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Geneva, 13–17 October 2008
Item 8 (b) of the provisional agenda*

Consideration of recommendations to the Conference of the Parties

Guidance on flame-retardant alternatives to pentabromodiphenyl ether (PentaBDE)

Note by the Secretariat

1. At its third meeting, the Committee suggested that the risk management evaluation of pentabromodiphenyl ether should include guidance on alternatives and Ms. Liselott Säll (Norway) and Mr. Bo Wahlström (Sweden) offered to make an initial effort to prepare guidance for commercial pentabromodiphenyl ether.[1]

2. Accordingly, the Secretariat entrusted Ms. Säll and Mr. Wahlström with the preparation of the document providing guidance on flame-retardant alternatives to pentabromodiphenyl ether (PentaBDE). The document is contained in the annex to the present note as submitted and has not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.4/1.

1 UNEP/POPS/POPRC.3/20, para 47.

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Annex

Guidance on flame-retardant alternatives to pentabromodiphenyl ether (PentaBDE)

Preface

Comment [J1]: Should this preface reflect further work in the Alternatives Working Group of the POPRC?

In 2005 Norway nominated the brominated flame retardant pentabromodiphenylether (PentaBDE) as a persistant organic pollutant (POP) to be evaluated for inclusion in the Stockholm convention. Based on the Risk Profile developed in 2006 and the Risk Management Evaluation Report developed in 2007 the POP Review Committee (POPRC) concluded that global action on PentaBDE is warranted. At the POPRC meeting in November 2007 Norway was commissioned to issue a guide of alternative flame retardants to PentaBDE. The Norwegian Pollution Control Authority (SFT) has therefore commissioned Swerea IVF (Sweden), to perform this guide that will be presented to the POPRC-meeting in Geneva in October 2008.

SFT, Oslo, June 2008

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Comment [J2]: This guidance document focuses on drop-in chemical solutions. However, alternatives to PentaBDE also include non-chemical alternatives such as barrier technologies,. These are listed in the pentaBDE Risk Management Evaluation and should be part of any product that emerges from the Alternatives Working Group.

In addition, alternatives include durable inherent flame-retardant materials. These are listed in Table 3.4 in UNEP / POPs / POPRC.3 / INF/23 the "Other Information" document. Ironically, the data in Table 3.4 come from the Norwegian EPA and should also be present in this document.

Summary

Flame retardants **resist the spread of fire and include chemical additives and non-chemical techniques.** ~~represent a large group of~~**Flame retardant** chemicals ~~that~~ mainly consist of inorganic and organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides. They are either additive or reactive. **Non-chemical techniques such as design changes can eliminate the need for flame retardants.**

Comment [J3]: Flame retardancy is not limited to chemicals but also include non-chemical alternatives and techniques.

Reactive flame-retardants are added during the polymerisation process and become an integral part of the polymer and forms a co-polymer. The result is a modified polymer with flame retardant properties and different molecule structure compared to the original polymer molecule.

Additive flame-retardants are incorporated into the polymer prior to, during, or more frequently after polymerisation. Additive flame-retardants are monomer molecules that are not chemically bo~~u~~nded to the polymer. They may therefore, in contrast to reactive flame retardants, be released from the polymer **during normal use** and thereby also discharged to the environment.

Non-chemical techniques such as design changes or barrier technologies can also provide fire resistance. Some manufacturers have re-designed products to eliminate flammable materials such as filling material in furniture. Barrier technologies have the widest commercial applicability and involve layers of materials that provide fire resistance.

In contrast to most additives, **chemical** flame-retardants can appreciably impair the properties of polymers. The basic problem is the trade-off between the decrease in performance of the polymer caused by the flame-retardant and the fire **retardancy** requirements. In addition to fulfilling the appropriate mandatory fire requirements and rules, a feasible flame-retardant shall, at most, fulfil the whole range of physical, mechanical, health and environmental properties and simultaneously be cost efficient for the market.

