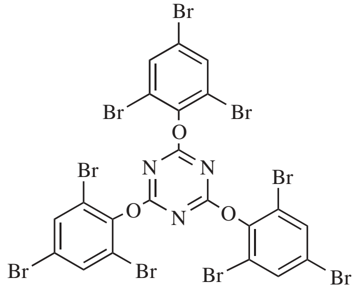
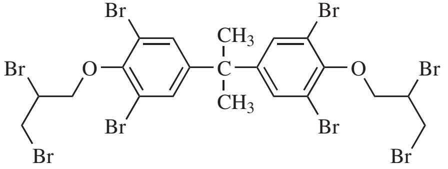
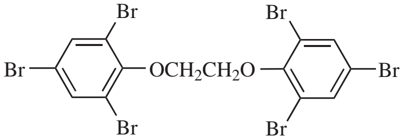
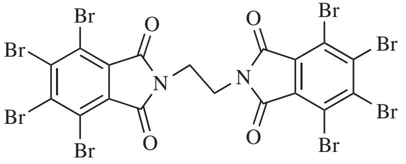
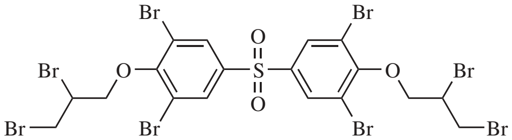
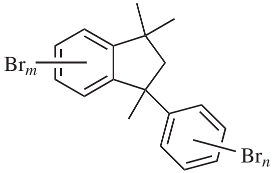
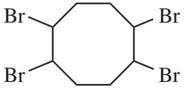
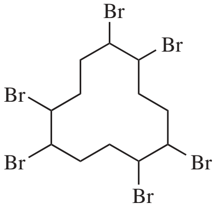
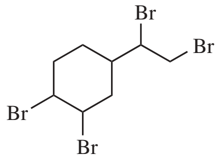
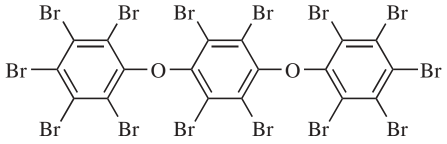
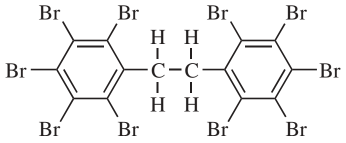
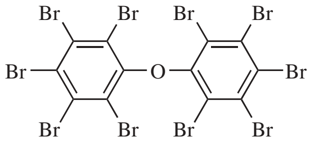
tris(tribromophenyl) triazine	[25713-60-4]		67		FR-245 (Dead Sea Bromine)
tetrabromobisphenol-A, bis(2,3-dibromopropylether)	[21850-44-2]		68	95	SAYTEX HP800 A (Albemarle) FR720 (Dead Sea Bromine) PE68 (Great Lakes)
1,2-bis(2,4,6-tribromophenoxy)ethane	[37853-59-1]		68	224	FM 680 (Great Lakes)
ethylenebistetrabomophthalimide	[32588-76-4]		68	445	SAYTEX BT93 (Albemarle) SAYTEX BT93W (Albemarle)

Table 5 (*Continued*)

Name	CAS registry number	Structure	Br, %	Mp, °C	Trade name (Company)
tetrabromobisphenol *S*-bis(2,3-dibromo-propylether)	[42757-55-1]		70.8	52–55	NonNen #52 (Marubishi Oil Chemical Co)
octabromo-1-phenyl-1,3,3,-tri-methylindan	[155613-93-7]	 ($m + n = 7$–8)	73	240–255	FR-1808 (Dead Sea Bromine)
tetrabromocyclooctane	[3194-57-8] [31454-48-5]		74.7	73	SAYTEX BC-48 (Albemarle)
hexabromocyclododecane	[3194-55-6]		74.7	175–195	SAYTEX HP-900 (Albemarle) FR-1206 (Dead Sea Bromine) CD-75P (Great Lakes)

dibromoetyldibromo-cyclohexane	[3322-93-8]		74.7	72	SAYTEX BCL-462 (Albemarle)
tetradecabromodi-phenoxybenzene	[58965-66-5]		82	370	SAYTEX 120 (Albemarle)
ethane-1,2-bis(pentabromophenyl)	[84852-53-9]		82.3	350	SAYTEX 8010 (Albemarle)
decabromodiphenyl oxide	[1163-19-5]		83	305	SAYTEX 102E (Albemarle) FR-1210 (Dead Sea Bromine) DE-83 (Great Lakes)

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[a] Commercial products are a mixture of isomers and have a melting range depending on isomer distribution.

