Survey and technical assessment of alternatives to Decabromodiphenyl ether (decaBDE) in plastics

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Preface

Polybrominated diphenylethers (PBDEs), among some other hazardous substances, are not allowed for use in electrical and electronic equipment put on the market from 1 July 2006, according to Directive 2002/95/EC on the restrictions of the use of certain hazardous substances in electrical and electronic equipment. PDBEs have a flame retardant function and they are added to plastics in many different kinds of products. The commercially used PBDEs are penta-, octa- and decaBDE. Penta- and octaBDE are already banned in EU in all uses, whilst decaBDE has not been restricted in EU for other uses than in electrical and electronic equipment.

Many companies have already phased out the use of decaBDE in their products and other have an ongoing work to change over to alternatives. There are at present discussions whether or not it is possible to use alternatives to decaBDE in different applications. To clarify the issue IFP Research AB was commissioned to carry out this survey on alternatives to decaBDE in different kind of plastics in different applications in electrical and electronic equipment.
Sammanfattning

Denna rapport är en teknisk översikt inom ett forsknings och industrimässigt område med en historia på över 40 år tillbaka i tiden, om man betraktar den moderna flamskyddskemin. Miljö och hälsorelaterade frågor kring flamskyddsmedel kommer inte att behandlas, då det pågår en riskbedömning av dekaBDE (dekabromdifenyletter) inom ramen för EU:s förrådning 793/93/EEC för existerande ämnen.

På uppdrag av Kemikalieinspektionen har IFP Research genomfört en studie av dekaBDE och en rad, till dekaBDE alternativa flamskyddsmedel, som finns tillgängliga idag för plaster som används i elektriska och elektroniska produkter och är nämda i RoHS –direktivet (2002/95/EG).

Uppdraget innefattar

- Översikt av alternativ för flamskydd av plaster
- Beskrivning av applikationer där dessa alternativa flamskyddande system kan användas.
- Beskrivning av vilka funktionskrav som skall uppfyllas i olika applikationer.
- Beskrivning av tekniska bedömningar som tillämpas, för att avgöra om alternativen uppfyller de brandkrav som ställs i de applikationer i vilka de förekommer.


Det ideala flamskyddsmedlet ska vara kompatibelt dvs inte förändra det aktuella materialets mekaniska egenskaper, ej ge färg, ha god ljusstabilitet, vara stabilt mot åldring och hydrolys, ge det behandlade materialet termisk stabilitet, ej orsaka korrosion, inte orsaka fysiologisk skada, inte emittera eller åtminstone emittera låga halter av toxiska gaser samt vara billig. Tesen att flamskyddande system ska vara så billiga som möjligt på marknaden är inte alltid sann. Tekniska polymerer är exempel på material där priset har mindre betydelse än deras funktion och prestanda. Detta innebär att de relativt billiga och etablerade flamskyddsmedlen, inklusive dekaBDE, kan bromsa eller rent av förhindra utvecklingen av alternativ som skulle kunna utvecklas för att komma så nära det ideala flamskyddsmedlets egenskaper som möjligt.


Slutsatsen av studien är att det finns en rad tillgängliga alternativa flamskyddande system till dekaBDE för många, om inte alla, polymera applikationer i elektronisk och elektrisk utrustning som innefattas av RoHS-direktivet.
Summary

This report is a technical review in a research and industrial area, which has its roots over 40 years back in time, if we consider modern flame retardant chemistry. Health- and environmental aspects of flame-retardants will not be discussed since it was not within the scope of the assignment and there is an ongoing risk assessment on DecaBDE in the Existing Substances Regulation within EU.

On behalf of the Swedish National Chemicals Inspectorate, IFP Research has surveyed and carried out a technical assessment of flame retardant alternatives to decabromodiphenyl ether (decaBDE) currently available for plastics in electrical and electronic products that are included in the RoHS directive (2002/95/EEG)

The assignment comprises

• A review of the alternative techniques available at present for fire retardation of plastics.
• A description of applications in which the alternatives may be used
• A description of what functional requirements have to be met in different applications
• A technical assessment of whether the alternatives fulfil the requirements set for flame retardant properties in the applications in which they could be used

Plastics have to fulfil flame retardancy regulatory requirements as mandatory specifications. Compliance with the flame retardancy requirements for plastics is controlled with well-defined flammability tests such as the International Electro technical Commission (IEC), or in the regulations and approval procedures of the Underwriters’ Laboratories Inc. (UL), the latter mainly operating on the US market. These fire regulations are mandatory for the market, and it is important to mark that there are no fire regulations that require the use of certain flame-retardants in order to manage these regulations or standards. It is up to the manufacturer to decide which flame-retardants to use, of the wide range of the 70 different commercial available flame-retardants.

The ideal flame retardant should be compatible i.e. not alter the mechanical properties of the plastic, not change colour, have good light stability, resistant towards ageing and hydrolysis, match and begin its thermal behaviour before the thermal decomposition of plastics, not cause corrosion, not have harmful physiological effects, not emit or at least emit low levels of toxic gases and be as cheap as possible. It is not always the ultimate truth that the flame retarding system needs to be as cheap as possible. Since we talk about engineering polymers, function is more important than price. This means that certain “popular”, relatively cheap and established flame-retardants, such as decaBDE, may inhibit the development and use of alternatives to come closer to the theoretical properties of the ideal flame-retardant.

A survey was carried out among some of the largest manufacturers of electronic devices in the world. A questionnaire with six questions was sent out. The purpose with these questions was to get a better understanding of their use of commercial common flame-retardants in the context of required customer governed fire protection. The companies involved in the survey were Ericsson Network Technologies, Electrolux, Sony Ericsson, Atlas Copco, Hewlett Packard and The Swedish Association of IT and Telecom. The answers from the survey show that these companies already have phased out, or have an ongoing process to phase out PBDEs in their products. The phase out is parallel with product development for the use of alternative flame-retardants, based on TBBPA, organic phosphate esters or inorganic salts, depending on the electronic application involved.

The conclusion that can be made from the technical assessment and the survey is that there seems to be alternatives available for fire protection of many, if not all, polymeric applications in electric and electronic equipment covered by the RoHS-directive.
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Appendix 1: Statement concerning flame retardants from the Nordic IT companies associations:
“Flame retardants in Information Technology (IT) Products”

Appendix 2: A selection of common international standards and regulations for electric and electronic devices
Foreword
The Research and Technology Organisation, IFP Research AB (www.ifp.se), an independent national research institute that serves the international industry, is an active partner in several international projects, financed by the European commission, and engaged in research projects on a national and Nordic basis in the areas of fibrous and polymer materials. IFP Research has essentially two owners namely its industrial member association with 85 members, mainly large industrial and trading companies, and Swerea, the parent company owned by the Swedish government.