Halogenated flame-retardants are primarily based on chlorine and bromine. A large group of additive flame-retardant**s** is the polybrominated diphenylethers (PBDEs), which include all congeners of commercial pentaBDE (C-PentaBDE). PBDEs are used in many different applications worldwide, and have the second highest production volume of brominated flame retardants currently used (today mainly represented by decabromodiphenylether).

C-PentaBDE has been produced in Israel, Japan, US and the EU, but production in these regions ceased in the beginning of this millenium. There are indicative reports of an expanding production of brominated flame retardants in China. No official information is available for production of C-PentaBDE in China **and**~~,~~ this is also the case for Israel and Eastern European countries outside **the** EU.

PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 ~~up to~~ - -30% by weight. The main historic use of C-PentaBDE was in flexible polyurethane foam (PUR), but it has also been used in epoxy resins, PVC, unsaturated thermoset polyesters (UPE), rubber, paints and lacquers, textiles and hydraulic oils. The quantities used for each specific application are not publicly available.

Like any other additives, a flame retardant will be selected for the particular properties it imparts to make the final product satisfy the specifications established by the customer. New flame retardant solutions are constantly introduced and some disappear from the market for a number of reasons. However, there is a variety of optional chemical **and non-chemical** systems available on the market that actually work as alternatives to C-PentaBDE. Their use in commercial applications are illustrated in table 4, and their environmental and health properties are described in table 7 in this report. However, it needs to be clearly understood that each flame retardant application is specific and unique and there are no single universal solutions for fire protection of materials and applications.

Even though there are toxicological and ecotoxicological data gaps for the potential alternatives to C-PentaBDE, the data available clearly show that there are commercially available alternative **chemical** flame retardants **and non-chemical alternatives** that are less hazardous than C-PentaBDE. **Given the range of alternative flame retardants available, a wise course would be to examine the manufacturing processes, evaluate the use of synthetic materials, and give preference to those that pose the least risk.**~~It is important to search for further health and environmental data on a sound scientific basis for potential~~

~~alternative flame retardants and avoid those flame retardants that may pose any risk to health and the environment.~~

1. Introduction

1.1 Flame retardants

With the increasing use of thermoplastics and thermo sets on a large scale for applications in buildings, transportation, electrical engineering and electronics, a variety of flame-retardant systems have been developed over the past 40 years. They mainly consist of inorganic and organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides. **More recently, a variety of non-chemical techniques for flame retardation have been developed and implemented.** Today, these flame-retardant systems fulfil the multiple flammability requirements developed for the above-mentioned applications (EHC 1921997).

Chemical f Flame-retardants are either additive or reactive. Reactive flame-retardants are added during the polymerisation process and become an integral part of the polymer and forms a co-polymer. The result is a modified polymer with flame retardant properties and different molecule structure compared to the original polymer molecule. This prevents them from leaving the polymer and keeps the flame retardant properties intact over time with very low emissions to the environment (Danish EPA 1999). Reactive flame-retardants are mainly used in thermosets, especially polyester, epoxy resins and polyurethane's (PUR) in which they can be easily incorporated (Posner 2006).

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 monomer molecules that are not chemically bound to the polymer. They may therefore be released from the polymer and thereby also discharged to the environment.

1.2 Categories of flame retardants

Chemical f 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 chemical flame retardant substances are described in literature, with no specific reference to national or international fire regulations. Such a reference would strengthen the case for the use of the particular substance, for any specific market.

The Index of Flame retardants 1997, an international guide, contains more than 1000 **chemical** flame retardant products (preparations and substances) listed by trade name, chemical name, application and manufacturer. This index describes around 200 flame retardant substances used in commercial flame retardant products.

There are four main families of flame retardant chemicals **and several types of design changes that can provide fire resistance**.