Decabromodiphenyl Oxide. Decabromodiphenyl oxide [1163-19-5] is the largest volume brominated flame retardant used solely as an additive. It is prepared by the bromination of diphenyl oxide in neat bromine (bromine is reactant and solvent) using $AlCl_3$ as a catalyst (32). The commercially available grades are >97% decabromodiphenyl oxide with the remainder essentially being the nonabromo species. Testing has shown that resins containing decabromodiphenyloxide generate no detectable brominated dioxins or debrominated species when subjected to normal processing conditions and even recycling (33).

Decabrom is thermally stable and can be employed with polymer systems that require high processing temperatures where it is usually used in conjunction with antimony oxide. The largest volume use of decabrom is in high impact polystyrene (HIPS) that is used to manufacture television cabinets though this volume is being eroded by non Deca brominated Flame Retardants. Decabrom has poor uv stability in styrenic resins and causes significant discoloration. The use of uv stabilizers can minimize, but not eliminate, this effect. For styrenic applications that require uv stability, several other brominated flame retardants are more suitable.

Decabrom is used in virtually every class of polymer, including ABS (see Acrylonitrile-Butadiene-Styrene (ABS) Polymers); engineering thermoplastics such as polyamides (qv) and polyesters (qv) (see Engineering Thermoplastics); polyolefins; thermosets, ie, epoxies and unsaturated polyesters; PVC; and elastomers (qv). It is also widely used in textile applications as the flame retardant in latex-based back coatings.

Tetrabromobisphenol-A. Tetrabromobisphenol-A [79-94-7] (TBBPA) is the largest volume brominated flame retardant. TBBPA is prepared by bromination of bisphenol-A under a variety of conditions. When the bromination is carried out in methanol, methyl bromide [74-80-9] is produced as a coproduct. With the phasing out of methyl bromide (MeBr) due to the Montréal Protocol some producers have switched from the methanol process to other process that do not co-produce MeBr. For example, Albemarle now uses ethanol in a continuous process in two new plants (34). Others like Dead Sea Bromine use methylene chloride as a solvent, which avoids MeBr formation, and the HBr is oxidized to bromine using hydrogen peroxide (35). TBBPA is used both as an additive and as a reactive flame retardant. It is used as an additive primarily in ABS systems. In ABS, TBBPA is probably the largest volume flame retardant used, and because of its relatively low cost is the most cost-effective flame retardant. In ABS, it provides high flow and good impact properties. These benefits come at the expense of distortion temperature under load (DTUL) (36). DTUL is a measure of the use temperature of a polymer. TBBPA is more uv stable than decabrom and uv stable ABS resins based on TBBPA are produced commercially.

Ethane-1,2-bis(pentabromophenyl). The additive ethane-1,2-bis(pentabromophenyl) (SAYTEX 8010) [84852-53-9] is prepared by the bromination of diphenyl ethane in neat bromine (bromine is reactant and solvent) using $AlCl_3$ as a catalyst (37). It is a high melting solid with 82.3% aromatic bromine that exhibits high thermal stability and better uv stability than Deca. In a 100% recycle study, Saytex 8010 in high-impact polystyrene exhibited excellent physical properties, flammability and color retention after being recycled five times. Extruded and injection-molded formulations (single and multiple injection molding cycles) did not contain any detectable quantities of brominated dioxins or furans and met the German Dioxin Ordinance (38).

Tetradecabromodiphenoxybenzene. The additive tetradecabromodiphenoxybenzene [58965-66-5] (SAYTEX 120) finds its main applications in high performance polyamides, linear polyesters and engineering resins. It is also suitable for use in wire and cable applications (polyolefins) and styrenic resins. It has better uv stability than Deca as well as better thermal stability and low blooming.

Octabromo-1-Phenyl-1,3,3,-Trimethylindan. The additive octabromo-1-phenyl-1,3,3,-trimethylindan [155613-93-7] (FR-1808) is prepared by the dimerization of alpha methyl styrene to make 1,3,3-trimethyl-1-phenylindane followed by bromination (39). Its bromine content is lower than that of Deca (73%) so higher loadings are required for the same flame retardancy levels. The product has a lower melting range (240–255°C) than Deca and so is melt blend able in certain resins like HIPS resulting in improved flow and impact strength. Like ethane-1,2-bis(pentabromophenyl), octabromo-1-phenyl-1,3,3,-trimethylindan structure precludes the formation of poly brominated dibenzodioxins and dibenzofurans and testing in both neat form and in compounded HIPS has shown this to be the case.

Tris(tribromophenyl) Triazine. The additive tris(tribromophenyl) triazine [25713-60-4] (FR-245) is prepared by reacting cyanuric chloride with three moles of tribromophenol in a suitable solvent with a base (40). The product has good uv stability and imparts good flow though its lower bromine content compared to Deca requires higher loadings for the same flame retardancy level. FR-245 major applications is in HIPS and ABS where it good uv, impact and flow properties. It is often blended with higher bromine content flame retardants to offset its tendency to cause afterglow in the UL-94 test.

