

Deca-BDE and Alternatives in Electrical and Electronic Equipment

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Preface

Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) specifies that, from 1 July 2006, new electrical and electronic equipment (EEE) put on the market are not to contain polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE), lead (Pb), mercury (Hg), cadmium (Cd) or hexavalent chromium (Cr⁶⁺) for specified equipment categories.

Article 5(1) (b) of the RoHS-directive makes it possible to exempt materials and components of electrical and electronic equipment from the ban in the directive if their elimination or substitution via design changes or materials and components which are not banned by the directive is technically or scientifically impracticable. Furthermore the provision also makes it possible to grant an exemption where the negative environmental, health and/or consumer safety impacts caused by substitution are likely to outweigh the environmental, health and/or consumer safety benefits thereof.

In accordance with a procedure referred to in Article 7(2) of the Directive, during 2005 the Commission evaluated the applications of one of the PBDEs, Deca-BDE. With the Commission Decision 2004/717/EC of 13 October 2005, Deca-BDE in polymeric applications was added to the list of exemptions.

Denmark has instituted legal proceedings against the Commission's decision to exempt Deca-BDE from the ban decreed by the RoHS Directive.

This report forms part of the scientific documentation that is needed to support the case before the Court of Justice of the European Communities. The purpose of the study is to identify and describe suitable alternatives to the brominated flame retardant Deca-BDE, and to determine whether substitution of the alternative substances is possible from a scientific or technical point of view. The Danish Environmental Protection Agency has concurrently initiated an environmental and health assessment of selected alternatives in order to compare any negative environmental or health impacts caused by substitution with the environmental and health benefits of the substitution.

The study has been guided by a Steering Group consisting of Torben Nørlem and Frank Jensen, Danish Environmental Agency, and Carsten Lassen, COWI.

The report has been prepared by Carsten Lassen and Sven Havelund, COWI A/S (Denmark), André Leisewitz, Öko-Recherche GmbH (Germany), and Peter Maxson, Concorde East/West Sprl (Belgium).

The information presented here reflects the combined view of the authors. The publication of the report does not necessarily imply that the contents reflect the views of the Danish EPA.

Executive Summary

Overall evaluation

This study has not identified any application of Deca-BDE in electrical and electronic equipment for which substitution is not possible, from the scientific or technical point of view. For all EEE materials and components presently using Deca-BDE, technically acceptable alternatives are available on the market. The widespread use of alternatives, and availability of EEE components without Deca-BDE, is indicated by the fact that a large number of the world's major manufacturers of EEE have phased out the use of Deca-BDE in their products.

The study

The study summarises information on the use of Deca-BDE and its alternatives in electrical and electronic equipment. The information was obtained mainly from the literature and from public information available on web-sites of manufacturers, trade organisations, institutions, etc. Due to the fact that the study is part of the scientific documentation supporting a case before the Court of Justice of the European Communities, the documentary emphasis was laid on published information. Only limited additional information was obtained by personal communication with companies and trade organisations.

It was beyond the scope of this study to undertake an environmental and health assessment of Deca-BDE and selected alternatives, or to compare any negative environmental or health impacts caused by substitution with the environmental and health benefits of the substitution. These aspects are covered by a separate environmental and health assessment initiated concurrently by the Danish EPA.

Applications of Deca-BDE

The global market demand for Deca-BDE in 2001 was about 56,100 tonnes. The market demand in Europe was 7,600 tonnes, considerably lower than the demand in the Americas and Asia. A significant part of the volume is used in electrical and electronic equipment (EEE).

The main EEE application has traditionally been enclosures made of High Impact Polystyrene (HIPS), especially for TV-sets, but also for printers, scanners, fax machines, etc. Other EEE applications are connectors, switches, and other internal parts made of engineering plastics like thermoplastic polyesters (PBT/PET) and nylon (PA), and wires and communication cables made of polyolefins (PP and PE).

As part of the European Commission's RoHS stakeholder consultation, the manufacturers of brominated flame retardants have specifically pointed at difficulties in the substitution of Deca-BDE in the plastics HIPS, ABS, and PBT, citing the lack of cost-effective alternative flame retardants that can provide good flame retardancy and good mechanical properties.

Alternatives to Deca-BDE

Table 1 lists 25 selected flame retardants, and shows the types of plastic in which each may be used. The list is not considered comprehensive. Only flame retardants that can be used to obtain plastics meeting the UL 94 vertical

flame test, V-0 have been included. V-0 grade is typically required for plastic parts in connectors, switches, and other components in contact with current-bearing metal parts of EEE. In the USA, V-0 grade plastics are also required for TV-set enclosures, whereas the European standard has less strict requirements.

Two brominated flame retardants – bis(pentabromophenyl) ethane and ethylene bis(tetrabromophthalimide) – have application spectra very close to the spectrum for Deca-BDE, and they have been produced and marketed as general purpose alternatives to Deca-BDE by the same companies that produce Deca-BDE. For most applications the two compounds have superior technical properties (except for colour) compared to Deca-BDE, but the two substances are more expensive than Deca-BDE.

The flame retardants in Table 1 can all be used to reach a high level of flame retardancy, but some of the flame retardants may, for some applications, fail to be a viable substitute for Deca-BDE for other technical reasons. In particular, the application of some of the non-halogenated alternatives may significantly change the properties of the flame-retarded plastics. The list may be considered a gross list; more information on the specific alternatives is provided in Chapter 3 of this report.

Enclosures

Enclosures for TV-sets are typically made of HIPS, ABS, or copolymers like PC/ABS, PPE/HIPS and PPE/PS. The addition of PC or PPE makes the resins themselves less flammable, and the flammability requirements can then be met using less efficient and/or smaller quantities of flame retardants. Personal computer monitors are mainly made from ABS and PC/ABS because these plastics have higher impact strength and are less susceptible to cracking than HIPS. In the USA, enclosures for TV-sets have traditionally been made from HIPS with Deca-BDE, and this application has accounted for around 80% of the use of Deca-BDE in the USA. In Europe, due to the lower flame-retardancy requirements for TV-set enclosures, HIPS without flame retardants has been used, in particular for the lower-price market segment for TV-sets. In response to fire statistics indicating significantly more fires in European produced TV-sets than in American ones, the major European producers today use a higher level of flame-retardancy than required by the European standard. The materials of choice are copolymers with non-halogen organo-phosphorous flame retardants. The discussion of alternatives is exemplified by the case of enclosures for TV-sets, as most information is available on this product group, and the observations are equally applicable to enclosures for other equipment.

A number of other brominated flame retardants are available for use in HIPS. A review of price estimates has been compiled on the basis of information from a major supplier of HIPS compounds for the TV sector. The prices of the compounds (consisting of resin, flame retardants and other additives) based on brominated alternatives are 10-20% higher than similar HIPS with Deca-BDE. The prices of the copolymers with organo-phosphorous flame retardants (FRs) are about 60-70% higher than HIPS with Deca-BDE, corresponding to a price increase of the raw materials of an average TV-set with CRT technology (27.5-inch screen) of about 5 €. With typical total manufacturing costs of 300 € for the average CRT TV-set, the difference in raw material costs corresponds to about 2%. Any additional costs of research and development, and changes of moulds and other process equipment by the enclosure manufacturer, may be relatively small if substitution takes place coinci-

dently with design changes and introduction of new products, e.g. TV-sets with LCD screens or plasma display panels.

The volume of flame retarded (also abbreviated as FR) plastic in enclosures of an average LCD panel TV-set, in which the back cover is typically flame retarded, is nearly the same as in an average CRT TV-set, because of the larger screen size of the LCD panel TV-sets. Therefore, the price estimate for FRs in CRT TV-sets may also be applied to the LCD panel TV-sets.

Deca-BDE has traditionally not been used in ABS because octa-BDE was superior in this resin. With the ban of octa-BDE, Deca-BDE may have taken over a part of this market, but other brominated flame retardants have superior technical properties in ABS, and have been marketed as the recommended octa-BDE alternatives for use with ABS.

Connectors, switches, etc.

Small plastic parts of electrical connectors, switches, etc. made of flame retarded thermoplastic polyesters (PBT/PET) or polyamide (PA) are present in almost all EE products. These two plastic groups account for about 60% of the consumption of plastics for electrical components of EEE. Deca-BDE, in turn, accounts for about 10% of the global consumption of flame retardants used in PBT/PET in EEE, and for about 6% of the global consumption of flame retardants used in polyamide in EEE. Contrary to the situation for the enclosures, replacement of these plastics by other types of plastic is generally not an option. As a general rule, in both PBT/PET and PA, Deca-BDE is a lower cost solution, but tends to be less acceptable in terms of compatibility and mechanical properties. The most widely used FRs in PBT/PET are brominated carbonate oligomers and brominated epoxy oligomers. Halogen-free FR alternatives have only recently been commercially available for PBT/PET. These are based on organic phosphinates. For PA in EEE, the most widely used FRs are halogenated – polybrominated styrenes, or brominated polystyrenes, which have a market share 10 times higher than the market share of Deca-BDE. A number of halogen-free FRs for PA have also been available for many years and are widely used. The halogen-free FRs are based on red phosphorous, melamine cyanurate, melamine polyphosphate, magnesium dihydroxide or organic phosphinates. For some applications they are economically competitive with the brominated flame retardants. It has not been possible to identify any applications of electrical connectors, switches, etc. for which Deca-BDE cannot be readily replaced by other brominated flame retardants or halogen-free flame retardants.

Wires and cables

Deca-BDE has been reported to be used for some types of wire and cable that are fabricated with insulation made of polyolefins (PE and PPP). Wires and cables belong to a very diverse product group, with a number of different plastics and rubber used for cable insulation, and employing a variety of flame retardants. It has not been possible to identify any recent quantification of the use of Deca-BDE and alternative flame retardants in cables of EEE. In any case, a number of both halogen-containing and halogen-free flame retardants are available for V-0 grade polyolefins.

Companies that have phased out Deca-BDE

A large number of companies in the EE sector specifically state that they have phased out Deca-BDE and other PBDEs in all of their products, among these, Dell, Hewlett-Packard Company (including Compaq), Sony, IBM, Ericsson, Apple, Matsushita (including Panasonic), Intel and B&O. Some of

the main driving forces for these commitments have been eco-labels, customer requirements (e.g. “green procurement” initiatives) and preparedness for the RoHS Directive and other legislation. Some of the companies replaced Deca-BDE already in the 1990s. These companies have typically managed the phase-out of Deca-BDE by enforcing specifications prohibiting its use in the products and components supplied by sub-contactors, but they generally have not specified which flame retardants should be used as substitutes. The specific flame retardants used in products are generally considered confidential, but a typical replacement scheme seems to be the use of copolymers with halogen-free organo-phosphorous compounds for enclosures and other large parts, and the use of alternative brominated flame retardants for the small parts (<25 g) in connectors, switches, etc. In this manner, the products still meet the most strict criteria of eco-labels.

Product chain and industry structure

Based on a description of the product chain of equipment containing Deca-BDE, the impact of a Deca-BDE ban on the different industrial sectors is briefly discussed. The impact is highly dependent on whether Deca-BDE is replaced with other brominated flame retardants with nearly the same properties as Deca-BDE, or whether it is replaced with halogen-free flame retardants, sometimes including changes of the resin as well. In the first case the impact is mainly implying the use of more expensive flame retardants. Any shift to halogen-free alternatives in EEE is, on the other hand, not driven by the introduction of a ban on Deca-BDE, but should rather be seen as part of a more general ongoing movement toward the use of halogen-free flame retardants driven by consumer demand, eco-labels, NGO actions, etc.

Table 1 Deca-BDE and selected alternative flame retardants for relevant V-0 grade plastics in EEE

Flame retardant	Enclosures				Connectors, etc		Wires	
	HIPS	ABS	PC/ABS	PPE/HIPS	PA	PBT/PET	PP	PE
Halogen-containing FRs								
Deca-BDE / ATO	X	X	X	X	X	X	X	X
Ethane-1,2-bis(pentabromophenyl) / ATO	X	X	X	X	X	X	X	X
Ethylene bis(tetrabromophthalimide) / ATO	X	X	X	X	X	X	X	X
Brominated epoxy polymer / ATO	X	X	X		X	X		
Tetrabromobisphenol-A (TBPPA)/ ATO	X	X						
TBBPA carbonate oligomer / ATO			X	X		X		
TBBPA bis (2,3-dibromopropyl ether) / ATO	X						X	
Tetradecabromodiphenoxybenzene / ATO	X				X	X		X
Tris(tribromophenoxy) triazine / ATO	X	X						
Bis(tribromophenoxy) ethane / ATO		X						
Tris(bromopentyl) phosphate / ATO							X	
Poly(pentabromobenzyl acrylate) / ATO					X		X	
Brominated polystyrene / ATO					X	X		
Poly(dibromostyrene) / ATO						X		
Chloroparaffins / ATO							X	
Dodecachlorododecahydro-dimethanodibenzocyclooctene / ATO or other synergists					X	X		
Non-halogen organo-phosphorous FRs								
Resorcinol bis(diphenylphosphate) (RDP)			X	X				
Bisphenol A bis(diphenylphosphate) (BDP)			X	X				
Triphenyl phosphates (TPP)			X	X				
Other non-halogen FRs								
Intumescent FR systems based on phosphor and nitrogen compounds							X	X
Red phosphorous					X			X
Melamine cyanurate					X		X	
Melamine polyphosphate					X			
Organic phosphinates					X	X		
Magnesium dihydroxide					X		X	

ATO: Antimony trioxide used as synergist

Abbreviations and acronyms

ABS	Acrylonitrile-butadiene-styrene
ATO	Antimony trioxide, Sb ₂ O ₃
BAPP	Bisphenol A diphosphate (same as BDP)
BDP	Bisphenol A diphosphate (same as BAPP)
BEO	Brominated epoxy oligomer
BFR	Brominated flame retardant
BrPS	Brominated polystyrene
BSEF	Bromine Science and Environmental Forum
CEFIC	European Chemical Industry Council
CRT	Cathode ray tube
DBDO	Decabromodiphenyl oxide (same as Deca-BDE)
DBDPO	Decabromodiphenyl oxide (same as Deca-BDE)
Deca-BDE	Decabromodiphenyl ether (same as DBDO)
DEFRA	UK Department for Environment, Food and Rural Affairs
EBFRIP	European Brominated Flame Retardant Industry Panel
EE, E&E	Electrical and electronic
EEE	Electrical and electronic equipment
EFRA	European Flame Retardants Association
EN	European Norm
EP	Epoxy
EPDM	Ethylene-propylene-diene terpolymer
EU	European Union
EVA	Ethylene-vinyl acetate
FPTV	Flat panel TV-set
FR	Flame retardant or flame retarded
HB	UL 94 horizontal burn test
HBCD	Hexabromocyclododecane
HF	Halogen-free
HIPS	High Impact Polystyrene
HIPS/PPO	Copolymer of HIPS and PPO (same as PPE/HIPS)
IEC	International Electrotechnical Commission
IR	Ignition resistant
IT	Information technology
LCD	Liquid crystal display
MFI	Melt flow index
OBDPO	Octabromodiphenyl oxide (same as Octa-BDE)
Octa-BDE	Octabromodiphenyl ether
OECD	Organisation for Economic Co-operation and Development
PA	Polyamide; Nylon
PA6	Polyamide 6; Nylon6
PA66	Polyamide 66; Nylon6-6
PAEK	Polyaryletherketone
PBB(s)	Polybrominated biphenyl(s)
PBDD(s)	Polybrominated dibenzodioxin(s)
PBDE(s)	Polybrominated diphenyl ether(s)
PBDF(s)	Polybrominated dibenzofuran(s)
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PC/ABS	Copolymer of PC and ABS
Penta-BDE	Pentabromodiphenyl ether

PES	Polyethersulfone
PET	Poly(ethylene terephthalate)
PF	Phenol formaldehyde (phenolic)
PP	Polypropylene
PPE	Polyphenylene ether (same as PPO)
PPO	Polyphenylene oxide (same as PPE)
PPO/PS	Copolymer of PPO and PS (same as PS/PPE)
PS	Polystyrene
PS/PPE	Copolymer of PS and PPE (same as PPO/PS)
PSU	Polysulfone
PVC	Polyvinyl chloride
R&D	Research and Development
RDP	Resorcinol bis(diphenylphosphate)
RoHS	Restriction of the use of certain hazardous substances in electrical and electronic equipment (Directive)
SAN	Styrene acrylonitrile (copolymer)
Sb	Antimony
SBR	Styrene butadiene rubber
SME	Small- and medium-sized enterprises
TBBPA	Tetrabromobisphenol A
TPP	Triphenyl phosphate
TPU	Thermoplastic polyurethane
UK	United Kingdom
UL	Underwriters Laboratories Inc.
UL 94	Tests for Flammability of Plastic Materials from Underwriters Laboratories Inc.
UPE	Unsaturated polyester
US(A)	United States (of America)
UV	Ultraviolet (light)
V-0, V-1, V-2	UL 94 Vertical burn tests
WEEE	Waste electrical and electronic equipment

1 Introduction

By the European Commission decision of 13 October 2005 (2005/717/EC), "*DecaBDE in polymeric applications*" was added to the Annex to Directive 2002/95/EC, the RoHS Directive [**Fejl! Bogmærke er ikke defineret.**].

The background for the exemption, and the history of this development in Europe, has recently been reviewed by the Washington State Department of Health and the Washington State Department of Ecology, and the reader is referred to this source for a quick overview [1].

1.1 Methodology

This report summarises information on the use of Deca-BDE and its alternatives in electrical and electronic equipment. The information has mainly been obtained from the literature and from public information available on the web-sites of manufacturers, trade organisations, institutions, etc.

Due to the nature of the study, comprising part of the scientific documentation to support a case before the Court of Justice of the European Communities, all information sources consulted, except for market surveys that are not authorised to be passed to third parties, are to be enclosed with the report submitted to the Court of Justice. This requirement also applies to personal communications, and consequently, only very limited information obtained through personal communications with companies and trade organisations is quoted in the report. The usual practice of guaranteeing confidentiality to information sources within companies has therefore not been possible, which obviously reduces the opportunities for obtaining and presenting new and updated information. Even beyond the concern of disclosing company-specific information, several companies have explicitly expressed their reluctance at being exposed as contributors to the study. In particular, these limitations may have seriously compromised the comprehensiveness of the evaluation of the potential costs of substitution of Deca-BDE.

Moreover, in response to requests for updated information on the use of Deca-BDE in Europe, the four organisations: CEFIC, EFRA, BSEF and EBFRIP have jointly responded that, in view of current legal proceedings, they were not in a position to respond to the requests [2]. The information on the use of Deca-BDE presented in this report has consequently been obtained mostly by combining information from a variety of published sources.

1.2 Definitions

As mentioned above, the Commission's exemption refers specifically to "*DecaBDE in polymeric applications*".

Deca-BDE

It is presumed that the term Deca-BDE is used for the commercial product, "Deca-BDE". The commercial product may contain up to 3% of other

PBDEs, which are otherwise restricted by the RoHS Directive (further discussed in chapter 2).

Polymeric applications

The Oxford Advanced Learner's Dictionary gives for polymer the following definition: "*a natural or artificial substance consisting of large molecules (= groups of atoms) that are made from combinations of small simple molecules.*" [3] A polymer is made by covalently linking small simple molecules, so-called monomers, together.

The Kirk-Othmer Encyclopedia of Chemical Technology introduces the chapter on polymers with the following: "*Polymers are the materials from which plastics, rubbers, and most fibers, surface coatings, and adhesives are made. Biopolymers are important constituents of living organisms.*" [4]

Wikipedia, the free web encyclopedia, introduces the term polymer as follows: "*Polymer is a term used to describe a very large molecule consisting of structural units and repeating units connected by covalent chemical bonds. The term is derived from the Greek words: polys meaning many, and meros meaning parts [1]. The key feature that distinguishes polymers from other molecules is the repetition of many identical, similar, or complementary molecular subunits in these chains.*"[5]

Examples of natural polymers are cellulose, wool or caoutchouc (natural rubber). Synthetic polymers are made from one or more synthetic monomers and form the basic matrix of a range of materials like plastics, silicones and synthetic rubbers.

Polymers are seldom used in their pure forms in electrical and electronic equipment; instead, the base polymer is usually mixed or chemically combined with a number of additives: pigments, stabilisers, flame retardants, fillers, etc. to form different types of plastics, rubbers and silicones. In the same manner, the cellulose base polymer is naturally combined with other substances to form wood. In the following text, the base polymer (or monomer) will be designated as the "resin".

Therefore, the term "polymer applications" is considered here to apply to all materials used in electrical and electronic equipment (EEE) that are based on polymers: plastics, rubbers, silicones, wood, textiles.

In practice, plastics account for nearly 100% of the applications of Deca-BDE in EEE, so the study has focused on these applications. However, it cannot be ruled out that small amounts of Deca-BDE may be used with other polymeric applications.

