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**Survey and technical assessment of
alternatives to TBBPA and HBCDD**

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Summary

On behalf of the Swedish Chemicals Inspectorate, IFP Research has surveyed a technical assessment of tetrabromobisphenol –A (TBBPA) and hexabromocyclododecane (HBCDD) and possible alternatives, from a quality and a fire protective perspective, that are commercially available on the market.

TBBPA and HBCDD are two of the most commonly used halogenated flame retardants, mainly used in polymers for electronic devices and building insulation materials. There is a minor use for HBCDD in coated textiles. In contrast to the additive flame retardant HBCDD, TBBPA can be applied both as reactive and additive flame retardant depending of the kind of application. Around 57% of all TBBPA manufactured on the global market is applied as a reactive flame retardant. Since reactive flame-retardants are added during the polymerisation process and become an integral part of the polymer it results in a modified polymer with flame retardant properties. The flame retarded polymer is therefore different in its molecule structure compared to the original polymer molecule. Since there is almost no reactive TBBPA left in the modified polymer that can be emitted, the flame retardant properties will stay intact over time with no emission to the environment.

Around 43% of all TBBPA produced on the global market is applied as additive flame-retardants either as TBBPA itself or as derivatives, which means that the TBBPA has been chemically modified. The derivatives to TBBPA are only described very shortly in this review.

Since additive flame-retardants are only physically bonded to the polymer as monomer molecules, they may therefore be released from the polymer and thereby also emit to the environment. This is also the case for the additive flame retardant HBCDD.

TBBPA is mainly used in epoxy resins on the market as a reactive flame retardant. It also occurs as an additive flame retardant at a lesser extent in high impact polystyrene (HIPS) and styrenics, which is a collective name for various styrene based resins, such as acrylonitrile butadiene styrene (ABS), styrene – acrylonitrile (SAN), styrene butadiene rubber (SBR), styrene butadiene latexes (SBL), unsaturated polyester resins (UPR).

There are a number of reactive nitrogen and phosphorous compounds and additive inorganic alternatives, mainly aluminium trihydrate that are used on a commercial basis as alternative non-halogen flame retardants in epoxy resins instead of TBBPA. For ABS there is no obvious alternative to TBBPA. In literature boron salts and other inorganic flame retardants are described as alternatives but there is contradictory information as well. In some cases ABS is replaced by combinations between polycarbonate (PC) and ABS that are flame retarded with organic phosphorous compounds.

HBCDD is mainly applied as an additive flame retardant in expanded polystyrene (EPS) and extruded polystyrene (XPS) used for insulation materials in building and construction industry. This flame retardant is also used to a minor extent in HIPS for casings materials and in textile back coatings.

Alternative commercial non halogen flame retardants do not exist on the market for EPS. There are however some examples described in literature, where boron and metal salts have been used, but there are doubts about their commercial applicability. For textile

coatings phosphor organic flame retardants and the intumescent systems are described as alternatives to HBCDD, but there are doubts about the technical qualities i.e durability in certain applications for the intumescent systems.

To sum up, TBBPA and HBCDD can be replaced by alternative commercial non-halogen flame-retardants in many cases. When commercial technically applicable non-halogen alternatives are discussed in various sources they are not recommended from a cost efficiency point of view. The term cost efficiency has to be clarified by the stakeholders for a better understanding of the ability and possibility of selection of functional commercial alternative flame retardants, having in mind that each flame retarded application is unique concerning its mechanical and fire retarded properties, which have to be assessed for each individual application vis a vis the appropriate quality and fire requirements on the market. It is of concern to highlight that the fire regulations and international standards that rule the fire security of polymer applications don't address the use of certain flame-retardants to manage particular fire requirements for that application.

Sammanfattning

På uppdrag av Kemikalieinspektionen har IFP Research genomfört en teknisk studie av tetrabrombisfenol –A (TBBPA) samt hexabromcyklododekan (HBCDD) och tänkbara alternativa flamskyddsmedel, som klarar såväl kvalitets och brandkrav, och som finns kommersiellt tillgängliga på marknaden.

TBBPA och HBCDD är två av de vanligaste förekommande halogenerade flamskyddsmedlen med huvudsaklig användning i elektroniska produkter och isolationsmaterial till byggindustrin. HBCDD används även i mindre omfattning i belagda textilier. Till skillnad från det additiva flamskyddsmedlet HBCDD, så kan TBBPA appliceras både som reaktivt och additivt flamskyddsmedel beroende på användningsområde.

Omkring 57 % av TBBPA som produceras på världsmarknaden används som reaktivt flamskyddsmedel. Reaktiva flamskyddsmedel tillförs under polymerisationen och blir en integrerad del av en modifierad polymer med flamhämmande egenskaper som i sin molekylära struktur skiljer sig från den ursprungliga molekylen. Eftersom det nästan inte finns någon monomer TBBPA kvar i den modifierade polymeren som kan emitteras, så behåller sina flamhämmande egenskaper under lång tid utan emissioner till miljön.

Omkring 43 % av världproduktionen av TBBPA appliceras additivt, antingen som TBBPA eller i form av derivat, som innebär att TBBPA kemiskt modifierats till andra flamskyddsmedel. I denna rapport beskrivs derivaten till TBBPA endast i korthet. Eftersom additiva flamskyddsmedel endast är fysikaliskt bundna till polymeren som monomerer, innebär detta att de kan emitteras från polymeren och spridas till miljön. Beroende på sina inneboende farliga egenskaper kan spridningen medföra risker för hälsa och miljö. Detta gäller även för det additiva flamskyddsmedlet HBCDD. TBBPA används främst i epoxy på marknaden som ett reaktivtflamskyddsmedel. Den förekommer även i mindre omfattning i ”high impact polystyrene” (HIPS) och ”styrenics”, som är ett samlingsnamn på en rad styrenebaserade hartser och polymerer såsom akrylbutadien styren (ABS), styren akryl nitril (SAN), styren butadien gummi (SBR), styren butadien latex (SBL) samt omättade polyestrar (UPR).

Det finns ett antal reaktiva kväve- och fosforföreningar samt additiva oorganiska salter, främst aluminium hydroxid, som på kommersiella grunder används som alternativa icke halogenerade flamskyddsmedel i epoxy istället för TBBPA. När det gäller alternativa flamskyddsmedel i ABS så är det inte lika uppenbart med alternativ till TBBPA. Litteraturen beskriver bor och andra oorganiska salter som tänkbara alternativ, men det finns även motsatta uppfattningar i denna fråga. I några fall är ABS ersatt av kombinationer av polymerer av polykarbonat (PC) och ABS som behandlats med organiska fosforbaserade flamskyddsmedel.

HBCDD appliceras som ett additivt flamskyddsmedel i framförallt expanderad polystyren (EPS) och extruderad polystyren (XPS), som används som isoleringsmaterial i byggindustrin. Flamskyddsmedlet används i mindre omfattning i ”high impact polystyrene” (HIPS) för höljen och i belagda textilier.

Det finns inga alternativa flamskyddsmedel för EPS på marknaden. Det finns exempel i litteraturen där även bor och metallsalter har använts som flamskyddsmedel, men det är

tveksamt om deras kommersiella tillämpning. För belagda textilier är fosfororganiska föreningar och de intumescenta systemen beskrivna som alternativ till HBCDD, men det är tveksamt om de intumescenta systemens tekniska kvaliteter t.ex beständighet mot vatten i vissa applikationer.

Sammanfattningsvis kan TBBPA och HBCDD ersättas av alternativa kommersiella icke-halogenflamskyddsmedel i många fall. När kommersiella icke halogenerade alternativ diskuteras i olika källor rekommenderas de inte av kostnadseffektivitetsskäl. Begreppet kostnadseffektivt bör klarläggas av marknadens olika aktörer för bättre förståelse för vilka möjligheter vid valet av kommersiella alternativa flamskyddsmedel med vetskapen om att hänsyn måste tas till att varje tillämpning är unik avseende sina tekniska och flammhämmande egenskaper. Det är dock viktigt att påpeka att de brandkrav och internationella standarder som reglerar brandsäkerheten hos polymera applikationer inte hänvisar till särskilda flamskyddsmedel för att klara aktuella brandkrav.

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Introduction

On behalf of the Swedish Chemicals Inspectorate, The Research and Technology Organisation (IFP Research AB, www.ifp.se) has surveyed and carried out a technical assessment of flame retardant alternatives to tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD) currently available for polymers and textiles. IFP Research AB is an independent national research institute in the areas of fibrous and polymer materials.