IFP Research has comprehensive processing equipment and well-equipped laboratories for chemical analyses and testing of materials. The staff, from associate professors to engineers, study and investigate aspects of materials characteristics, design, processing and recycling in close collaboration with industry and universities. The institute is also actively engaged in knowledge transfer regarding new technologies relevant to polymer and fibrous materials.

Stefan Posner graduated 1983 with a Masters degree in cellulose and polymer chemistry from Chalmers Technical University in Gothenburg. He has been and is project leader for national and international projects for a number of years at IFP Research, where he has been employed since 1984. He has since then been involved in research and industrial projects concerning polymer, textile and cellulose chemistry and related environmental issues.

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On behalf of the Swedish Chemicals Inspectorate, IFP Research has surveyed and carried out a technical assessment of flame retardant alternatives to decabromodiphenyl ether (decaBDE) currently available for use in plastics in electric and electronic products that are included in the RoHS directive (2002/95/EEG)

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The authors thank all colleagues from Ericsson Network Technologies, Electrolux, Sony Ericsson, Atlas Copco, Hewlett Packard and The Swedish Association of IT and Telecom for their valuable assistance with answers to all questions in the users survey carried out in this report.
**Introduction**

This report is a technical review in a research and industrial area, which has its roots over 40 years back in time if we consider modern flame retardant chemistry. The review gives a detailed overview of a large number of commercial additive and reactive flame-retardants used today. Any detailed description of certain polymer applications in the context of certain systems of these flame-retardants is beyond the scope of this review. Furthermore, a users survey, including five large international producers of electronic equipment, was carried out. The result and conclusions from this survey are presented in this review together with a fresh eco-policy from the Nordic IT companies associations (appendix 1) concerning the use of flame retardant in electronic devices. This review will not discuss any physiological aspects of flame-retardants, especially not regarding decaBDE, for which there is an ongoing risk assessment programme within EU. [11].

Fires are among the most common causes of harm to property and people around the world. A number of risk-benefit analyses based on actual fires has been performed in the last decades. Statistics from these risk-benefit analyses indicate a clear reduction in the number of deaths and severe injuries due to improved fire safety, where one factor is increased and improved applications of various forms of fireproof materials. These forces have driven development ahead towards functionally better and more effective systems for fire protection among other flame-retardants, and legislation has been tightened up at the same time.

**Plastics are polymers**

Many common classes of polymers are composed of hydrocarbons and are combustible. These polymers are made of small units, monomers, bonded into long chains. Carbon makes up the backbone of the molecule and hydrogen atoms are bonded along the backbone. There are polymers that contain only carbon and hydrogen. Such polymers are polyethylene, polypropylene, polybutylene and polystyrene. Even though the basic makeup of many polymers is carbon and hydrogen, other elements can also be involved. Oxygen, chlorine, fluorine, nitrogen, silicon, phosphorus and sulphur are other elements that are found in the molecular makeup of polymers. Polyvinyl chloride (PVC) contains chlorine. Polyamide (nylon) contains nitrogen. Teflon contains fluorine. Polyester and polycarbonate contain oxygen.

For various electrical applications, transportation and other industries such as building and textile industry, plastics have to fulfil flame retardancy regulatory requirements as mandatory specifications. Compliance with the flame retardancy requirements for plastics is controlled with well-defined flammability tests, which are described in more detail later in this review. A large number of flame-retardants have been developed due to the flammability requirements and plastics have to meet all these flammability requirements. However, it is important to mark that there are no flammability standards that stipulate the use of certain flame-retardants to fulfil these specific demands.

**Flame retardant mechanisms**

The term flame protection does not mean that the material is unable to burn but that there is a delay before the material in question catches fire or is in some other way affected by the heat generated in a fire. It is essential to differentiate between materials that delay fire, known as flame retardant materials, and materials that resist fire, known as flame resistant materials.

In order to understand the benefits and applications of different flame-retardants, meaning all kinds of design, materials and chemicals that prevent fire, it is essential to understand the process
of fire in polymer materials. The process, known as *pyrolysis*, can be briefly described as thermal decomposition of the material and it is schematically illustrated in Figure 1 below.

![Figure 1: Process of combustion for polymer material](image)

Combustion is a combination of chemical and physical processes that generate combustible and toxic gases that mix with the oxygen in the air and these in turn are combusted with increased heat generation. This means that the process maintains itself until all the material, which acts as a kind of fuel, is consumed. The role of the flame retardant is to interrupt this combustion process in various ways.

The traditional classification of flame-retardants is often based on the predominant mechanism of the flame retardant performance in connection with the process of combustion. Flame-retardants can act primarily

- In the gaseous phase, such as *halogenated flame-retardants* in combination with *antimony trioxide* (synergene).
- In the condensed phase, also known as the liquid phase, such as *metal salts* and *phosphorous compounds*.
- By physical action, mainly through *inorganic salts*.

Flame-retardants intended to act in the *gaseous phase* interact with the volatile substances formed when combustion takes place. A condition, which has to be met for the flame retardants to be able to do this, is that they form volatile substances that can react with the volatile substances in the combustion process in such a way that the new volatile substances formed are not
combustible. Flame-retardants that act in the condensed phase interfere with the process of pyrolysis so that they reduce the formation of combustible gases and change their properties so that the combustibility of the gases is reduced. Flame retardants based on physical action in the combustion process act in both the gaseous phase and the condensed phase. Many of these flame-retardants that react through a physical process are inorganic. If they are to have the desired effect on the fire process, they need to be applied in large quantities at up to 60% by weight in the polymer material. The primary physical effect can be

- To reduce heat generation, such as alumina trihydrate
- To form a protective non-combustible layer, such as phosphorous compounds
- “Dilution” of the organic combustible material, such as alumina trihydrate

Almost all commercial flame-retardants in use today are active in both the condensed phase and the gaseous phase. Phosphorus-based systems are primarily active in the condensed phase, while halogen-based flame-retardants primarily react in the gaseous phase, where they disrupt and finally stop the chemical reactions that occur there. The primary task of metal hydroxides is to absorb heat and thereby lower the temperature in the combustion process. In conjunction with this thermal process, the metal hydroxide generates inert gases such as water vapour that “dilute” the gaseous phase and by doing so prevent continued progression of the fire.