Tetrabromobisphenol-A, Bis(2,3-dibromopropylether). The additive tetrabromobisphenol-A, bis(2,3-dibromopropylether) [21850-44-2] is prepared by reacting TBBPA with allyl chloride followed by the addition of two moles of bromine. This material has 34% aliphatic bromine and 34% aromatic bromine and its lower melting point range means it is melt blend able. It is suitable for use in polyolefin and styrenic resins and it works very well for UL-94 class V-2 ratings. It does however have a blooming issue in polyolefins, its sulfur analog tetrabromobisphenol *S*-bis(2,3-dibromopropylether) [42757-55-1] has less of an issue.

Tris-dibromopropyl Isocyanurate. The additive tris-dibromopropyl isocyanurate [52434-90-9] (FR-930) is prepared by the addition of three moles of bromine to tris allyl isocyanurate in a suitable solvent followed by recrystallization and drying. It contains 65.8% of aliphatic bromine and finds its major use in polyolefins (41).

Hexabromocyclododecane. There are three flame retardants obtained from the bromination of cyclic oligomers of butadiene (see Butadiene). These are hexabromocyclododecane [25637-99-4] (HBCD), tetrabromocyclooctane [31454-48-5], and dibromoethyldibromocyclohexane [3322-93-8]. Each has a theoretical bromine content of 74.7%. They differ primarily in melting point and solubility. Hexabromocyclododecane is the only one used in large volume. The primary use of HBCD is in polystyrene foam (EPS and XPS) and it is prepared by the bromination of CDT (cyclododecatriene) in a suitable solvent (42). The product of the reaction is a mixture of three principal isomers, alpha, beta and gamma. The gamma isomer is the predominant product from the reaction and has the highest melting point (205°C). Thermal stability is often correlated with melting point range and hence to high gamma content. There are many commercial grades available with high and low gamma contents and different melting points ranges. The melting point however has been shown not to correlate to the stability of the compound during processing (43). Other factors such as levels of minor impurities and particle size are at least as important. Compared to brominated aromatic flame retardants, the thermal stability of HBCD is considerably lower, limiting use to situations where the processing temperature is low. Thermal stabilizers are often needed and there are many commercial grades containing thermal stabilizers available.

1,2-Bis(2,4,6-tribromophenoxy)ethane. The additive 1,2-bis(2,4,6-tribromophenoxy)ethane [37853-59-1] (FM-680) is a white crystalline powder having the good thermal stability expected of a brominated aromatic. It is prepared by the reaction of tribromophenol [75-80-9] and ethylene dibromide [106-93-4] in the presence of a base. The principal market for FM-680 is in ABS resins. It imparts good impact and reasonable flow properties at the expense of DTUL and has better uv stability compared to tetrabromobisphenol-A.

Ethylenebis(tetrabromophthalimide). The additive ethylenebis(tetrabromophthalimide) [41291-34-3] (SAYTEX BT93 and BT93W) is prepared from ethylenediamine and tetrabromophthalic anhydride [632-79-1]. It is an extremely stable product that exhibits a high degree of uv stability and finds its uses in many high end applications. It is used in engineering thermoplastics and polyolefins because of its thermal stability and resistance to bloom (44). It is used in styrenic resins because of its uv stability (45). This flame retardant has been shown to be more effective on a contained bromine basis than other brominated flame retardants in polyolefins (10).

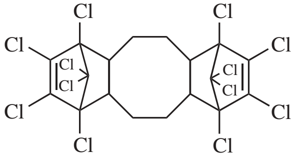
Bis(2-ethylhexyl)tetrabrom Phthalate. The additive bis(2-ethylhexyl) tetrabrom phthalate [26040-51-7] is prepared by reacting two moles of 2-ethylhexanol with tetrabromophthalic anhydride. It is the brominated version of di-octylphthalate and is a flame-retardant plasticizer (45% bromine) that finds its main application in PVC coatings. It is more effective than phosphate esters in thermal stability and flame retardancy and is used as a diluent for primary plasticizers allowing LOI >40 to be obtained without adversely affecting properties of the PVC (46).

Table 6 is a general listing of chlorinated compounds used as additive flame retardants.

Bis(hexachlorocyclopentadieno)cyclooctane. The di-Diels-Alder adduct of hexachlorocyclopentadiene [77-47-4] and cyclooctadiene (47) is a flame retardant having unusually good thermal stability for a chlorinated aliphatic. In fact, this compound is comparable in thermal stability to brominated aromatics in some applications. Bis(hexachlorocyclopentadieno)cyclooctane is used in several polymers, especially polyamides (48) and polyolefins (49) for wire and cable applications. Its principal drawback is the relatively high use levels required compared to some brominated flame retardants.