IFP Research has comprehensive processing equipment and well-equipped laboratories for chemical analysis 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.

The assignment comprises

- A review of the alternative flame-retardants to TBBPA and HBCDD available at present for fire protection of polymers and textiles.
- 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 present and coming known fire requirements set for flame retardant properties in the applications in which they could be used
- A review of applications where there are no alternatives to TBBPA and HBCDD

Economic, health- and environmental aspects of flame-retardants are not discussed in this report.

The ideal flame-retardant

In contrast to most additives, flame-retardants can appreciably impair to properties of polymers. The basic problem is the compromise between the decrease of performance of the polymer 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

1. Be easy to incorporate in the polymer involved
2. Be compatible with the polymer involved
3. Not alter the mechanical properties of the polymer
4. Be colourless
5. Have good light stability
6. Be resistant towards ageing and hydrolysis
7. Match and begin its thermal behaviour before the thermal decomposition of polymer
8. Not cause corrosion
9. Not emit or at least emit low levels of toxic gases
10. Not have harmful physiological and environmental effects
11. Be commercially available and cost efficient

These qualities are of course impossible to reach for any single application. However, many formulations have been and have to be developed for each polymer application in order to give as good properties as possible.

Since numerous fire regulations and international standards rule the fire security of polymer applications they don't address the use of certain flame-retardants. It is therefore the responsibility of the polymer producer (the compounder) to optimise as many of the ideal properties as possible in customer applications that harmonise with high standards of fire security.

Flame-retardants are either *additive* or *reactive*. *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 retardant properties and 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 keeps the flame retardant properties intact over time with no emission to environment. Reactive flame-retardants are mainly used in thermosets, especially polyester, epoxy resins and polyurethane's (PUR) in which they can be easily incorporated.

Additive flame-retardants are incorporated into the polymer prior to, during, or more frequently after 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. They may therefore be released from the polymer and thereby also emit to the environment. Depending on the inherent dangerous properties, the flame retardant might pose a risk to human health and the environment.

Groups of flame retardants

Flame-retardants are added to various kinds of polymers, both synthetic and natural, to enhance the flame retardant properties of the polymers. Around 350 different substances of flame-retardants are described in literature with no specific reference to certain national or international fire regulations, which have to be met for the application to exist on the market. . *The Index of Flame retardant*, an international guide contains more than 1000 flame retardant products by trade name, chemical, application and manufacturer that describe around 200 chemicals used in commercial flame retardant products [2,3]

There are four main families of flame retardant chemicals [2].

Inorganic flame-retardants are metal hydroxides such as aluminium trihydrate, magnesium hydroxide, ammonium polyphosphate, boron salts and the element red phosphorous. Both aluminium hydroxide, also called aluminium trihydrate, and magnesium hydroxide are used as halogen free alternatives to brominated flame-retardants and they also function as smoke suppressants. Inorganic phosphor compounds are widely used as substitutes to bromine. Inorganic flame-retardants are added as fillers into the polymer and are considered immobile in contrast to the organic additive flame-retardants.

Antimony trioxide and zinc borate are also used but as synergists in combination with halogenated flame-retardants.

The whole group of inorganic flame-retardants represents around 50% by volume of the global flame retardant production, mainly as aluminium trihydrate, which is in volume the biggest flame retardant category in use on the market.

Organophosphorous flame-retardants are primarily phosphate esters and represent around 20% by volume the global production. This category is widely used both in polymers and textile cellulose fibres. Of the halogen-free organ phosphorous flame-retardants in particular triaryl phosphates (with three benzene rings attached to a phosphorous group) as alternatives to brominated flame-retardants. Organ phosphorous flame-retardants may in some cases contain bromine or chlorine.

Nitrogen based organic flame-retardants inhibit the formation of flammable gases and are used in polymers containing nitrogen such as polyurethane and polyamide. Some nitrogen-based flame-retardants are melamines and melamine derivatives and they are used for a minor group of polymers and act as intumescent (swelling) systems.

Halogenated flame-retardants are primarily based on chlorine and bromine. These flame-retardants react with flammable gases to slow or prevent the burning process. The brominated flame-retardants TBBPA and HBCDD are included in this group. The group of halogenated flame-retardants represent around 25% by volume of the global production, where the brominated flame-retardants dominate the international market.

Brominated flame-retardants can be divided into three classes namely **Aromatic**, including TBBPA, PBDEs and PBB¹s.

Cycloaliphatic, including hexabromocyclododecane (HBCDD)

Aliphatic, which are globally representing a minor group of substances.

Tetrabromobisphenol -A (TBBPA) and derivatives

TBBPA is a brominated organic compound and is primarily used as a reactive intermediate in the manufacture of flame retarded epoxy and polycarbonate resins and is therefore an integral part of the polymer. It may also be used as an additive flame retardant and only physical bonded to the polymer, for example in the manufacture of acrylonitrile-butadiene-styrene resins (ABS) and phenolic resins [1,2]. When TBBPA is used as an additive flame retardant it is generally together with the synergist antimony trioxide which is not the case when it is used as a reactive flame retardant.

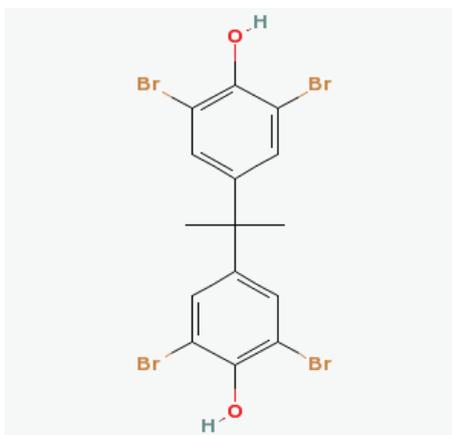


Figure 1: Chemical structure of TBBPA

¹ PBBs are not manufactured anymore. Production stopped globally 2000.

As far as known today TBBPA is also used for the manufacture of derivatives to TBBPA - dimethylether, TBBPA-dibromopropylether, TBBPA-bis (allylether), TBBPA-bis (2-hydroxyethyl ether), TBBPA-brominated epoxy oligomers and TBBPA-carbonate oligomers. These derivatives are mainly used as flame retardants in certain applications as described in table 1 below.

TBBPA is produced in USA, Japan, Jordan and Israel but not officially in the EU anymore. The annual global production in 2004 was estimated at more than 170.000 tonnes. Around 57% of the global production of TBBPA is used for epoxy resins in circuit boards and around 25% TBBPA is used as an additive flame retardant for casings materials, around 8% is used for the manufacture of derivatives and the last 10% of TBBPA is used as additives for other polymers such as ABS in combination with HIPS and thermoplastic polymers. [21]

Figure 2: Main use of TBBPA worldwide in percent.

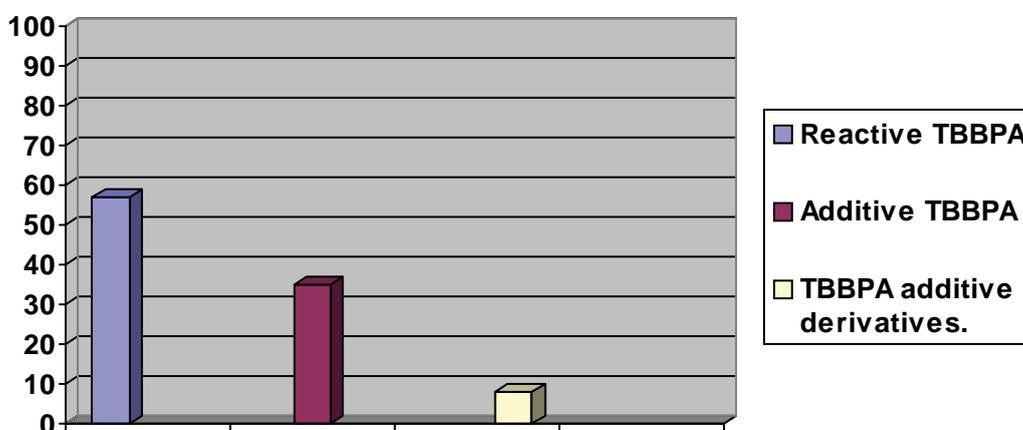


Table 1: Main use of TBBPA and derivatives [2,8,21]

Chemical	Reactive	Additive	Main occurrence in polymers
TBBPA	Yes No No No	No ³ Yes Yes Yes	Epoxy resins Phenolic resins High impact polystyrene (HIPS) Acrylonitrile butadiene styrene terpolymers (ABS)
TBBPA carbonate oligomer	No	Yes	Acrylonitrile butadiene styrene terpolymers (ABS) in blends with PC Engineering thermoplastics
TBBPA-bis (2,3-bibromopropyl ether)	No	Yes	Polyolefin's, polystyrene
TBBPA-bis (allyl ether)	Yes	No	Polystyrene foam (EPS) ⁴
TBBPA epoxy oligomer	No	Yes	Styrenics ⁵ , Polybutadieneterephthalate (PBT)
TBBPA-bis (2-hydroxyethyl ether)	No	Yes	Engineering plastics Textile coatings

³ [2] mention that TBBPA is used as a reactive flame retardant totally or partially.