The term synergistic effects is used in connection with the development of flame-retardants. This term means that the desired effect of two or more components working together is greater than the effect of each of the components separately. Perhaps one of the most important synergistic effects historically in flame retardant chemistry is the one between halogen and antimony, where antimony reacts in the form of antimony trioxide with the formation of radicals, finally forming antimony tribromide and antimony oxybromide or their chlorinated equivalents. These flame-retardants react in the gaseous phase and usually contain halogens of the chlorine or bromine type. The other halogens, iodine and fluorine, do not function at all as flame-retardants. Organic iodine compounds are too unstable, while organofluorine compounds are too stable for the reactions that take place in the gaseous phase in combustion.

Flame-retardants may be either reactive or additive. Reactive flame-retardants are added during the polymerisation process and become an integral part of the polymer. The result is a modified polymer with flame protective properties but different in its molecule structure compared to the original polymer molecule. Since the reacted monomers of the flame retardant is a part of the modified polymer, this prevents them from leaving the polymer and keep the flame retardance properties intact over time with no emission to environment.

*Typical reactive flame-retardants for polymers are*

- Bis (2-hydroxyethylamino)octachlorbiphenyl
- Diethyl N, N-bis (2-hydroxyethyl) aminoethylphosphonate
- Chlorendic anhydride
- Tetrabromophtalic anhydride
- Tetrachlorophtalic anhydride

Additive flame-retardants are incorporated into the plastic either prior to, during, or more frequently following polymerisation. They are used especially in thermoplastics. If they are compatible with the plastic they act as plasticizers, otherwise they are considered as fillers. Additive flame-retardants are only physical bonded to the polymer as monomer molecules, and if
they are exposed to environment there will be a possible impact depending on the original characteristics of this particular molecule.

Combinations of reactive and additive flame-retardants with other additive flame-retardants may cause either additive, synergetic or antagonistic effects. While the additive effect is a sum of all individual effects, the synergetic or antagonistic effect may be higher or lower than the individual effects. Synergetic effects have already been mentioned in this review and their practical importance is of great value.

Typical additive flame-retardants in polymers are
Ammonium phosphate
Alumina trihydrate
Brominated paraffins
Chlorinated paraffins
Decabromodiphenylether (decaDBE)
Octabromodiphenylether (octaBDE)
Tricresyl phosphate
Triocyl phosphate
Triphenyl phosphate
Tris (2,3-di bromopropyl)phosphate
Tris (trichloropropyl)phosphate

Common polymeric additive flame retardants
Brominated polycarbonate
Brominated polystyrene
Chlorinated polyethylene
Polyvinyl chloride (PVC)

In contrast to most additives, flame-retardants can appreciably impair to properties of plastics. The basic problem is the compromise between the decrease of performance of the plastic caused by the flame retardant and the flame requirements. An ideal flame-retardant shall, beside to fulfilment of the appropriate mandatory fire requirements and rules
  * Be easy to incorporate in the plastic involved
  * Be compatible with the plastic involved
  * Not alter the mechanical properties of the plastic
  * Be colourless
  * Have good light stability
  * Be resistant towards ageing and hydrolysis
  * Match and begin its thermal behaviour before the thermal decomposition of plastics
  * Not cause corrosion
  * Not have harmful physiological effects
  * Not emit or at least emit low levels of toxic gases
  * Be as cheap as possible

These qualities are of course impossible to reach for any single application. However, many formulations have been and have to be developed for each plastic in order to give as good properties as possible. Since fire regulations and international standards rule the use of flame retardants, it is essential for the key actor in this process, namely the polymer producer, to optimise as many of the ideal properties as possible in the future electronic application with high
standards of fire security in mind. It is not always the ultimate truth that the flame protective system needs to be as cheap as possible. This is truly an industrial aspect but has less importance when it comes to fire security and quality aspects on the final product, especially when we talk about engineering polymers where function is more important than price. The fact that a flame retardant shall be as cheap as possible, the low cost of certain “popular” and established flame-retardants, such as decaBDE, may inhibit the development and use of alternatives with a number of good properties close to the ideal flame-retardant.

**Flame-retardants in plastics**

**Introduction**

There are around 370 different chemical flame retardants described in literature, among them around 70 are commercially available, where 15 of these components represent more than 70% of the amounts used in electronic products and textiles [9].

**Characteristics of decaBDE**

The aromatic polybrominated flame-retardants (PBDE) enter into compounds with five, eight or ten bromine atoms in the structure. Decabromodiphenylether, or shortened decaBDE, consists of ten bromine atoms.

![Figure 2: Structural formula of decabromodiphenyl ether, also called decabromobiphenyl oxide [9]](image)

DecaBDE is the additive flame retardant produced in the greatest quantity around the world in terms of tonnes per year among the organic aromatic bromine compounds. [12] Around 90% of world production ends up in electronics and plastics, while the other approximately 10% ends up in coated textiles, upholstered furniture and bedding products. Of all polybrominated diphenylethers (PBDE), decaBDE stands for approximately 80% of the world market today [11].

Since decaBDE is an additive flame retardant it may be exposed to environment and influence the surrounding depending on its specific physiological, chemical and physical characteristics, which is described and investigated in an ongoing risk assessment programme within EU [11].
**Halogen containing flame retardants other than decaBDE**

Especially two halogenated flame-retardants are common beside decaBDE in electronic devices. These are tetrabromobisphenol A, shortened TBBPA, and hexabromocyclododecane (HBCD),

![TBBPA](image)

*Figure 3: TBBPA*

![HBCD](image)

*Figure 4: 1,2,5,6,9,10 HBCD*

**Phosphorous containing flame retardants**

Phosphorus containing flame-retardants mainly influence the reactions during fire that take place in the condensed phase. They are particularly effective in materials with high oxygen content, such as oxygen containing plastics as well as cellulose and its derivates. The range of phosphorous containing flame-retardants is extraordinary versatile since, in contrast to halogen compounds, it extends over several oxidation states. Thus phosphines, phosphine oxides, phosphonium compounds, elemental red phosphorous and phosphates are all used as flame-retardants. In some cases phosphorous/halogen compounds are used to increase the effectiveness of the flame retardant. Many of the phosphorous flame-retardants are liquid and have plasticizer properties.

Commercial phosphoric acid esters, such as aryl phosphates and their alkyl-substituted derivates are mainly used as additives with plasticizing properties in PVC, polyamides and polyethylene ether (PPE). Phosphorinanes are used for transparent formulations, for example in polymethylmetacrylate (PMMA).