Chlorinated Paraffins. The term chlorinated paraffins covers a variety of compositions. The prime variables are molecular weight of the starting paraffin

Table 6. **Chlorinated Compounds Used as Additive Flame Retardants**

Common name	CAS registry number	Molecular formula	Halogen %	Mp, °C	Sources
dodecachloropenta-cycloctadeca-7,15 diene	[13560-88-9]		65.1	350	Dechlorane Plus (OxyChem)
pentabromochloro-cyclohexane	[25495-99-2]	$C_6H_5ClBr_5$	78	170	Nissei Chemical Industries Co
chlorinated paraffin	[63449-39-8] [61788-76-9][a]		39–70		Dover Chemical Ferro Corporation Caffaro SpA Chimprom Firma Chemiczna INEOS Chlor LEUNA-TENSIDE GmbH Novacke Chemicke Zavody, a.s Quimica del Cinca SA Asahi Denka Kogyo KK Tosoh Corp Ajinomoto Co., Inc.,
bromo/chloro alpha olefin and paraffins	[82600-56-4][b]		24–35	liquid	Dover Chemical
	[68955-41-9][a]		19–35		Ferro Corporation

[a] No unique CAS registry number.

[b] No unique formula.

and the chlorine content of the final product. Typical products contain from 12–24 carbons and from 40–70 wt% chlorine. Liquid chlorinated paraffins are used as plasticizers (qv) and flame retardants in paint (qv) and PVC formulations. The solid materials are used as additive flame retardants in a variety of thermoplastics. In this use, they are combined with antimony oxide, which acts as a synergist. Thermal stabilizers, such as those used in PVC (see Vinyl Acetal Polymers), must be used to overcome the inherent thermal instability.

4.3. Polymeric/Oligomeric Flame Retardants. There are several halogenated oligomeric/polymeric flame retardants and their high molecular weight provide numerous advantages such as, low volatility, low toxicity, easy handling (no dust) and resistance to bloom and plate-out. In some cases they are used at levels high enough that the resulting flame-retarded resin should properly be viewed as a polymer blend or alloy. The main oligomeric/polymeric flame retardants are shown in Table 7.

Brominated Carbonate Oligomers. There are two commercial brominated carbonate oligomer (BCO) products. Both are prepared from tetrabromobisphenol-A and phosgene. One has phenoxy end caps [28906-13-0] and the other tribromophenoxy [71342-77-3] end caps. These are used primarily in PBT and polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) blends.

Brominated Epoxy Oligomers. Brominated epoxy oligomers are prepared in several ways. One method involves the reaction of tetrabromobisphenol-A and epichlorohydrin. This can give materials having molecular weights from as low as 1600 to as high as 60,000 with bromine contents ranging from 52–54%. In some cases, the terminal epoxy groups are capped by reacting with phenol or tribromophenol to improve thermal stability. End capping with phenol lowers the bromine content slightly whereas end capping with tribromophenol raises it slightly. The lower molecular weight products are used primarily in styrenic resins, eg, HIPS and ABS while the higher molecular weight products are used in engineering thermoplastics, eg, PBT. In HIPS and ABS, they offer good flow and uv resistance. Their effect on physical properties is difficult to characterize because it is dependent on the molecular weight.

Homopolymers of a Dibromo/Tribromo Styrene Monomer. Poly(dibromostyrene) [62354-98-7] (PDBS) is a homopolymer of dibromostyrene [31780-26-4] (50), which contains 59% bromine (PDBS-80 from Great Lakes). The primary applications for this material are in high temperature polyamides and PET. The material has excellent flow characteristics and good thermal stability (51). The primary weakness of this product is the bromine content relative to brominated polystyrene which typically has 68% bromine which translates into a $\sim$3 parts difference in the load level needed in the polymer to give equivalent flame retardant performance. To partially address the weakness of the lower bromine content a series of new homopolymers based upon a brominated monomer with 64–65% has been developed. PBS-64 and PBS-64 HW are homopolymers of a dibromo/tribromo styrene monomer and are targeted at the high temperature polyamides and PET area. PBS-64 HW has a higher molecular weight than PBS-64 so the flow is reduced but physical properties are improved over the lower molecular weight product (52).

Brominated Polystyrene. Brominated polystyrene (BrPS) is prepared by the bromination of polystyrene. The initial product [57137-10-7] (Pyro-Chek