⁴ Not used in Europe according to European Brominated Flame Retardant Industry Panel (EBFRIP)

⁵ Styrene based resins such as polystyrene (PS), acrylo nitrile styrene (ABS), styrene – acrylonitrile (SAN), styrene butadiene rubber (SBR), styrene butadiene latexes (SBL), unsaturated polyester resins (UPR).

Hexabromocyclododecane (HBCDD)

HBCDD is a cycloaliphatic brominated additive flame retardant. Around 85% the global production of HBCDD is used in flame retarded expanded polystyrene (EPS and extruded polystyrene (XPS) mainly used as a rigid insulation in panel/boards for building and construction. Around 10% is used in textile back coatings and the last 5% is used in high impact polystyrene (HIPS) for casings materials [2,4].

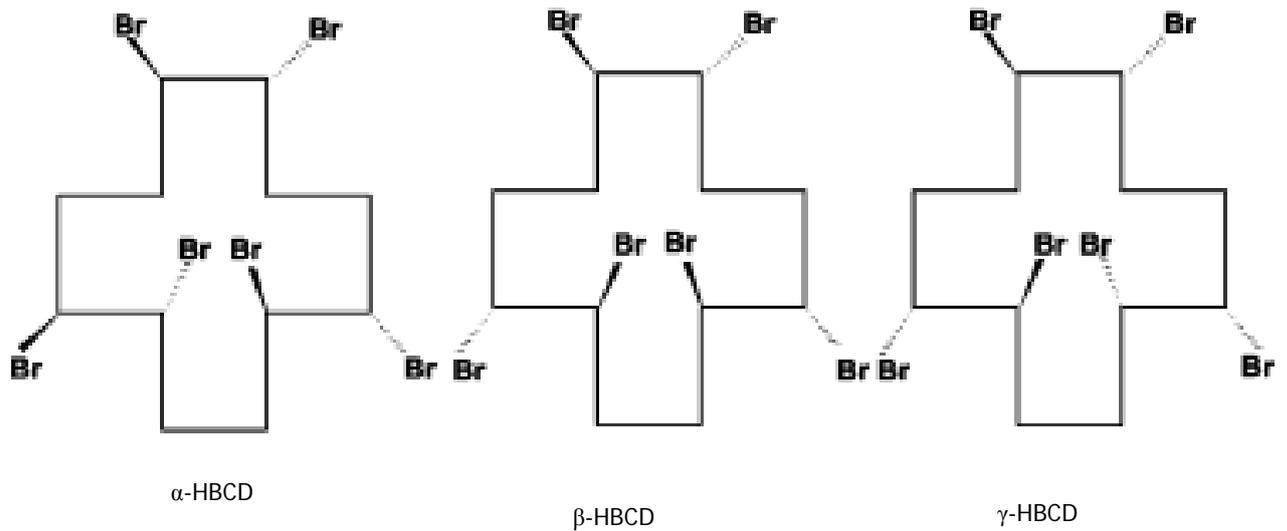


Figure 3: Chemical structure of HBCDD.



Figure 4: Main use of HBCDD worldwide in percent.

Alternative flame retardants in certain polymers to TBBPA, its derivatives and HBCDD

Epoxy resins

Epoxy resins are mainly used as encapsulation material of electric components and multiplayer laminates in printed circuit boards. It may be flame retarded by the introduction of certain halogenated compounds into part of the system. Those flame-retarded materials are manufactured with reactive TBBPA there is virtually no monomer TBBPA left in the end product.

Epoxies may also be added with additive inorganic flame-retardants such as aluminium trihydrate or magnesium hydroxide or reactive nitrogen and phosphorous constituents in some applications. There are however still some applications in electronics where non-halogen alternatives are hard to find, such as printed circuit boards. These alternatives are considered less cost efficient than the halogens, having the same fire safety performance in mind. [2]. It is however unclear what is fully meant by less cost efficient in terms of price, processing conditions etc.

High impact polystyrene (HIPS)

Traditionally brominated flame-retardants (BFR) have been applied for housing of business electronics and TV sets from HIPS, PC and ABS. Two of these BFRs are TBBPA and deca bromobiphenylether, used as additive flame-retardants. Some commercial non-halogen flame retardant alternatives used in HIPS are organic aryl phosphorous compounds such as;

- Resorcinol bis (biphenyl phosphate)
- Bis phenol A bis (biphenyl phosphate)
- Polymeric biphenyl phosphate
- Diphenyl cresyl phosphate
- Triphenyl phosphate

Styrenics

Styrenics is a group name of a number of polymers that are styrene based resins such as polystyrene (PS), acryl nitrile styrene (ABS), styrene – acrylonitrile (SAN), styrene butadiene rubber (SBR), styrene butadiene latexes (SBL) and unsaturated polyester resins (UPR).

For a number of categories of styrenics alternative halogenated and non-halogenated flame-retardants are used, but since the volume is comparably small in relation to the use of TBBPA, only some of the more important styrenics are described below.

Acrylonitrile Butadiene-Styrene (ABS)

ABS is a strong and high impact polymer used for instance for housings in electronic devices. Among the most commonly used flame-retardants for ABS are etylene bis (tetrabromophtalimide), decaBDE, TBBPA (additive) and TBBPA carbonate oligomer, with ABS is in combination with polycarbonates (PC). Small amounts of antimony oxide may be used as synergist. There are non-halogen alternatives to BFR s described in literature [2, 3, 8, 10, 17, 18] with reference to table 1 below, but also uncertainties concerning commercial alternatives to BFR s in ABS on the market. In a Danish report [2] there are non-halogen blends of polyethylene ether (PPE)/ PS or PC/ABS with organic

phosphorous compounds such as resorcinol bis (biphenyl phosphate), Bis phenol A bis (biphenyl phosphate) and triphenyl phosphate, that are used as flame retarded polymer alternatives to ABS on the market

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. Beside the use of TBBPA there is a wide range of flame-retardants used, based on halogenated paraffin's and phosphate and inorganic fillers. Also reactive organic flame-retardants, such as chlorendic anhydride, tetrabromophtalic anhydride tetrachlorophtalic anhydride may be used. [10, 21]

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 and expandable polystyrene (EPS) bead board are dibromoethyldibromocyclohexane, pentabromochlorocyclohexane, TBBPA-bis (allyl ether) and hexabromocyclododecane (HBCDD). 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 polystyrene⁶. In this case a most common used flame retardant system is decaBDE together with antimony oxide. Alternative non-halogen flame-retardants do not exist on the market for EPS. Around 58% of all EPS contained HBCDD on the European market⁷ some years ago. There are some examples described in literature [10], where boron and metal salts have been used, but there are doubts about their commercial applicability.

⁷ According to a EUMEPS study from 2003 and 2004

Table 2: Overview of commercially used flame-retardants used as alternatives for TBBPA and HBCDD and their relevant applications. [2,8]

Polymer materials	Applications	Fire requirement(s)	Main use of and/or HBCDD	Commercial halogenated flame retardant alternatives ⁸	Commercial halogen free flame retardant alternatives alone and/or in combination	Alternative polymer material, non flammable or containing halogen free flame retardants
Epoxy resins	Printed circuit boards Electronic components encapsulations Technical laminates	UL94 (see appendix 2) FR4	TBBPA (reactive)	Decabromodiphenylether/ATO Decabromodiphenylethane/ATO Ethylene-bis(tetrabromophthalimide)/ATO	Aluminium trihydrate Ammonium polyphosphate Red phosphorous (incap) Phosphorous polyols Dihydrooxaphosphananthrene oxide Metal phosphinates	Polyethylene sulphide ⁹
HIPS	Housings of electronic products. Wiring parts	UL94	TBBPA (additive)/ATO HBCDD	Decabromodiphenylether/ATO Decabromodiphenylethane/ATO Ethylene-bis(tetrabromophthalimide)/ATO Brominated epoxies/ATO Chlorinated paraffins/ATO	Resorcinol bis (biphenyl phosphate) Bis phenol A bis (biphenyl phosphate) Polymeric biphenyl phosphate Diphenyl cresyl phosphate and triphenyl phosphate	Polyethylene that contains magnesium hydroxide
EPS	Insulation of foundation Ground deck parking deck etc	Euro classes, (see appendix 4)	TBBPA- bis (allyl ether) HBCDD	No alternatives	No alternatives	No information available
ABS (Within the category of styrenics)	Housings for business machines, dashboards, toys, equipments for refrigerator, telephones, and other consumer electronics	UL94	TBBPA (additive)/ATO TBBPA-carbonate oligomer ¹⁰	Decabromodiphenylether/ATO Decabromodiphenylethane/ATO Ethylene-bis(tetrabromophthalimide)/ATO Brominated epoxies/ATO	No alternatives	PPE ¹¹ /PS blends or PC/ABS blends with organic phosphorous compounds such as resorcinol bis (biphenyl phosphate), Bis phenol A bis (biphenyl phosphate) and triphenyl phosphate

⁸ If antimony trioxide is added as a synergist, it is marked with ATO in context to the halogenated flame retardant.