- Inorganic
- Organophosphorous
- Nitrogen based
- Halogenated flame retardants
- **Barrier technologies**

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Inorganic flame-retardants are metal hydroxides (such as aluminium hydroxide and magnesium hydroxide), ammonium polyphosphate, boron salts, inorganic antimony, tin, zinc and molybdenum compounds, and elemental red phosphorous. Both aluminium hydroxide, also sometimes called aluminium trihydrate (ATH), and magnesium hydroxide are used as halogen free alternatives to brominated flame retardants and they also function as smoke suppressants. Inorganic phosphorus compounds are widely used as substitutes to brominated flame retardants. 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 primarily used as synergists in combination with halogenated flame-retardants. Alternative synergists include zinc hydroxystannate (ZHS), zinc stannate (ZS), and certain molybdenum compounds. 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 of the total global production. This category is widely used both in polymers and textile cellulose fibres. Of the halogen-free organophosphorous flame-retardants in particular, triaryl phosphates (with three benzene rings attached to a phosphorous group) are used as alternatives to brominated flame-retardants. Organophosphorous flame-retardants may in some cases also contain bromine or chlorine.

Nitrogen based organic flame-retardants inhibit the formation of flammable gases and are primarily used in polymers containing nitrogen such as polyurethane and polyamide. The most important nitrogen-based flame-retardants are melamine~~'s~~ and melamine derivatives and these 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 polybrominated diphenylethers (PBDEs) are included in this group, where all the isomers of PentaBDE are represented. The group of halogenated flame-retardants represent around 30% by volume of the global production, where the brominated flame-retardants dominate the international market (SRI Consulting 2005).

Halogenated flame-retardants can be divided into three classes:

- ***Aromatic***, including PBDEs in general and PentaBDE in particular.
- ***Cycloaliphatic,*** including hexabromocyclododecane (HBCDD).
- ***Aliphatic***, globally representing a minor group of substances.

***Barrier technolgies* have the widest immediate commercial applicability and involve layers of materials that provide fire resistance. These include boric acid-treated cotton materials used in mattresses; blends of natural and synthetic fibers used in furniture and mattresses (VISIL, Basofil, Polybenzimidazole, KEVLAR, NOMEX and fiberglass); and high performance synthetic materials used in firefighter uniforms and space suits.**

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2. Requirements for feasible flame retardants

2.1 Fire requirements

Tightened legislation and tougher fire requirements are the major forces that have driven ~~forward development towards functionally better and more effective~~**increased use of chemical** flame retardants. **However, concerns over the toxicity of chemical flame retardants have also driven the development of less toxic alternatives and design changes that provide fire resistance without the addition of chemical substances**. ~~In the light of this trend, a~~**A** large number of specific fire standards with unique fire requirements have been developed internationally for various widely differing situations. Customer's requirements are absolute, whether they are public institutions, international organisations or businesses on the market. If the fire requirements are not met, there is no market for the individual supplier and the manufacturer. On the other hand, ***there are no prescriptive fire requirements at all stipulating that particular flame retardants have to be used to meet the requirements. The choice of flame retardants is left entirely to the manufacturer of the final product.***

Comment [J4]: The tobacco industry has also been a major force in pushing for flammability standards in furniture to avoid regulation of its own products. For example see this Washington Post article: http://www.washingtonpost.com/wp-dyn/content/article/2008/01/25/AR2008012503170_2.html?sub=AR

Comment [J5]: For example see Science (2007) 318: 194 – 196, The Fire Retardant Dilemma

In some cases the requirements are so strict that the alternatives are not economically feasible or the environmental requirements or regulations in that part of the world do not make the manufacturers choice of flame retardants possible to apply. Worse quality characteristics may also be limiting factors in the manufacturer's choice of flame retardants (Posner 2005).

2.2 Quality properties on fire retarded materials

In contrast to most additives, **chemical** flame-retardants can appreciably impair the properties of polymers. The basic problem is the trade-off between the decrease of performance of the polymer caused by the flame-retardant and the fire requirements. In addition to fulfilling the appropriate mandatory fire requirements and rules, a feasible flame-retardant shall, at most, fulfil all of the qualities mentioned below.

Fire retardant properties

- Commence thermal activity before and during the thermal decomposition of the polymer
- Not generate any toxic gases beyond those produced by the degrading polymer itself
- Not increase the smoke density of the burning polymer

Mechanical properties

Comment [J6]: Should extractability for recyclability be part of this list somewhere?