1.3 Fire regulations and material classifications

The use of plastics in electrotechnical products entrains special fire precautions because fire hazard is inherent in any energised equipment. Potential ignition sources within electrical and electronic equipment include overheated current-carrying parts, overheated terminals, sparks and arcs. When a part is ignited, flames may develop and migrate to adjacent combustible materials. Special fire tests have been developed to simulate as realistically as possible actual ignition risks.

A large number of standards and test procedures for electrotechnical products exist, both internationally (IEC) and at national/regional level.

In the EU, consumer electronics such as TV-sets, amplifiers, CD-players, tape recorders, etc. are regulated by standard EN 60065. This standard describes a series of test methods that have evolved from the American Standard UL 94 (see below). EN 60065 includes no flammability requirements for plastic materials, which are otherwise well protected from internal ignition sources by means of fire enclosures or minimum distances from potential ignition sources. For TV-sets, back plates and front plates are permitted to be made from materials that fulfil the requirements of the UL 94 horizontal burn test, HB (see below). The requirements of EN 60065 are different from those of the American standard (UL 1410) which, among other things, has stricter flammability requirements for TV-set enclosures. [32]

Electronic products such as computers, printers, telephone systems, photocopiers and other office machines are regulated in the EU by EN 60950, which has essentially the same flammability requirements as the international (IEC 950) and the American (UL 1950) standards [32]. Standard 60950 comprises several different test methods and classifications for the different parts from which appliances are made. These test methods for materials have also evolved from the American Standard UL 94.

Electrical household appliances are regulated by the European standard EN 60335. This standard has a number of sub-standards depending on the type of appliance - washing machine, hairdryer, vacuum cleaner, etc.

When the efficiency of flame retardants or the flame retardancy of plastic materials is compared, the UL 94 flammability classification is usually applied.

UL 94 tests on plastic materials

UL 94 refers to the material flammability test of the American Underwriters Laboratories.

There are two types of pre-selection test programs conducted on plastic materials to measure flammability characteristics. The first program determines the material's tendency either to extinguish or to spread the flame once the specimen has been ignited. This is described in UL 94, The Standard for Flammability of Plastic Materials for Parts in Devices and Appliances, which is now harmonized with IEC 60707, 60695-11-10 and 60695-11-20 and ISO 9772 and 9773. The second test program measures the resistance of the plastic to electrical ignition sources. The material's resistance to ignition and surface tracking characteristics is described in UL 746A, which is similar to the test procedures described in IEC 60112, 60695 and 60950. [6]

UL 94 flammability classifications

There are 12 flammability classifications specified in UL 94 that are assigned to materials based on the results of these small-scale flammability tests. These classifications, listed below in descending order of flammability resistance, are used to distinguish a material's burning characteristics after test specimens have been exposed to a specified test flame under controlled laboratory conditions. [6]

Six of the classifications relate to materials commonly used in manufacturing enclosures, structural parts and insulators found in consumer electronic products (5VA, 5VB, V-0, V-1, V-2, HB).

The other six classifications are assigned to low-density foam materials commonly used in fabricating speaker grills, sound-proofing material and very

thin films – all materials that are generally not capable of supporting themselves in a horizontal position.

Horizontal versus vertical testing orientation

Depending on the specifications of the relevant test method, specimens moulded from the plastic test material are oriented in either a horizontal or vertical position, and are subjected to a defined flame ignition source for a specified period of time. In some tests, the test flame is applied only once, as is the case in the horizontal burning (HB) test, while in other tests the flame is applied twice or more.

A HB flame rating indicates that the material was tested in a horizontal position and was found to burn at a rate less than the specified maximum.

The three vertical ratings, V-2, V-1 and V-0 indicate that the material was tested in a vertical position and self-extinguished within a specified period of time after the ignition source was removed. The vertical ratings also indicate whether the test specimen dripped flaming particles that ignited a cotton indicator located below the sample. In testing for the strictest 5VA or 5VB classification, UL 94 describes a method in which the test flame is applied five times. These small-scale tests measure the propensity of a material to extinguish or spread flames once it has been ignited.

Material classification range

Therefore, the UL 94 material flammability classifications range from HB (the lowest standard) to successively more stringent vertical burning tests (Class UL 94 V-2, V-1, V-0 and 5V). In short, ranging from least to most flammable, the classifications are: UL 94 V5 > V-0 > V-1 > V-2 > HB.

The ignition resistance of a plastic part depends also on the thickness of the part - a thicker part (made of the same plastic) being more resistant. Along with the flammability classification of a plastic material, the thickness of the material would usually be specified as well. A certain plastic compound may, for example, be classified V-0 at 1/8-inch (~0.32 cm) thickness, but only V-2 at 1/16-inch (~0.16cm) thickness.

1.4 Flammability of plastics

The flammability of base resins varies considerably, and can be characterised by the limiting oxygen index.

The limiting oxygen index indicates the minimum percentage of oxygen required in the combustion atmosphere to sustain ignition and combustion. If the limiting oxygen index is 20% (atmospheric concentration) or lower, the resin will continue burning when ignited in the normal atmosphere. There is no simple relationship between a UL 94 rating and the oxygen index, but the oxygen index gives a broad indication of the flammability performance of the material.

Oxygen indexes of a number of resins are shown in Table 1.1. The oxygen index of the resins may vary somewhat, and slightly different values may be found in different information sources. The oxygen index is also dependent on the addition of reinforcement materials. The addition of glass fibres, for instance, lowers the oxygen index of the plastic material, and requires a higher flame retardant loading to obtain a desired FR classification.

Resins with a limiting oxygen index of more than about 30% are self-extinguishing, i.e. they can achieve a flame retardant grade without addition of flame retardant substances. Three of the resins included in Table 1.1 - polysulfone, polyaryletherketone and polyethersulfone - have such high oxygen indexes that flame retardant grades are achieved without addition of flame retardants.

By mixing a resin with a low limiting oxygen index, e.g. polystyrene, with a resin with a higher index, e.g. polyphenylene, a copolymer with a higher limiting oxygen index than the pure polystyrene can be obtained. With a higher limiting oxygen index, the copolymer can meet a desired FR classification at lower FR loading, or with the use of less efficient flame retardants.

Table 1.1
Limiting oxygen index of base resins [7]

Base polymer	Abbreviation	Limiting oxygen index of base polymer * (%)
Polystyrene	PS	18
Polyketone	PK	20 **
Polybutylene terephthalate	PBT	22
Polyamide	PA	24.5
Polyphenylene ether	PPE	28
Polycarbonate	PC	29
Polysulfone	PSU	29.5
Polyaryletherketone	PAEK	37
Polyethersulfone	PES	38

* Oxygen indexes derived in [7] from Gareiß, B. 1995. Halogen-free flameproofing for engineering plastics. In: Polymers, BASF AG, Ludwigshafen (except for polyketone).

** Derived in [7] from Londa, M., Gingrich, R.P., Kormelink, H.G. & Proctor, M.G. 1995. Development of flame retardant aliphatic polyketone compounds. Shell Chemical Company, Houston.

2 Applications of Deca-BDE

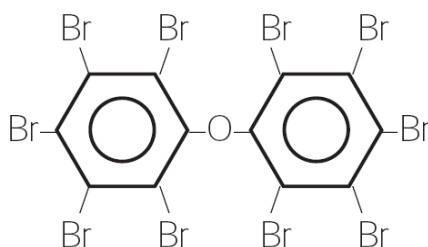
Polybrominated diphenyl ethers (PBDEs) are a group of aromatic brominated compounds in which one to ten hydrogens in the diphenyl oxide structure are replaced by bromine.

Three different PBDEs have been commercially available. They are referred to as penta-, octa- and decabromodiphenyl ether, but each product is, in fact, a mixture of brominated diphenyl ethers.

Decabromodiphenyl ether, or Deca-BDE, as indicated by the name, has ten bromine atoms attached to the diphenyl oxide structure, and a bromine content of 82-83%, making it a very efficient flame retardant.

The CAS No (chemical identification number) of decabromodiphenyl ether is 1163-19-5. The substance is also known as decabromodiphenyl oxide (DBDO) or bis(pentabromophenyl) ether.

Figure 2.1
Chemical structure of Deca-BDE (from [8])



Commercial Deca-BDE is marketed, among other names, as SAYTEX® 102E (Albemarle Corp.) [8], Great Lakes DE-83 RTM (Great Lakes Corp.) [9] and FR 1210 (ICL Industrial Products) [10].

The commercial Deca-BDE contains small impurities. In 1995, the US and European producers committed themselves to producing Deca-BDE with an average purity of 97% or better [11]. The remaining part have typically mainly been made up by nonabromodiphenyl ether (with nine bromine atoms) [17]. According to the European Union Risk Assessment Report – Bis(pentabromophenyl) ether, "*The actual composition of the products from different producers/suppliers is regarded as confidential information.*" [16] The EU Risk Assessment applies to the commercial Deca-BDE [16].

Deca-BDE is the most widely used of the PBDEs, with a global demand of about 56,100 tonnes in 2001 (see Table 2.1) and 56,418 tonnes in 2003 [18], according to the manufacturers of FRs.

As indicated in Table 2.1, the U.S. market for Deca-BDE is significantly larger than the European market. A recent US study of alternatives to Deca-BDE prepared by the Lowell Center for Sustainable Production [12] reported that roughly 80% of Deca-BDE use in the U.S. is thought to be in electronic enclosures (housings, casings), with the vast majority used in the back and front plates of television sets. The majority of TV-set enclosures in the U.S.

are, according to the study, made from HIPS with Deca-BDE, whereas enclosures in Europe are primarily made either without FRs or with other FRs.

Table 2.1
Market demand for PBDEs and two other major brominated flame retardants, by region, in 2001 (tonnes) [18]

Metric tons	Americas	Europe	Asia	Rest of the World	Total
TBBPA	18,000	11,600	89,400	600	119,700
HBCD	2,800	9,500	3,900	500	16,700
Deca-BDE (DBDPO)	24,500	7,600	23,000	1,050	56,100
Octa-BDE (OBDPO)	1,500	610	1,500	180	3,790
Penta-BDE (PBDPO)	7,100	150	150	100	7,500
TOTAL	53,900	29,460	117,950	2,430	203,790

TBBPA: Tetrabromobisphenol A; HBCD: Hexabromocyclododecane

Combining the information in Table 2.1 and Table 2.2, it can be estimated that Deca-BDE accounted for about 2% of the total European FR market for all applications in 2001.

According to the recent progress report on "The Voluntary Emissions Control Action Programme for the brominated flame retardant Deca-BDE", the textile and plastics industries in the UK, France, Germany, Italy, Belgium and the Netherlands are responsible for more than 95% of the Deca-BDE consumption in the EU [13].

Table 2.2
European market for flame retardants, 2001 (based on [14])

Flame retardant	Market supply	
	Tonnes	%
Brominated FR	51,000	11,8
Chlorinated phosphates	42,000	9,1
Non halogenated phosphorous based	172,000	9,7
Aluminium trihydroxide	20,000	40,0
Magnesium dihydroxide	9,000	4,7
Melamine and its salts	25,000	2,1
Antimony trioxide	71,000	5,9
Cloroparaffins	2,000	16,5
Borates	51,000	0,4
Overall total	430,000	100

Deca-BDE is a flame retardant with a wide application spectrum in plastic resins and textiles. It is an additive flame retardant, which means that it does not chemically react with the plastic resin. Deca-BDE is always used in conjunction with antimony trioxide (ATO), which acts as a synergist.

Current applications of Deca-BDE, according to information from the Bromine Science and Environmental Forum (BSEF), are shown in Table 2.3

Table 2.3
Applications of Deca-BDE, according to the Bromine Science and Environmental Forum [15]

Deca-BDE (DECABROMODIPHENYL ETHER)	
HIPS (High Impact Polystyrene)	E&E equipment <ul style="list-style-type: none"> ■ housings of TVs ■ audio and video equipment ■ mobile phone ■ remote control
Textiles	Households/ furniture appliances <ul style="list-style-type: none"> ■ Upholstery textiles – e.g. (sofas, office chairs)
PE – Polyethylenes	E&E <ul style="list-style-type: none"> ■ Wire and cables – e.g. (Heat shrinkable tubes)
PP - Polypropylene	Packaging <ul style="list-style-type: none"> ■ closures ■ refrigerated housewares
PBT - Polybutylene Terephthalate	E&E <ul style="list-style-type: none"> ■ communications cables ■ capacitor films ■ building cables
LUPE - Unsaturated PolyEsters	Building/Construction applications <ul style="list-style-type: none"> ■ pipes ■ stadium seats, etc... ■ lamp holders
Nylon	Households <ul style="list-style-type: none"> ■ lamp sockets ■ kitchen hoods
	E&E applications (connectors in E&E equipment)
	Building/Construction (reinforced plastics)
	Transportation (reinforced plastics)
	E&E appliances <ul style="list-style-type: none"> ■ connectors in E&E equipment ■ circuit breakers, ■ coils of bobbins

Note: Nylon = polyamide = PA

According to the European Union Risk Assessment Report – Bis(pentabromophenyl) ether, the main application for Deca-BDE is in HIPS for TV-set back plates: *"Industry information indicates that decabromodiphenyl ether is used at loadings of 10-15% weight in polymers and is always used in conjunction with antimony trioxide. The major application for decabromodiphenyl ether is in high impact polystyrene (HIPS) which is used in the television industry for cabinet backs. It is also used in a large number of other polymers with end-uses in electrical and electronic equipment (e.g. computers, connectors, electrical boxes, wire and cable etc.). Examples include polypropylene (for electronics), acetate copolymers (EVA (ethylene-vinyl acetate) and other ethylene copolymers for wire and cable), EPDM (ethylene-propylene-diene terpolymer) and thermoplastic elastomers (for wire and cable) and polyester resins (for electronics). Other minor uses include styrenic rubbers, polycarbonates, polyamides and terephthalates, and small amounts are also reported to be used in hotmelt adhesives"* [16]

The most recent breakdown of global consumption of Deca-BDE among various applications in an official report dates back to the early 1990's. At that time the global consumption of 30,000 tonnes of Deca-BDE was broken down as follows: 30% polystyrene (HIPS), 20% thermoplastic polyesters (PBT, PET), 15% polyamide (PA), 10% styrenic rubber (SBR), 5% polycarbonate (PC), 5% polypropylene (PP) and 15% other polymer applications [17].

This consumption pattern is most probably significantly different today, but no comprehensive updated breakdown of consumption has been identified.

Leisewitz *et al.* (2001) reports that Albemarle Corp. declares that 85% of Deca-BDE is used in HIPS for casings of EE appliances [22].

According to a presentation by Munro et al., of Great Lakes Chemical Corp., at ADDCON 2004, Deca-BDE more recently represents about 10% of the FR consumption for thermoplastic polyesters used in EEE, corresponding to 1,500 tonnes; and 6% of the FR consumption for polyamides used in EEE, corresponding to 840 tonnes [56]. Assuming the global consumption of Deca-BDE in 2003 was 56,418 [18] tonnes, it may be estimated that consumption of Deca-BDE for polyesters and polyamide in EEE applications represents about 2.7% and 1.5%, respectively, of the total global consumption of Deca-BDE. One reason for this substantial reduction – compared to the early 1990s – in the use of Deca-BDE for polyesters and polyamide may be that other brominated flame retardants have taken over the majority of the FR market for these resins, as discussed in section 3.3.

The European Brominated Flame Retardant Industry Panel, in its comments to the European Commission's Stakeholder Consultation, emphasised in particular the difficulties of finding alternatives for three resin types with which Deca-BDE is used: "*Alternatives are not always available: In certain plastic resins like HIPS, ABS, and PBT, there are currently no cost-effective alternative flame retardants which can provide good flame retardancy and good mechanical properties.*" [19]

The advantages of Deca-BDE emphasised by manufacturers are high bromine content, good thermal stability and cost effectiveness, as noted in the following quotations:

Albemarle Corp.: "*SAYTEX 102E flame retardant is a prime candidate for most applications due to its overall performance and cost effectiveness. Its good thermal stability makes it a candidate for applications in which resistance to high temperature is required. Because of its high bromine content SAYTEX 102E flame retardant is highly effective in achieving desired levels of flame retardancy.*" [8]

ICL Industrial Products: "*Its high bromine content coupled with its exceptional thermal stability makes it the material of choice for a large variety of applications.*" [10]

Great Lakes: "*Great Lakes DE-83R™ is a high purity fully brominated aromatic flame retardant with excellent thermal stability. It offers outstanding cost/performance.*" [20]

It should be noted that the thermal stability of Deca-BDE seems to be shared with other brominated flame retardants as shown in the following chapter, in which Deca-BDE is compared to a number of alternatives for different applications.

3 Substitutes to Deca-BDE by application

3.1 Overview of substitution approaches

Substitution of Deca-BDE in a given polymer application can basically take place at three levels:

1. Deca-BDE can be replaced by another flame retardant with adequate properties without changing the resin.
2. The plastic material, i.e. the resin with flame retardants and other additives, can be replaced by another plastic material (incl. copolymers) with adequate properties.
3. The need for flame retardants can be eliminated by design changes, or the entire product can be replaced by a different product with adequate performance.

An example of the latter type of substitution in EEE could be a solution where a reduction of the risk of flame propagating is achieved using a metal sheet to cover the plastic in contacts with current-carrying parts. Although level-3 substitution may be feasible for some applications, this study has focused on level-1 and -2 substitutions.

“Adequate properties” means that a plastic part manufactured from an alternative plastic material can meet the same fire-safety standards as the Deca-BDE application, and that the technical specifications of the part are also acceptable for the application.

Often, when seeking a substitute for undesirable substances, it is not possible to find one substance that has similar technical properties and can substitute for the undesirable substance in all of its applications. Such an alternative would, unfortunately, very likely also share the undesirable properties.

For this reason it may be necessary to search for different alternatives for different applications. In this study an “alternative” is defined as a flame retardant that can substitute for Deca-BDE for a specific application.

The application spectrum of Deca-BDE and selected brominated FR alternatives in EEE, according to Albemarle, is shown in Table 3.1. The application of Deca-BDE in foams, textiles and coatings is not shown, as they are not within the scope of this study. Other manufacturers may identify other applications of Deca-BDE, e.g. in wire and cables made of PP.

As indicated in the table, the flame retardant ethane-1,2-bis(pentabromophenyl) has the same application spectrum as Deca-BDE for the relevant polymers, while the application spectrum for ethylene bis(tetrabromophthalimide) differs with respect to a few base polymers. It should be noted that the table indicates only whether or not these FR sub-

stances can be used in the different plastics, and does not imply that the different FR substances have similar properties in the plastics.

Table 3.1
Application spectrum of Deca-BDE and selected brominated FR alternatives in EEE, according to Albemarle Product Selector [21]

Application	SAYTEX				
	102E	8010	BT-93 BT-93W	120	CP-2000
Solid thermoplastics					
ABS	●	●	●	●	●
HIPS	●	●	●	●	●
Nylon	●	●		●	
Thermoplastic polyester	●	●	●	●	
Polycarbonate	●	●	●	●	⚡
Polypropylene	●	●	●	●	
Polyethylene	●	●	●	●	
SAN	●	●			
Alloys (PC/ABS, HIPS/PPO)	●	●	●	●	
Thermoplastic elastomers	●	●	●		
Wire and cable					
Silicone	●	●	●	●	
PVC	●	●			
EPDM	●	●	●	●	
Thermosets					
Epoxy	●	●	●		⚡
Phenolic	●	●	●		●
Unsaturated polyester	●	●	●		⚡
Vinyl esters	●	●	●		⚡

102E: Deca-BDE
BT-93/BT-93W: Ethylene bis(tetrabromophthalimide)
8010: Ethane-1,2-bis(pentabromophenyl)
120: Tetradecabromodiphenoxybenzene
CP-2000: TBBPA
●: used additively ; ⚡: Used reactively

3.2 Substitutes for Deca-BDE in housings/enclosures

Globally, the sources cited previously confirm that the major application of Deca-BDE appears to be in flame retarded HIPS used for housings/enclosures of electronic equipment.

Table 3.2 shows the percentage of enclosures of different types of electronic equipment made from different resins, as presented by Tony Kingsbury, Chairman, American Plastics Council E&E Work Group, at the BFR Roundtable, September 2002. The figures present the situation in the US around 2002, which, at least with regard to TV-sets, is different from the situation in Europe. Similar data for the European market have not been identified.

Ignition resistant (i.e., flame retarded) HIPS is widely used for enclosures of TV-sets in the US, whereas personal computer monitors are mainly made

from ABS and PC/ABS because these resins have higher impact strength and are less susceptible to cracking [12]. According to the US data, HIPS is also used for a significant percentage of the enclosures of printers, fax machines and scanners, but without flame retardants. This seems not to be the case in the European market. Both Danish [7] and German [22] studies have reported the use of flame retardants in enclosures of printers, especially laser printers.