⁹ Polyethylenesulphide (PES) is a high crystalline sulphur containing flame inherent polymer used as a surface and thermoplastic material.

¹⁰ In combination with PC

Textile back coatings	Protective clothing Carpets Curtains Upholstered fabrics Tents Interior in public transportation Other technical textiles	See appendix 3	HBCDD		Reactive phosphorous constituents Ammonium polyphosphate Diammonium phosphate Intumescent systems ¹²	
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Fire regulations for applications related to the use of TBBPA and HBCDD

Electronic and electric applications

Polymers used in electrical and electronic applications have to meet fire performance requirements. The flammability tests are globally 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)* mainly related to the US market.

A number of IEC standards are moving towards European standards within the European standardisation organisation CEN. The best mythology for testing electro technical products with regard to fire hazard is to duplicate exactly the conditions occurring in practice. There are no existing standards, which refers to the use of any specific 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.

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 one of the most important tests for polymers namely UL 94, The Standard for Flammability of Plastic Materials for Parts in Devices and Appliances, which is harmonized with IEC 60707. Similar ignitability tests are described in a number of other standards, including: IEC 60065, IEC 60950, IEC 60695-11-10, IEC 60695-11-20, ISO 9772 and ISO 9773. Burning behaviour of compounded thermoplastics is not just a material characteristic. It is also dependent on the shape and wall thickness of the application. Components or parts may, under faulty conditions or overload conditions, attain a temperature such that they are unduly affected or such that they will ignite parts in the nearby area. The ignitability classification attained from UL94 (or similar standards) relates to a specific formulation and thickness of the material tested. In all product standards the producer must test their components and

¹¹ Polyphenyleneoxide (PPE) often described as poly(2,6-dimethyl-1,4-phenyleneoxide), is an amorphous heat resistant polymer for electronic equipment, pump housings etc. often used in combination with polystyren

¹² According to Prof. R. Horrocks at Bolton Institute, UK (2004), the intumescent systems are solely charformers at the back of the fabric and do not prevent ignition and flame spread. Most of the commercially available intumescent systems are water soluble and are consequently removed during soaking prior to flame testing.

materials at the thickness used in the product. Should the same material be used at different thicknesses it should be tested for all thicknesses or (in cases where thickness varies little) for the smallest thickness.

The Glow Wire Test simulates thermal stresses, which may be 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, IEC 60695 and IEC 60950 and IEC 60065. In Europe, flammability is tested using Glow Wire Tests according to IEC 60695-2-1 and/or the Needle Flame test according to IEC 60695-2-2.

Significantly modern standardisation of electrical and electronic appliances is moving towards performance-based requirements. Presently the IEC standardises safety requirements of consumer electronics and IT equipment through the activities of Technical Committee (TC) 108. This committee has responsibility for the maintenance of IEC 60065 and IEC 60950 until the finalisation of a new common approach to safety for all products covered by these two existing, prescriptive standards. Previously the prescriptive approach has solely relied on requirements that would minimise the chance of internal ignition of electrical and electronic products. The new performance based requirement has expanded the remit the safety committee to include both internal and external ignition. This means that external housing, which previously needed to be protected from internal ignition (something that could be relatively easily achieved through sufficient spacing from internal parts), now needs to be protected from external, small open flame ignition which can most effectively be done by the judicious choice of ignition resistant material. Present indications from the standardisation committees is that the performance requirement of the external housing will correspond to UL94 (V-1). Adoption of this new standard lies at least 1-2 years in the future but it will potentially effect the use of flame-retardants in such applications.

FR4 – an industrial standard for printed circuit boards laminates

FR4 is a category of double and multi layer laminates made of glass fibre reinforced epoxy resin that that is under high temperature stress during use. The double or multi layer laminate is coated with a layer of copper of various thickness.

Building and construction materials

In Europe a system for fire testing and classification has been introduced. It is called the Euroclasses system. Testing according to the Euro class system is carried out through a number of harmonised European testing methods (EN) that have been issued by the European Standardisation organisation CEN.

The Euro class-system for construction products affects mainly surfaces and floorings. There are seven main classes of surfaces. They are called A1, A2, B, C, D, E and F. Which class is required in the various EU countries is the provision of their national building legislation The system is described in more detail in appendix 4. [19]

Textile applications

Tightened legislation and more restricted fire requirements are the major forces that have driven forward development towards functionally better and more effective flame-retardants. This trend is particularly clear in the English-speaking countries. *The United Kingdom, Ireland and the United States, especially California*, have carried out extensive large-scale risk-benefit studies. In the light of this trend, a large number of specific fire standards with unique fire requirements have been developed internationally for various widely differing situations. The overview of international fire requirements, presented in appendix 3, of this report is not intended to be complete, but is an attempt to present the most important and most prominent international requirements occurring in the area of fire protected textiles.

Market opinion on brominated flame-retardants and their non-halogen alternatives

There are reports that describe that for some applications and polymers fire retardant properties are hard, or even not possible, to achieve with non-halogen alternatives. The Bromine Science and Environmental Forum (BSEF) describe this situation [16] as below.

- *Higher quantities of non-halogen flame-retardants are required in order to get the same level of fire protection. This would mean, as far as BSEF is concerned, that higher production of non-halogen alternatives would lead to increase in manufacturing and transportation costs.*
- *Since BFRs are loaded in less amounts into the polymers the BFRs impair less to the qualities of the polymer than the non-halogen flame-retardants at reasonable costs.*
- *In certain plastics such as HIPS, ABS and PBT, there are currently no cost effective alternative flame-retardants, which can provide good flame retardance and good mechanical properties. The BFR s environmental characteristics are well understood since there have been detailed studies during the past 10 years.*

A report from the Danish Environmental Protection Agency [2] mention that there are no present commercial non-halogen flame-retardants available today for ABS and PBT/PET polymers. For ABS, where TBBPA is often used, alternative materials to ABS, such as ABS/PC blends containing organic phosphorous flame-retardants and melamines are suggested.

For EPS, that is often flame retarded with HBCDD, there is no information available of commercial non-halogen flame retardant alternatives [2]

For HIPS however there are organic phosphorous compounds used on the market as alternative non-halogen flame retardants [2]. This is also confirmed by another source [8].

In context to this market situation for certain polymers, a number of global major manufacturers of electronic devices and equipment, have developed programmes and policies for their action concerning their relation to brominated flame retardants. Some of these actions are described below.

Dell

Dell has a public policy to phase out of all applicable OSPAR chemicals (see appendix 4). Through industry partnerships, Dell is actively working to help establish supply chain Capability and capacity of viable alternative materials needed to realize our goal to eliminate all remaining uses of brominated flame-retardants, including TBBPA in circuit boards, by 2015. Dell will continue to strive to meet our public goals to eliminate the use of environmentally sensitive materials in our products, as well as continue to evaluate the viability of halogen-free flame retardant alternatives. Dell is committed to replacing BFRs, including TBBPA, with halogen free alternatives [11, 22].

Hewlett Packard (HP)

HP has a public policy to phase out of some OSPAR chemicals. Since the early 90s HP has replaced PBBs and PBDEs in product covers with halogen free alternatives in 95% of its products. In a re-cent press release from 1st of November 2005, HP announced that they would replace all halogenated flame retardants including additive TBBPA from the remaining 5% of external case parts of all new HP brand products introduced after 31st of December 2006 [11, 12]. HP will continue to use reactive TBBPA in printed wiring board (PWB) material as non-halogenated alternatives have not been identified which meet both technical and environmental specifications. In addition, HP has no intention to start using decaBDE, even if it will not be regulated.