**Inorganic non-phosphorous flame-retardants**

Inorganic flame-retardants are suitable for use in plastics since these compounds are too inert to be effective in the decomposition of plastics in the temperature region of 150°C to 400°C, where most plastic materials decompose. Apart from antimony trioxide, which is a synergene to halogen flame-retardants, the most widely used inorganic flame-retardants are aluminium hydroxide and boron containing compounds that affect the combustion process of plastics by physical means. Unlike organic flame retardants, inorganic flame retardants do not evaporate under the influence of heat, but they emit non-flammable gases such as water or carbon dioxide, which dilute the mixture of flammable pyrolysis gases and forms a protective layer on the surface against further oxygen attack and against further propagation of the fire.
Smoke suppressants
Fires cause the release of toxic gases and smoke. The level of smoke development depends on numerous factors such as the
- Source of ignition
- Oxygen availability
- Constitution of the combustible material

The smoke development is hard to describe since it depends on a large number of factors. The scale of smoke production from plastics and the decrease of smoke with smoke suppressants can vary considerably depending whether it has its origin in the pyrolysis or flames and the condition involved.

As flame-retardants, smoke suppressants probably act physically or chemically in the condensed phase. Physical action means the formation of glassy coatings or intumescent foams or dilution of the combustible material, which prevents further formation of pyrolysis products and hence smokes.

Smoke emission may be limited by chemical means mainly by oxidation of aromatic soot precursors or by the soot itself. As an example, certain compounds such as ferrocene cause condensed phase oxidation reactions, which are visible as a glow. Much work has been carried out to clarify how smoke suppressants may be used to prevent certain plastics such as PVC, polystyrene, polyurethane and some unsaturated polyesters to generate smoke. PVC has been most in focus to generate effective smoke suppressants of common plastics used.

Applications of smoke suppressants can be found in building materials, which are not relevant in this review, but also in transportation which are of relevance in this review. Fillers are often used since they are cheap additives and can obtain adequate limitation of smoke development. Common additives are aluminium hydroxide, magnesium hydroxide and calcium carbonate. Ferrocene and its derivates and molybdenum trioxide are rarely used since they are relatively expensive.

To comply with fire regulations for reducing smoke release, other systems have been developed without smoke suppressants additives. These alternatives are thermo sets, for example phenolics, which practically do not release any smoke at all.

General overview of flame-retardants in plastics
Like any other additive, a flame retardant will be selected for the particular properties it imparts to make it fulfil the specifications for the final product, established by the customer. Products are constantly being changed and new products are introduced to the market, meaning that polymers used today might not be used tomorrow. A more detailed list of polymers, their common use in electrical and electronic products, and the flame retardants used for each certain polymer is described later in this chapter.

AcrylonitrileButadiene-Styrene (ABS)
ABS is a strong and high impact polymer used for instance for housings in electronic devices. Among the most common flame retardants for ABS are tris (tribromophenoxy)ethane, octaBDE and TBBPA. Small amounts of antimony oxide may be used as synergene, and PVC is often used as a flame retardant added to ABS to form as ABS/PVC alloy.
Epoxies
Epoxies are mainly used as encapsulation material of electric components. It may be flame retarded by the introduction of certain halogenated compounds into part of the system. Those flame-retarded materials contain TBBPA or TCBPA. Epoxies may also be filled with inorganic fillers for flame protection.

Polyamide
Polyamide (PA) could be flame retarded with several different chemicals, including alicyclic chlorine compounds together with antimony oxide or ferric oxide as a synergist. Brominated epoxy, brominated polystyrene, poly(dibromophenylene)oxide, magnesium hydroxide, red phosphorous, melamine cyanurate, melamine polyphosphate and a new family of metal phosphinates could also be used as flame-retardants. Some are recommended for PA 6\(^1\) and some for PA 6,6\(^2\) [13], depending on the specifications of certain applications.

Polyesters
Polyesters are used for electric fittings and insulations. Polyester, particularly unsaturated polyesters, burns readily and therefore it is very important to protect these of polymers with flame-retardants. There is a wide range of flame-retardants used, based on halogenated paraffins and phosphate and inorganic fillers. Also reactive organic flame-retardants, such as chlorendic anhydride, tetrabromophthalic anhydride tetrachlorophthalic anhydride may be used.

Polyolefines
Polyolefines, namely polyethylene and polypropylene, are used in electrical wires and cable insulations. They burn readily and need therefore to be flame retarded. Among the most common flame retardants used in polyolefines are chlorinated cyclic compounds, which are chlorinated paraffins with antimony oxide as synergist. There are also aromatic bromine compounds, dithiopyrophosphate and magnesium hydroxide. Depending on the properties of the polyolefine polymer there are different amounts of flame-retardants and synergens added to the polymer concerned.

Polystyrene
These polymers are used for computers, cabinets for display units and equipments for refrigerators. Among the most common flame-retardants used in extruded foam or expandable polystyrene (EPS) bead board are dibromoethyl dibromocyclohexane, pentabromochlorocyclohexane and hexabromocyclododecane (HBCD). The use of antimony oxide is not very common in these materials. However, antimony oxide is more used in impact grade polystyrene compounds, which are used for TV-cabinets and other domestic housing equipment and these are more difficult to flame retard than general-purpose polystyrene. In this case a most common used flame retardant system is decaBDE together with antimony oxide.

Polyurethane
Polyurethanes are among the most widely used polymers used in a wide range of applications, among them refrigerators. Compact foams are, in contrast to flexible foams, often not prepared with flame retardants, since their oxygen content is low compared to flexible foams.
A big amount of flame retardants and synergists are used in polyurethanes, including antimony oxide, namely chlorinated paraffins, PVC, hexachloroendoethylentrahydrophthalic acid, (HET

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1 Polyamide from epsilon-caprolactam
2 Polyamide that is a polycondensate from hexamethylenediamine and adipic acid
acid), dibromoethyl dibromocyclohexane, dibromoneopentyl glycol, red elementary encapsulated phosphorous and aluminium hydroxide.

**Styrene-acrylonitrile (SAN)**
SAN copolymer resins are used in reflectors, refrigerator doors and battery cases. They behave like polystyrene during burning. Common used flame-retardants are alicyclic bromine compounds.

**PVC**
This polymer in itself inherently flame-retardant contains 57% chlorine, and it is mainly used in isolation materials, pipes and for electrics devices. Many flame retardant chemicals, such as alumina trihydrate, antimony oxide, barium borate, chlorinated paraffins, phosphate esters and zinc borate, are added to PVC when needed. To rigid PVC, tricresyl phosphate is sometimes added as a flame retardant plastizer.