- Not significantly alter the mechanical properties of the polymer
- Be easy to incorporate into the host polymer
- Be compatible with the host polymer

Physical properties

- Be colourless or at least non-discolouring
- Have good light stability
- Be resistant towards ageing and hydrolysis
- Not cause corrosion

Health and envrionmental properties

- Not have harmful health effects
- Not have harmful environmental properties

Commercial viability

- Be commercially available and cost efficient

3. Characteristics of C-PentaBDE

Brominated diphenylethers (PBDEs) are a large group of additive brominated flame retardants with a versatile use in many applications worldwide. PBDEs are the second highest production group of brominated flame retardants currently used, mainly represented today by the fully brominated ~~decabromodiphenylether~~**Decabromodiphenylether (decaBDE)**.

Commercial pentabromodiphenylether (C-PentaBDE) is a mixture of two major congeners i.e. 2,2`,4,4´´tetrabromodiphenylether (BDE-47), and 2,2´,4,4´,5-pentabromodiphenylether (BDE-99). Trace amounts of 2,2´,4-tri-bromodiphenylether (BDE-17) and 2,4,4´-trisbromodiphenylether (BDE-28) are also present in C-PentaBDE. Both BDE-17 and BDE-28 are precursors in the formation of major congeners in C-PentaBDE such as BDE-47.

Comment [J7]: Do you want to say synthetic precursors?

Continued bromination of BDE-47 yields mainly BDE-99 and 2,2´,4,4´,6-pentabromodiphenylether (BDE-100). Percentages of BDE-99 and BDE-100 are 35% and around 7% respectively. Further bromination yields 2,2´,4,4´,5,5´-hexabromodiphenylether (BDE-153) and 2,2´,3,4,4´,5´,6 – heptabromodiphenylether (BDE-154), that are also present in C-PentaBDE (Alaee et. al 2003).

C-PentaBDE is also subject to debromination. Studies of the marine food web in Bohai Bay, North China observed changes in the relative concentrations of BDE-47 and BDE-99 with trophic level (zooplankton to gulls) which led to the conclusion that BDE-99 was biotransformed to BDE-47. In other studies, carp fed with food spiked with BDE congeners debrominated approximately 9.5% of the BDE-99 in the gut to BDE-47. Debromination of both BDE-47 and BDE-99 has also been observed in anaerobic microbes.

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Comment [J8]: Yi Wan, Jianying Hu, Kun Zhang and Lihui An (2008), 'Trophodynamics of Polybrominated Diphenyl Ethers in the Marine Food Web of Bohai Bay, North China', *Environ. Sci. Technol*., 42: 1078-1083

Comment [J9]: Stapleton, H.M., Letcher, R.J. and Baker, J.E. (2004), 'Debrominated Diphenyl Ether Congeners BDE 99 and BDE 183 in the Intestinal Tract of the Common Carp (*Cyprinus carpio*)', *Environ. Sci. Technol*. 38: 1054-1061

Comment [J10]: Robrock KR, Korytar P, Alvarez-Cohen L (2008), 'Pathways for the anaerobic microbial debromination of polybrominated diphenyl ethers', Environ Sci Technol 42: 2845 - 2852

Table 1 Composition of C-PentaBDE.

Categories of PBDEs	~~Tridiphenyl~~**TriBDE** ethers		~~Tetradiphenyl~~**TetraBDE** ether	~~Pentadiphenyl~~**PentaBDE** ethers		~~Hexadiphenyl~~**HexaBDE** ether	~~Heptadiphen~~**ptaBDE** ether
Congeners	**BDE-17**	**BDE-28**	**BDE-47**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**
Content	Traces	Traces	Major	Major	Minor	Minor	Traces

PentaBDE is widespread in the global environment. Levels of components of C-PentaBDE have been found in humans in all UN regions. Most trend analyses show a rapid increase in concentrations of PentaBDE in the environment and in humans from the early 1970s to the middle or end of the 1990s, reaching plateau levels in some regions in the late 1990s, but continuing to increase in others. The levels in North America and the Arctic are still rising. Vulnerable ecosystems and species are affected, among them several endangered species. Some individuals of endangered species show levels high enough to be of concern. Toxicological studies have demonstrated reproductive toxicity, neurodevelopmental toxicity and effects on thyroid hormones in aquatic organisms and in mammals. The potential for the toxic effects in wildlife, including mammals, is evident.