Table 7. **Polymeric and Oligomeric Brominated Additive Flame Retardants**

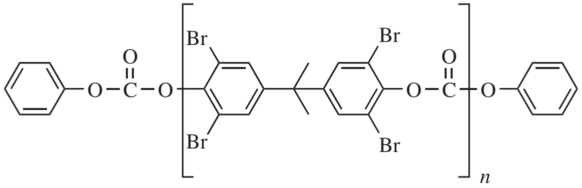
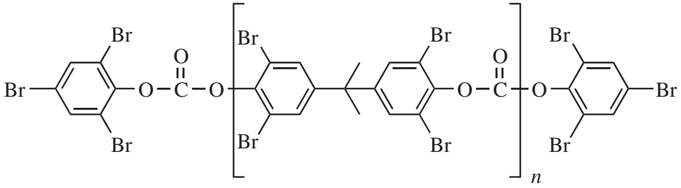
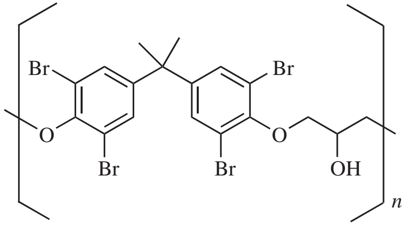
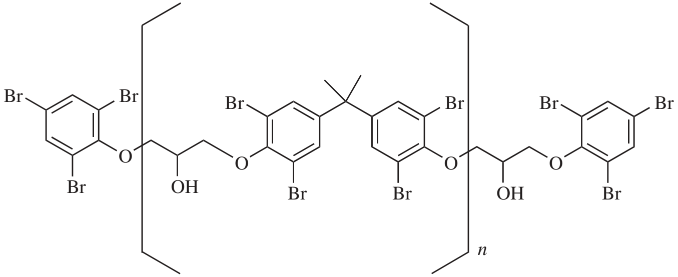
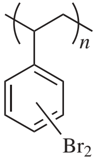
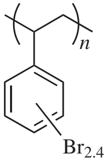
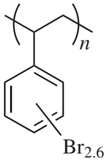
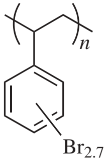
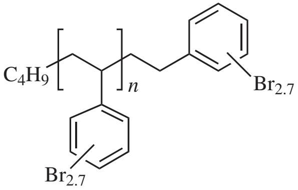
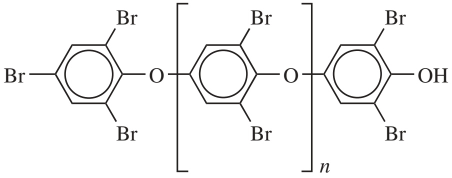
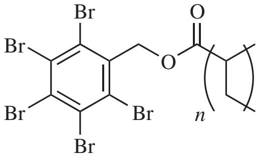
Name	CAS registry number	Structure	Br, %	Mp, °C	Trade name (Company)
tetrabromobisphenol-A carbonate oligomer, phenoxy end capped	[94334-64-2] [28906-13-0]		52	210–230	BC-52 (Great lakes) FG-7500 (Teijin)
tetrabromobisphenol-A carbonate oligomer, tribromophenoxy end capped	[71342-77-3]		58	230–260	BC-58 (Great Lakes) FG-8500 (Teijin)
epoxy oligomers of TBBPA	[68928-70-1]		52–54		Dead Sea Bromine Dainippon Ink Mitsubishi Gas Tohoto Kasei

Table 7 (*Continued*)

Name	CAS registry number	Structure	Br, %	Mp, °C	Trade name (Company)
epoxy oligomers of TBBPA end-capped with tribromophenol or phenol	[139638-58-7] [135229-48-0]		55–58		Dead Sea Bromine Dainippon Ink Mitsubishi Gas Tohoto Kasei
poly (dibromo-styrene)	[148993-99-1]		59	140	PDBS-80 (Great Lakes)
poly (dibromo/ tribromostyrene)	[148993-99-1]		64 64	137 156	Firemaster PBS-64 (Great Lakes) Firemaster PBS-64HW (Great Lakes)

brominated polystyrene	[88497-56-7]		66 (Br) 1.5 (Cl)	195	Pyro-chek 68PB (Albemarle) FR 803 (Dead Sea Bromine) Firemaster BP 411 (Great Lakes)
brominated polystyrene	[88497-56-7]		68	182	SAYTEX HP-7010 (Albemarle)
brominated anionic polystyrene	[88497-56-7]		68	162	SAYTEX HP-3010 (Albemarle)
poly(2,6-dibromo phenylene oxide)	[69882-11-7]		64	225	UNIPLEX FRP-64 (Unitex)
poly(2,3,4,5,6-penta bromobenzyl acrylate)	[59447-57-3]		71	190–220	FR-1025 (Dead Sea Bromine)

68PB) has a minimum of 66% bromine, corresponding to 2.6 bromines per aromatic ring as well as 1.5% chlorine as bromine chloride is used in the bromination (53). This material has a degree of polymerization of about 1800 and is widely used in glass filled engineering thermoplastics, eg, polyamides and thermoplastic polyesters. Other companies now offer similar products as Pyro-Chek 68PB is the major brominated polystyrene for engineering thermoplastics. Stability of these types of brominated polystyrene is inferior to homopolymers of dibromo/tribromo styrene monomer but this has been addressed by Albemarle with the introduction of a product based on the bromination of polystyrene using bromine (54). The product Saytex HP-7010 is a high molecular weight product with 68% aromatic bromine and superior thermal stability and low color. It is particularly suited for engineering resins, such as PET, PBT, and polyamides. The higher molecular weight of these brominated polystyrenes is a disadvantage in certain resins like high temperature polyamides where extremely high flow is required as well as high thermal stability. This trend has become more pronounced as the electronic connectors that these resins go into require thinner walls (hence the molds are harder to fill) and the advent of lead-free solder which leads to higher processing temperatures. Albemarle has developed a new class of brominated polystyrene that is based on brominating an anionic polystyrene, which has a very low molecular weight, low polydispersity and is free from defects. Saytex HP-3010 is the first in this class of materials and shows extremely high flow and the best thermal stability seen to date for any brominated polystyrene, it is designed for high temperature polyamides where high flow and high thermal stability are required (55).