Apple

Apple has a public policy to phase out most OSPAR chemicals. Apple is committed to phasing out all PBDEs, but does not commit to halogen free alternative to decaBDE. Apple does not have a phase out target for TBBPA, but are actively looking for equally effective alternatives with better environmental features than TBBPA [11,13].

IBM

IBM has a public policy to phase out of some OSPAR chemicals. In 1991, IBM phased out all PBDEs¹², and is actively working to evaluate safe and functionally acceptable alternatives to TBBPA in electronic components and printed circuit boards. [11, 14,15]

Toshiba

Toshiba is in compliance with the RoHS directive, which means phasing out PBDEs Despite a comprehensive website dedicated to Toshibas environmental initiatives, it is unclear whether or not the company are globally phasing out other chemicals other than those targeted in the RoHS directive [11].

Conclusions

The sources for this review are public and open references from authorities and scientifically literature since it was very hard to get enough relevant technical information from the market. The conclusions from the review are that:

- There is a range of alternative commercial non halogen flame retardants to TBBPA and HBCDD to a number of important polymer materials with the exception for EPS and ABS, that manage the stringent fire requirements of UL94 and similar European fire standards. However ABS in blends with polycarbonate (PC) or the alternative polymer combination to ABS consisting of polyphenylene ether (PPE) and polystyrene (PS) are optional when treated with organic phosphorous flame-retardants.
- In epoxy and polycarbonate resins, TBBPA is added as a reactive flame retardant during the polymerisation process and become an integral part of the polymer. The result is a modified polymer with flame retardant properties and 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 TBBPA from leaving the polymer and keeps the flame retardant properties intact over time with no emission to environment.
- Although there are commercially available non-halogen flame alternatives to additive TBBPA and HBCDD respectively, it is not easy to verify to what extent that they are applied in electronic devices, building materials and coated textile materials.
- Less cost efficiency, technical requirements, for instance in printed circuit boards, and specific fire requirements in individual cases are mentioned as reasons for not using commercially available non-halogen alternatives today. Since there are non-halogen alternatives to additive TBBPA and HBCDD applicable in several applications, it is recommended that the stakeholders clarify the term cost efficient.
- For EPS and XPS, mainly used in construction products for insulation in buildings, there are no commercial alternatives found in the publications studied in this review. In those cases flame protection is required according to the so called Euroclasses, the only flame retardant commercially available is HBCDD. In Sweden most EPS is not treated with flame-retardants. One reason for this situation could be related to poor fire regulations for buildings in Sweden.
- Fire regulations and international standards rule the fire security of polymer applications but they don't address the use of certain flame-retardants.

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Appendix 1

An overview 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 polymers 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). UL94 is described in detail in appendix 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 60332-1-2

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

Appendix 2

UL 94

UL94(V-0 to V2)

1. The test specimen is hanged vertically above a piece of cotton fabric where a gas flame is applied to the bottom edge.
2. The gas flame is immediately withdrawn after 10 seconds where the afterflame time (t1) is registered
3. The procedure above is repeated to register the second afterflame time (t2)
4. This procedure, 1 to 3, is repeated 5 times.
5. The afterglow time for the second repetition (t3) is registered.

The sum of the after flame is calculated of the material/application. Due to the result of this sum after flame and afterglow in context to ignition of the holder clamp, the material is classified accordingly. The holding cotton fabric must also not be ignited by flames and drippings from the material/application.

Table A-1: The different fire regulatory classes of UL94

UL94 class	Criteria 1 [sec]	t2 + t3 [sec]	Sum afterflame [sec]
V-0	$t1 + t2 < 50$	< 30	See criteria 1
V-1	$t1 > 30$ $t2 > 30$	≤ 60	≤ 250
V-2	$51 \leq t1 + t2 \leq 55$	V-0 or V-1	251 to 255

UL94 (V-5A)

A rod shaped specimen is placed vertically and an attempt is made to ignite the specimen five times for 5 seconds. It must not continue to burn or glow for more than 60 seconds after the burner has been removed. The material must not drip.

UL94(V-5B)

Sheets of the same thickness are tested in a horizontal position. The flame is applied to the centre of the specimen. Classification is done in V-5B if the specimen exhibits burn through hole, other criteria as for UL94 (V-5A).

Materials classified for UL94 (V-5A) or UL94 (V-5B) shall also comply with the requirements for materials classified for V-0, V-1 and V-2.

UL94(HB)

A test where 3 specimen of the cabinet material are placed in an angle of 45 degrees and ignited if possible with a burner. In order to be classified HB the burning rate must not exceed 40 mm/min over a 75 mm span for specimen thicker than 3 to 13 mm and 75 mm/min for specimen thinner than 3 mm. In each case the specimen must cease burning before the 100 mm reference mark.

UL94 (HF1 and HF2)

These regulations are for foamed products. In this method 2 sets of 5 specimen stored under different conditions are tested; an attempt is made to ignite the test specimen with a

fishtail burner. The flame is kept under the specimen for 60 seconds. The following conditions must be met

1. Only one specimen must burn more than 2 seconds
2. No specimen must burn more than 10 seconds
3. No specimen must glow for more than 30 seconds
4. No specimen must burn or glow at a distance of 60 mm from the ignition point
5. For HF-1 no drops must ignite the underlying surface
6. For HF-2 the underlying surface is allowed to be ignited

If a set of 5 specimen does not comply with the requirements because of one of the following situations, another set of 5 specimen subjected to the same conditions shall be tested.

1. A single specimen flames more than 10 seconds or
2. 2 specimens flame for more than 2 seconds but less than 10 seconds or
3. 1 specimen flames more than 2 seconds but less than 10 seconds, and a second specimen flames more than 10 seconds or
4. 1 specimen does not comply with the additional criteria.

All specimens from this second set shall comply with the requirements in order for the foamed plastic material in that thickness and density to be classified HF-1 or HF-2.

Appendix 3

An overview of fire requirements for textile applications.

Some examples of fire requirements and corresponding building standards based on the *Flammable Fabrics Act* (FFA) in the United States, which was adopted by the US Congress as long ago as 1953, the UK *Furniture and Furnishings Fire Safety Regulations* and the fire-safety requirements from 1988 still in force, and some important standards of other European countries and international transport organisations

Table A-2: Some important fire regulations for textile applications

Product type	Type of fire source	Example of risk	Standard or equivalent
Seating	Smouldering cigarette	Smoking in furniture	Testing according to EN 1021-1. National requirements in several EU Member States
Seating	Smouldering cigarette	Smoking in furniture	Testing according to UFAC (<i>The Upholstered Furniture Action Council</i>) Voluntary industry requirements, followed by many manufacturers in the US
Seating	Ignition with small gas flame	Carelessness with open fire	Testing according to EN 1021-2. National requirements in some EU Member States. Requirements for low flammability in purchasing for example for hotels
Seating Etc.	Ignition with burning wood	Carelessness with open fire	Testing according to BS 5852, fire source 5. Requirements for consumer environment for upholstery materials for furniture, mattresses and cushions in the UK. Medium risk level for public environment in the UK according to BS 7176
Seating	Ignition with burning wood	Carelessness with open fire / arson	Testing according to BS 5852, fire source 7. High and very high risk level for public environment in the UK according to BS 7176
Seating, ships	Smouldering cigarette and small gas flame	Carelessness with open fire	Testing according to IMO Resolution A.652 (16): 1989. Requirement for low flammability
Seating, trains	Ignition with burning wood	Carelessness with open fire / arson	Testing according to BS 5852, fire source 7. Requirement for seats in X2000 trains

Seating, trains	Ignition with burning paper	Carelessness with open fire / arson	Testing according to UIC 564-2, app. 13. Used by Central European train companies
Seating, airplanes	Ignition with oil burner	Fire on board	Testing according to FAA 23.853. Requirement for self-extinguishing is applied by most airlines
Mattresses, beds	Ignition with cigarette	Smoking in bed	Testing according to EN 597-1. Requirement for low flammability in several European countries
Mattresses, beds	Ignition with cigarette	Smoking in bed	<i>Code of Federal Regulations (CFR)</i> Testing according to 16 CFR part 1632 (USA) General requirements for low flammability in the USA
Mattresses, etc. ships	Smouldering cigarette and small gas flame	Smoking Carelessness with open fire	Testing according to IMO Resolution A.688 (17): 1991. Requirements for low flammability
Mattresses, beds	Ignition with burning wood	Carelessness with open fire	Testing according to BS 6807, fire source 5. Medium risk level for public environment in the UK according to BS 7177
Mattresses, beds	Ignition with burning wood	Carelessness with open fire / arson	Testing according to BS 6807, fire source 7. High and very high-risk level for public environment in the UK according to BS 7177.
Mattresses, beds	Ignition with gas burner	Carelessness with open fire / arson	Testing according to California Technical Bulletin 603. Requirement for limited heat and smoke generation from 2005. Other states are expected to follow suit.
Curtains and drapes	Gas flame + heat radiator	Carelessness with open fire	Testing according to EN 1101, EN 1102 and EN 13772 and classification according to EN 13773. These standards are expected to gradually replace existing national standards.
Curtains and drapes	Large gas flame	Carelessness with open fire	NFPA (<i>National Fire Protection Association</i>) NFPA 701 (USA). Requirement for self-extinguishing
Curtains and drapes, ships	Gas flame	Carelessness with open fire	Testing according to IMO res. A.471 (XII), 1981 Requirement for self-extinguishing products.