Based on the information in the risk profile, PentaBDE, due to the characteristics of its components, is likely, as a result of long-range environmental transport and demonstrated toxicity in a range of non-human species, to cause significant adverse effects on human health or the environment, such that global action is warranted.

Comment [J11]: This should reference the POPRC decision and Risk Profile document

4. Commercial use and production of PentaBDE

4.1 Historic production of PentaBDE

Based on the latest available information from Bromine Science and Environmental Forum (BSEF), the total market demand of C-PentaBDE has decreased from 8,500 tons in 1999 to 7,500 tons in 2001. The estimated cumulative use of C-PentaBDE since 1970 was in 2001 estimated to 100 000 t (BSEF 2001),(UNEP/POPS/POPRC.3/20/Add1 2007).

Table 2 C-PentaBDE volume estimates: Total market demand by region in 2001 in metric tons (and by percent) (BSEF 2001).

	Americas	**Europe**	**Asia**	**Rest of the world**	**Total**	**% of total world usage of BFR**
Penta-mix PBDE formulation	7100	150	150	100	7500	4

C-PentaBDE has been produced in Israel, Japan, US and the EU. Today there is no production in Japan and C-PentaBDE was voluntarily withdrawn from the Japanese market in 1990 (UNECE 2007). There is no offical information available from Israel of any present production or use of PentaBDE.

The sole producer of C-PentaBDE in the US, the Great Lakes Chemical Corporation (now Chemtura), voluntary ended their production of C-PentaBDE by 1st of January 2005[2]. Before the phase-out in US the majority of C-PentaBDE formulation produced globally was used in North America (>97%). At the end of

[2] Landry S Albermarle, personal communication (2008)

2004, in the US, approximately 7.5% of the more than 1 million tonnes of flexible polyurethane foam produced each year in the US contained the C-PentaBDE formulation (UNECE 2007).

Production in the EU ceased in 1997. Usage in EU ha**d**~~s~~ been declining during the second half of the 1990´s and was estimated to be 300 metric tonnes in year 2000, used solely for PUR production (EU 2000). The use of C-PentaBDE was banned in the EU in 2004 through the restrictions on marketing and the use of dangerous substances in the Council directive 2003/11/EC. From 1st of July 2006 PentaBDE was restricted in electrical and electronic appliances through the RoHS –directive [2002/95/EC].

Results from a survey conducted in Canada in 2000 indicated that approximately 1300 tonnes of PBDE commercial products were imported into Canada. Based on quantities reported, C-PentaBDE was imported in the greatest volume. Now PentaBDE is on the list of toxic substances in the Canadian Environmental Protection Act (CEPA 1999).

Investigations through direct contacts with industry and studies of relevant sources information on any historic or present production or use of C-PentaBDE in Eastern European countries outside the EU have been sought, but no information of such activities was found.

4.2 Historic use of PentaBDE

PBDEs are used in different resins, polymers, and substrates at levels ranging from 5~~-up to~~ - 30% by weight. The quantities used for each specific application are not publicly available (USEPA (Dfe) 2004). **PentaBDE has been used mainly in the manufacture of flexible polyurethane (PUR) foam for furniture and upholstery in homes and vehicles, packaging, and to a smaller extent non-foamed PUR in casings and electric and electronic equipment (EE). It has also been used in building materials and textiles.**

Table 3 Historic use of PentaBDE in various materials and applications (EHC 162, 1994), (Danish EPA 1999), (Renner 2000),(UNEP/POPS/POPRC.3/20/Add1).