Table 3.2
Resins used in electronic enclosures in the USA [23]

Resin	Percentage of enclosures of:				
	Televisions	Monitors	Printers	Fax machines	Scanners
IR-HIPS	98+%	3%			
IR-ABS	<2%	34%			
IR- PC/ABS		61%			
IR-PC/PS		<1%			
IR- PPO/PS		<1%			
IR-PC		<1%			
HIPS			20%	34%	20%
ABS			75%	57%	75%
PC/ABS			5%	5%	5%
Blends w/ PVC				<4%	

Note: IR = ignition resistant = flame retarded

According to Lowell (2005), HIPS for TV-sets accounts for the major part of Deca-BDE use in the USA: *"Roughly 80% of deca-BDE use in the U.S. is thought to be in electronic enclosures, with the vast majority used in the back and front plates of television sets."* [12] *"DecaBDE is used in TV enclosures because it is an inexpensive, highly efficient flame retardant that is very compatible with inexpensive high impact polystyrene (HIPS). In a TV enclosure, the back plastic panel and in some cases the front panel will be made from decaBDE HIPS containing roughly 12% decaBDE by weight in combination with antimony trioxide (ATO) at a ratio of roughly three parts decaBDE to one part ATO."* [12]

In accordance with this U.S. reference, Great Lakes Corp. wrote in 2006: *"TV housings are the largest use of decabromodiphenyl oxide (Great Lakes DE-83R™) as a flame retardant in HIPS."* [24]

In Europe, the application pattern as concerns TV-sets is quite different. According to a market report on the European flame retardant chemicals industry in 1998: *"The market for brominated flame retardants in HIPS resins has largely collapsed, due to relaxed requirements for television sets in Europe and environmental concerns. Outside of Germany, the Netherlands and the Nordic countries there is limited use of decabromodiphenyl oxide, at about 10-12%, and perhaps also octabromodiphenyl oxide and decabromodiphenyl."* [25] Note: "decabromodiphenyl" should probably read "decabromobiphenyl".

The difference in the use of Deca-BDE for HIPS between Europe and the USA, as mentioned above, has mainly been driven by differences in flame retardancy requirements and environmental concerns.

In the USA, UL 94 V-0 grade FR, which greatly limits the risk of external ignition by an open flame, is required by UL 1410 for TV-set back plates. In

Europe, TV-set back plates have to comply with the EN/IEC 60065 standard, in which the aim is to prevent ignition of the TV-set by inner sources of ignition. The European standard allows major plastic parts of TV-set back plates and housings to be made from materials that fulfil the requirements of the less demanding UL 94-HB (horizontal burn test) standard [32], provided that design measures are taken to adequately isolate flammable materials from potential internal ignition sources.

According to investigations by Stiftung Warentest in Germany, the share of (new) TV-set housings with halogenated FR dropped from 60-70% in 1993/1994 to approximately 25% in 1995 and under 10% in 1996/1997. By the end of the 1990s, the European manufacturers of TV-sets had mostly renounced FRs in favour of structural solutions, and used plastics that achieved the UL 94 HB standard [26;44]. This is still the case for some European manufacturers.

However, in response to fire statistics indicating that the number of TV-set fires in Europe in the late 1990's was an order of magnitude higher than the number in the USA [26], an extensive discussion of the relevance of external sources of ignition (e.g. a burning candle) took place, and there has been a partial revival of the use of FR polymers for TV-set housings, especially among international "brand name" European manufacturers. Panasonic, Philips, Sony and Finlux, in November 2004, signed a commitment to voluntarily meet the higher fire safety classification V-1 (or equivalent) for all of their CRT models as of 1st January 2006 [27] [28].

Today a significant percentage of CRT-TV housings sold on the European market are still made from HIPS without FR, but the major European manufacturers of TV-sets now seem to be using copolymers like PC/ABS, PS/PPE or PPE/HIPS either without FRs, or with non-halogenated FRs (details in section 3.2.4).

Meanwhile, CRT TV screens are in the process of being replaced by flat panel TV-sets (FPTV) with LCD panels or plasma display panels. General Electric [29] calculated the global plastic consumption for FPTV-sets in 2005 at approximately 42% PC/ABS, 33% HIPS, 14% FR-HIPS, 10% modified PPE and 1% other. The weight of the enclosures and materials used are virtually the same as in CRT TV-sets, and the discussion regarding TV-set enclosures applies as well to flat panel TV-sets, as discussed further in section 3.2.4.

For office equipment, American and European standards have essentially the same flammability requirements, with minor differences. According to EN/EIC 69950, applied in Europe, enclosures of moveable office machines (<18 kg weight) have to comply with UL 94 V-1, whereas enclosures of stationary and larger movable office machines (>18 kg weight) have to comply with UL 94 V-5.

In effect, a range of resins can be used for enclosures of TV-sets, office equipment and other electronic equipment. Deca-BDE and octa-BDE, in particular, have been used over the years to obtain FR HIPS and FR ABS, respectively.

Alternative solutions that have been used by industry include either replacing Deca-BDE in HIPS or ABS with another flame retardant, or using other co-

polymer resins in which the same level of flame retardancy can be achieved by using other BFRs or halogen-free FRs.

3.2.1 Enclosures of HIPS

As mentioned, Deca-BDE is widely used for enclosures made of HIPS. Deca-BDE is the cheapest FR for V-0 grade HIPS, but has some technical disadvantages for some applications (see below). The selection of the most suitable flame retardant depends heavily on the requirements of the final application, and the price/loading of the flame retardant.

A number of flame retardants are marketed for use in HIPS. Table 3.3 lists eight commercially available flame retardants that may be used to achieve V-0 HIPS besides Deca-BDE, and indicates the section of this report in which further characteristics of the substances can be found.

Table 3.3
Examples of commercially available flame retardants for V-0 grade HIPS

Substance	Examples of commercial products	Loading for V-0 grade	Synergist ATO	Cf. section of this report
Deca-BDE	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	12-13% [30] *	4-5%	1
Ethane-1,2-bis(pentabromophenyl)	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	12-13% [30] *	4-5%	5.1
Ethylene bis(tetrabromophthalimide)	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	12-13% [30] *	4-5%	5.2
Brominated epoxy polymer **	FR 2300 (ICL Industrial Products)	n.a.	n.a.	5.9
Tetrabromobisphenol-A	SAYTEX® CP-2000 (Albemarle Corp.) BA-59P (Great Lakes Corp.) FR-1524 (TBBA) (ICL Industrial Products)	14-20% [30] *	4%	5.5
Chloroparaffin **	n.a.	n.a.	n.a.	n.a.
Tetrabromobisphenol A bis (2,3-dibromopropyl ether)	SAYTEX® HP-800AG (Albemarle Corp.) PE-68 (Great Lakes Corp.) FR-720 (ICL Industrial Products)	5% [30] *; *** (in "styrenic based resins")	5%	5.6
Tetradecabromodiphenoxybenzene	SAYTEX® 120 (Albemarle Corp.)	12% [30] *	4%	5.4
Tris(tribromophenoxy) triazine	FR 245 (ICL Industrial Products)	14.3 [35]	6%	5.12

* Data on the product from Albemarle only. The data are provided by SpecialChem S.A., an Internet-based knowledge and solution provider in the domain of specialty chemicals, with direct reference to Albemarle.

** The class of substances is included in a list summarised March 2006 by J. Troitzsch [31], editor of the Plastics Flammability Handbook [32]. The substance group was not assessed further.

*** The low loadings indicate that the "styrenic based resins" may be styrenic based copolymers.

n.a. Not assessed.

In Table 3.4 the properties of Deca-BDE in HIPS are compared to a few of the recommended substitutes that have an application spectrum close to that of Deca-BDE. As indicated in the table, based on information from Albemarle Corp., Deca-BDE (102E) shows poorer performance as to bloom resistance, UV stability and physical properties in comparison with BFRs based on Ethylene bis(tetrabromophthalimide) (BT-93, BT-93W) and Ethane-1,2-bis(pentabromophenyl) (8010). It should also be noted that SAYTEX® BT-93 achieves UL 94 V-0 only at 1/8-inch polymer thickness, whereas SAYTEX® 8010 achieves the UL 94 V-0 rating at both 1/8-inch and 1/16-inch thickness [33].

Table 3.4
Comparison of Albemarle FRs recommended for HIPS (based on [34])

Properties	SAYTEX			
	BT-93	BT-93W	8010	102E
Bloom Resistance	++	++	-	--
Thermal Stability	++	++	+	+
UV Stability	++	++	+	-
Physical Properties	+	+	+	-
Electrical Properties	+	+	+	+
FR Efficiency	+	+	+	+
Melt Flow Index (MFI)	+	+	+	+
WEEE compliant	Yes	Yes	Yes	No

Notes:

++ Very Good + Good - Fair -- Poor

BT-93 and BT-93W: Ethylene bis(tetrabromophthalimide)

8010: Ethane-1,2-bis(pentabromophenyl)

102E: Deca-BDE

The term "WEEE complaint" probably means "RoHS compliant".

According to the table, Deca-BDE does not provide any of the listed technical properties that cannot be provided by the other flame retardants. As pointed out by Albemarle, "*Flame retarded HIPS based on SAYTEX BT-93 or SAYTEX 8010 show an excellent balance of physical properties, UV stability, lower formulation cost and result in thermally stable, easily recyclable, non-blooming formulations. This allows FR HIPS compounds currently based on other flame retardants to be replaced as well as substituting FR HIPS based on Saytex BT93 and S8010 for other resins, like FR ABS and FR PC/ABS.*" [34]

Also according to Albemarle Corp: "*Saytex 8010 is the most cost effective non-decabromodiphenyl-oxide (DECA) flame retardant for HIPS.*" [85]

The technical disadvantages of Deca-BDE are also addressed by the Dead Sea Bromine Group in a paper in *Plastics Additives & Compounding*, April 2001: "*Existing flame retardant products for these applications seldom meet all of the required properties. Decabromodiphenyl oxide (Deca) is cost efficient in HIPS but has poor UV stability and is not melt blendable during injection moulding.*" [35] And further: "*In both HIPS and ABS, FR-245 is cost efficient and offers an excellent combination of melt flow, impact and light stability properties.*" [35] FR-245 consists of Tris(tribromophenyl) cyanurate; see section 5.12.

The main advantage of Deca-BDE is its price. Prices of HIPS compounds with different flame retardant systems are discussed further in section 3.2.4.

Another advantage of Deca-BDE that has been emphasised is that plastics containing Deca-BDE can be recycled several times while maintaining their flame retardant properties. However, there is some concern that the recycling of Deca-BDE HIPS may promote the formation of polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs).

The suitability of an FR plastic for recycling is a property shared with several of the potential FR substitutes, as indicated by Albemarle Corp.: "*The results of the recycling study show that HIPS/S-8010 and HIPS/BT-93 are not only easily recyclable, but were also found to meet the requirements of the German Dioxin Ordinance.*" [36] And further, in another paper: "*The V-0 HIPS resin with EBP was also analyzed for the polybrominated dibenzofurans and dibenzodioxins after*

five injection molding cycles (Table III). Even after recycling no detectable level of these species was found, and the recycled V-0 FR HIPS easily conforms to the specified maximum allowable quantities of the German Hazardous Substances Ordinance." [37]

It has not been possible to identify any commercially available halogen-free flame retardants that can achieve V-0 grade HIPS or ABS. Manufacturers of EEE who demand enclosures without brominated flame retardants can usually replace HIPS with a copolymer of PPE/HIPS or PC/ABS, as further discussed in section 3.2.3.

3.2.2 Enclosures of ABS

Traditionally Octa-BDE, rather than Deca-BDE, has been the flame retardant of choice for ABS. The OECD monograph from 1994 on selected brominated flame retardants states, concerning octa-BDE: "*The bulk of its applications are for compounds based on acrylonitrile butadiene styrene (ABS), where this brominated chemical offers the comparative advantage in terms of melting range and colour.*" [17] ABS is not included in the OECD monograph's list of Deca-BDE applications, or the list of Deca-BDE applications mentioned by BSEF, referred in Table 2.3.

Deca-BDE may, to some extent, have replaced Octa-BDE after the EU ban on Octa-BDE, and ABS is mentioned by the European Brominated Flame Retardant Industry Panel (EBFRIP) in the panel's comment to the European Commission's Stakeholder Consultation: "*Alternatives are not always available: In certain plastic resins like HIPS, ABS, and PBT, there are currently no cost-effective alternative flame retardants which can provide good flame retardancy and good mechanical properties.*" [19]

However, marketing materials recommend other brominated flame retardants than Deca-BDE as alternatives to Octa-BDE in ABS. Great Lakes Corp. wrote in the pamphlet, "Flame Retardant Alternatives to Octa-PBDE in ABS:" "*The recommended alternatives to octa-PBDE in ABS are Firemaster® FF-680 and Great Lakes BA-59P™.*" [93] These alternatives are based on bis(tribromophenoxy)ethane and TBBPA, respectively. Deca-BDE is not mentioned in the pamphlet.

The *Risk Reduction Strategy for Octabromodiphenyl Ether* prepared for the UK Department for Environment, Food and Rural Affairs (DEFRA) listed the following alternatives to Octa-BDE in ABS, in cases where the polymer itself was not substituted: TBBPA, ethane 1,2-bis (pentabromophenyl) and bis(tribromophenoxy) ethane [38]. Again, Deca-BDE was not mentioned as a FR of any importance for use with ABS.

A number of flame retardants are marketed for use in ABS. Table 3.5 lists, in addition to Deca-BDE, six commercially available flame retardants that can be used to achieve V-0 ABS.

Table 3.5
Examples of commercially available flame retardants for V-0 grade ABS

Substance	Examples of commercial products	Loading for V-0 grade	Synergist ATO	Cf. section in this report
Deca-BDE	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	13-15% *	5%	1
Ethane-1,2-bis(pentabromophenyl) ***	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	n.a.	n.a.	5.1
Ethylene bis(tetrabromophthalimide) ***	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	n.a.	n.a.	5.2
Brominated epoxy polymer ***	FR 2300 (ICL Industrial Products)	n.a.	n.a.	5.9
Tetrabromobisphenol-A	SAYTEX® CP-2000 (Albemarle Corp.) BA-59P (Great Lakes Corp.) FR-1524 (TBBA) (ICL Industrial Products)	22% [93] **	5%	5.5
Bis(tribromophenoxy) ethane	FF-680 (Great Lakes Corp.)	17% [93]	5%	5.3
Tris(tribromophenoxy) triazine	FR 245 (ICL Industrial Products)	14.3 [35]	6%	5.12

* As Deca-BDE traditionally has not been used for ABS, no technical data on the Deca-BDE loading has been identified. The Deca-BDE loading may be assumed to be slightly lower than the octa-BDE loading of 16% [93]

** Data on the product from Great Lakes Corp. only.

*** The substances are included in a list summarised March 2006 by J. Troitzsch [31]. The loadings of the substance have not been assessed further.

n.a. Not assessed.

Other manufacturers mention the use of TBBPA as well in ABS. ICL Industrial Products states in the data sheet for FR-1524 (TBBA): "*It is also cost-effective as an additive flame retardant in applications such as ABS...*" [98]

The Dead Sea Bromine Group wrote in a paper published in *Plastics Additives & Compounding*, April 2001: "*Tetrabromobisphenol A (TBBA) is cost efficient and melt blendable in ABS but has low thermal stability, poor impact properties and may not meet UV stability standards. Moreover, it lowers heat distortion temperature.*" [35] And further: "*In both HIPS and ABS, FR-245 is cost efficient and offers an excellent combination of melt flow, impact and light stability properties.*" [35] FR-245 is the company's trade name for tris(tribromophenyl triazine).

The cost considerations for replacing Deca-BDE in ABS are quite comparable to the considerations regarding the replacement of octa-BDE. The above-mentioned Risk Reduction Strategy for octa-BDE, produced by DEFRA, includes a detailed assessment of the cost of substituting octa-BDE in ABS. The cost estimate was prepared for the substitution of 1,2-bis(pentabromophenyl) ethane for octa-BDE in ABS, which, according to the assessment, represented the greatest cost increase of any of the substitutes. The increase in polymer price with the substitute flame retardant was estimated at 25%. (The price of octa-BDE was estimated at 3.6 €/kg, and the price of ABS flame retarded with 15% octa-BDE was 1.4 €/kg. All figures are assumed to be based on 2002 prices). The increase using TBBPA as a substitute would be lower. Furthermore, the cost estimate included an estimate for research and development

(R&D) by companies using octa-BDE. The total research and development costs for UK manufacturers were estimated at 0.5 m€, while the cost due to the increased price of flame retardants was estimated at 1.2 m€/year. To this was added the costs of replacing moulds: *"Costs of new moulds, depending upon the size and complexity of the product have been estimated at £50-100,000 (€80-160,000). The British Plastics Federation has indicated that a typical SME in ABS processing would have around 15 to 20 moulds."* [38] The total costs of replacing moulds, including the cost of downtime for polymer processing companies, were estimated at 4.8 m€

If the increased costs are passed on to the consumer, the increase in the average price of products would be less than 1%: *"Thus, the total estimated costs to industry, taking into account the likely increased cost of substitutes and the potential need to replace moulds is around €7.5 to €12 million over five years. If these increased costs were passed on to the consumer, the percentage increase in the average price of products would be between 0.19% and 0.30%, taking into account an estimated 3 million products on the market per year"*. [38]

The price of Deca-BDE may be slightly lower than the price of octa-BDE, and consequently, the price difference between Deca-BDE and alternatives may be slightly higher. Further, it should be noted that the "average" price increase of products referenced above would be significantly lower than the price increase of those products that include large parts made of ABS, e.g. TV-sets with ABS enclosures. This is further discussed in section 3.2.4.

3.2.3 Enclosures of copolymers

PPE/HIPS and PC/ABS copolymer blends have been marketed by a number of resin suppliers as substitutes for brominated HIPS and ABS resins. As mentioned before, these copolymers are also used for more demanding applications, e.g. in information technology (IT) equipment.

PPE refers to polyphenylene ether homopolymer or copolymer. The polymer may also be designated polyphenylene oxide (PPO) and the copolymer PPO/HIPS or PPO/PS. The addition of 17 to 20 percent PPE by weight enhances the HIPS charring ability and therefore improves flame retardancy [12]. From a processing standpoint, PPE/HIPS blends have very similar flow properties to HIPS. Flow properties are important in the injection moulding process, as resin substitutes with similar flow properties to HIPS mean similar opportunities for the design of products with fine structural parts, and fewer changes to the expensive tooling and moulds used in the moulding process.

PC/ABS and PC polymers typically contain a very small amount of fluoropolymer (roughly 0.3%) for drip resistance, so the polymers are consequently not 100% halogen-free [12].

A number of both halogen and non-halogen flame retardants are marketed for use in HIPS/PPO and PC/ABS copolymers. Table 3.5 lists, besides Deca-BDE, seven commercially available flame retardants for V-0 PC/ABS or PPE/HIPS. In practice, European manufacturers of TV-sets, as mentioned in section 3.2, usually use V-1 grade or lower.

Halogen-free V-0 and V-1 grades are both available from a number of compound suppliers. As an example, halogen-free V-0 grade PC/ABS is marketed by Bayer (Bayblend®) [39] and RTP Company (RTP 2500 FR-110) [40]. Halogen-free V-0 grade PS/PPE is marketed by GE Plastics (NORYL®)

LS175) [41], and V-0 grade halogen-free PPO/HIPS is available from Total Petrochemicals (FT-878) [42].

According to the Kingsbury 2002 reference, RDP is the dominant FR in PC/ABS and PPO/PS on the American market, while the use of BDP is growing, and the use of TPP is shrinking [23].