**Thermosetting plastics**
Some thermosetting plastics do not require the addition of flame-retardants simply because their combustion characteristics are good enough to meet many specifications. Some of these plastics, such as melamines, are sometimes also used as flame-retardants. Thermo set polyesters and epoxies do need flame retardants to meet fire specifications. In these cases HET acid and its anhydride and bromoneopentyl glycol are used as flame-retardants. When phenolics are flame treated often TBBPA and p-bromobenraldehyde are added in addition to phosphorous oxychloride and boric acid. Sometimes chlorinated paraffins and some bromine compounds are used, usually with antimony oxide as a synergist.

There are around 370 different chemical flame retardants described in the literature, of which around 70 are commercially available and only 15 flame retardant chemicals represent more than 70% of the amount used in electronic products and textiles. Many of these chemicals have vague or in some cases unknown environmental and health characteristics, beside their flame protective properties. In table 5 below, a large but not complete number of these commercial flame-retardants are listed in the context of their use in corresponding polymers. However, many formulations have been or have to be developed for each plastic application in order to give as good properties as possible. Since fire regulations and international standards rule the use of fire protective systems, among them flame retardants, it is essential for the key actor in this process, namely the polymer producer, to optimise as many of the ideal properties as possible in the future electronic application with high standards of fire security in mind.
Table 5: Plastics and other polymers applied in products included in the RoHS-directive with their corresponding flame-retardants used [4,5,6,7].

<table>
<thead>
<tr>
<th>Plastics</th>
<th>Examples of common electric and electronic applications</th>
<th>Possible presence of decaBDE</th>
<th>Used halogenated flame retardants, other than decaBDE</th>
<th>Used non halogen flame retardants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefin’s (for instance polyethylene and polypropylene)</td>
<td>Toys, isolation of cables, pipes for electrics, phones, switch panels, cabinet to kitchen machines</td>
<td>Yes</td>
<td>Brominated paraffin’s, Brominated polystyrene, Chlorinated paraffin’s, Hexabromocyclododecane, Octabromo diphenyloxide, Pentabromodiphenyloxide</td>
<td>Alumina trihydrate, Ammonium polyphosphate, Barium metaborate, Dithiopyrophosphate, Magnesium hydroxide, Neoalkoxy tri (dioctyl phosphate) titanate, Red phosphorous (encapsulated) Sodium antimonite, Zinc borate.</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Computers, cabinets for display units, equipments for refrigerator</td>
<td>Yes</td>
<td>Brominated polystyrene, Chlorinated paraffins, Chlorinated polystyrene, Dibromoethyl dibromocyclohexane, Hexabromomicyclodecan, Octabromodiphenyloxide, Pentabromochlorocyclohexane, Pentabromodiphenyloxide, Pentabromomethylbenzene, Penta bromophenyl benzate, Trichloromethyltetramobenzene, Tris (betachloropropyl) phosphate, Tris (dichloropropyl) phosphate</td>
<td>Alumina trihydrate, Ammonium polyphosphate, Barium metaborate, Cresyl biphenyl phosphate, Magnesium hydroxide, Neoalkoxy tri (dioctyl phosphate) titanate, Octyl diphenyl phosphate, Red phosphorous (encapsulated) Sodium antimonite, Tributoxy ethyl phosphate, Tributyl phosphate, Tricresyl phosphate, Triisopropylphenyl phosphate, Trixylenyl phosphate, Zinc borate.</td>
</tr>
<tr>
<td>Material Type</td>
<td>Uses</td>
<td>Flame Retardants</td>
<td>Fire Retardants</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>-----------------------------------------------------</td>
<td>------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>ABS (acrylonitrile-butadiene-styrene terpolymer)</td>
<td>Housings for business machines, dashboards, toys, equipments for refrigerator, telephones, and other consumer electronics</td>
<td>Yes</td>
<td>Brominated polystyrene Chlorinated paraffins Halogenated hydrocarbons Octabromodiphenyloxide Pentabromomethylbenzene Penta bromophenyl benzoate Polyvinyl chloride Tetrabromobisphenol A Trichloromethyltetramobromobenzene Tris (tribromophenoxy)ethane</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Alumina hydrate Ammonium polyphosphate Barium metaborate Magnesium hydroxide Octyl diphenyl phosphate Red phosphorous (encapsulated) Sodium antimonite Triphenyl phosphate Zinc borate</td>
<td></td>
</tr>
<tr>
<td>Polyamide (Nylon)</td>
<td>Handles, wheels, carpet</td>
<td>No</td>
<td>Brominated epoxy Brominated polystyrene Hexabromobenzene Octabromodiphenyloxide Poly (dibromophenylene) oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ferric oxide Red phosphorous (encapsulated)</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>Safety glazing, light covers, housings for electrical applications</td>
<td>No</td>
<td>Tetrabromobisphenol A Tetrachlorobisphenol A Tris (betalchloroethyl) phosphate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Alumina trihydrate Ammonium polyphosphate Barium metaborate Bisphenol A Calcium sulphate Magnesium hydroxide Red phosphorous (encapsulated) Sodium antimonite Zinc borate</td>
<td></td>
</tr>
<tr>
<td>PMMA (methyl meta acrylate)</td>
<td>Ceiling light cope</td>
<td>N/A</td>
<td>N/A</td>
<td>Phosphorinanes</td>
</tr>
<tr>
<td>SAN (Styrene acrylonitrile)</td>
<td>Reflectors, refrigerator doors, battery cases</td>
<td>Yes</td>
<td>No</td>
<td>Red phosphorous (encapsulated)</td>
</tr>
<tr>
<td>PPO (Polyphenylene oxide)</td>
<td>Telecommunications equipment, microwaveable packaging</td>
<td>Yes</td>
<td>Many kinds of brominated flame-retardants are used.</td>
<td>Tripropylphenyl biphenyl phosphate Tricresyl phosphate Triphenyl phosphate</td>
</tr>
<tr>
<td>Unsaturated polyesters</td>
<td>Electric fittings, electric insulation</td>
<td>Yes</td>
<td>Chlorinated paraffins Chloroendic anhydride Dibromoneophenyl glycol Hexabromocyclododecane (Pentabromobenzy)acylate Pentabromodiphenyloxide</td>
<td>Alumina trihydrate Ammonium polyphosphate Barium metaborate Calcium sulphate Di-(polyoxoethylene) hydromethyl monophonate Magnesium carbonate Magnesium hydroxide Molybdic oxide Neoalkoxy tri(diocetyl phosphate) titanate Red phosphorous (encapsulated) Sodium antimonate</td>
</tr>
<tr>
<td>Epoxy resins</td>
<td>Encapsulation of electric components</td>
<td>Yes</td>
<td>Brominated polystyrene Chlorinated paraffins Chloroendic anhydride Dibromopentyl glycol Pentabromophenol Pentabromo diphenyl oxide Tetrabromobisphenol A Tetrachlorobisphenol A</td>
<td>Alumina trihydrate Ammonium phosphate Barium metaborate T-butyl phenyl diphenyl phosphate Cresyl phenyl phosphate Neoalkoxy tri (dioctyl phosphate) titanate</td>
</tr>
<tr>
<td>Flame Retardants</td>
<td>Sealing, damper, covers, electric insulation</td>
<td>Yes</td>
<td>Polyurethanes</td>
<td>Sealing, damper, covers, electric insulation</td>
</tr>
<tr>
<td>-------------------------------------------------------</td>
<td>---------------------------------------------</td>
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<td>---------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Tetrachlorophtalic anhydride</td>
<td>Tetrachlorophtalic anhydride</td>
<td></td>
<td></td>
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<tr>
<td>Tribromophenol</td>
<td>Tribromophenol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (betachloroethyl) phosphate</td>
<td>Octyl diphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (dichloropropyl) phosphate</td>
<td>Red phosphorous (encapsulated)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (betachloroethyl) phosphate</td>
<td>Sodium antimonite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (dichloropropyl) phosphate</td>
<td>Tributoxyethyl phosphate</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Tricresyl phosphate</td>
<td>Tricresyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripropylphenyl phosphate</td>
<td>Tripropylphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Triphenyl phosphate</td>
<td>Triphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc borate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brominated paraffins</td>
<td>Alumina trihydrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorenedic anhydride</td>
<td>Aluminium hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorinated paraffins</td>
<td>Ammonium polyphosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibromoethyldibromocyclohexane</td>
<td>Ammonium bromide</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Dibromoneopentyl glycol</td>
<td>Barium metaborate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexabromocyclodecane</td>
<td>T-butyl phenyl diphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachloroendomethylenetetrahydrophthalic acid (HET acid)</td>
<td>Cresyl diphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentabromodiphenyl oxide</td>
<td>O, O-diethyl-1-N-N bis (2-hydroxyethyl) aminomethyl phosphonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentabromo phenol</td>
<td>Di- (polyoxyethylene)hydroxymethyl phosphonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrabromophthalic anhydride</td>
<td>Magnesium hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachlorophthalic anhydride</td>
<td>Molybdcic oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrabromoneopentyl alcohol</td>
<td>Neoalkoxy tri (dioctyl phosphate) titanate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (betachloroethyl) phosphate</td>
<td>Octyl diphenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (dichloropropyl) phosphate</td>
<td>Red phosphorous (encapsulated)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tris (chloropropyl) phosphate</td>
<td>Sodium antimonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triphenyl phosphate</td>
<td>Triscreyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triphenyl phosphate</td>
<td>Triethyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triisopropyl phenyl phosphate</td>
<td>Triisopropyl phenyl phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc borate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Users review – results from questionnaire among multinational users.**