Poly(2,6-dibromophenylene oxide). Poly(2,6-dibromophenylene oxide) [69882-11-7] is a light tan melt-process able solid flame retardant containing 64% aromatic bromine. The main applications are in unfilled and filled engineering thermoplastics (PBT, PET, polyamide resins (nylon, 6 and 66) useful in the manufacture of electrical/electronic component parts (eg, electrical connectors). Since it is a polymeric flame retardant, it does not bloom or migrate from the plastic or cause plate-out during injection molding.

Poly(2,3,4,5,6-pentabromobenzyl acrylate). Poly(2,3,4,5,6-pentabromobenzyl acrylate) [59447-57-3] is made from the polymerization of pentabromobenzyl acrylate and has a high aromatic bromine content along with good thermal stability. Again its main applications are in engineering thermoplastics, PET, PBT and polyamides as well as styrenic copolymers.

4.4. Reactive Flame Retardants. Reactive flame retardants are reacted into the polymer by either becoming a part of the backbone or by grafting onto the backbone. The choice of reactive flame retardant is a great deal more complex than that of an additive type as the reactive flame retardant can exert an enormous effect on the final properties of the polymer. Some reactive halogenated compounds are also used as intermediates for other flame retardants. Tables 8 and 9 list the commercially available reactive flame retardants and intermediates.

Tetrabromobisphenol-A. TBBPA is the largest volume reactive flame retardant. Its primary use is in epoxy resins (see Epoxy Resins) where it is reacted with the bis-glycidyl ether of bisphenol-A to produce an epoxy resin having 20–25% bromine. This brominated resin is typically sold as a 80% solution in

Table 8. **Brominated Reactive Flame Retardants and Intermediates**

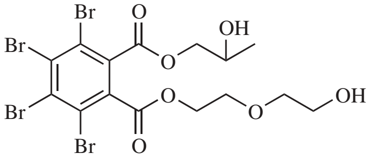
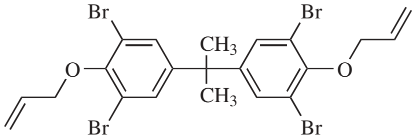
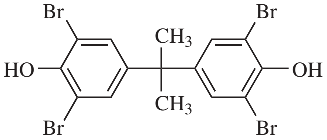
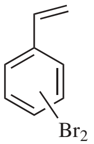
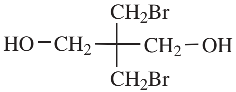
Compound	CAS registry number	Structure	Bromine, %	Mp, °C	Sources
diester/ether diol of tetrabromophthalic-anhydride	[77098-07-8]		46	liquid	SAYTEX RB-79 (Albemarle) PHT4-Diol (Great Lakes)
tetrabromobisphenol-A-bis(allyl ether)	[25327-89-3]		51.2	119	PHE-65 (Great Lakes)
tetrabromobisphenol-A	[79-94-7]		58.4	180	CP-2000 (Albemarle) FR-1524 (Dead Sea Bromine) BA-59P (Great Lakes) Flamecut 120G(Tosoh) Firegaurd 2000(Tejin)
dibromostyrene	[31780-26-4]		59	liquid	DBS (Great Lakes)
dibromoneopentylglycol	[3296-90-0]	 $HO{-}CH_2{-}C(CH_2Br)_2{-}CH_2{-}OH$	61	109	FR-222 (Dead Sea Bromine)

Table 8 (*Continued*)