Albemarle Corp. has written about NcendX (based on BDP): "*PC/ABS and PPO/HIPS blends are the material of choice for higher end electronic enclosures. NcendX® P-30 liquid phosphorus flame retardant is an outstanding performer in PC/ABS and PPO/HIPS blends. It actually improves resin melt flow and exhibits outstanding thermal stability, excellent hydrolytic stability, low migration and low volatility*" [119]

HIPS/PPO with halogen-free FRs may not match all properties of HIPS with BFR, as pointed out by Great Lakes regarding the UV stability of the blend: "*Where a non-halogen flame retardant is required, HIPS requires another polymer such as PPO to achieve the UL-94 V-O flammability requirement. The addition of this polymer dramatically changes the processing conditions for injection molding as well as resulting in higher costs for this type of system, and in general cannot achieve the level of UV stability which can be reached with selected brominated fire retardant systems* [43]

Table 3.6
Examples of commercially available flame retardants for V-0 grade PC/ABS and
PPE/HIPS

Substance	Examples of commercial products	Loading for V-0 grade	Synergist	Cf. section in this report
Halogenated				
Deca-BDE **	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	n.a.	n.a.	1
Ethane-1,2-bis(pentabromophenyl) **	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	n.a.	n.a.	5.1
Ethylene bis(tetrabromophthalimide) **	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	n.a.	n.a.	5.2
Brominated epoxy polymer **	FR 2300 (ICL Industrial Products)	n.a. only mentioned for PC/ABS	n.a.	5.9
Tetrabromobisphenol-A carbonated oligomer **	Great Lakes BC-52 (Great Lakes Corp.) Great Lakes BC-58HP (Great Lakes Corp.)	n.a.	n.a.	5.11
Non halogenated				
Resorcinol bis(diphenylphosphate) (RDP)	Reofos® RDP (Great Lakes Corp.) Fyrolflex® RDP (Akzo Nobel/Supresta)	about 10% in PC/ABS*	-	5.14
Bisphenol A bis(diphenylphosphate) (BDP)	Reofos® BAPP (Great Lakes Corp.) NcendX P-30 (Albemarle Corp.) Fyrolflex® BDP (Akzo Nobel/Supresta)	10-14% in PC/ABS *	-	5.15 5.16
Triphenyl phosphate (TPP)	Reofos® TPP (Great Lakes Corp.) Fyrolflex® TPP (Akzo Nobel/Supresta) Disflamoll® TP (Lanxess)	8-12% in PC/ABS *	-	5.18

* Loading for V-0 grade PC/ABS [44]

** The substances are included in a list summarised March 2006 by J. Troitzsch [31]. The loadings of the substance have not been assessed further.

n.a. Not assessed.

Examples of flame retardants in copolymers and their uses are shown in the following table taken from Lowell (2005) [12].

Table 3.7
Phosphate Flame Retardants Used in Electronic Enclosure Applications (cut from [12])

Flame Retardant	Acronym (s)	Applicable Resin Systems and Other Notes	Known uses	Manufacturer: Trade Name
Resorcinol bis diphenyl phosphate	RDP	<ul style="list-style-type: none"> • 11% phosphorus • V0 rating achieved when used in PPO/HIPS blends • <i>Dominate flame retardant in PC/ABS and PPO/HIPS systems</i> 	<ul style="list-style-type: none"> • Bayer Bayblend PC/ABS resins • GE Plastics PC/ABS resins • Used in Dell PC/ABS CRT Monitor 	<ul style="list-style-type: none"> • Azko Nobel: Fyroxflex®RDP 10 • Great Lakes: Reofos RDP
Bisphenol A diphosphate	BPADP, BAPP, BDP	<ul style="list-style-type: none"> • Usage growing in PC/ABS and PPO/HIPS applications • 9% phosphorus 	<ul style="list-style-type: none"> • Dow Chemical PC/ABS 7560, used in the Sharp AQUOS LCD TV 	<ul style="list-style-type: none"> • Great Lakes: Reofos BAPP • Albemarle NcendX P-30 • Azko Nobel: Fyroxflex®BDP
Diphenyl cresyl phosphate	DPK	<ul style="list-style-type: none"> • Used in PC/ABS 		
Proprietary monophosphate		<ul style="list-style-type: none"> • PC/ABS 	<ul style="list-style-type: none"> • Low migration, hydrolysis resistant 	<ul style="list-style-type: none"> • Great Lakes: Reofos 507
Triphenyl phosphate	TPP	<ul style="list-style-type: none"> • Also known as triaryl phosphate • Usage shrinking in PC/ABS and PPO/HIPS applications 		<ul style="list-style-type: none"> • Great Lakes: Reofos TPP •

Sources: Kingsbury 2002, Great Lakes Chemical Company Website, Azko Nobel Website, German EA 2000, GE Plastics Website, Bayer website, Azko Nobel website.

The price of the PPE/HIPS and PC/ABS copolymer blends is compared to HIPS with Deca-BDE in the next section.

3.2.4 Summary of substitutes for enclosures and price comparison

Deca-BDE may potentially be used in enclosures of a range of EE products like TV-sets, printers, photocopiers and hair dryers. For all identified applications of Deca-BDE in enclosures, alternatives without Deca-BDE are available.

The following section will focus primarily on TV-set enclosures (although CRT TV-sets are in the process of being phased out), because most information is available on this product group, and the results for TV-set enclosures can be applied to other product groups.

Polymers and flame retardants for TV-set enclosures

Whereas HIPS with Deca-BDE seems to be the material of choice for TV-set enclosures in the USA, major European producers of TV-sets today use HIPS without FR, or copolymers with non-halogenated flame retardants.

A number of products in the lower price segment of the market still use HIPS without flame retardants, which meets the current standard (UL 94 HB). An example of HIPS without flame retardants advertised for use for TV-set enclosures is BASF's Polystyrol 496 F [45].

Table 3.8 summarises information on resins and FRs used by five important producers of TV-sets for the European market. Although the major producers have returned to V-1 or V-0 grade housings, they have not returned to Deca-BDE.

Table 3.8
Resins and FRs used by five important producers of TV-sets for the European market

TV-set equipment manufacturer	Resin	FR	Flammability grade
Philips [46]	Mostly PC/ABS	Non-halogenated FR; Partially TBBA	UL 94 V-0, V-1
Panasonic [47]	Mostly PS/PPE	Non-halogenated FR; PBDE prohibited	UL 94 V-0
Sony [48]	HIPS/PPO, PC/ABS	Non-halogenated FR; PBDE prohibited	UL 94 V-0, V-1
Loewe Opta [49]	HIPS/PPO, PC/ABS	PBDE prohibited	Fire protection under the IEC 60065 regulation
Metz [50]	HIPS; HIPS/PPO; PC/ABS	Halogenated FRs are not used	Fire protection under the IEC 60065 regulation; UL 94 HB, V-1, V-0

According to Lowell (2005) [12], roughly 20,000 tonnes of resorcinol bis(diphenyl phosphate) (RDP) are used annually for the European TV market, but this figure has not been confirmed in this study.

Costs for Deca-BDE substitution in TV-set enclosures

As described for ABS in section 3.2.2, the cost of substitution is dependent on the difference in price of the raw materials, research and development costs, and possible changes of moulds and other tools. The costs of changes in moulds, if necessary, may be a significant part of the total costs.

The raw material costs for plastic enclosures depend on a number of factors, including the cost of the resin itself, the cost of the flame retardant and any volume pricing adjustments. The raw material costs frequently differ from region to region (e.g. Europe vs. USA or Asia), depending on regional market conditions.

The one-time costs of mould changes depend heavily on the timing. With a longer transition period, the costs can be lowered by introducing substitutes when the moulds are changed along with periodic design changes. As described by AEA Technology Environment (1999) [51], the time scale of changes in basic elements of a TV-set, like the chassis, may be longer than the time scale for changes in models. A TV model is typically produced for only about a year, but may be on sale for 2-3 years. Although a specific TV model has a relatively brief market life, manufacturers utilise some basic building blocks like the chassis, the heart of a TV-set, for a longer period of time. The chassis may have a useful life of 5-7 years. The new model TVs produced each year are derivatives of the original chassis, with minor electronic enhancements, as well as different cosmetic designs; no manufacturer completely redesigns its product range over a mere 1-2 year period [51]. The typical time scale for changes in enclosures is not assessed in this study.

It is beyond the scope of the present study to undertake a detailed assessment of all costs related to the substitution of Deca-BDE in enclosures, but in the following, the incremental costs of plastic raw materials are briefly discussed.

The price of plastic raw materials depends on product quality, purchased volumes, market conditions, etc. In Table 3.9, indicative price levels of HIPS with different flame retardants (information from Total Petrochemicals) is shown. Total Petrochemicals, with a market of about 30,000-40,000 tonnes

HIPS and HIPS/PPE for TV-set enclosures in Europe, supplies not only standard HIPS but also HIPS with brominated FR and halogen-free FR [52] (the precise FRs used are proprietary). HIPS with Deca-BDE is only marketed by Total Petrochemicals in Southeast Asia, and the indicated price consequently reflects this market. It should be noted that Total Petrochemicals maintains a strategy of being a high quality supplier of HIPS and compounds, and therefore the prices shown in the table will not necessarily be the lowest on the market.

For the following paragraph, average prices in table 3.9 is applied. Using average prices, for the brominated alternatives, the price about 109% (for V-1 grade) and 121% (for V-0 grade) of the price of HIPS with Deca-BDE. The extra cost corresponds to approximately 0.15 €/kg to 0.35 €/kg. Similar price increases for V-0 grade HIPS have been reported by Panasonic when replacing Deca-BDE with other BFRs in their TV-sets in the USA [53]. The price of the halogen-free HIPS/PPE is approximately 158% of Deca-BDE HIPS, corresponding to a cost increase of 0.95 €/kg. Total Petrochemicals does not market PC/ABS, but estimates the price of competitive products to be 2.60 – 2.80 €/kg (spring 2006). The price of PC/ABS has decreased since 2005, due to lower PC raw material costs. This means that the price of PC/ABS is about 164% that of Deca-BDE HIPS, corresponding to a cost increase of 1.05 €/kg.

These prices reflect the experiences of only one major compounder, but indicate the order of magnitude of price differences between compounds with Deca-BDE and alternatives.

To put these prices in perspective, the extra raw material cost of the full enclosure of an average TV-set (front and rear enclosure) may be estimated. Lowell (2005) has estimated the weight of the front and rear enclosure of an average 27.5-inch TV-set to be 5.45 kg [12]. Using the prices of compounds from Total Petrochemicals, the extra cost of using the alternative materials PPE/HIPS or PC/ABS would be about 5-6 €. The extra cost of using other BFRs would be 0.8-1.9 €, depending on the flammability grade. Note that these estimated costs are for the raw materials only. If the total production cost of a 27.5-inch TV-set, according to information obtained from Panasonic [53], is roughly 300 €, then the extra material cost of these alternatives can consequently be estimated at 0.5-2% of the production cost, with the higher part of that range applicable to the halogen-free HIPS/PPE.

Table 3.9
Indicative price levels of HIPS compounds (information from Total Petrochemicals), spring 2006 [54]

Polymer/compound	European price range (€/kg)	Comments
Standard HIPS	0.95 – 1.25	HB fire standard
HIPS + deca-BDE	1.50 – 1.80	This HIPS+Deca-BDE price reflects the Southeast Asia market, since Total Petrochemicals does not sell HIPS with Deca-BDE in Europe. In addition to the basic PS price, the compound price reflects primarily the fire rating (V-2 at the lower end of the price range, and V-0 at the upper end), as well as the volume purchased, the specific FR used, etc.
HIPS + other BFR:		
- UL 94 V-0	1.90 – 2.10	
- UL 94 V-1	1.70 – 1.90	
HIPS/PPE + halogen-free FR	2.30 – 2.90	

CRT-based TV-sets are soon to be relegated to history, but the cost estimates above can quite well be applied to new LCD panel TV-sets. In the US, the back cover of the LCD panel TV-set has to comply with UL 94 V-0, whereas European standards have less strict requirements. In the USA, the weight of the back cover of an average LCD panel TV-set (50-inches) is about 4 kg [53].

As discussed previously, the costs of moulds and other tools may be significant, but can be greatly reduced if new materials are introduced concurrently with new designs/products. The extra material costs of some 5 € for a new TV-set is, of course, more critical for a product in the low price market segment, competing above all on retail price, than it is for a product in the high end of the market, competing on technical features, environmental profile, etc.

Cost calculations in other studies

The costs associated with the replacement of octa-BDE and Deca-BDE by other flame retardants have been discussed in a few other studies.

In Lowell (2005) [12] the incremental material cost for an average 27.5-inch CRT TV-set, with a front and rear enclosure weight of 3.5 kg and 1.95 kg respectively, is estimated. The result is shown in Table 3.10. The price of the HIPS with Deca-BDE material is nearly the same as shown in Table 3.9, whereas the prices of HIPS/PPE and PC/ABS are significantly higher, which may reflect actual differences between the European and American markets, including a greater European demand for copolymers with non-halogenated FRs.

It should be noted that the figures are estimates only, and that thin-walling and volume related pricing are not factored into the calculations, nor are other cost increases or decreases due to changes in energy use, yield, or cycle time. The Lowell (2005) study estimated that the extra cost of raw materials corresponded to an increase of 1.5 to 2.5% of the total price of the TV-set.

Table 3.10
Prices of various V-0 systems for enclosures on the American market in 2004 (based on Lowell, 2005 [12])

Resin	Flame retardant	Resin costs €/kg *	Resin cost for "average" TV-set rear enclosure € *, **	Resin cost for "average" TV-set front & rear enclosure € *, **
FR HIPS ***	Deca-BDE	1.6 – 1.8	13.0	20.3
FR ABS	TBBPA or Brominated epoxy oligomer	1.9 – 2.5	16.8	26.4
FR ABS/PC	Halogenated FR	2.5 – 3.0	21.0	33.0
FR PC	Halogenated FR	3.0 – 3.6	25.4	39.9
PR HIPS/PPO	Halogen-free FR	3.4	26.6	41.8

* All prices by the truckload except HIPS (railcar). Converted here from \$/lb using 1 \$ = 0.824 €; 1 lb = 0.454 kg.

** "Average" TV-set is a 27.5-inch CRT unit with front and rear enclosure weights of 3.5 and 1.95 kg, respectively.

*** HIPS with Deca-BDE

As discussed in section 3.2.2, the assessment prepared for the UK Department for Environment, Food and Rural Affairs (DEFRA) included an estimate of the cost of replacing octa-BDE in ABS enclosures. The cost of replacing Deca-BDE in similar enclosures can be assumed to be comparable, although probably slightly higher. In the assessment it is estimated that, if the increased cost were passed on to the consumer, the percentage increase in the average product price would be between 0.19% and 0.30%, assuming an estimated 3 million products on the market per year [38]. The DEFRA study does not include a separate cost assessment for TV-sets or other products in which the FR plastic part accounts for a large part of the product.

As part of the development of the Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan, the additional cost of substituting Deca-BDE was assessed as well. It should be noted that the estimate reflects the US market, where Deca-BDE HIPS has dominated the market for TV-set enclosures. In the Action Plan it was concluded:

"A wide range of values have been reported regarding what the final price increase would be. The Lowell report estimates the materials-based cost shift between 1.5 percent and 2.5 percent of the final product prices for televisions, although it may not fully cover the costs. Personal conversations with four manufacturers of finished products currently making deca-BDE-free products estimated the increase at between 5 and 15 percent. Another company indicated a price increase of less than 0.5%. Ecology finally estimated the cost increase between 5 to 15 percent for the final product (finished products and components of finished products). This is despite the fact that the plastic itself may increase in price by more than 50 percent and despite the fact that the price of the alternative itself may be doubled. However, some manufacturers say the material is not the only basis for the cost shift, and cite greater energy, down time and form retooling. Thus there is a difference between the expected cost shift and the expected price shift, although there may be no difference between the expected cost shift and a diminishment of the expected price reduction. The latter is very difficult to quantify from market data." [55]

3.3 Connectors, circuit breakers, etc.

As indicated in Table 2.3, small inner parts of electrical and electronic equipment like connectors, circuit breakers, etc. made of PBT or polyamide (PA) are among the main application areas of Deca-BDE.

According to a presentation by Munro et al., of Great Lakes Chemical Corp., at ADDCON 2004, electrical internals account for 27% of the total global consumption of FR polymers [56]. Of this total, PBT accounts for 28%, PET for 10%, PA for 31%, PC/PPS for 15% and other polymers for 16%.

PBT is one type of thermoplastic polyester and, together with PET, is often designated as a "thermoplastic polyester" or - as in some of the quotations below - simply a "polyester," where "thermoplastic" is implicitly understood from the context.

Polyamide is also known as "PA" or "nylon." Different types of PA may require different flame retardants. Common types are PA6 and PA66. Deca-BDE is, for thermal reasons, generally only used in PA6.

Circuit breakers, connectors, etc. are typically in contact with current-bearing parts of EEE, and therefore the FR requirement is usually V-0 grade.

Flame retarded thermoplastic polyesters and PA are today mainly based on brominated FR technology, as presented by Munro et al.: *"The majority of flame retardant polyester and polyamide compounds used in the electrical and electronic market segment are based on brominated flame retardant technology. There are a wide variety of brominated flame retardants that are used in both resins which all give different performance advantages with increasing costs for the superior technical performance."* [56]

The global flame retardant additive consumption in thermoplastic polyesters and polyamide, based on a presentation by Great Lakes Corp. in 2004, is shown in Table 3.11.

Table 3.11
Global flame retardant additive consumption in polyesters and polyamides in EEE (based on [56])

Polyesters (15,000 tonnes FR)	Percentage	Polyamides (14,000 tonnes FR)	Percentage
Deca-BDE	10%	Deca-BDE	6%
Non-deca	5%	Other halogenated	13%
Other halogenated	3%	Polybrominated styrenes/ brominated polystyrenes	66%
Brominated carbonate oligomers *	44%	Melamine derivatives	7%
Brominated epoxy oligomers	24%	Red phosphorous	8%
Polybrominated styrenes/ brominated polystyrenes	13%		
Non-halogen	1%		
Total	100%		100%

* Assumed to be tetrabromobisphenol-A carbonate oligomer.

Deca-BDE represents about 10% of the FR consumption for thermoplastic polyesters, corresponding to 1,500 tonnes, and 6% of the FR consumption for polyamides, corresponding to 840 tonnes globally. Considering the global consumption of Deca-BDE in 2003 to be 56,418 tonnes [18], it may be estimated that Deca-BDE consumption for polyesters and polyamide in electrical internals represents about 2.7% and 1.5%, respectively, of total Deca-BDE consumption.

The significant difference between these percentages and the data from the early 1990's, when thermoplastic polyesters and polyamide were reported to account for 20% and 15%, respectively, of global Deca-BDE consumption, may be an indication of the gradual replacement of Deca-BDE by other BFRs.

The figures for the entire market (not only for EEE as in table 3.11) for flame retarded polyamide in Western Europe in 1998 show a significantly different pattern, with non-halogen FRs accounting for 42% of the total (Table 3.12). To what extent this difference reflects differences between the Western European market and other markets, or reflects the fact that non-halogen FRs have a higher market share of FRs for non-EEE applications in Western Europe, has not been investigated.

Table 3.12

Western European market for flame retardants for all applications of PBT/PET and PA in 1998, according to IAL Consultants' Market Report [25]

PBT/PET (9,900 tonnes FR)	Percentage	Polyamides (11,210 tonnes FR)	Percentage
Brominated flame retardants	84%	Brominated flame retardants	33%
Antimony trioxide *	16%	Antimony trioxide *	16%
		Organochlorine FRs	8%
		Magnesium compounds	8%
		Melamine	19%
		Red phosphorous	10%
		Zinc compounds	5%
	100%		100%

* used as synergist with halogenated flame retardants

The advantage of Deca-BDE for these applications is its low cost, whereas other BFRs provide superior mechanical properties as stated by Munro *et al.*: *"As a general rule the monomeric additives are lower cost solutions but tend to suffer in terms of compatibility and mechanical properties. These include additives such as decabromodiphenyl oxide and decabromodiphenyl ethane. The polymeric solution such as brominated epoxies, carbonates and styrenes give superior mechanical properties and compatibility over the monomeric systems. The ability to change the molecular weight of the polymeric systems can be used to give different flow performance while changing the monomers and copolymer components can lead to improved compatibility and high temperature performance."* [56] Note: Decabromodiphenyl oxide is synonymous for Deca-BDE.

According to the paper, non-halogenated flame retardants accounted globally for only 1% of the FR used in thermoplastic polyesters, and 15% of the FRs used in PA. The percentage in Europe may quite well be higher.

That Deca-BDE is not the principal FR choice for connectors is also indicated by the fact that Albemarle's Flame Retardants web-page for "Connectors" does not include Deca-BDE in the list of 9 flame retardants for use in connectors [102].

3.3.1 Parts made of thermoplastic polyesters

Thermoplastic polyesters, mainly PBT and PET, are employed in applications requiring high FR performance levels. Applications in EEE include plug-in connectors, connector strips, switching systems, housings for automatic overload protectors, capacitor pots, in coil formers, lamp parts, personal computer fans, power supply components, parts for electric drives, sheathing for waveguides and many other products [57].

The characteristics of PBT that are most difficult to substitute are high dimensional stability and low water absorption. Beside these characteristics, PBT has great stiffness and strength, high resistance to chemicals and heat distortion, good dielectric properties, and high gloss and surface hardness.

Until recently, only halogenated flame retardants have been able to provide FR PBT, and brominated flame retardants have accounted for nearly 100% of this market.

The main properties of Albemarle Corp's flame retardants for PBT, according to SpecialChem S.A (with explicit reference to Albemarle Corp.) are shown in Table 3.13.