Materials/polymers/resins	**Applications**	**Commercial commodities for the applications**
Epoxy resins	Circuit boards, protective coatings	Computers, ship interiors, electronic parts.
Polyvinylchloride (PVC)	Cable sheets	Wires, cables, floor mats, industrial sheets.
Polyurethane (PUR)	Cushioning materials, packaging, padding	Furniture, sound insulation packaging, padding panels, wood imitations, transportation.
Unsaturated (Thermoset) polyesters (UPE)	Circuit boards, coatings	Electrical equipment, coatings coatings for chemical processing plants mouldings, military and marine applications: construction panels.
Rubber	Transportation	Conveyor belts, foamed pipes for insulation.
Paints/lacquers	Coatings	Marine and industry lacquers for protection of containers
Textiles	Coatings	Back coatings and impregnation for carpets, automotive seating, furniture in homes and official buildings, aircraft, underground.
Hydraulic oils	Drilling oils, hydraulic fluids	Off shore, coal mining

There is no data available on the proportions of use of C-PentaBDE for the different applications in table 3.

4.3 Present use and trends in production of PentaBDE

Since there should be no current production of C-PentaBDE in Europe, Japan, Canada, Australia and the US, remaining production would be located in other parts of the world. The bromine industry has representation worldwide beside Europe, Japan and North America. ~~Though~~ **Despite** direct personal contacts with the bromine industry, no information was provided of any production or use of C-PentaBDE in Africa, other Asian countries than China and South and Latin America.[3],[4].

China's flame retardant market has seen rapid growth in the last five years aided by favorable economic growth, increasing demand from the end user market, ~~increasing awareness on fire safety issues~~ and numerous other factors. China's flame retardant market is one of the most dymanic flame retardant markets around the world, and establishment and implementation of government regulations and standards are playing an important role in the growth of the market. The current growth levels are expected to continue with more environment**ally**-friendly non-halogenated types driving the growth of the market.

Xu Dan, Industry Analyst for the Chemicals, Materials and Food Group of Frost & Sullivan's Asia Pacific reveals that, "China has increasingly become the global production base for electronic products and the main region for consumption of plastics." She declares, "The increase in demand for E&E equipments, as well as the development of Building & Construction, and Automotive industries is driving the growth of the flame-retardant market in China." (Frost & Sullivan 2007).

In China there are two major global suppliers, and possible producers, of C-PentaBDE that have been identified through the internet. There is no official data available of any possible production of C-PentaBDE in China[5]. However, China has its own RoHS since 2006, where the use of PBDEs in electronics is banned (SJ/T 11363 2006).

Comment [J12]: Maybe a conversation or email exchange with the Chinese delegation would be more appropriate than this personal communication.

Comment [J13]: I believe China ROHS bans the use of pentaBDE and octaBDE but not decaBDE.

5. Alternative flame retardants and alternative technical solutions to PentaBDE

Like any other additives, a flame retardant will be selected for the particular properties it imparts to make it satisfy the specifications for the final compound established by the customer **in compliance with flame retardant regulations**. As mentioned earlier, different flame retardants **or non-chemical alternatives** may be chosen to give different levels of fire protection depending on the specific levels defined by the customer and that particular market. New flame retardant solutions are constantly introduced and some disappear from the market for a number of reasons. Therefore table 4 is a on-the-spot account and cannot be complete, but only act as a guide that illustrates the variety and optional chemical systems that are available and actually work as viable alternatives to C-PentaBDE. However, it needs to be clearly understood that each flame retardant application is specific and unique, and there are no single universal solutions for fire protection of materials and applications.

[3] Dr. Didier, M Trimbos, Eurobrom, personal communication (2008)
[4] Baker A, Dead Sea bromine Ltd, personal communication (2008)
[5] DiGangi J, personal communication (2008)

Table 4 Overview of use of alternative flame retardants to PentaBDE in several materials and applications. (EHC 162 1994), (UNEP/POPS/POPRC.3/INF/23 2007), (KemI 2006), (Timpe 2007), (Haglund 2000), (Troitzsch 2007),(Supresta 2008).