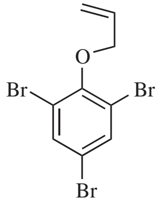
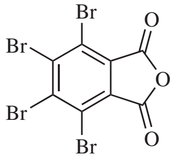
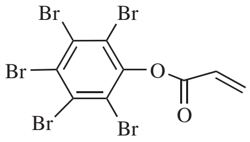
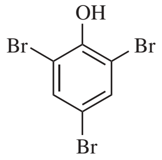
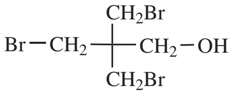
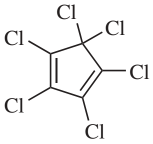
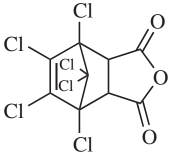
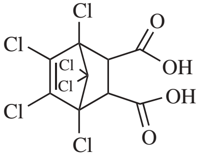
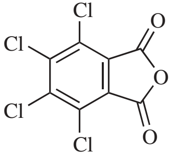
Name	CAS registry number	Structure	Br, %	Mp, °C	Trade name (Company)
tribromophenyl allyl ether	[26762-91-4] [3278-895]		64.2	74–76	PHE-65 (Great Lakes)
tetrabromophthalic anhydride	[632-79-1]		68	270	SAYTEX RB-49 (Albemarle) PHT-4 (Great Lakes)
pentabromobenzylacrylate	[59447-55-1]		71	117	FR-1025M (Dead Sea Bromine)
2,4,6-tribromophenol	[75-80-9] [118-79-6]		72.5	95.5	FR-613 (Dead Sea Bromine) FM PH-73 (Great Lakes) Manac
tribromoneopentyl alcohol	[1522-92-5]	$\mathrm{Br-CH_2-\overset{CH_2Br}{\underset{CH_2Br}{+}}-CH_2-OH}$	73.6	62–67	FR-513 (Dead Sea Bromine)

Table 9. **Chlorinated Reactive Flame Retardants and Intermediates**

Compound	CAS registry number	Structure	Chlorine, %	Mp, °C	Trade names and sources
hexachlorocyclo-pentadiene	[77-47-4]		78.0	11[a]	HEX (Velsicol Chemical Corporation)
chlorendic anhydride	[115-27-5]		57.7	240	Velsicol Chemical Corporation Nippon Kayaku
chlorendic acid	[115-28-6]		55.0	[b]	HET acid (Durez)
tetrachlorophthalic anhydride	[117-08-8]		49.6	255–257	Tetrathal (Solutia)

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[a] 239°C bp.

[b] Decomposes to the anhydride.

a solvent and is used in printed wiring board manufacture (PWB). TBBPA is also used in the production of brominated epoxy oligomers (BEO's) and brominated carbonate oligomers (BCO), which are used as additive flame retardants. It is also used to make other flame retardants such as tetrabromobisphenol-A, bis(2,3-dibromopropylether) and tetrabromobisphenol-A-bis(allyl ether).

Tetrabromophthalic Anhydride. Tetrabromophthalic anhydride [632-79-1] TBPA is prepared in high yield and high purity by the bromination of phthalic anhydride in 60% oleum (56). The sulfur trioxide present in the oleum oxidizes the HBr by-product back to bromine so that all bromine ends up on the aromatic ring.

TBPA is widely used as a reactive flame retardant in unsaturated polyesters as well as the precursor to a number of other fire retardants. Polyesters prepared from this compound have relatively poor photochemical stability and tend to discolor upon exposure to light. This tendency to discolor can be reduced, but not eliminated, by the use of uv stabilizers.

Diester/Ether Diol of Tetrabromophthalic Anhydride. The diester/ether diol of tetrabromophthalic anhydride [77098-07-8] is prepared from TBPA in a two-step reaction. First TBPA reacts with diethylene glycol to produce the half ester and the acid group of the half ester is reacted with propylene oxide to form the diester. The final product, is a diol having one primary and one secondary hydroxyl group. It is an extremely viscous product (typically 100,000 cps) with a hydroxyl value ~220 and it used primarily as a flame retardant for rigid polyurethane foam (57,58).

Dibromoneopentyl Glycol. Dibromoneopentyl glycol [3296-90-0] (DBNPG) is prepared by the stepwise hydrobromination of pentaerythritol [115-77-5] to yield a product in which about half of the hydroxyl function has been replaced, a carboxylic acid is typically used as a catalyst (see ALCOHOLS, POLYHYDRIC; GLYCOLS). The impure commercial form which typically contained 80–82 wt% DBNPG, 5–7% monobromoneopentyl triol [19184-65-7], and 13–15 wt% tribromoneopentyl alcohol [1522-92-5] has been replaced by a pure commercial form of DBNPG by Dead Sea Bromine (FR-522).

The principal use of DBNPG is in rigid polyurethane foam systems (see FOAMS). It can be used by itself to produce Class II foams or with phosphorus co agents to produce Class I foams as evaluated by the ASTM E84 test (59). DBNPG is also used in unsaturated polyester resins where it can be used to replace part of the regular glycol to yield a resin having the desired bromine content. A preferred method of using the compound is to prepare a resin using DBNPG as the sole glycol. This technique gives a resin solid containing 45 wt% bromine, which may be blended with either a non-halogenated or halogenated resin to give a product having the desired degree of flame-retardant properties (60).

Tribromoneopentyl Alcohol. Like dibromoneopentyl glycol tribromoneopentyl alcohol [1522-92-5] is prepared by the stepwise hydrobromination of pentaerythritol. Tribromoneopentyl alcohol is a reactive flame retardant containing approx. 73% aliphatic bromine. It is exceptionally stable for an aliphatic bromine source and is particularly suitable where thermal, hydrolytic and light stability are required. Major uses are a reactive flame retardant for flexible and rigid polyurethanes where it reacts through its single hydroxyl function to form pendant urethane groups.