As quoted in the previous section, a number of the other flame retardants have superior properties to Deca-BDE (102E in the table), which has a high rating only on "colour".

Table 3.13
Comparison of Albemarle FRs recommended for PBT [58]

Properties	SAYTEX						
	HP-7010	PBT-620	BT-93	BT-93W	120	8010	102E
Bloom Resistance	++	++	++	++	+	-	--
Thermal Stability	++	++	+	+	-	-	--
UV Stability	-	-	++	++	+	+	-
Physical Properties	+	++	+	+	+	+	-
Electrical Properties	++	++	+	+	+	+	+
FR Efficiency	+	+	+	+	+	+	+
MFI	+	++	+	+	+	+	+
Gloss	+	+	--	--	-	-	-
Colour	+	++	--	-	++	+	++
WEEE compliant	Yes	Yes	Yes	Yes	No		

Notes:

++ Very Good + Good - Fair -- Poor

HP-7010, PBT-620: Brominated polystyrene

BT-93; BT-93W: Ethylene bis(tetrabromophthalimide)

120: Tetradecabromodiphenoxybenzene

8010: Ethane-1,2-bis(pentabromophenyl)

102E: Deca-BDE

A list of commercially available flame retardants for V-0 grade PBT/PET is shown in Table 3.14. For some of the flame retardants, relative formulation costs are indicated on the basis of information from Great Lakes Corp.[56], and the formulation costs can only be considered indicative for the commercial products from this company.

Recently, Clariant GmbH has developed a new class of halogen-free phosphorous based flame retardants, more specifically alkyl phosphinic acid salts marketed under the trade name Exolit® OP, which are effective flame retardants for engineering plastics like PA and PBT [59].

Polyester compounds using this flame retardant system are marketed exclusively by the compounder Ticona [60]. The new Celanex XFR range consists of four grades: one unreinforced and three reinforced with 10, 20 or 30 percent glass fibres. The compounds can meet UL 94 V-0 down to 0.8 mm material thickness. According to Ticona, four main features distinguish Celanex XFR from other phosphorous-containing flame retardant systems: high efficacy, thermal stability up to 300°C, virtual absence of migration and emissions, and problem-free coloration of the compounds. According to Ticona, Celanex XFR is suitable for use in 20% of the European PBT market [60].

Table 3.14
Examples of commercially available flame retardants for V-0 grade PBT

Substance	Examples of commercial products	Loading for V-0 grade	Synergist ATO	Formulation costs *	Cf. section of this report
Halogenated					
Deca-BDE	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	10.4 % *	4%	1	1
Ethane-1,2-bis(pentabromophenyl)	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	10.4 % *	4%	2	5.1
Ethylene bis(tetrabromophthalimide)	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	12-14 % **	5%		5.2
Brominated epoxy polymer	FR 2300 (ICL Industrial Products)	15.8 % *	4%	2	5.9
Tetrabromobisphenol-A carbonate oligomer	Great Lakes BC-52 (Great Lakes Corp.) Great Lakes BC-58HP (Great Lakes Corp.)	14.5 % *	4%	3	5.11
Brominated polystyrene	SAYTEX® PBT 620 (Albemarle Corp.) Firemaster® PBS-64 (Great Lakes Corp.) Firemaster® CP-44HF (Great Lakes Corp.)	12.9 % *	4%	5	5.7
Brominated polystyrene	Firemaster® BP-411 (Great Lakes Corp.)	12.1 % *	4%	4	
Poly(dibromostyrene)	PDBS-80 (Great Lakes Corp.)	14.5 % *	4.4%	5	5.8
Tetradecabromodiphenoxybenzene	SAYTEX® 120 (Albemarle Corp.)	12-14 % **	5%		5.4
Dodecachlorododecahydrodimethanodibenzocyclooctene	Dechlorane Plus® (Occidental Petroleum Corp.)	11-18% [114]	3-9%		5.13
Non halogenated					
Organic phosphinates	Exolit® OP 1312 M1 (Clariant GmbH)	about 23% [61]	yes, but loading not indicated		5.25

*1 Data on the product from Great Lakes Corp. only [56]. Formulation costs: 1=low; 5=high

** Source: [58]. It is not specifically mentioned that the loading is for V-0 grade, but it is indicated that the FR efficiency of the substance is similar to that of Deca-BDE.

For the brominated alternatives used with PBT, as indicated in Table 3.14, ethane-1,2-bis(pentabromophenyl) and brominated epoxy polymer are the cheapest alternatives. As Deca-BDE represents only 10% of the market, it is evident that the higher price of the alternatives is outweighed by their superior technical properties.

It has not been possible to confirm from independent sources the relative price difference between PBT flame retarded with Deca-BDE, and PBT using the new halogen-free alternatives. According to the manufacturer, Clariant GmbH, in 2004, *"Flame retarding polyamide or polyester with Exolit phosphinates will result in compounds which are (at current prices) comparable or only slightly more expensive than compounds with brominated flame retardants like PBDEs, brominated polystyrene or brominated benzacrylates. Phosphinates are more expensive on a per kg flame retardant basis, however, realistically the price per volume of flame retarded polymer compound should be compared. The necessary dosage of phosphinates is lower compared to brominated flame retardant systems"*

which usually consist of the brominated flame retardant plus antimony trioxide as a synergist, i.e. phosphinates are more effective." [59]

In the next section, the price of V-0 grade, glass-fibre-reinforced PA, flame retarded with organic phosphinates, is compared to a similar PA, flame retarded with Deca-BDE. The incremental price of the PA with phosphinates is estimated at 27%, which may roughly indicate the order of magnitude of the price increase for PBT as well.

In 2004 the production capacity of FR phosphinates was limited to several thousand tons from Clariant GmbH, which is the only supplier [59].

Unlike the situation for enclosures, in which HIPS and ABS can be replaced by copolymers, the properties of the thermoplastic polyesters and polyamides cannot easily be obtained by use of other resins. Lassen *et al.* (1999) [7] discussed briefly the options for replacing FR PBT with other plastics: The constraint on replacing bromine-containing PBT with halogen-free polyamide is not the price, but the different technical properties of the two types of plastic. Other options would be to use resins that are inherently less flammable. Halogen-free polyketone could be a possible alternative, but is about 50% more expensive than PBT and polyamide, and this price difference could be a constraint to replacing, e.g. PBT/PET with this plastic. The price of high performance thermoplastics such as polysulfone, polyaryletherketone (PAEK) or polyethersulfone (PES) is significantly higher than the price of PBT and PA. In general terms, the price varies from 2x for polysulfone, to significantly more for the most expensive [7].

No examples of changes of resin in order to avoid the use of brominated FR-containing PBT or ABS have been identified.

In conclusion, for all identified applications of Deca-BDE in EEE parts made of PBT/PET, alternatives without Deca-BDE are available.

3.3.2 Parts made of polyamide

Polyamide is also known as PA or nylon. Common types of polyamide are PA6 and PA66.

Polyamide is widely used for injection molding applications, often with glass fibre reinforcement. Flame retarded polyamide is used for connectors, circuit breakers and other internal parts of EEE.

Contrary to PBT, a large range of flame retardants have been applied in different types of polyamide.

According to the information presented in Table 3.11, brominated flame retardants account, globally, for the majority of flame retardants used with polyamide for applications in EEE. Different types of PA may require different flame retardants.

A comparison of the technical properties of Albemarle's FRs recommended for use with polyamide shows nearly the same pattern as seen for the other resins. Deca-BDE gives poor performance with regard to bloom resistance and thermal stability, very good performance with regard to colour, and is considered a lower cost solution. It has not been possible to identify any PA application in EEE for which Deca-BDE cannot be replaced by other flame

retardants. As shown in Table 3.11, brominated polystyrene is the most widely used FR in polyamide for EEE, with a market share ten times higher than the market share of Deca-BDE.

Table 3.15
Comparison of Albenarle FRs recommended for use with polyamide (based on [62])

Properties	SAYTEX					
	HP-7010	BT-93	BT-93W	120	8010	102E
Bloom Resistance	++	++	++	+	-	--
Thermal Stability	++	+	+	-	-	--
UV Stability	-	++	++	+	+	-
Physical Properties	+	+	+	+	+	-
Electrical Properties	++	+	+	+	+	+
FR Efficiency	-	+	+	+	+	+
MFI	+	+	+	+	+	+
Gloss		--	--	-	-	-
Colour	+	--	-	++	+	++
WEEE compliant	Yes	Yes	Yes	No		

Notes:

++ Very Good + Good - Fair -- Poor

HP-7010: Brominated polystyrene

BT-93; BT-93W: Ethylene bis(tetrabromophthalimide)

120: Tetradecabromodiphenoxybenzene

8010: Ethane-1,2-bis(pentabromophenyl)

102E: Deca-BDE

Twelve flame retardants that can be used in addition to Deca-BDE to achieve V-0 grade PA are listed in Table 3.16.

A number of halogen-free flame retardants are available for use in polyamide, and they are widely used. According to Table 3.11, melamine and red phosphorous each represent about 8% of the global FR market for PA made into EE components. According to the information in Table 3.12, the halogen-free FRs accounted for 42% of the total European FR market for PA for all applications in 1998, with melamine accounting for 19% of the total market.

According to SpecialChem, "*Melamine cyanurate, is a halogen free, thermally stable flame retardant which has established itself as the flame retardant of choice to achieve UL 94 V-0 especially in unfilled and mineral filled polyamide 6 and 66. Cost effectiveness, excellent electrical and mechanical properties as well as health and safety considerations and freedom of colour are the main advantages of melamine cyanurate.*" [63] However, as shown in Table 3.16, only V-2 can be obtained in fibre-glass-reinforced PA, which is the most demanding PA application for FRs.

Red phosphorous has been used for many years as a FR in polyamide. Red phosphorous can actually be used as a flame retardant additive for a wide variety of plastics. However, it is most efficient in oxygen-containing polymers such as polycarbonate and PA [17]. The red phosphorous concentration required in polyamide for UL 94 V-0 rating, according to the OECD monograph, is about 7% [17]; however, in glass-fibre-reinforced polyamide 66, 10-13% red phosphorous is needed (Table 3.16). According to one producer of polyamide containing red phosphorous (quoted in [7]), the mechanical properties of polyamide are hardly impaired by the small quantities of red phosphorous. One disadvantage of red phosphorous is that, due to its reddish colour, the polyamides can only be offered in the colours grey and black. There

are also certain risk factors associated with working with red phosphorous, including flammability and auto-ignition.

Table 3.16
Examples of commercially available flame retardants for V-0 grade PA

Substance	Examples of commercial products	Loading for V-0 grade wt%	Synergist	Cf. section in this report
Halogenated				
Deca-BDE	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	16-18 % *	6-7 % ATO	1
Ethane-1,2-bis(pentabromophenyl)	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	16-18 % *	6-7 % ATO	5.1
Ethylene bis(tetrabromophthalimide)	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	n.a.	n.a.	5.2
Brominated epoxy polymer ***	FR 2300 (ICL Industrial Products)	n.a.	n.a.	5.9
Brominated polystyrene	SAYTEX® HP-7010 (Albemarle Corp.)	19-21 % *	6-7% ATO	
Tetradecabromodiphenoxybenzene	SAYTEX® 120 (Albemarle Corp.)	16-18 % *	6-7 % ATO	5.4
Poly (pentabromobenzyl acrylate)	FR-1025 (PBB-PA) (ICL Industrial Products)	n.a.	n.a.	5.10
Dodecachlorododecahydrodimethanodibenzocyclooctene	Dechlorane Plus® (Occidental Petroleum Corp.)	18-20% [114]	9-10% ATO	5.13
Non halogenated				
Red phosphorous	Exolit® RP 690 and other in the RP series (Clariant GmbH)	10-13% in glass-reinforced polyamide 66 [131]		5.21
Melamine cyanurate	MELAPUR® MC XL (CIBA) FR-6120 (ICL Industrial Products)	PA 6 unfilled: 10-12 % PA 66 unfilled: 6-8 % PA 6 and PA 66 mineral filled: 13-15 wt% PA 6 and PA 66 glass filled V-2 only, at 15-20 wt% **		5.24
Melamine polyphosphate	MELAPUR® 200/70 (Ciba)	PA 66 glassreinforced: 25% [134]		5.23
Organic phosphinates	Exolit® OP 1312 M1 ; Exolit® OP 1311 and others in the series (Clariant GmbH)	15-20% [139]		5.25
Magnesium hydroxide	MAGNIFIN® H-7 C (Albemarle Corp.)	45% ****		5.20

* Source: [62]. It is not specifically mentioned that the loading is for V-0 grade, but it is indicated as typical loading, and the FR efficiency of the substances is similar to that of Deca-BDE.

** Loadings for products from Ciba [136].

*** The substance is included in a list summarised March 2006 by J. Troitzsch [31]. The loadings of the substance have not been assessed further.

**** Source: Clariant GmbH [64].

It has not been possible to identify any detailed independent assessment of the cost of replacing Deca-BDE with other flame retardants in PA.

Therefore, in the following discussion, an estimate is made on the basis of information obtained from Clariant GmbH - Business Unit Plastic Industries, Germany. Clariant is a major global actor in the field of specialty chemicals, and a manufacturer of a number of halogen-free flame retardants, among which, ammonium polyphosphate, red phosphorous and organic phosphinates. On request, Clariant has provided information for comparison of its newly developed organic phosphinates with three other flame retardants for PA [64]. The price estimates of three other flame retardants are based on recent information from market surveys. Any price comparison is, of course, highly dependent on the type of PA and the filling, and this estimate should only be considered as an example indicating the order of magnitude.

The calculation is made for glass-fibre-reinforced flame retarded V-0 grade Polyamide 6 (FR PA 6 GF). It is assumed that the glass fibre loading is 20% (typical loadings are 10-30%). The price of the pure PA 6 is assumed to be 2.3 €/kg (typical range 2.1-2.5 €/kg), and the price of the glass fibre assumed to be 1.95 €/kg (typical range 1.7-2.2 €/kg). The total material price for the PA 6 GF (20%) is then 2.23 €/kg.

In Table 3.17, cost estimates are shown for V-0 grade FR PA 6 GF, flame retarded variously with Deca-BDE, brominated polystyrene, magnesium hydroxide and organic phosphinates. No data on red phosphorous or melamine polyphosphate, two other options, were identified. The prices of the three alternatives range from 84% to 127% of the Deca-BDE option. It should be noted that the high loading of magnesium hydroxide required to achieve V-0 grade may hinder its use for certain applications in spite of the low price. For a 25 g plastic part, these price differences correspond to a cost difference of (-)0.02 to 0.03 €.

Table 3.17
Comparison of material prices of V-0 grade PA 6 GF with four different flame retardants

Flame retardant	Price of flame retardant /kg	FR loading	FR price per kg FR PA 6	Total material price for FR PA 6 GF /kg average	Total material price Percentage of Deca-BDE PA 6 GF average
Deca-BDE + ATO	Deca-BDE: 2.75 ATO: 2.75	14% Deca-BDE + 5% ATO	0.52	2.33	100%
Brominated polystyrene + ATO	BrPS: 4.00-5.25 ATO: 2.75	21% BrPS + 5% ATO	0.98-1.03 average: 1.00	2.65	114%
Magnesium hydroxide	1.00-1.50	45%	0.45-0.68 average: 0.563	1.79	84%
Organic phosphinate (OP 1312)	6.80-7.40	15%	1.02-1.10 average: 1.06	2.96	127%

Note: Due to differences in density of the FRs, the volume of 1 kg final material will be slightly different. In fact, for the user, the comparison should be done for the same volume, but it is clear that the result would be only slightly different from these estimates. Basic prices and loadings according to [64].

In conclusion, for all identified applications of Deca-BDE in EEE parts made of PA, alternatives without Deca-BDE are available.

3.4 Substitutes to Deca-BDE in cables, sheets and films made of PP and PE

According to the information from the Bromine Science and Environmental Forum shown in Table 2.3, Deca-BDE is used in the polyolefins PP and PE for the following applications:

- Wire and cables - e.g. heat shrinkable tubing;
- Communication cables;
- Building cables;
- Capacitor films.

Building cables, power capacitors and, to some extent, communication cables are beyond the scope of the RoHS Directive.

“Wire and cables” is a very diverse product group, with a number of different plastics and rubber used for cable insulation, as well as several different flame retardants. It has not been possible to identify any source that has quantified the use of Deca-BDE and alternative flame retardants in cables of EEE, nor to identify any specific applications where Deca-BDE provides exceptional properties. According to Bromine Science and Environmental Forum, wire and cabling accounted for 2% of the EE industry's BFR consumption (probably in the late 1990's) [65]

A number of brominated flame retardants are available for use with PE and PP. Properties of FRs from Albemarle Corp. are compared in Table 3.18, showing a similar pattern to that seen for other resins.

Regarding the use of Deca-BDE (SAYTEX® 102E) and two brominated alternatives for cables and wire, Albemarle Corp. wrote : *"SAYTEX® 102E flame retardant is a very effective flame retardant with high % bromine (83%) and high thermal stability (approximately 300°C). Although it is a common FR used in wire & cable, it "blooms," which affects appearance, moisture resistance, and electrical properties. With good UV resistance, very good thermal stability and low blooming characteristics, thermally stable and high-bromine SAYTEX 8010 flame retardant is well-suited for applications requiring color stability, or where recycling is anticipated. SAYTEX BT-93 brominated flame retardant is very thermally stable (over 450°C), with excellent flame retardant efficiency. It does not bloom, which leads to better moisture resistance and electrical properties."* [66]

Regarding the brominated alternatives, the situation is very much the same as for HIPS and PA, and the price differences estimated for the latter two resins may roughly be applied to the polyolefins.

Table 3.18
Comparison of Albemarle FRs recommended for polyolefins (based on [69])

Properties	SAYTEX				
	BT-93	BT-93W	120	8010	102E
Bloom Resistance	++	++	+	-	--
Thermal Stability	+	+	+	-	--
UV Stability	++	++	+	+	-
Physical Properties	+	+	+	+	-
Electrical Properties	+	+	+	+	+
FR Efficiency	+	+	+	+	+
MFI	+	+	+	+	+
Colour	--	-	++	+	++

Notes:

++ Very Good + Good - Fair -- Poor

HP-7010: Brominated polystyrene

BT-93; BT-93W: Ethylene bis(tetrabromophthalimide)

120: Tetradecabromodiphenoxybenzene

8010: Ethane-1,2-bis(pentabromophenyl)

102E: Deca-BDE

Halogen-free flame retardants that can be used with polyolefins include intumescent systems and magnesium hydroxide.

Halogen-free solutions for polypropylene, based on intumescent technologies, have been commercially available for many years, but their use and acceptance has been somewhat restricted due to product limitations, especially as regards processing, water extraction, cost performance, and the high load levels required, which cause degraded mechanical properties [142]. The mechanism of FRs based on intumescent technologies is to cause the plastic, when heated, to swell (intumesce) into a thick, insulating char that protects the underlying material from burning by providing a physical barrier to heat and mass transfer.

Many of the existing halogen-free solutions are based on ammonium polyphosphate, combined with different nitrogen sources and other co-additives.

An example is Clariant's ammonium polyphosphate based flame retardant Exolit AP 750: *"In comparison to other non-halogen flame retardants, such as aluminum or magnesium hydroxide, Exolit AP 750 is much more effective. The UL 94 standard (Class V-0), which is important in the electrical and electronics industry, is thus achieved with substantially lower dosages."* [68]

Another halogen-free FR system, based on melamine phosphate, is Reogard® 1000 (CN-2616): *"CN-2616 steps beyond the performance limitations of existing flame retardant solutions for polyolefins with a unique set of properties. It is versatile enough to meet MVSS 302, UL-94 V0 and V5 requirements, and initial results following European test protocols have also been positive."* [142]

"We believe that the reduced loading of CN-2616 required to meet UL 94-V0 test requirements and the superior performance in terms of water resistance, electrical and physical properties will lead to increased use of halogen-free polyolefin compounds." [142]

The following table lists Deca-BDE and 12 other flame retardants used with polyolefins to achieve V-0 grade.

In conclusion, for all identified applications of Deca-BDE in EEE parts made of polyolefins, alternatives without Deca-BDE are available.