Interior materials in cars	Gas flame	Carelessness with open fire	Testing according to ISO 3795 and equivalent. Requirement for limited rate of flame spread is specified in FMVSS 302 (USA), Directive 95/28/EC and by individual car manufacturers.
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Table A-3: EU standards covering personal protective clothing

Type of risk	Example of risk	Corresponding EU standard
Small flames	All activity in the vicinity of flames	EN 533
Larger flames and convective heat	Proximity to small fires	EN 531 level B1
Radiated heat	Proximity to ovens	EN 531 level C1
Heat and flames	Fire-fighting	EN 469
Drops of molten metal	Welding and cutting work with oxygen	EN 470-1
Splashes of molten metal	Foundry, smelting plant	EN 531 level D1 and E1

Table A-4: Classification of textile fabrics according to the FFA (the Flammable Fabrics Act).

Class		Time for spreading of flame
Class 1	Normal flammability	4 seconds or more
Class 2	Intermediate flammability	Between 4 and 7 seconds before fabric ignites
Class 3	Rapid and intense burning	Less than 4 seconds. Dangerous and flammable. Unsuitable for clothing.

Appendix 4

An overview of fire requirements for building and construction applications [19]

Table A-5: Euro classes of reaction to fire for construction products except floorings (*)

Class	Test method(s)	Classification criteria	Additional classification
A1	EN ISO 1182 (1); and	$DT \leq 30 \text{ }^\circ\text{C}$; and $Dm \leq 50 \%$; and $t_f = 0$ (i.e. no sustained flaming)	-
	EN ISO 1716	$PCS \leq 2.0 \text{ MJ.kg}^{-1}$ (1) and $PCS \leq 2.0 \text{ MJ.kg}^{-1}$ (2) (2a) and $PCS \leq 1.4 \text{ MJ.m}^{-2}$ (3) and $PCS \leq 2.0 \text{ MJ.kg}^{-1}$ (4)	-
A2	EN ISO 1182 (1) or	$DT \leq 50^\circ\text{C}$; and $Dm \leq 50\%$; and $t_f \leq 20\text{s}$	-
	EN ISO 1716 and	$PCS \leq 3.0 \text{ MJ.kg}^{-1}$ (1) and $PCS \leq 4.0 \text{ MJ.m}^{-2}$ (2) and $PCS \leq 4.0 \text{ MJ.m}^{-2}$ (3) and $PCS \leq 3.0 \text{ MJ.kg}^{-1}$ (4)	-
	EN 13823 (SBI)	$FIGRA \leq 120 \text{ W.s}^{-1}$; and LFS < edge of specimen and $THR_{600s} \leq 7.5 \text{ MJ}$	Smoke production (5), and flaming droplets/ particles (6)
B	EN 13823 (SBI) and	$FIGRA \leq 120 \text{ W.s}^{-1}$; and LFS < edge of specimen; and $THR_{600s} < 7.5 \text{ MJ}$	Smoke production (5), and flaming droplets/ particles (6)
	EN ISO 11925-2(8): Exposure = 30s	$F_s \leq 150 \text{ mm}$ within 60s	
C	EN 13823 (SBI) and	$FIGRA \leq 250 \text{ W.s}^{-1}$; and LFS < edge of specimen; and $THR_{600s} \leq 15 \text{ MJ}$	Smoke production (5), and flaming droplets/ particles (6)
	EN ISO 11925-2(8): Exposure = 30s	$F_s \leq 150\text{mm}$ within 60s	

D	EN 13823 (SBI) and	$FIGRA \leq 750 \text{ W.s}^{-1}$	Smoke production (5), and flaming droplets/ particles (6)
	EN ISO 11925-2(8): Exposure = 30s	$F_s \leq 150 \text{ mm within 60s}$	
E	EN ISO 11925-2(8): Exposure = 15s	$F_s \leq 150 \text{ mm within 20s}$	Flaming droplets/ particles (7)
F	No performance determined		

(*) The treatment of some families of products, e.g. linear products (pipes, ducts, cables etc.), is still under review and may necessitate an amendment to this decision.

(1) For homogeneous products and substantial components of non-homogeneous products.

(2) For any external non-substantial component of non-homogeneous products.

(2a) Alternatively, any external non-substantial component having a PCS $\leq 2.0 \text{ MJ.m}^{-2}$, provided that the product satisfies the following criteria of EN 13823(SBI) : $FIGRA \leq 20 \text{ W.s}^{-1}$; and LFS < edge of specimen; and $THR_{600s} \leq 4.0 \text{ MJ}$; and s1; and d0.

(3) For any internal non-substantial component of non-homogeneous products.

(4) For the product as a whole.

(5) s1 = $SMOGRA \leq 30 \text{ m}^2.\text{s}^{-2}$ and $TSP_{600s} \leq 50 \text{ m}^2$; s2 = $SMOGRA \leq 180 \text{ m}^2.\text{s}^{-2}$ and $TSP_{600s} \leq 200 \text{ m}^2$; s3 = not s1 or s2.

(6) d0 = No flaming droplets/ particles in EN13823 (SBI) within 600s; d1 = No flaming droplets/ particles persisting longer than 10s in EN13823 (SBI) within 600s; d2 = not d0 or d1; Ignition of the paper in EN ISO 11925-2 results in a d2 classification.

(7) Pass = no ignition of the paper (no classification); Fail = ignition of the paper (d2 classification).

(8) Under conditions of surface flame attack and, if appropriate to end-use application of product, edge flame attack.

Definitions

ΔT	Increase in temperature
Δm	Weight loss
t_f	Durability of flaming
PCS	Calorimetric heat value
FIGRA	Speed of fire
THR_{600s}	Total combustion heat
LFS	Horizontal flame

Material: A single basic material or an uniform distributed mix of basic materials for instance stone, wood, mineral wool with equally distributed binder, polymers.

Homogen product: A product consisting of one single material with the same density and composition throughout the whole product..

Inhomogeneous product: A product that does not fulfil the requirements for a homogeny product. It is a product that has a composition of several constituents,

	spread
SMOGRA	Speed of smoke development
TSP _{600s}	Total smoke production
Fs	Flame spread

important or not.

Table A-6: Euro classes of reaction to fire for floorings

Class	Testing method(s)	Classification criteria	Additional classification
A1_{FL}	EN ISO 1182 (1); and	$\Delta T \leq 30^{\circ}\text{C}$; and $\Delta m \leq 50\%$; and $t_f = 0$ (no continues flames)	-
	EN ISO 1716	$\text{PCS} \leq 2,0 \text{ MJ.kg}^{-1}$ (1); and $\text{PCS} \leq 2,0 \text{ MJ.kg}^{-1}$ (2); and $\text{PCS} \leq 1,4 \text{ MJ.m}^{-2}$ (3); and $\text{PCS} \leq 2,0 \text{ MJ.kg}^{-1}$ (4)	-
A2_{FL}	EN ISO 1182 (1); or	$\Delta T \leq 50^{\circ}\text{C}$; and $\Delta m \leq 50\%$; and $t_f \leq 20\text{s}$	-
	EN ISO 1716; and	$\text{PCS} \leq 3,0 \text{ MJ.kg}^{-1}$ (1); and $\text{PCS} \leq 4,0 \text{ MJ.m}^{-2}$ (2); and $\text{PCS} \leq 4,0 \text{ MJ.m}^{-2}$ (3); and $\text{PCS} \leq 3,0 \text{ MJ.kg}^{-1}$ (4)	-
	EN ISO 9239-1 (5)	Critical heat flow (6) $\geq 8,0 \text{ kW.m}^{-2}$	Smoke production (7)
B_{FL}	EN ISO 9239-1 (5) and	Critical heat flow (6) $\geq 8,0 \text{ kW.m}^{-2}$	Smoke production (7)
	EN ISO 11925-2 (8) : Time of exposure = 15s	$F_s \leq 150\text{mm}$ within 20s	-
C_{FL}	EN ISO 9239-1 (5) and	Critical heat flow (6) $\geq 4,5 \text{ kW.m}^{-2}$	Smoke production (7)
	EN ISO 11925-2 (8) : Time of exposure = 15s	$F_s \leq 150\text{mm}$ within 20s	-
D_{FL}	EN ISO 9239-1 (5) and	Critical heat flow (6) $\geq 3,0 \text{ kW.m}^{-2}$	Smoke production (7)
	EN ISO 11925-2 (8): Time of exposure = 15s	$F_s \leq 150\text{mm}$ within 20s	-
E_{FL}	EN ISO 11925-2 (8):	$F_s \leq 150\text{mm}$ within 20s	-