Brominated Styrene. Dibromostyrene [31780-26-4] is a reactive monomer containing 59% bromine that will readily form homopolymers or copolymers. It is used in unsaturated polyesters for electronics, for making copolymer latex for textile applications as well as making homopolymers, which find applications in engineering thermoplastics.

Tribromophenol. Tribromophenol [75-80-9] is prepared through bromination of phenol and is used as an intermediate to make other flame retardants such as tribromophenyl allyl ether [21850-44-2], 1,2-bis(2,4,6-tribromophenoxy) ethane [37853-59-1], Tris(tribromophenyl) triazine [25713-60-4] and epoxy oligomers.

Bromine as a Reactive Flame Retardant. Bromine and chlorine are the starting materials for all of the commercial compounds described. Bromine is also used in a somewhat different way to impart flame retardancy. That is, it is used to brominate the resin in interest directly. This is practiced commercially in the case of unsaturated polyesters (61).

Hexachlorocyclopentadiene. Hexachlorocyclopentadiene [77-47-4] is a reactive intermediate and is used to manufacture flame retardant for use in the wire and cable industry as well as the preparation of chlorendic anhydride, which is used as a reactive intermediate in the manufacture of flame retardant, unsaturated polyesters.

Tetrachlorphthalic Anhydride. Tetrachlorphthalic anhydride [117-08-8] (TCPA) is manufactured by the ferric chloride catalyzed chlorination of phthalic anhydride. The relatively low chlorine content and the lower flame retardant efficiency of the aromatic chlorides limit use to unsaturated polyester resin formulations that do not require a high degree of flame retardancy.

Chlorendic Acid. Chlorendic acid [115-28-6] (HET Acid) and its anhydride [115-27-5] are widely used flame retardants. Chlorendic acid is synthesized by a Diels-Alder reaction of maleic anhydride and hexachlorocyclopentadiene (see Cyclopentadiene and Dicyclopentadiene) in toluene followed by hydrolysis of the anhydride using aqueous base (62). The anhydride can be isolated directly from the reaction mixture or can be prepared in a very pure form by dehydration of the acid. The principal use of chlorendic anhydride and chlorendic acid has been in the manufacture of unsaturated polyester resins. Because the esterification rate of chlorendic anhydride is similar to that of phthalic anhydride, it can be used in place of phthalic anhydride in commercial polyester formulations. Besides having a degree of fire resistance, polyesters containing chlorendic anhydride often exhibit a significant degree of uv stability and corrosion resistance. The double bond in chlorendic acid is not reactive as a cross-linking site; hence, reactive monomers such as maleic anhydride must be included in the polyester backbone to achieve cross-linking. Other applications are in alkyds, polyurethanes, and epoxy resins.

5. Economic Aspects

There are a relatively small number of producers of halogenated flame retardants, especially for brominated flame retardants, where three producers account for greater than 80% of world production. Table 10 gives the volumes of brominated and chlorinated flame retardants used worldwide. Prices of

Table 10. **Consumption of Halogenated Flame Retardants**

		Volume × 10^3t		
Region	Flame retardant	1989[a]	1998[b]	2001[b]
Western Europe	brominated	28	48	38.5
	chlorinated	19.6	51	50.5
Japan	brominated	28.7	48	47.4
	chlorinated	4.85	5.1	4.73
United States	brominated	46.5	68.3	60.3
	chlorinated	16	18.5	17.5
Total	*brominated*	*103.2*	*164.3*	*146.2*
	chlorinated	*40.45*	*80.6*	*72.73*

[a] Ref. (63).

[b] Ref. (64).

halogenated flame retardants vary from less than $2.00/kg to as high as $13.00/kg. Cost to the user depends on the level of use of the specific flame retardant and other factors such as the use of stabilizers.

6. Health and Safety Factors

Halogenated flame retardants, which are primarily brominated, come in variety of structural classes. Their potential effects are related to their non-halogenated substructures, and thus should be considered individually with respect to their health and environmental profiles.

In general, the acute toxicity of the halogenated flame retardants currently in use is quite low. They typically have high oral and dermal LD_{50} values and are not skin or eye irritants. Most are not mutagens. Most brominated flame retardants examined to date have relatively high no adverse effect levels on repeated doses, and do not affect fetal development. Many can be considered persistent in the environment, although there are notable exceptions. Because of persistency, it is generally recommended that they not be released to the environment through waste or water discharges. Brominated flame retardants generally are not toxic to aquatic organisms, again with a few notable exceptions. The few that do show some evidence of bioaccumulation typically do not induce chronic effects.

Specific information on each individual flame retardant can be acquired from the manufacturer. The latest MSDS should always be consulted prior to use, the appropriate personal protective gear worn during use, and proper disposal utilized.

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