Table 3.19
Examples of commercially available flame retardants for V-0 grade polyolefins

Substance	Examples of commercial products	Loading for V-0 grade		Synergist ATO		Cf. section in this report
		PP	PE	PP	PE	
Halogenated						
Deca-BDE	SAYTEX® 102E (Albemarle Corp.) Great Lakes DE-83 RTM (Great Lakes Corp.) FR 1210 (ICL Industrial Products)	20-30% **	20-30% **	6-10%	6-10%	1
Ethane-1,2-bis(pentabromophenyl)	SAYTEX® 8010 (Albemarle Corp.) Firemaster® 2100 (Great Lakes Corp.)	20-30% **	20-30% **	6-10%	6-10%	5.1
Ethylene bis(tetrabromophthalimide)	SAYTEX® BT-93 (Albemarle Corp.) BT-93 (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)	20-30% **	20-30% **	6-10%	6-10%	5.2
Tetradecabromodiphenoxybenzene	SAYTEX® 120 (Albemarle Corp.)		20-30% **		6-10%	
Brominated epoxy polymer (PP only) *	FR 2300 (ICL Industrial Products)	n.a.		n.a.		5.9
Tetrabromobisphenol A bis (2,3-dibromopropyl ether)	SAYTEX® HP-800AG PE-68 (Great Lakes Corp.) Safety Data Sheet FR-720 (ICL Industrial Products)	9-12% **		3-4%		5.6
Poly pentabromobenzyl acrylate [67]	FR-1025 (ICL Industrial Products)	n.a.		n.a.		5.10
Chloroparaffins *	n.a.	n.a.	n.a.	n.a.	n.a.	-
Dodecachlorododecahydrodimethanodibenzocyclooctene	Dechlorane Plus® (Occidental Petroleum Corporation)	30 % [114]		10%		5.13
Non halogenated						
A Blend of: Pentaerythritol Phosphate Alcohol, Melamine Phosphate and Cryst Silica Quartz	CN-2616; Reogard® 1000 (Great Lakes Corp.)	20% [142]		-		5.26
Ammonium polyphosphate	Exolit® AP-750 (Clariant GmbH)	26- 30% [68]	30-35% [68]	-		5.23
Red phosphorous (PE only)*			n.a.		n.a.	
Magnesium hydroxide *	MAGNIFIN® H-7 C (Albemarle Corp.)	n.a.		n.a.		5.20

* The substances are included in a list summarised March 2006 by J. Troitzsch [31]. The loadings of the substance have not been assessed further.

** Source: SpecialChem [69]. The loading refers to products from Albemarle Corp.

4 Examples of companies that have phased out Deca-BDE

4.1 Manufacturers of EEE

A number of the major manufacturers of EEE state that they currently do not use Deca-BDE and other PBDEs in their products.

Below are statements quoted from the following major EEE brand name companies: Dell, HP, Compaq, Sony, IBM, Ericsson, Apple and Panasonic. The companies jointly cover all major product groups of consumer electronics and IT equipment.

Some of the main drivers behind Deca-BDE-free products have been eco-labels, customer requirements (e.g. "green procurement" guidelines) and compliance with the RoHS Directive and other legislation. Companies typically implement the phase-out of Deca-BDE simply by adding specifications prohibiting its use in the products and components supplied by subcontractors, but generally the companies do not specify which flame retardants should be used as substitutes. The types of flame retardants used in products are generally considered confidential, but a typical replacement scheme would be to use copolymers together with halogen-free organo-phosphorous compounds for enclosures and other large parts, and to use other brominated flame retardants instead of Deca-BDE for the small parts (<25g) in connectors, switches, etc. In this manner, the products still meet the most strict eco-label criteria, e.g. the Nordic Swan criteria for consumer electronics and personal computers [70]. Whereas the Nordic Swan criteria require the entire EE device to be PBDE-free, the EU Flower eco-label accepts PBDEs in parts <25g.

The large number of major companies that have phased out Deca-BDE in their products clearly indicates that Deca-BDE-free electronic components are available on the market, and that the requirement for "Deca-BDE-free" is not an obstacle to manufacturing any EEE.

Hewlett-Packard Company

Products from the Hewlett-Packard Company include the "HP" and "Compaq" brand names. According to the web-site of Hewlett-Packard Company, *"HP eliminated the use of two brominated flame retardants (BFR's) PBB and PBDE years before they were included in the RoHS directive."* [71]

At the Third Annual International Consortium for Fire Safety, Health and the Environment Workshop, 12-13 Sep 2005, a representative of HP stated in his presentation:

"- Since 1995, all PBBs, PBOs and PBDEs (24 CAS-numbers in total), have been phased out in our products. Note: Even if the Commission would allow decaBDE, we will not start to use it!" [72]

HP listed a number of drivers behind changing its environmental requirements in the E&E sector: Legislation (e.g. WEEE, RoHS, REACH), custom-

ers (e.g. public green procurement), recyclers, shareholders, employees, standardisation organisations (e.g. eco-design and Environmental Product Declarations, NGOs, media, consultants, eco-labelling organisations (EU Flower, German Blue Angel, Nordic Swan, TCO) and competition. [72]

"Examples of flame retardants that we use instead of halogens are mainly different types of organic phosphate esters, see below:

Substance	CAS number
DEEP, diethylethylphosphonate	78-38-6
DPK, diphenylcresylphosphate	247-693-8
RDP, resorcinol bis (diphenylphosphate)	57583-54-7
TEP, triethylphosphate	78-40-0
TCP, tricresylphosphate	1330-78-5
TPP, triphenylphosphate	115-86-6

Some other possible solutions contain aluminum, manganese, zinc and red phosphorous, but a lot of work remains before we can consider any of these new alternatives as we have to be sure these meet all applicable electrical safety standards. " [73]

"Our expectations: - non-halogenated FR alternatives for mainly ABS, PC/ABS, PC and HIPS. AND, extensive eco-toxicological testing / data is a must for any new alternative". [72]

Dell

Dell posted on their web-site in December 2005 the document, "Dell's Position on Brominated Flame Retardants (BFRs)." [74] The document included the following statement:

"Since 2002, four years ahead of the EU RoHS Directive, Dell has prohibited the use of all polybrominated biphenyls (PBB) and polybrominated diphenyl (PBDE) ethers, including DecaBDE, in our products, worldwide."

Requested how Dell managed to substitute Deca-BDE, the company answered: *"The short answer to the substitution question is that we avoid the use of DecaBDE by enforcing specifications prohibiting its use and by avoiding plastics that contain this FR."* [75]

Sony

According to Sony's Corporate Social Responsibility Report 2005, PBDEs were to be prohibited immediately in Sony's products [76]. Sony's "Management regulations for the environment-related substances to be controlled which are included in parts and materials," 5th Edition of 2006, included the following statement[77]:

Substances: Polybrominated diphenylethers (PBDE) (including decabromodiphenyl ether [DecaBDE])		
Targets		Effective date of the ban on the delivery
Level 1	- All uses (e.g. flame retardants contained in plastics)	Banned since the establishment of this Standard
	- The parts manufactured using the molding dies, which were made in or before December 2002 (Applicable only to the bodies of the displays and TV sets shipped to countries and regions other than European ones) The parts whose molding dies have been made since January 2003 must not contain PBDE.	Banned since January 1, 2005

IBM

IBM's "Engineering Specification 46G3772 Baseline Environmental Requirements for Materials, Parts, and Products for IBM Logo Hardware Products," of 8 February 2006, included the following statement:

"Octa- and pentabromo diphenyl ethers are prohibited above 0.1% by mass in any Homogenous Material by EU Directive, but IBM prohibits the Intentional Addition of any PBDE in any Homogenous Material. There are no applications of PBDE permitted by IBM. IBM does not exempt decabromo diphenyl ether from this restriction." [78]

Ericsson

Ericsson's "Sustainability Report 2003" stated: *"Three of the substances banned by the RoHS Directive, PBB, PBDE and mercury, are included in the Ericsson list of banned substances and already phased out from new Ericsson products."* [79]

Apple

Apple stated on their web-page (February 2006) under "Apple and the Environment - Materials Selection," the following:

"Substances Banned from Products.... Polybrominated diphenyl ethers (PBDEs)" [80]

Matsushita

Products from Matsushita include, among others, the Panasonic trademark.

The "Environmental data book 2005" from the Matsushita Group included the statement: *"Discontinue immediately: Specified brominated flame retardants (PBB, PBDE)"* [81]. Furthermore, the "Matsushita Electric Group's Chemical Substances Management Rank Guidelines" of October 2005 stated that Deca-BDE (identified by CAS. No.) is prohibited in the company's products [82]. The guidelines listed 9 prohibited brominated flame retardants, and 47 different brominated flame retardants for reduction, which illustrates yet again the diversity of flame retardants used for these products.

Intel

Intel stated in their Material Declaration Data Sheets, *"To the best of our knowledge, the following materials are not present in Intel products and are restricted by Intel's Environmental Product Content Specification for Suppliers and Outsourced Manufacturers (<http://supplier.intel.com/ehs/environmental.htm>): ".... Polybrominated biphenyls and their ethers (PBB, PBDE)"* [83].

B&O

B&O stated in a pamphlet about environmental policy *"For at kunne sælge vores produkter efter juli 2006 skal de være fri for bly, cadmium, kviksølv, hexavalent chrom, PBB og PBDE. De to sidste stoffer er to bromerede flammehæmmere som typisk her været tilsat for at nedsætte brandbarheden. Disse to stoffer har vi udfaset fra alle vore produkter i begyndelsen af 90erne."* [84] Literally translated: [In order to be able to sell our products after July 2006, they have to be free of lead, cadmium, mercury, hexavalent chromium, PBB and PBDE. The two latter substances have typically been added in order to reduce the flammability. We have phased out these two substances from all our products at the beginning of the 1990s].

4.2 Major plastic suppliers

In Germany the association of plastics manufacturers, VKE (Verband der Kunststoffherzeugenden Industrie e.V.), and the association for the textile additives industry (TEGEWA) declared in 1986 a voluntary phase-out of the use of PBDEs, including Deca-BDE (voluntary commitments from 1 Dec 1986 and 22 Dec 1986 [22]).

Likewise, a number of the major European suppliers of plastic compounds, providing a wide range of FR plastics, specifically certify that their products do not contain PBDEs in concentrations above 0.1%:

Bayer

"In common with other well-known German plastics manufacturers, we have not used any polybrominated diphenyl ethers (PBDEs) or polybrominated biphenyls (PBBs) in the production of flame retardant plastics since 1989." [148]

Ticona

"In addition, flame retardants containing PBDE (polybrominated diphenyl ethers) or PBBE (polybrominated biphenyl ethers) must be treated separately in the recycling process. Ticona polymers don't contain these elements and flame retardants." [150]

BASF

Absence declaration	
BASOTECT®	STYROLUX®
CAPRON	STYROFLEX®
ECOFLEX	STYROPOR®
LURAN®	TERBLEND® N
LURAN® S	TERLURAN®
NEOPLEN®	TERLUX®
NEOPOR®	ULTRADUR®
POLYSTYROL	ULTRAFORM®
STYROBLEND®	ULTRAMID®
	ULTRASON®

Please be advised that based on the information available to us from our raw material suppliers, the current products offered in the product lines listed above do not contain as intentional additives, any of the below referenced materials as referenced in the subject EU Directive 2003/11/EC. To the best of our knowledge, none of these materials are generated during production.

Polybrominated diphenyl ethers (PBDEs)
Polybrominated biphenyls (PBBs)
Pentabromodiphenyl ethers
Octabromodiphenyl ethers

[149]

Dupont

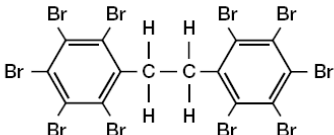
"DuPont EP is committed to full compliance with RoHS ● Use of PBDEs stopped 20 years ago." [151]

5 Substitutes for Deca-BDE by substance

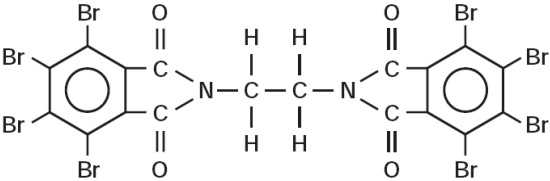
The following chapter includes information on flame retardants that can substitute for Deca-BDE in V-0 grade plastics for one or more application. Flame retardants with a proprietary CAS No and chemical name are not included. For convenience, the indicated lists of resins exclude applications in foams, thermosets, textiles and coatings which are out of the scope of this study. V-0 grade may not be obtainable for all indicated resins.

The indicated market volumes include all applications of the substance as FR.

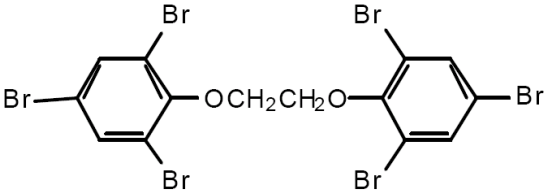
5.1 Ethane-1,2-bis(pentabromophenyl)

CAS No.	84852-53-9	Ref.
Chemical name	Ethane-1,2-bis(pentabromophenyl) (EBP)	
Synonyms	Ethane-1,2-bis(pentabromophenyl) (SAYTEX® 8010) Decabromodiphenylethane, DBDE (Firemaster® 2100) Benzene, 1, 1'-(1, 2-ethanediy)bis[2, 3, 4, 5, 6-pentabromo- (Firemaster® 2100) 1,2 Bis(pentabromophenyl) ethane EBP	
Chemical formula		[87]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>ABS, HIPS, PA, PBT/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPE, Thermoplastic elastomers, silicone, PVC, EPDM</p> <p><i>"SAYTEX® 8010 flame retardant is the most cost effective non-decabromodiphenyl-oxide (DECA) flame retardant for HIPS"</i></p> <p><i>"SAYTEX 8010 flame retardant can be used in a wide range of high performance applications. In particular it finds use in styrenic polymers, engineering resins, wire & cable and elastomers."</i></p> <p><i>"Firemaster 2100 is a general purpose, brominated, high-purity, non-DPO based flame retardant for a variety of polymers including styrenics, engineering polymers, polyolefins, and elastomers."</i></p>	[85] [87] [86]
Examples on trade names	<p>SAYTEX® 8010 (Albemarle Corp.) [87]</p> <p>Firemaster® 2100 (Great Lakes Chemicals Corp.) [88]</p>	
Extent of the application	Western Europe: 2,500 tonnes in 1998	[25]

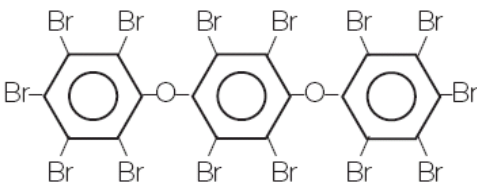
5.2 Ethylene bis(tetrabromophthalimide)

CAS No.	32588-76-4	Ref.
Chemical name	Ethylene bis(tetrabromophthalimide)	
Synonyms	Ethylene bistetrabromophthalimide (SAYTEX® BT-93) 1,2-bis (tetrabromophthalimido) ethane N,N'-Ethylenebis-3,4,5,6-tetrabromophthalimide	
Chemical formula		[89]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>ABS, HIPS, PBT/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPE, Thermoplastic elastomers, silicone, PVC, EPDM</p> <p><i>"It finds use in polyolefins, high-impact polystyrene (HIPS), thermoplastic polyesters (PBT, PET, etc.), polycarbonate and elastomers."</i></p> <p><i>"Combining high UV resistance with very effective flame retardancy and recyclability, SAYTEX BT-93 is a popular choice for resins used in office automation equipment, such as photocopiers and printers where UV stability is an important performance criterion."</i></p>	[89] [85]
Examples on trade names	<p><u>SAYTEX® BT-93</u> (Albemarle Corp.)</p> <p><u>BT-93</u> (Jiangsu Huading Refining Chemical Industry Co. Ltd., China)</p>	[89] [90]
Extent of the application	Western Europe: 5,250 tonnes in 1998	[25]

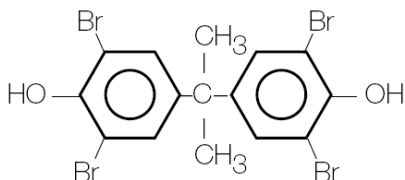
5.3 Bis(tribromophenoxy)ethane

CAS No.	37853-59-1	
Chemical name	Bis(tribromophenoxy)ethane	
Synonyms	1,2-Bis(tribromophenoxy)-ethane (Great Lakes Corp.)	
Chemical formula		[91]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>HIPS, ABS, PC, UPE</p> <p><i>"The recommended alternatives to octa-PBDE in ABS are Firemaster FF-680 and Great Lakes BA-59P™"</i></p> <p><i>"High bromine content, excellent thermal stability and good UV stability makes Great Lakes FF-680 an outstanding flame retardant for HIPS, ABS, polycarbonate, thermoplastic, elastomers, unsaturated polyesters, adhesives, coatings, and textiles. Great Lakes FF-680 is especially efficient for applications in which thermal stability at high processing temperatures is important."</i></p>	[92] [93] [91]
Examples on trade names	<u>FF-680</u> (Great Lakes Corp.)	[94]
Extent of the application	No data	

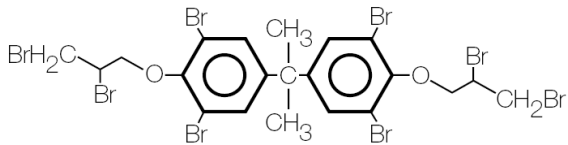
5.4 Tetradecabromodiphenoxybenzene

CAS No.	58965-66-5	
Chemical name	Tetradecabromodiphenoxybenzene	
Synonyms		
Chemical formula		
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>ABS, HIPS, PA, PBT/PET, PC, PP, PE, SAN, PC/ABS, HIPS/PPE, silicone, EPDM</p> <p>"SAYTEX 120 flame retardant finds application in high performance polyamide and linear polyester engineering resins and alloys. It also finds application in polyolefins, wire & cable, and styrenic resins."</p>	[95]
Examples on trade names	SAYTEX 120 (Albemarle Corp.)	[95]
Extent of the application	No data	

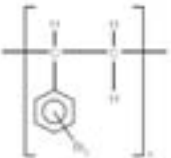
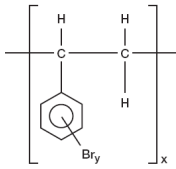
5.5 Tetrabromobisphenol A (TBBPA)

CAS No.	79-94-7	
Chemical name	Tetrabromobisphenol A (TBBPA)	
Synonyms		
Chemical formula		[96]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>ABS, HIPS, PC</p> <p><i>"As an additive flame retardant, SAYTEX CP-2000 flame retardant is widely used in ABS."</i></p> <p><i>"Great Lakes BA-59P, tetrabromobisphenol A, is a brominated aromatic flame retardant used in thermoplastic and thermoset resin systems."</i></p> <p><i>"It is also cost-effective as an additive flame retardant in applications such as ABS..."</i></p>	[96] [97] [98]
Examples on trade names	<p>SAYTEX® CP-2000 (Albemarle Corp.)</p> <p>BA-59P (Great Lakes Corp.) Safety Data Sheet</p> <p>FR-1524 (TBBA) (ICL Industrial Products) MSDS</p>	[96] [97] [98]
Extent of the application	Western Europe: 11,600 tonnes in 2001 (probably mainly reactive use)	[18]

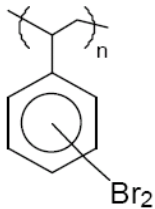
5.6 Tetrabromobisphenol A bis (2,3-dibromopropyl ether)

CAS No.	21850-44-2	
Chemical name	Tetrabromobisphenol A bis (2,3-dibromopropyl ether)	
Synonyms		
Chemical formula		[99]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>HIPS, PP, PE, crystal PS</p> <p><i>"SAYTEX HP-800A flame retardant is designed for use in PP (homopolymer and copolymer) and high impact polystyrene (HIPS) applications, mostly UL 94 V2."</i></p> <p><i>Very effective in PP and in HIPS at low dosage. Along with the melting characteristics of SAYTEX HP-800A flame retardant, this results in minimal impact on mechanical properties of the resin. • Good thermal stability • Usually used with antimony trioxide for maximum flame retardant performance"</i></p> <p><i>"Great Lakes PE-68 is recommended as an additive flame retardant for polyolefin resins"(Great Lakes Corp.)</i></p>	[99] [99]
Examples on trade names	<p>SAYTEX® HP-800A, HP-800AG, and HP-800AGC (Albemarle Corp.)</p> <p>PE-68 (Great Lakes Corp.) Safety Data Sheet</p> <p>FR-720 (ICL Industrial Products)</p> <p>403AF (LG Chem) (HIPS with Tetrabromobisphenol A bis (2,3-dibromopropyl ether))</p>	[99] [100] [101]
Extent of the application	Western Europe: 1,500 tonnes in 1998 (mainly reactive use)	[25]