	<i>Time of exposure = 15s</i>		
F_{FL}		No performance determined	

- (1) For homogenous products and important constituents of inhomogeneous products
- (2) For all non important outer constituents in inhomogeneous products
- (3) For all non important inner constituents in inhomogeneous products
- (4) For the product as a unit
- (5) Durability of testing = 30 minutes
- (6) Critical heat flow is defined as the lowest value of heat flow where flames extinguish or the heat flow after a testing 30 min meaning the heat flow that contribute to the largest spread of flames.
- (7) **s1** = Smoke emissions ≤ 750 %.min; **s2** = not s1
- (8) In those cases the flame is applied at the surface and, if applicable, to the field of application for the product in those cases the flame is applied to the edge.

Appendix 5

ANNEX 7
(Ref. § 7.3)

**OSPAR CONVENTION FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF
THE NORTHEAST ATLANTIC**

MEETING OF THE OSPAR COMMISSION (OSPAR)

REYKJAVIK: 28 JUNE – 1 JULY 2004

OSPAR List of Chemicals for Priority Action (Update 2004)

(Reference number 2004-12)

Type	Group of substances / substances	CAS No	EINECS No	Identified at †: Lead country: Background document
A: CHEMICALS WHERE A BACKGROUND DOCUMENT HAS BEEN OR IS BEING PREPARED				
<i>Aromatic hydrocarbon</i>	4-tert-butyltoluene	98-51-1	202-675-9	OSPAR 2000: Germany: Published 2003 (ISBN 1-904426-09-3)
<i>Metallic compound</i>	cadmium			OSPAR/MMC 1998: Spain: Published 2002 (ISBN: 0 946956 93 6)
<i>Metal/organometallic compounds</i>	lead and organic lead compounds			OSPAR/MMC 1998: Norway: Published 2002 (ISBN 1-904426-00-X)
	mercury and organic mercury compounds			OSPAR/MMC 1998: United Kingdom: Published 2000 (ISBN: 0 946956 54 5)
<i>Organometallic compounds</i>	organic tin compounds *			OSPAR/MMC 1998: The Netherlands: Published 2000 (ISBN: 0 946956 56 1) addressing TBT and TPT
<i>Organic ester</i>	neodecanoic acid, ethenyl ester	51000-52-3	256-905-8	OSPAR 2001: United Kingdom
<i>Organohalogens</i>	perfluorooctanyl sulphonic acid and its salts (PFOS) *	1763-23-1	217-179-8	OSPAR 2003: United Kingdom
	tetrabromobisphenol A (TBBP-A)	79-94-7	201-236-9	OSPAR 2000: United Kingdom: Published 2004 (ISBN: 1-904426-39-5)
	hexachlorocyclopentadiene (HCCP) *	77-47-4	201-029-3	OSPAR 2000: The Netherlands: Published 2004 (ISBN: 1-904426-40-9)
	1,2,3-trichlorobenzene	87-61-6	201-757-1	OSPAR 2000: Belgium & Luxembourg: Published 2003 (ISBN 1-904426-10-7)
	1,2,4-trichlorobenzene	120-82-1	204-428-0	OSPAR 2000: Belgium & Luxembourg: Published 2003 (ISBN 1-904426-10-7)
	1,3,5-trichlorobenzene	108-70-3	203-608-6	OSPAR 2000: Belgium & Luxembourg: Published 2003 (ISBN 1-904426-10-7)
	brominated flame retardants			OSPAR/MMC 1998: Sweden: Published in 2001 (ISBN: 0 946956 70 7) addressing: polybrominated diphenylethers; polybrominated biphenyls; hexabromocyclododecane
	polychlorinated biphenyls (PCBs) *			OSPAR/MMC 1998: Germany & Belgium: Published 2001 (ISBN: 0 946956 78 2)
	polychlorinated dibenzodioxins (PCDDs)			OSPAR/MMC 1998: Denmark & Belgium: Published 2002 (ISBN: 0 946956 92 8)
	polychlorinated dibenzofurans (PCDFs)			
	short chained chlorinated paraffins (SCCP)			OSPAR/MMC 1998: Sweden: Published 2001 (ISBN: 0 946956 77 4)
<i>Organic nitrogen compound</i>	4-(dimethylbutylamino)diphenylamin (6PPD)	793-24-8	212-344-0	OSPAR 2002: Germany
<i>Organophosphate</i>	triphenyl phosphine	603-35-0	210-036-0	OSPAR 2001: Germany: Published 2003 (ISBN 1-904426-13-1)

<i>Type</i>	Group of substances / substances	CAS No	EINECS No	Identified at †: Lead country: Background document
<i>Organosilicane</i>	hexamethyldisiloxane (HMDS)	107-46-0	203-492-7	OSPAR 2000: France: Published 2004 (ISBN: 1-904426-41-7)
Pesticides/Biocides/ Organohalogenes	dicofof	115-32-2	204-082-0	OSPAR 2000: Finland: Published 2002 (ISBN: 0 946956 97 9)
	endosulphan	115-29-7	204-079-4	OSPAR 2000: Germany: Published 2002 (ISBN: 0 946956 98 7)
<i>Pharmaceutical</i>	hexachlorocyclohexane isomers (HCH)			OSPAR/MMC 1998: Germany: Published 2002 (ISBN: 0 946956 94 4)
	methoxychlor	72-43-5	200-779-9	OSPAR 2000: Finland: Published 2002 (ISBN: 0 946956 99 5)
	pentachlorophenol (PCP)			OSPAR/MMC 1998: Finland: Published 2001 (ISBN: 0 946956 74 X)
	trifluralin	1582-09-8	216-428-8	OSPAR 2002: Germany: Published 2004 (ISBN: 1-904426-37-9)
	clotrimazole	23593-75-1	245-764-8	OSPAR 2002: France: Published 2004 (ISBN: 1-904426-38-7)
<i>Phenols</i>	2,4,6-tri-tert-butylphenol	732-26-3	211-989-5	OSPAR 2000: United Kingdom: Published 2003 (ISBN 1-904426-14-X)
	nonylphenol/ethoxylates (NP/NPEs) and related substances			OSPAR/MMC 1998: Sweden: Published 2001 (ISBN: 0 946956 79 0)
<i>Phthalate esters</i>	octylphenol	140-66-9	205-426-2	OSPAR 2000: United Kingdom: Published 2003 (ISBN 1-904426-15-8)
	certain phthalates: dibutylphthalate, diethylhexylphthalate			OSPAR/MMC 1998: Denmark & France
<i>Polycyclic aromatic compounds</i>	polyaromatic hydrocarbons (PAHs) §			OSPAR/MMC 1998: Norway: Published 2001 (ISBN: 0 946956 73 X)
<i>Synthetic musk</i>	musk xylene			OSPAR/MMC 1998: Switzerland: Published 2000 (ISBN: 0 946956 55 3) addressing musk xylene, musk ketone, moskene and musk tibetene. Revised Background Document: Published 2004 (ISBN: 1-904426-36-0)

<i>Type</i>	Group of substances / substances	CAS No	EINECS No	Identified at †: Lead country: Background document
B: CHEMICALS WHERE NO BACKGROUND DOCUMENT IS BEING PREPARED BECAUSE THEY ARE INTERMEDIATES IN CLOSED SYSTEMS ‡	Aliphatic hydrocarbons			
	1,5,9 cyclododecatriene ‡	4904-61-4	225-533-8	OSPAR 2002: not applicable
C: CHEMICALS WHERE NO BACKGROUND DOCUMENT IS BEING PREPARED BECAUSE THERE IS NO CURRENT PRODUCTION OR USE INTEREST*	cyclododecane ‡	294-62-2	206-033-9	OSPAR 2002: not applicable
	Organohalogenes			
	2-propenoic acid, (pentabromo)methyl ester	59447-55-1	261-767-7	OSPAR 2003: not applicable