A users survey, as a questionnaire, of five large international producers of electronic equipment namely Ericsson Network Technologies, Electrolux, Sony Ericsson, IBM, Atlas Copco, Hewlett Packard and The Swedish Association of IT and Telecom, was used. The questions asked and answers given are shown in table 6. In addition to the review these companies were asked about their policy concerning the use of flame-retardants in their products. Almost every one of the companies in the survey stated that they at the moment on a voluntary basis are phasing out PBDE including decaBDE from products ending up on the European market.

*Hewlett Packard* declared that they already had phased out PBBs and PBDEs, including decaBDE, in 1994, in all their products.

*Atlas Copco* stated that they have a strict policy towards their suppliers not to use flame retardants restricted in the RoHS –directive.
*Ericsson Network Technologies* declared that they only use halogen free flame protected materials in their products beside PVC and fluoropolymers.

*Electrolux* declared that they have an ongoing process to phase out PBB and PBDEs, including decaBDE, from products ending up on the European market. If possible, all bromorganic flame-retardants in general will be avoided.

*Sony Ericsson* declared that they phased out the use of halogenated flame-retardants in 2003 in printed circuit boards and charger enclosures. The aim is to phase out all halogenated flame-retardants by the end of 2005. Sony Ericsson has never used any PBBs or PBDEs, including decaBDE, as flame-retardants in their products.
Table 6: answers from manufacturers of electronic devices on the international market

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Company 1</td>
<td>Yes</td>
<td>IEC60332-3-XX, IEC 60332-1, UL910, UL1666, UL1685 UL VW-1</td>
<td>Mantle materials and in certain cases isolation materials.</td>
<td>Halogen free fire protected materials. PVC Fluoro polymers</td>
<td>Alumina trihydrate Antimony trioxide Magnesiumdihydroxide</td>
<td>Halogen free fire protected compounds (HFFR): 1700 PVC with flame retardants: 900</td>
</tr>
<tr>
<td>Company 2</td>
<td>Yes</td>
<td>No tests done, but requires fire proof according to UL94</td>
<td>Circuit board Charge cases</td>
<td>No in situ flame protected polymers</td>
<td>Phosphorous based, inorganic</td>
<td>No information</td>
</tr>
<tr>
<td>Company 3</td>
<td>Yes</td>
<td>No information</td>
<td>Printed circuit card Cover to display screens etc.</td>
<td>A number of additive phosphorous organic esters.</td>
<td>Tetrabromobisphenol A (TBBPA)</td>
<td>No information</td>
</tr>
<tr>
<td>Company 4</td>
<td>Yes</td>
<td>UL</td>
<td>Circuit board, cables and other plastic details</td>
<td>Materials that are not banned on our prohibited and restricted lists and mentioned in RoHS directive</td>
<td>Substances that are not banned on our prohibited and restricted lists and mentioned in RoHS directive</td>
<td>Around 50% of the products have some kind of flame-retardants, which is around 75,000 units or 150 tonnes.</td>
</tr>
<tr>
<td>Company 5</td>
<td>Yes</td>
<td>EN 60335-1 (IEC 335-1), IEC 695.2.2, UL 94</td>
<td>Plastic components that could potentially be &quot;heated up&quot;, e.g. motors, pumps, fans, lamp-P</td>
<td>PP, ABS, ABS-PC, PBT, PA, PS, PVC</td>
<td>Br, Cl, P (red P, polyphosphates), Mg (OH) 2 (Just some trials - unfortunately mechanical prop. are limiting applications),</td>
<td>We manufacture and sell approximately 55 million products worldwide</td>
</tr>
</tbody>
</table>
holders, safety supply hose, detergent dispenser, dryers, switches, door lock, thermostats, absorbers, connectors, connection boxes, boxes for electronic, electronic/electric components plastic case and covers, cables, supports

other intumescents and Al (OH) 3 annually and I would say that all of them contain FR plastics to some extent.
Global consumption of flame-retardants
The production of halogenated flame-retardants is equivalent to around 28% of the global production, where the brominated flame-retardants stand for 20% of the total world production of flame-retardants according to statistics from 2001 [1].