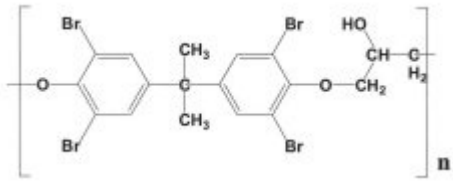
5.7 Brominated polystyrene

CAS No.	88497-56-7	
Chemical name	Brominated polystyrene	
Synonyms	Benzene, ethenyl, homopolymers, brominated	
Chemical formula	<p>SAYTEX® HP-3010</p>  <p>where x is proprietary and y is approximately 2.7</p> <p>SAYTEX® HP-7010G</p>  <p>where x and y are approximately 2000 and 2.7, respectively</p>	[103]; [104]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PA, PP, PBT/PET/PCT, PC/ABS, HIPS/PPO</p> <p><i>"For FR large connectors made of Polyamide, you won't find better cost-performance flame retardants than SAYTEX® HP-7010 or PYRO-CHEK® 68PB"</i></p> <p><i>"SAYTEX HP-7010 flame retardant provides outstanding thermal stability and electrical performance. It is particularly suitable for engineering plastic applications such as polyesters (PET, PBT, PCT) and polyamides (nylons)"</i></p> <p><i>"SAYTEX PBT-620 flame retardant is designed specifically for injection molding grades PBT"</i></p> <p><i>"Great Lakes PBS-64 is a polymeric flame retardant for polyamides and thermoplastic polyesters (PBT and PET)."</i></p>	[102] [104] [105] [106]
Examples on trade names	<p>SAYTEX® HP-3010 ; SAYTEX® HP-7010G ; SAYTEX® PBT-620 (blend with polyester resin); PYRO-CHEK® 68PB (Albemarle Corp.)</p> <p>FIREMASTER® PBS-64 (Great Lakes Corp.) Safety Data Sheet</p> <p>FIREMASTER®BP 411 (Great Lakes Corp.)</p> <p>Firemaster® CP-44HF (Great Lakes Corp.) Safety Data Sheet</p> <p>(Note: For CP-44HF and PBS-64 the Technical Data Sheet identifies CAS No. 148993-99-1 whereas the Safety Data Sheets identifies CAS No. 88497-56-7)</p>	[103]; [104]; [105]; [106] [107]
Extent of the application	No data	

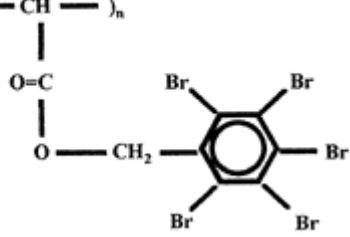
5.8 Poly(dibromostyrene)

CAS No.	148993-99-1	
Chemical name	Poly(dibromostyrene)	
Synonyms		
Chemical formula		[108]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PBT/PET, PA</p> <p><i>"Great Lakes PDBS-80 is a polymeric flame retardant for polyamides and thermoplastic polyesters (PBT and PET)"</i></p> <p><i>"Firemaster® CP-44HF is a polymeric flame retardant designed for polyamides and thermoplastic polyesters (PBT and PET). It is the preferred flame retardant for applications where improved flow is a requirement."</i></p>	[108]
Examples on trade names	<p>PDBS-80 (Great Lakes Corp.) Material Safety Sheet</p> <p>(Note: For CP-44HF and PBS-64 mentioned above Technical Data Sheet identifies CAS No. 148993-99-1 whereas the Safety Data Sheet identifies 88497-56-7)</p>	[108]
Extent of the application	No data	

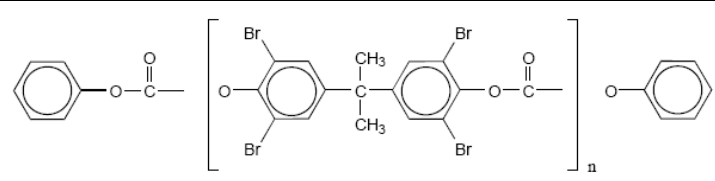
5.9 Brominated epoxy polymer

CAS No.	68928-70-1	
Chemical name	Brominated epoxy polymer	
Synonyms	Tetrabromobisphenol A - Tetrabromobisphenol A diglycidyl ether	
Chemical formula		[109]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PBT, HIPS, ABS, PC/ABS</p> <p>F-2300H is a high molecular weight brominated epoxy polymer, designed for use as a flame retardant additive for thermoplastic polyesters (PBT and PET), thermoplastic elastomers, alloys (e.g. PC/ABS) and others.</p>	[109]
Examples on trade names	FR 2300 (ICL Industrial Products) MSDS	[109]
Extent of the application	No data	

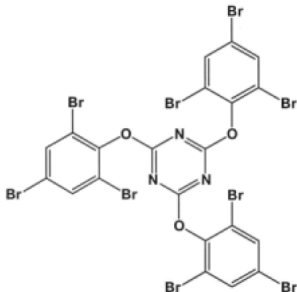
5.10 Poly pentabromobenzyl acrylate

CAS No.	59447-57-3	
Chemical name	Poly pentabromobenzyl acrylate	
Synonyms	PBB-PA, pentabromobenzyl polyacrylate	
Chemical formula	$\left(\text{---CH}_2\text{---CH---} \right)_n$ 	[110]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PBT, PET, PA, styrenic copolymers</p> <p><i>"FR- 1025 is a polymeric flame retardant with a high content of aromatic bromine and good thermal stability. It is especially suitable for engineering thermoplastics, PET, PBT, nylon and styrenic copolymers. FR-1025 exhibits inherent advantages over other halogenated FR additives currently offered for the same application, as a result of its oligomeric nature, high bromine content and excellent thermal stability."</i></p>	[110]
Examples on trade names	FR-1025 (PBB-PA) (ICL Industrial Products) MSDS	[110]
Extent of the application	No data	

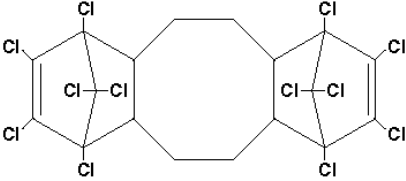
5.11 Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A

CAS No.	94334-64-2 71342-77-3	
Chemical name	Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	
Synonyms		
Chemical formula		[7]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PBT/PET, PC, ABS, PC/ABS, polysulfone, SAN</p> <p><i>"Great Lakes BC-52 is a brominated, aromatic flame retardant for thermoplastic resin systems. Great Lakes BC-52, a white powder, offers excellent thermal stability, UV stability and color in the final part. Great Lakes BC-52's unique combination of properties makes it a suitable flame retardant in PBT, PET, PET/PBT blends, PC, ABS, ABS/PC blends, Polysulfone, and SAN."</i></p>	[111]
Examples on trade names	<p>94334-64-2: Great Lakes BC-52 Safety Data Sheet (Great Lakes Corp.)</p> <p>71342-77-3: Great Lakes BC-58HP MSDS</p>	[111] [112]
Extent of the application	No data	

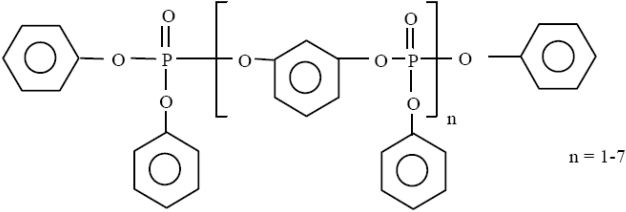
5.12 Tris(tribromophenoxy) triazine

CAS No.	25713-60-4	
Chemical name	Tris(tribromophenoxy) triazine	
Synonyms	2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine Tris(tribromophenyl) cyanurate	
Chemical formula		[113]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PE, ABS, HIPS <i>"In both HIPS and ABS, FR-245 is cost efficient and offers an excellent combination of melt flow, impact and light stability properties."</i>	[35]
Examples on trade names	FR 245 (ICL Industrial Products)	[113]
Extent of the application	No data	

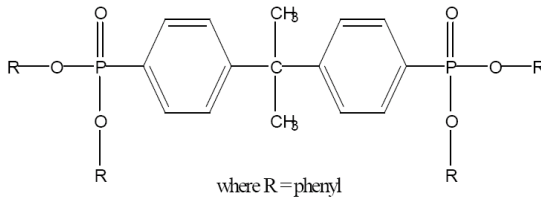
5.13 Dodecachloro dodecahydro dimethano dibenzocyclooctene

CAS No.	13560-89-9	
Chemical name	Dodecachloro dodecahydro dimethano dibenzocyclooctene	
Synonyms	1,2,3,4,7,8,9,10,13,13,14,14- dodecachloro- 1,4,4a,5,6,6a,7,10,10a,11,12,12a - dodecahydro- 1,4:7,10 - dimethanodibenzo (a,e) cyclooctene Dechlorane Plus	
Chemical formula		
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PA, ABS, PP, Epoxy <i>"Dechlorane Plus® is an excellent flame retardant for all nylons with or without glass fiber reinforcement. UL-94 V-0 ratings are possible to thicknesses of 1/64" (0.4 mm), while maintaining the excellent electrical and physical properties."</i> <i>"PBT has been successfully used in conjunction with Dechlorane Plus® to produce flame retardant connectors."</i> <i>"Dechlorane Plus® is more efficient flame retardant in ABS than some popular brominated additives."</i>	[114]
Examples on trade names	Dechlorane Plus® series (Occidental Petroleum Corporation) MSDS	[114]
Extent of the application	No data	

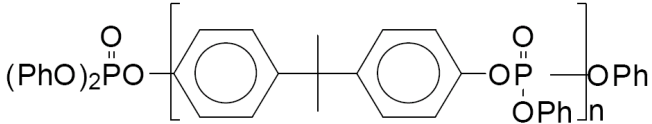
5.14 Resorcinol bis(diphenylphosphate) (RDP)

CAS No.	57583-54-7	
Chemical name	Resorcinol bis(diphenylphosphate) (RDP)	
Synonyms	Phosphoric trichloride, polymer with 1, 3-benzenediol, phenyl ester; Tetra-phenyl resorcinol diphosphate (Reofos RDP)	[115]
Chemical formula	 <p style="text-align: right;">n = 1-7</p>	[117]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PC/ABS</p> <p><i>"Reofos® RDP is a high molecular weight phosphate ester flame retardant which can impart superior flammability performance and lower volatility than is obtainable with conventional triaryl phosphates."</i></p> <p><i>"Fyrolflex RDP, an oligomeric phosphate ester flame retardant plasticizer, was designed for use in engineering resin applications such as polyphenylene oxide and PC/ABS. Fyrolflex RDP has demonstrated effectiveness as a process aid in ABS, HIPS, and other high-performance engineering plastic applications."</i></p>	<p>[116]</p> <p>[117]</p>
Examples on trade names	<p>Reofos RDP (Great Lakes Corp.) Safety Data Sheet</p> <p>Fyrolflex RDP (Supresta/Akzo Nobel)</p>	<p>[116]</p> <p>[117]</p>
Extent of the application	<p>EU: >1500 tonnes</p> <p><i>"Used throughout Europe - roughly 20,000 metric tons in the EU TV enclosure market"</i> This volume has not been confirmed by other sources and seems to be very high.</p> <p>Total tri-aryl/alkyl phosphates: Western Europe: 18,500 t</p>	<p>[118]</p> <p>[12]</p> <p>[25]</p>

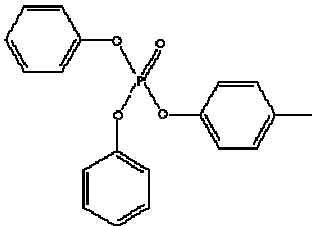
5.15 Bisphenol A bis(diphenyl phosphate) (BAPP)

CAS No.	181028-79-5	
Chemical name	Bisphenol A bis(diphenyl phosphate) (BAPP) - same as BDP	
Synonyms	Phosphoric trichloride, reaction product with Bisphenol A and phenol (Great Lakes Corp.)	
Chemical formula	 <p style="text-align: center;">where R = phenyl</p>	[120]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PC/ABS, PPE/HIPS blends</p> <p><i>"Reofos BAPP is recommended for thermoplastic applications, in particular PC/ABS, because of its ability to increase resistance to stress cracking, improve resistance to degradation during humid aging and impart flame retardancy. Also, Reofos BAPP has a much lower volatility than traditional triaryl phosphates."</i></p> <p><i>"PC/ABS and PPO/HIPS blends are the material of choice for higher end electronic enclosures. NcendX® P-30 liquid phosphorus flame retardant is an outstanding performer in PC/ABS and PPO/HIPS blends. It actually improves resin melt flow and exhibits outstanding thermal stability, excellent hydrolytic stability, low migration and low volatility"</i></p>	[120] [119]
Examples on trade names	Reofos BAPP (Great Lakes Corp.) Safety Data Sheet NcendX P-30 (Albemarle Corp.)	[120] [121]
Extent of the application	See for RDP above	

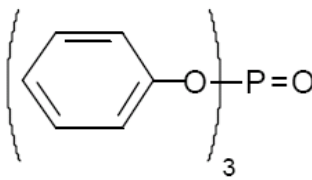
5.16 Bisphenol A bis(diphenyl phosphate) (BDP)

CAS No.	5945-33-5	
Chemical name	Bisphenol A bis(diphenyl phosphate) (BDP) - same as BAPP	[122]
Synonyms		[123]
Chemical formula		
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>ABS, HIPS, PPE/PC</p> <p><i>"Fyrolflex BDP, an oligomeric phosphate ester, was designed for use as a flame retardant plasticizer in engineering resin applications such as polyphenylene oxide and polycarbonate blends. Fyrolflex BDP has demonstrated effectiveness as a process aid in ABS, HIPS and other high-performance engineering plastic applications."</i></p>	[123]
Examples on trade names	Fyrolflex BDP (Akzo Nobel/Supresta)	[123]
Extent of the application	See for RDP above	

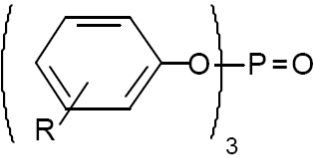
5.17 Cresyl diphenyl phosphate (CDP)

CAS No.	26444-49-5	
Chemical name	Cresyl diphenyl phosphate (CDP)	
Synonyms		
Chemical formula		[124]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PC/ABS, PF, Epoxy, PUR-foams <i>"Disflamoll DPK is used as a plasticizing flame retardant in flexible PVC. It has excellent flame retarding characteristics in PF and EP resins, in TPU's, PC/ABS blends and PUR foams (rigid and flexible). It is suitable for flame lamination."</i> *No data indicating that V-0 grade can be obtained is identified	[125]
Examples on trade names	Disflamoll® DPK (Lanxess)	[125]
Extent of the application	EU: >1500 t See for RDP above	[118]

5.18 Triphenyl phosphate (TPP)

CAS No.	115-86-6	
Chemical name	Triphenyl phosphate (TPP)	
Synonyms	Triaryl phosphate (Reofos TPP) Triphenyl phosphate (Fyrolflex TPP)	
Chemical formula		[126]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PC/ABS, modified PPO, Phenolic <i>"Reofos® TPP is a well-established plasticizer that imparts flame retardancy, permanence, good processing and good surface finish to a wide variety of resins. It is a traditional, cost effective non-halogen flame retardant."</i> <i>"Reofos TPP can be used to impart improved processing properties, flame retardancy and increased physical property performance in cellulose acetate, cellulose nitrate, PC/ABS, modified PPO and epoxy resins. End-use applications include films, lacquers and molding powders."</i>	[126]
Examples on trade names	Reofos TPP (Great Lakes Corp.) Safety Data Sheet Fyrolflex TPP (Akzo Nobel/Supresta) Disflamoll® TP (Lanxess)	[126] [127] [128]
Extent of the application	EU: >1500 t See for RDP above	[118]

5.19 Triaryl phosphates butylated

CAS No.	68937-40-6	
Chemical name	Triaryl phosphates butylated	
Synonyms		
Chemical formula	 <p>R = H or t-butyl</p>	[129]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PC/ABS</p> <p>"Reofos 507 is recommended for thermoplastic applications, in particular PC/ABS, because of its ability to increase resistance to stress cracking, improve resistance to degradation during humid aging and impart flame retardancy."</p> <p>*No data was identified indicating that V-0 grade can be obtained.</p>	[129]
Examples on trade names	Reofos 507 (Great Lakes Corp.) Safety Data Sheet	[129]
Extent of the application	No data	

5.20 Magnesium hydroxide

CAS No.	1309-42-8	
Chemical name	Magnesium hydroxide	
Synonyms	Magnesium dihydroxide; Magnesium hydrate	
Chemical formula	Mg(OH) ₂	
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>Thermoplastic polyester and elastomers, polyolefin, PVC, EPDM, PE/ EVA</p> <p>Regarding connectors: "<i>For halogen-free compounds, we suggest MAGNIFIN® flame retardants. MAGNIFIN products are the only additive that allows compounders to achieve UL 94 v-0 flame retardancy...</i>"</p>	[102]
Examples on trade names	MAGNIFIN® H-7 C (Albemarle Corp.)	[130]
Extent of the application	Western Europe: 2,400 tonnes in 1998 (all magnesium FRs)	[25]

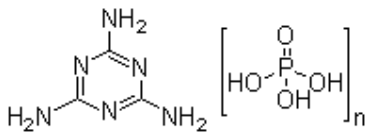
5.21 Red phosphorous

CAS No.	7723-14-0	
Chemical name	Red phosphorous	
Synonyms		
Chemical formula		
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PA, PE</p> <p>RED PHOSPHOROUS is normally used in flame-retardant-modified polymer compounds in a concentration range between 5 and 15% (w/w), which corresponds to 8 to 25% (w/w) Exolit RP 690 in the finished compound. In glass-fiber-reinforced polyamide 6.6, 10 to 13% (w/w) Exolit RP 690 is usually sufficient to obtain the UL 94 V-0 classification for electrical components (1.6 mm).</p>	[131]
Examples on trade names	Exolit RP 690 and others in the RP series (Clariant GmbH)	[131]
Extent of the application	Western Europe: 1,100 tonnes in 1998	[25]

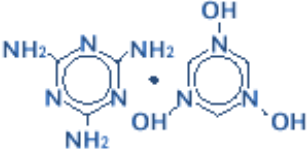
5.22 Ammonium polyphosphate

CAS No.	14728-39-9 68333-79-9	
Chemical name	Ammonium polyphosphate	
Synonyms		
Chemical formula	$(\text{NH}_4\text{PO}_3)_n$	
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PE, PP <i>"Exolit AP 750 may be used in a range of thermoplastics, especially polypropylene, polyethylene, ethylene/vinyl acetate copolymers and polyolefin blends. It is suitable both for extrusion and injection moulding applications. In addition Exolit AP 750 is suitable for use in hot melt adhesives or coating compounds."</i>	
Examples on trade names	<u>Exolit AP 750</u> (TP) and others in the AP series (Clariant GmbH)	[132]
Extent of the application	Western Europe: 7,750 tonnes in 1998 (all ammonium phosphate FRs)	[25]

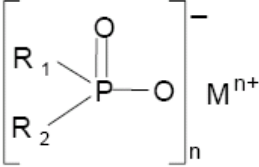
5.23 Melamine polyphosphate

CAS No.	218768-84-4	
Chemical name	Melamine polyphosphate	
Synonyms		
Chemical formula		[133]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PA, TPU <i>"MELAPUR 200/70 is a melamine based halogen free flame retardant for glass fiber reinforced polyamide 66."</i>	[134]
Examples on trade names	<u>MELAPUR® 200/70</u> (Ciba) <u>Exolit AP 750</u> (Clariant GmbH)	[134] [135]
Extent of the application	No data	

5.24 Melamine Cyanurate

CAS No.	37640-57-6	
Chemical name	Melamine cyanurate	
Synonyms	1,2,5-triazine-2,4,6 (1H,3H,5H)-trione, compound with 1,3,5 triazine-2,4,6 triamine (1:1) (MELAPUR® MC XL)	
Chemical formula		[137]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	PA, thermoplastic PUR <i>"MELAPUR MC XL is used as an effective flame retardant, primarily for electrical & electronic applications (connectors, switches, housings, etc) made from polyamide or TPU. In unfilled or mineral filled compounds it gives a UL 94 V-0 rating; in glass filled systems only a UL 94 V-2 rating is possible."</i>	[136]
Examples on trade names	<u>MELAPUR® MC XL</u> , MELAPUR® MC50, MELAPUR® MC25 (Ciba) <u>FR-6120</u> (ICL Industrial Products)	[136] [137]
Extent of the application	No data	

5.25 Organic phosphinates

CAS No.	225789-38-8	
Chemical name	Organic phosphinates	
Synonyms	Diethylphosphinic acid, aluminium salt	
Chemical formula		[138]
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PA, PBT</p> <p><i>"In glass-fiber-reinforced polyamide 6 or 6.6, a dosage of 15 to 20 % (by wt.) Exolit OP 1312 is usually sufficient to obtain the UL 94 V-0 classification for electrical components (at 1.6 as well as 0.8 mm thickness).</i></p> <p><i>Subject to the polymer grade, processing conditions and glass-fibre reinforcement the dosage of the flame retardant may vary."</i></p>	[139]
Examples on trade names	Exolit® OP 1312 M1 ; Exolit® OP 1311 and others in the series (Clariant GmbH)	[140] [141]
Extent of the application	No data	

5.26 Reogard 1000

CAS No.	A Blend of: Pentaerythritol Phosphate Alcohol CAS No 5301-78-0 Melamine Phosphate CAS No:- 41583-09-9 Cryst Silica Quartz CAS No:- 14808-60-7	[143]
Chemical name	A Blend of: Pentaerythritol Phosphate Alcohol, Melamine Phosphate and Cryst Silica Quartz	
Synonyms	CN-2616	
Chemical formula	-	
Resins to be used with the flame retardant (solid plastics and wire/cable only)	<p>PP</p> <p><i>"CN-2616 is a nitrogen-phosphorus proprietary flame retardant system for polyolefins. It is targeted primarily at the UL 94-V0 polypropylene applications but its performance benefits could also make it suitable for other polyolefin applications such as the wire and cable or building industries."</i></p>	[142]
Examples on trade names	Reogard 1000 (Great Lakes Corp.)	[143]
Extent of the application	No data	

6 Overall product chain and industry structure

In order to understand which businesses will be impacted by a ban of Deca-BDE in EEE, the product chain and implicated businesses are briefly described below.