<i>Type</i>	Group of substances / substances	CAS No	EINECS No	Identified at †: Lead country: Background document
	2,4,6-bromophenyl 1-(2,3-dibromo-2-methylpropyl) *	36065-30-2	252-859-8	OSPAR 2001: not applicable
	pentabromoethylbenzene*	85-22-3	201-593-0	OSPAR 2001: not applicable
	heptachloronorbornene*	28680-45-7 2440-02-0	249-153-7	OSPAR 2001: not applicable
	pentachloroanisole*	1825-21-4	-	OSPAR 2001: not applicable

<i>Type</i>	Group of substances / substances	CAS No	EINECS No	Identified at †: Lead country: Background document
<i>Organohalogenes (cont.)</i>	polychlorinated naphthalenes* ††			
	trichloronaphthalene*	1321-65-9	215-321-3	OSPAR 2001: not applicable
	tetrachloronaphthalene*	1335-88-2	215-642-9	OSPAR 2001: not applicable
	pentachloronaphthalene*	1321-64-8	215-320-8	OSPAR 2002: not applicable
	hexachloronaphthalene*	1335-87-1	215-641-3	OSPAR 2001: not applicable
	heptachloronaphthalene*	32241-08-0	250-969-0	OSPAR 2001: not applicable
	octachloronaphthalene*	2234-13-1	218-778-7	OSPAR 2001: not applicable
	naphthalene, chloro derivs.*	70776-03-3	274-864-4	OSPAR 2002: not applicable
	3,3'-(ureylenedimethylene)bis(3,5,5-trimethylcyclohexyl) diisocyanate*	55525-54-7	259-695-6	OSPAR 2001: not applicable
	<i>Pesticides/Biocides</i>	ethyl O-(p-nitrophenyl) phenyl phosphonothionate (EPN)*	2104-64-5	218-276-8
flucythrinate*		70124-77-5	274-322-7	OSPAR 2001: not applicable
isodrin*		465-73-6	207-366-2	OSPAR 2001: not applicable
tetrasul*		2227-13-6	218-761-4	OSPAR 2001: not applicable
diosgenin*		512-04-9	208-134-3	OSPAR 2002: not applicable
<i>Pharmaceutical</i>				

Endnotes

† The substances in this list were identified at the following OSPAR Commission meetings: OSPAR/MMC 1998: Agreement reference number 1998-16 (Annex 2 to the OSPAR Strategy with regard to Hazardous Substances);

(Note: When identifying the substances or groups of substances, OSPAR/MMC 1998 has not allocated CAS and EINECS registration numbers. Background documents adopted by the OSPAR Commission for these substances or groups of substances may indicate which substances have been addressed so far by OSPAR)

OSPAR 2000: Agreement reference number 2000-10;

OSPAR 2001: Agreement reference number 2001-2;

OSPAR 2002: Agreement reference number 2002-18;

OSPAR 2003: Agreement reference number 2003-19.

‡ The identification of these substances and the consequent action required is explained in § 7.6 of the OSPAR 2002 Summary Record. In brief, these substances have rankings in terms of persistency, liability to bioaccumulate and toxicity which are of equal concern as the other substances on this list. However, to the best of OSPAR's knowledge, on the basis of information from industry, OSPAR accepts that this substance is produced and used exclusively as an intermediate in closed systems in the production of other substances, under conditions where the safeguards applying are sufficient to avoid reasonable concerns that discharges, emissions or losses of the substance could reach the marine environment. Therefore, every five years, commencing in 2003, Contracting Parties and, where appropriate, observers representing the chemicals industries should report to OSPAR:

- a. whether they have found any evidence that these chemicals are being produced, used or discharged without being subjected to safeguards to avoid reasonable concerns that discharges, emissions or losses of the substances could reach the marine environment, and, if so, what that evidence is, and what action (if any) has been taken;
- b. whether there have been any cases where applications have been made for approvals involving these chemicals, and, if so, what decision was taken.

* The identification of these substances and the consequent action required is explained in § 4.13 of the OSPAR 2001 Summary Record. In brief, these substances have rankings in terms of persistency, liability to bioaccumulate and toxicity which are of equal concern as the other substances on this list. However, to the best of OSPAR's knowledge, there is no current production or use in the OSPAR states. Therefore, commencing in 2003 and every five years thereafter, or earlier, if information becomes available, Contracting Parties and, where appropriate, observers representing the chemicals industries should report to OSPAR:

- a. whether they have found any evidence that these chemicals are being produced, used or discharged, and, if so, what that evidence is, and what action (if any) has been taken; whether there have been any cases where applications have been made for approvals involving these chemicals, and, if so, what decision was taken.

†† Polychlorinated naphthalenes should be treated as a group of substances (OSPAR 02/21/1, § 7.7).

◆ PFOS is the highly persistent and toxic breakdown product of a number of perfluorooctanyl sulphonyl compounds. Several PFOS precursors have been selected on the OSPAR List of Substances of Possible Concern. The background document will identify these precursors and, if necessary, appropriate control measures will be proposed. CAS and EINECS numbers refer only to the acid form of PFOS.

§ The following substances belonging to the group of polyaromatic hydrocarbons have been deselected from the OSPAR List of Substances of Possible Concern on the grounds that they do not meet the cut-off values for persistence in the Selection Criteria used in the Initial Selection Procedure adopted by OSPAR 2001 (Reference Number: 2001-1) and are therefore not considered to be a priority for action by OSPAR: naphthalene, 2-methyl- (CAS No. 91576); 1-phenanthrenecarboxylic acid, 1,2,3,4,4a,4b,5,6,10,10a-decahydro-1,4a-dimethyl-7-(1-methylethyl)-

, methyl ester, [1R-(1.alpha.,4a.beta.,4b.alpha.,10a.alpha.)]- (CAS No. 127253); 1-phenanthrenemethanol, 1,2,3,4,4a,4b,5,6,7,9,10,10a-dodecahydro-1,4a-dimethyl-7-(1-methylethyl)- (CAS No. 127366); 7H-dibenzo[c,g]carbazole (CAS No. 194592); 13H-dibenzo[a,i]carbazole (CAS No. 239645); 1H-3a,7-methanoazulene, 2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl-, [3R-(3.alpha.,3.alpha.,7.beta.,8.alpha.)]- (CAS No. 469614); 1-phenanthrenemethanol, 1,2,3,4,4a,4b,5,6,10,10a-decahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,4b.alpha.,10a.alpha.)]- (CAS No. 666842); cedrene- (CAS No. 11028425); 1-phenanthrenemethanol, tetradecahydro-1,4a-dimethyl-7-(1-methylethyl)- (CAS No. 13393936); 1-phenanthrenecarboxylic acid, tetradecahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1.alpha.,4.alpha.,4.alpha.)]- (CAS No. 19941287).

♣ The following substance belonging to the group of organic tin compounds has been deselected from the OSPAR List of Substances of Possible Concern on the grounds that it does not meet the cut-off value for persistence in the Selection Criteria used in the Initial Selection Procedure adopted by OSPAR 2001 (Reference Number: 2001-1) and is therefore not considered to be a priority for action by OSPAR: stannane, tributyl(1-oxododecyl)oxy- (CAS No. 3090366).

♠ The following substance belonging to the group of polychlorinated biphenyls has been deselected from the OSPAR List of Substances of Possible Concern on the grounds that it does not meet the cut-off value for persistence in the Selection Criteria used in the Initial Selection Procedure adopted by OSPAR 2001 (Reference Number: 2001-1) and is therefore and is therefore not considered to be a priority for action by OSPAR: 1,1'-biphenyl, 4,4'-dichloro- (CAS No. 2050682).

♥ The OSPAR Background Document on Hexachlorocyclopentadiene adopted by OSPAR 2004 indicates that HCCP does not meet the cut-off values for persistence and bioaccumulation in the Selection Criteria Used in the Initial Selection Procedure adopted by OSPAR 2001 (Reference Number: 2001-1) and does not fulfil the bioaccumulation criterion in the EC Technical Guidance Document. A decision on whether to delete HCCP from the OSPAR List of Chemicals for Priority Action will await the finalisation of the risk assessment report under EU Council Regulation (EEC) 793/93.



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