An approximate distribution of major categories of flame-retardants produced worldwide is described in figure 1.

*Figure 1: Global distribution (%) of major categories of flame retardants [1]*

![Figure 1: Global distribution (%) of major categories of flame retardants](image)

Table 1. Consumption of all categories of flame-retardants based on geographical distribution a forecast to 2003. (millUSED)[1]

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>470</td>
<td>480</td>
<td>585</td>
<td>630</td>
<td>2.8-3.6</td>
</tr>
<tr>
<td>Western Europe</td>
<td>332</td>
<td>559</td>
<td>631</td>
<td>685</td>
<td>3.4</td>
</tr>
<tr>
<td>Japan</td>
<td>250</td>
<td>317</td>
<td>348</td>
<td>373</td>
<td>3.8</td>
</tr>
<tr>
<td>Asia excl Japan</td>
<td>na</td>
<td>na</td>
<td>&gt;244</td>
<td>&gt;290</td>
<td>5.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>&gt;1,052</td>
<td>&gt;1,356</td>
<td>&gt;1,808</td>
<td>&gt;2,078</td>
<td>3.5 - 4.0%</td>
</tr>
</tbody>
</table>

Na: not available

*Source: SRI Consulting (2000)*
Table 2. Consumption of flame retardants based on category and region (2001) [1]

<table>
<thead>
<tr>
<th>Total Quantity (ktonnes) (mill. USD)</th>
<th>USA</th>
<th>Western Europe</th>
<th>Japan excl Japan</th>
<th>Asia excl Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brominated compounds</td>
<td>60</td>
<td>42</td>
<td>47</td>
<td>90</td>
</tr>
<tr>
<td>Organophosphor compounds</td>
<td>58</td>
<td>83</td>
<td>26</td>
<td>&gt;19</td>
</tr>
<tr>
<td>Chlorinated compounds</td>
<td>17</td>
<td>51</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Aluminium trihydrate</td>
<td>285</td>
<td>168</td>
<td>40</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Antimony oxides</td>
<td>30</td>
<td>25</td>
<td>14</td>
<td>30</td>
</tr>
<tr>
<td>Others</td>
<td>43</td>
<td>39</td>
<td>11</td>
<td>Na</td>
</tr>
<tr>
<td><strong>Total</strong> (ktonnes)</td>
<td>493</td>
<td>408</td>
<td>143</td>
<td>&gt;173</td>
</tr>
<tr>
<td><strong>Total</strong> (mill. USD)</td>
<td>627</td>
<td>556</td>
<td>373</td>
<td>&gt;415</td>
</tr>
</tbody>
</table>

Source: SRI Consulting (2001)

Most present-day halogenated flame-retardants are used in the area of electronics in the manufacturing of circuit boards, and casings for home and office electronics, including mobile phone equipment. The plastics industry is by far the largest user of flame-retardants, the largest quantities of which are supplied to raw-material manufacturers. A smaller proportion of world production of flame-retardants goes to the textile and paper industries.

Flammability tests

Plastics used in electrical and electronic applications frequently have to meet fire performance requirements. The flammability tests are internationally used and described in the standards of the International Electro technical Commission (IEC), or in the regulations and approval procedures of the Underwriters’ Laboratories Inc. (UL), which is mainly related to the US market. A number of IEC standards are moving towards European standards within the European standardisation organisation CEN. The best method for testing electro technical products with regard to fire hazard is to duplicate exactly the conditions occurring in practice, but there are no existing standards, which refer to the use of any kind of flame-retardants. This choice has to be done in each single application by the manufacturer.

There are two types of pre-selection test conducted on plastic materials to measure flammability characteristics [8]. The first determines the material’s tendency either to extinguish or to spread the flame once the specimen has been ignited. The first test is described in UL 94, The Standard for Flammability of Plastic Materials for Parts in Devices and Appliances, which is harmonized with IEC 60707, 60695-11-10 and 60695-11-20 and ISO 9772 and 9773.

Burning behaviour of compounded thermoplastics is not just a material characteristic. It is also depending on the shape and wall thickness of the application. Components or parts may, under faulty or overloaded conditions, attain a temperature that they will have a negative impact or will ignite parts in the nearby area. The Glow Wire Test simulates thermal stresses, which may be

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3 Acts only as a synergene not a separate flame retardant in conjunction with halogenated flame retardants
produced by such sources of heat or ignition, for example the glowing elements of overloaded resistors, in order to assess by simulation technique the fire hazard. Thus, the second test measures the ignition 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. In Europe, flammability is tested using Glow Wire Tests according to IEC 695-2-1 and/or the Needle Flame test according to IEC 695-2-2.

Since there is a great amount of fire standards world wide, the list in appendix 2, illustrates a selection of common fire standard for electric and electronic applications where cables are one central part.

**Conclusions**

Flame-retardants do not give any added value to the final product in the perspective that flame retardation is a basic value and not an added value. The use of fire retardation systems is driven by international and national fire regulations and standards, which is a result of a number of tragic fire injuries and deaths in the past. However, these regulations and standards do not require the use of certain chemical flame-retardants.

It is of course important to understand that the polymer producer, who is responsible for the selection and addition of flame-retardants, has to take these mandatory regulations into consideration together with other quality aspects of the final product. It is not easy to understand that among 370 different chemical flame-retardants described in literature, where around 70 are commercially available, only 15 flame retardant chemicals represent more than 70% of the amounts used in electronic products and textiles. Many of these chemicals, such as decaBDE, have limited or in some cases unknown environmental and health characteristics, beside their flame protective properties. There are probably several explanations behind this narrow field of use, but the predominant factors are most likely economic and conservative, hopefully with motivated technical aspects. Since we talk about engineering polymers in most cases, function is more important than price. This means that certain “popular”, relatively cheap and established flame-retardants, such as decaBDE, may inhibit the development and use of alternatives to come closer to the theoretical properties of the ideal flame retardant.

Important major customers to the polymer producers, such as the companies asked in this review, do not want decaBDE to be contained in their products and they do not want an exemption of decaBDE in the RoHS directive. An exemption may lead to problems to comply with their own standards to avoid decaBDE, which they consider as a doubtful chemical from a health and environmental point of view. The message from the companies in this review is clear, they do not want decaBDE to be removed from the RoHS directive. If this narrow view of the use of flame-retardants continues, it could inhibit the development and use of alternative chemicals and techniques that may be better to health and environment and of course with satisfactory fire protective properties.