The principal life-cycle stages of Deca-BDE in the EU are shown in Each of these key industry sectors will be discussed briefly below.

Figure 6.1, derived from the draft update of the Deca-BDE Risk Assessment.

The industry sectors associated with the different EEE-related life-cycle stages are:

- Manufacturers of flame retardants;
- Manufacturers of plastic raw materials (resins, master batches and compounds);
- Manufacturers of plastic parts;
- Manufacturers of EE components;
- Manufacturers of EEE (original equipment manufacturers, OEM).

Each of these key industry sectors will be discussed briefly below.

Figure 6.1
 Flowchart of the principal life-cycle stages of Deca-BDE in the EU. Boxes with grey shading indicate use of powder. It should be noted that this chart does not include all life-cycle stages (e.g. foam rubber production is missing).
 Source: Risk assessment Update draft 2004 [144]



6.1 Manufacturers of flame retardants

Brominated flame retardants

According to the Bromine Science and Environmental Forum (BSEF), BFRs are produced mainly by three companies in the following parts of the world [18]:

BSEF companies	Albemarle	Chemtura	ICL Industrial Products (DSBG)
Countries with BFR production sites	USA France Belgium United Kingdom Germany Austria Jordan Japan	USA United Kingdom	Israel USA The Netherlands China

The three companies all manufacture bromine and a range of brominated compounds as their core business. Overall the three companies account for around 78% of the global bromine production [18]. Bromine is found principally in seawater, salt lakes and underground brines, and the resources are virtually unlimited. All three companies manufacture Deca-BDE. Besides brominated compounds, they also manufacture different halogen-free flame retardants like organo-phosphorous compounds and magnesium hydroxide.

The three companies referred to above are:

Albemarle, a leading global producer of chemicals, with two main business segments, polymer chemicals and fine chemicals. Headquarters in Richmond, Virginia (USA).

Chemtura, resulting from the merger between Crompton Corporation and Great Lakes Chemical Corporation. The company is among the world's largest producers and marketers of bromine and brominated specialty chemicals. Headquarters in the USA, and production plants in the USA and European countries, such as the United Kingdom and France.

ICL Industrial Products includes the former Dead Sea Bromine Group (DSBG) and Eurobrom. ICL Industrial Products is recognized to be the largest producer of elemental bromine. Headquarters in Beer Sheva, Israel, and installations in Israel, the Netherlands and China.

These three companies jointly formed the European Brominated Flame Retardant Industry Panel (EBFRIP) in the mid-1980's. The organisation is made up of these three main members, as well as a number of major polymer producers as associate members. Together with Tosoh Corporation, one of Japan's largest and most diversified chemical companies, the three companies also formed another organisation to promote the interests of the industry, the Bromine Science and Environmental Forum (BSEF), established in 1997.

According to the Minerals Yearbook from the US Geological Survey, 40% to 50% of the consumption of bromine in the USA was used in brominated flame retardants [145]. The large BFR manufacturing companies are thus very vulnerable to changes in the demand for BFRs. According to the Minerals Yearbook, the withdrawal of penta-BDE and octa-BDE from the market significantly decreased the demand for bromine: "*Between 40% and 50% of domestic demand for bromine is used in FR. Although usage fluctuates along with overall cycles in the economy, assuming sustained economic growth, demand was expected to grow by 4% per year. The ban on and voluntary withdrawal of two PBDE compounds resulted in a decrease in demand for bromine between 2001 and 2004.*" [145]

The effect on the BFR manufacturing companies of an EU ban on Deca-BDE in EEE will depend heavily on which alternatives will be used. Most likely, the first step in substitution, for many users, will be to use a more expensive alternative BFR. In the short term, in this case, a ban could actually increase sales in this sector, and perhaps even the volume of bromine used, assuming alternative BFRs would require a higher loading. Some users may, however, in the short or medium term, shift to halogen-free alternatives, resulting in a decreased demand for brominated flame retardants. It should be kept in mind that a ban on Deca-BDE in EEE will not by itself drive the market towards the use of non-halogenated FRs. The general resistance to halogenated flame retardants by consumers, NGOs, eco-labels, etc. would probably have a more significant influence in that direction than would a ban on Deca-BDE.

Halogen-free flame retardants

The halogen-free flame retardants that may serve as substitutes for Deca-BDE are, first of all, non-halogen organo-phosphorous FRs (RDP, BDP, TPP), intumescent FR systems based on phosphorous and nitrogen compounds, red phosphorous, melamine cyanurate, melamine polyphosphate, organic phosphinates and magnesium dihydroxide.

The manufacturers of alternatives would clearly be helped by a ban on Deca-BDE in EEE, although the impact in the short term may be moderate.

Flame retardants that may serve as alternatives to Deca-BDE in EEE are manufactured primarily by the following European companies:

Supresta (including the former Akzo Nobel), Netherlands, according to its web-site, is the industry leader in the manufacture, distribution, and service of organo-phosphorous flame retardants, plasticizers, lubricants, fluids, and wetting agents (www.supresta.com). They manufacture a wide range of organo-phosphorous flame retardants including RDP and BDP.

CIBA Speciality Chemicals, Germany, is a global company manufacturing a wide range of chemicals (www.cibasc.com). CIBA is a manufacturer of melamine-based FRs including melamine cyanurate and melamine polyphosphate.

Clariant Corp., Switzerland, according to its web-site, is a global leader in the field of fine and speciality chemicals (www.clariant.com). The Pigments and Additives Division manufactures, among other substances, flame retardants based on organic phosphinates, melamine polyphosphate and red phosphorous.

Nabaltec, Germany, is a medium-sized company that produces high-grade specialty products based on aluminium hydroxide and magnesium hydroxide (www.nabaltec.de).

Italmatch Chemicals S.p.A., Italy, is a relatively small company specialised in the production of phosphorous derivatives (<http://www.italmatch.it>). Italmatch manufactures red phosphorous, phosphorous melamine derivatives and a new product line based on a low oxidation state of phosphorous.

Martinswerk, Germany, according to its web-site, is the world's major supplier of specialty chemical products based on aluminium hydroxides and oxides (<http://www.martinswerk.de/eng/home.htm>). In addition to aluminium compounds, they manufacture magnesium hydroxide.

EFRA

The manufacturers of flame retardants have jointly formed the European Flame Retardants Association (EFRA). The association had, by 15 Feb 2006, 15 full members [146].

6.2 Manufacturers of plastic raw materials

Plastic resins are manufactured by relatively few large companies in Europe. The resins are mixed with additives (so-called "masterbatches") to form compounds, which are the raw materials for further processing. Compounding may take place by the resin manufacturer, by specialised compounders or by the company manufacturing the plastic parts.

At European level, manufacturers of resins and compounds are organised in PlasticsEurope, the Association of Plastics Manufacturers (<http://www.plasticseurope.org>).

Engineering thermoplastics

As regards the engineering thermoplastics market (PA, polyamide, PBT, PC

and acetal compounds), according to Applied Market Information Ltd., compounding is dominated by the large resin producers, notably Bayer, Dupont, BASF, GE Plastics and Ticona [147]. Only in the polyamide market have independent compounders taken control of a significant share of the supply, estimated at 40% of the tonnage by volume in 2002. For many polyamide compounders, a differentiated product and market positioning is evident, with several dedicated polyamide compounders strategically focusing on niche market sectors that may not be adequately served by the polyamide resin manufacturers. In the PBT and acetal markets, the independents have only a 7% and 5% share, respectively, in 2003.

Of the five main resin suppliers, Bayer[148], BASF [149], Ticona [150] and Dupont [151] have specifically stated that their products do not contain PBDEs. As stated by Bayer: "*In common with other well-known German plastics manufacturers, we have not used any polybrominated diphenyl ethers (PBDEs) or polybrominated biphenyls (PBBs) in the production of flame retardant plastics since 1989.*" [148]

Deca-BDE containing compounds are probably produced by some of the smaller independent EU compounders. Therefore, a ban on Deca-BDE may shift this market towards compounds from the major resin/compounds producers.

Polystyrene

The major General-Purpose Polystyrene (GPPS) and High-Impact Polystyrene (HIPS) producers of the world in 2004 were Dow Chemical (2.2 million t), BASF (1.6 million t), Total Petrochemicals (1.4 million t) and NOVA Chemicals (1.0 million t), followed by Chi Mei Corp., Chevron Phillips, Eni Chemical and Shinho Petrochemical (these production volumes exclude expanded polystyrene, EPS/XPS) [152].

HIPS supplied in Europe by the two largest European producers of polystyrene, BASF [149] and Total Petrochemicals [54], does not contain Deca-BDE. Deca-BDE containing compounds are probably provided by a number of small and medium-sized compounders. Therefore, a ban on Deca-BDE may shift this market towards compounds from the major resin/compounds producers.

6.3 Manufacturers of plastic parts

This category includes manufacturers of housings and larger structural parts of EEE, and manufacturers of small plastic parts for components.

Whereas the market for compounds is dominated by relatively few large actors, the market for plastic parts is characterized by many small and medium sized firms. The UK Risk Reduction Strategy and Analysis of Advantages and Drawbacks of Octa-BDE [38] provided details of plastics manufacturers in the UK according to a number of size categories (defined by number of employees), as well as the average turnover of the companies within those categories. Of the total 14,540 plastics manufacturers in the UK, 5,260 companies fell within the category of small companies (those with fewer than 50 employees), of which the majority (3,365) were micro-enterprises (0-9 employees). With regard to the situation for the EU as a whole, the study stated that there are 55,000 companies manufacturing rubber and plastics in the EU. Of these companies, the average enterprise size was given as 25 employees.

Figure 6.2
Number of companies and average turnover for manufacture of plastics in the UK [33]

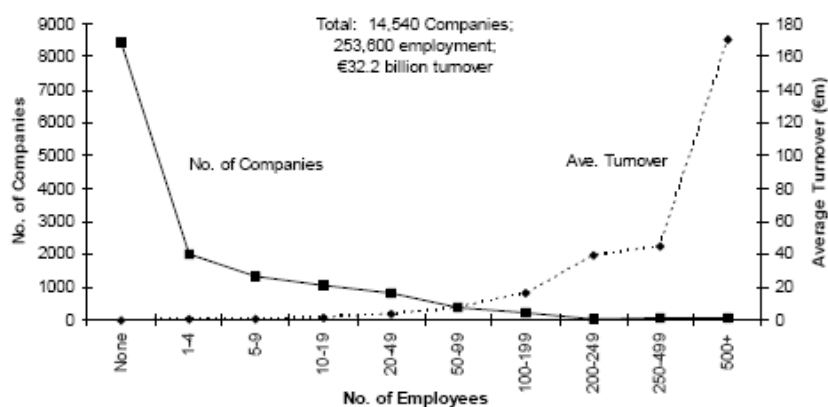


Figure 4.1: Number of Companies and Average Turnover for Manufacture of Plastics in the UK (DTI, 2001)

There are no data indicating how many manufacturers of plastic parts may be influenced by a ban on Deca-BDE in EEE. The total consumption of plastics for E&E in Europe in 2000 was 2.67 million tonnes, of which about 1.48 million tons in EEE is covered by the WEEE Directive [153]. If it is assumed that half of the consumption of 7,000 tonnes of Deca-BDE (in 2003) was used for this equipment, it can be roughly estimated that 30,000 tonnes of plastics with an average content of 12% Deca-BDE were used for EEE. Under these assumptions, Deca-BDE containing plastics consequently accounted for about 2% of the plastics used in manufacturing of EEE.

For plastic part manufacturers actually using Deca-BDE containing compounds, a Deca-BDE ban may result in research and development costs, as well as the purchase of new moulds and other tools. If Deca-BDE is replaced by other brominated flame retardants, the impact will be small and will mostly imply the use of more expensive compounds.

In particular for large parts like the housings of TV-sets, the original equipment manufacturer (OEM) may use the situation introduced by a ban as an excuse to make a full change to halogen-free housings, and in such a case may also change sub-contractor, selecting one with more experience in, e.g. co-polymer moulding.

6.4 Manufacturing of EE components

Connectors, switches, etc.

European manufacturers of connectors, switches, etc. are organised by the Electronic Packaging and Interconnection Association (EPIA), under the umbrella of the European Electronic Component Manufacturers Association (EECA) (<http://www.eeca.org/epia.htm> and <http://www.eeca.org/>). In 2004, EPIA covered the electro-mechanical components, which include bare PCB's (printed circuit boards), connectors, connector/cable assemblies, relays, switches, etc.

According to EPIA, *"This sector of the electronic components industry has a low barrier to entry; i.e. small scale companies are both possible and viable, entry costs*

are relatively low and technology is not overwhelmingly demanding. Therefore, this sector of the industry consists of many more companies than the other sectors within EECA. Typically, the companies are relatively small and many of the products are tailored to the needs of specific customers or even specific customer products. However, there are also many standard products produced by the sector with many end-uses and customers." [154]

The number of companies operating within the sector is not indicated.

Cables

National associations of cable manufacturers are collectively members of The European Confederation of National Associations of Manufacturers of Insulated Wire and Cable, known as Eurocable (<http://www.europacable.com>). Eurocable represents approximately 90% of the European industry and, through National Associations, more than 200 individual cable manufacturers. It is not indicated how many of these produce wires and cables for EEE, but "information cables" represented in 2004 a production turnover of € 2.3 billion, of a total of € 10.8 billion for the whole sector [155].

The manufacturers of electronic components and cables are obliged to respond to the requirements of the manufacturers of finished EE products. If Deca-BDE is banned, the market may shift to suppliers who have already replaced this compound. If Deca-BDE is replaced by other brominated flame retardants, however, the impact may be assumed to be small, and will mostly imply the use of more expensive compounds.

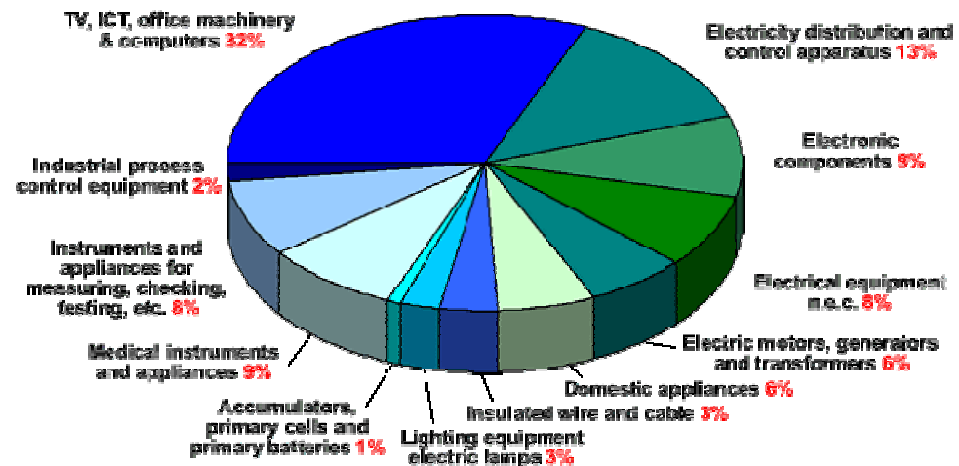
6.5 Original equipment manufacturers

At European level, manufacturers of electrical and electronic equipment are organised in the Liasion Group of the European Mechanical, Electrical, Electronic and Metalworking Industries, ORGALIME (<http://www.orgalime.org>).

The distribution of EEE production within the EU by the various EE sub-sectors is indicated in the figure below. The total value of the production in 2005 was 511.6 billion € [156].

Figure 6.3

ORGALIME Electrical and electronic industry production (Nace codes 29.7, 30 to 33) by sector - 23 member countries. Percentages of total turnover in euros [157]



According to a survey of the Association of Plastics Manufacturers in Europe (now PlasticsEurope) published in 2000 [153] about 12 percent of all plastics used in the EE sector contained flame retardants. The percentage of plastics treated with FRs ranged from 65% in IT & Telecommunication to 1% in large household appliances (see Table 6.1).

As estimated in section 6.3, Deca-BDE containing plastics probably accounted for about 2% of the plastics used in manufacturing of EEE in Europe, but it is based at the present information not possible to point out exactly which sectors would be most affected by a ban of Deca-BDE (e.g. contacts) as consumption figures by sector is not available, and components containing Deca-BDE in principle may be used in any electrical or electronic appliance.

Table 6.1
Percentage of plastics treated with flame retardants in EEE produced in Europe (about 2000) [153]

Equipment	Percentage of plastics treated with flame retardants	Weight of plastics treated with flame retardants (x 1000 tonnes)
IT and telecommunications: Data processing - PCs and monitors	65	110
IT and telecommunications: Office equipment - printers and copiers	20	18
Consumer equipment - TVs and very small amount of audio equipment	55	74
Small household appliances - inner parts	2	3
Large household appliances - inner parts	1	5
Total		210

As indicated by the fact that a number of major manufacturers of EEE, representing a wide range of EEE, do not use Deca-BDE, the availability of Deca-BDE free components seems not to be a barrier for the manufacturing of Deca-BDE free final equipment although the price of the components may be higher.

The most impacted of the original equipment manufacturers will be manufacturers of equipment in which Deca-BDE is present in casings and other structural part designed specifically for the equipment in question. In particularly manufacturers of equipment for the low price market segment, with a strong competition on the price, may be impacted by the higher price of plastic parts with Deca-BDE alternatives

7 Companies and organisations contacted

Organisations

Bromine Science and Environmental Forum (BSEF), Belgium
Danish Plastics Federation, Denmark
European Brominated Flame Retardant Industry Panel (EBFRIP), Belgium
European Flame Retardants Association (EFRA), Belgium
The European Chemical Industry Council (Cefic), Belgium
Umweltbundesamt, Germany
Verband der Automobilindustrie e.V. (VDI), Germany
Verband der Elektroindustrie (VDE), Germany
Verband der Kunststoffherstellenden Industrie e.V./Plastics Europe, Germany
Washington State Dept. of Ecology, Washington State, USA
Washington State Dept. of Health, Washington State, USA

Companies

Albemarle Corporation, USA
Albemarle Europe Sprl, Belgium
Amco Plastic Materials Inc., USA
Apple, USA
B&O, Denmark
BASF AG, Germany
Bayer AG, Germany
cfb Budenheim Ibérica, Spain
BSH Bosch und Siemens Hausgeräte GmbH, Germany
Chemtura/Great Lakes Sales (Europe) GmbH, Switzerland
Ciba Specialty Chemicals Inc., Switzerland
Clariant International Ltd., Germany
Clariant Masterbatches Deutschland GmbH, Germany
DaimlerChrysler AG, Germany
Dell, USA
DOW Europe SA, Germany
Eurobrom ICL-IP, Israel
General Electric/GE Advanced Materials, Germany
General Electric/GE Plastics - Customer Technical Field Support, Germany
Great Lakes Technology NV, Belgium
Grundfos, Denmark
Hewlett Packard, USA, Sweden
ICL-Industrial Products / Eurobrom, The Netherlands
Lanxess AG, Germany
Loewe Opta GmbH, Germany
Lowell Center for Sustainable Production, University of Massachusetts, USA
Metz-Werke GmbH & CO KG, Germany
Omya, UK
Panasonic Deutschland GmbH, Germany
Panasonic Europe Ltd., Germany
Panasonic Shikoku Electronics Corp. of America, USA
Paul Polymer Production, Sweden
Philips Consumer Electronics, Germany

PolyOne Th. Bergmann GmbH, Germany
Rego Polymer Systeme GmbH, Germany
Rhodia Polyamide Polska, Germany
Romira GmbH, Pinneberg, Germany
Siemens AG, Germany
Sony Deutschland GmbH, Germany
Sony, Japan
Thomson Consumer Electronics GmbH &CO OHG, Germany
Total Petrochemicals/PetroFina sa nv, Belgium
Volkswagen AG, Wolfsburg/Germany

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