The conclusion that can be made from the technical assessment and the survey is that there seems to be alternatives available for fire protection of many, if not all, polymeric applications in electric and electronic equipment covered by the RoHS-directive.
References

1. SRI Consulting, statistics (2000 and 2001)


6. www.jamplast.com


8. www.ul.com


10. P. Swaraj PP Polymer AB “State of the art study for the flame retardancy of polymeric materials with some experimental results” (2001)

11. http://ecb.jrc.it/existing-chemicals/

12. www.bsef.org

13. V. Beddoes ”The Polymer Lexicon – acronyms and abbreviations” RAPRA Technology Inc. (1998)
Appendix 1

**Flame retardants in Information Technology (IT) products**

For information technology and telecom products to be safe, certain product parts like covers/housing, printed circuit boards, cables and some components must be flame retarded to meet applicable electrical safety standards like EN60950. In case of an electrical fault inside the product, resulting in a locally heated area, a spark or a flame, the function of the flame retardant is to reduce the heat emission, thereby delaying the fire. In practice, this leads to extended time to discover and put out the fire as well as longer time for building evacuation.

The most effective and commonly used flame retardant systems include Bromine. In total, some 70 different flame retardant chemical systems are used by the IT industry.

Flame-retardants are for the same reason also used in many other electric and electronic products and appliances like home electronics and white goods. Flame-retardants must be added to all relatively easy to ignite materials such as textiles and plastics in aircrafts, buses, cars, furniture, trains etc in order to meet fire safety regulation. Metal is not an alternative, it cannot be used for electrical shock reasons and wood can seldom be used because it does not meet fire safety regulations.

The environmental properties of flame-retardants have been debated and investigated since the end of the 80s. However, according to Directive 2003/11/EC, 24th amendment to 76/769/EEC, penta- and octaBDE is regulated within the European Union. According to the EU RoHS Directive, 2002/95/EC, new electrical and electronic equipment put on the market after July 1st 2006, must not contain PBBs and PBDEs. For some other 10 brominated flame retardants (incl decaBDE and TBBPA) the EU Commission is currently carrying out scientific risk assessments as base for possible future regulative measures, see: [http://ecb.jrc.it/existing-chemicals](http://ecb.jrc.it/existing-chemicals)

It is, however, important to note that the absolute majority of the member companies of the above organisations have, on a voluntary basis, already since the mid 90s phased out the use of PBBs and PBDEs in plastic parts for which suitable alternatives have been identified. For some products, e.g. printed circuit boards, the Industry standard flame retardant system is based on TBBPA (TetraBromoBisPhenol A). Other systems have been tried, however some with unacceptable technical disadvantages.

Industry self declaration systems of product environmental attributes exist both from ECMA, [www.ecma.ch](http://www.ecma.ch) since 1997 and the Nordic IT Eco Declaration since 1996. At present some 3.000 such IT Eco Declarations have been issued, all of them address the flame retardant families of PBBs and PBDEs.

PBBs and PBDEs have also been restricted in voluntary ECO labels for IT products like TCO, Nordic Swan, German Blue Angel and European EU Flower. The actual number of ECO labelling licenses per IT product category can be found on the Internet of the individual ECO labelling organisations.

For more information about the IT Eco Declaration system, see: [www.itecodeclaration.org](http://www.itecodeclaration.org)

Many of the member companies have these IT Eco Declarations available on their Internet home pages. For specific product brand information, contact the individual manufacturer.

European producer organizations that can give more information are:

- Association of Plastic Manufacturers Europe, [www.apme.org](http://www.apme.org)
- Bromine Science and Environmental Forum, [www.bsef.com](http://www.bsef.com)
- European Brominated Flame Retardant Industry Panel, [www.ebfrip.org](http://www.ebfrip.org)
Appendix 2.

A selection of common international standards and regulations for electric and electronic devices

UL 94 – Test for flammability of plastic materials for parts in devices and appliances
One of the most important tests for plastics is the UL 94 flammability test. It contains procedures for testing materials in horizontal position (UL 94 HB) and in vertical position (UL 94 V-0, V-1 and V-2).

UL 746A - Polymeric Materials - Short-Term Property Evaluations
Include following tests, which means to determine the resistance to ignition of polymeric materials. Hot Wire Ignition (HWI), High-Current Arc Ignition (HAI), High Voltage Arc Resistance to Ignition (HVTR), Glow-Wire Ignitability Test (GWIT, GWFI)

IEC 695-2-1/0 – Fire hazard testing: Glow-wire flammability test methods – general
This glow-wire test simulate the effect of thermal stresses which may be produced by heat sources such as glowing elements or overloaded resistors, for short periods, in order to assess the fire hazard by a simulation technique.

IEC 695-2-1/1 – Fire hazard testing: Glow-wire end-product test and guidance
This method specifies the details of the glow-wire test when applied to end products for fire hazard testing.

IEC 695-2-1/2 – Fire hazard testing: Glow-wire flammability test on materials
This method is applied to specimens of solid electrical insulating materials or other solid combustible materials for flammability testing.

IEC 695-2-1/3 – Fire hazard testing: Glow-wire ignitability test on materials
This method is applied to specimens of solid electrical insulating materials or other solid combustible materials for ignitability testing.

IEC 332 -1 Test on a single vertical insulated wire or cable

IEC 332 -2 Test on a single vertical insulated wire or cable

IEC 332 -3 Test on bunched wires or cables

UL 910 Test method for fire and smoke characteristics of electrical and optical fiber cables used in air handling spaces

UL 1581 Reference standard for electrical wires, cables, and flexible cords

UL 1666 Standard test for flame propagation height of electrical and optical-fiber cable installed vertically in shafts
UL 1685 Fire test of limited-smoke cables
Applied on material

UL 1950 Safety of information technology equipment (flammability test description)

IEC 60332-1-1
Tests on electric and optical fibre cables under fire conditions
Part 1-1: Test for vertical flame propagation
For a single insulated wire or cable – Apparatus

IEC 60332-1-2
Tests on electric and optical fibre cables under fire conditions
Part 1-2: Test for vertical flame propagation for a single insulated wire or cable - Procedure for 1 kW pre-mixed flame

IEC 60332-1-3
Tests on electric and optical fibre cables under fire conditions
Part 1-3: Test for vertical flame propagation for a single insulated wire or cable - Procedure for determination of flaming droplets/particles

IEC 60332-3-XX
Tests on electric cables under fire conditions –
Part 3-XX: Test for vertical flame spread of vertically mounted bunched wires or cables

UL VW-1 Vertical Wire Flame Test