Materials /polymers /resins	**Inorganic alternatives to PentaBDE**	**Phosphorous/ nitrogen organic alternatives to PentaBDE**	**Halogen organic alternatives to PentaBDE**	**Alternative flame inherent materials**	**Applications**	**Commercial commodities for the application**
Epoxy resins	Aluminium hydroxide (ATH) Magnesium hydroxide Ammonium poly phosphate Red phosphorous Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Metallic phosphinates Reactive nitrogen anc phosphorous constituents (unspecified) DOPO[6]	Tetrabromobis phenol A (reactive) Ethylenebis (tetrabromo) phtalimide	Polyethylene sulphide	Circuit boards, protective coatings	Computers, ship interiors, electronic parts.
Polyvinylchloride (PVC)	Aluminium hydroxide (ATH) Zinc borate Zinc-molybdenum compounds (together with phosphate esters) Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Tricresyl phosphate (also plasticizer)	Tris (dichloropropyl) phosphate Vinylbromide	Rigid PVC is flame inherent itself	Cable sheets	Wire end cables, floor mats, industrial sheets.
Polyurethane (PUR)	Ammonium poly phosphate Red phosphorous Reofos (non-halogen flame retardant)	Melamine (nitrogen based) Dimethyl propane phosphonate (DMPP)	Bromoalkyl phosphates Tetrabromophthalic anhydride Tris(chloroethyl) phosphate (TCPP) (together with brominated polyols or red phosphorous)	Intumescent systems	Cushioning materials, packaging, padding	Furniture, sound insulation packaging, padding panels, wood imitations, transportation.

Comment [J14]: Do you mean "retardant"? Inherent does not make sense...

[6] DOPO=Dihydrooxaphosphaphenanthrene oxide

Materials /polymers /resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Unsaturated (Thermoset) polyesters (UPE)	Ammonium polyphosphate Aluminium hydroxide (ATH) Magnesium hydroxide Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Triethyl Phosphate Dimethyl propane phosphonate (DMPP)	Dibromostyrene Tetrabromophthalic anhydride based diol, Tetrabromophtalic anhydride Bis (tribromophenoxy) ethane	Intumescent systems	Circuit boards, coatings	Electrical equipment, coatings coatings for chemical processing plants mouldings, military and marine applications: construction panels.
Rubber	N/A	Alkyl diaryl phosphates (nitrile rubber)	N/A	Intumescent systems	Transportation	Conveyor belts, foamed pipes for insulation.
Paints/lacquers	N/A	Triaryl phosphates (unspecified)	Tetrabromo phthalate diol Tetrabromophthalatic anhydride based diol Bis (tribromophenoxy) ethane	Intumescent systems Silicone rubber	Coatings	Marine and industry lacquers for protection of containers
Textiles	Aluminium hydroxide Magnesium hydroxide Ammonium compounds (unspecified) Borax	Tetrakis hydroxyyimethyl phosphonium salts such as chloride (THCP) or ammonium (THPX) Dimethyl phosphono (N-methylol) propionamide Diguanidine hydrogen phosphate Aromatic phosphates (unspecified)	Trichloropropyl phosphate	Intumescent systems Aramide fibres (certain protective applications) Wool Modacrylic	Coatings	Back coatings and impregnation for carpets, automotive seating, furniture in homes and official buildings, aircraft, underground.

Materials /polymers /resins	Inorganic alternatives to PentaBDE	Phosphorous/ nitrogen organic alternatives to PentaBDE	Halogen organic alternatives to PentaBDE	Alternative flame inherent materials	Applications	Commercial commodities for the applications
Textiles cont.		Dimethyl hydrogen phosphite (DMHP) Melamine (nitrogen based) Phospho nitrilic chloride (PNC)				
Hydraulic oils	N/A	Butylated triphenyl phosphate esters	N/A	N/A	Drilling oils, hydraulic fluids	Off shore, coal mining

N/A : not available or not applicable

6. Present manufacture and use of alternative flame retardants to PentaBDE

6.1 Inorganic flame retardants and synergists

6.1.1 Aluminium hydroxide (ATH)

ATH has been used as a flame retardant and smoke suppressant since the 1960´s and it is available in a variety of particle sizes as commercial products. Flame retardation by ATH has been shown to be partly due to the heat sink effect and partly due to the dilution of combustible gases by the water formed as a result of dehydroxylation. Alumina which is formed as a result of thermal degradation of ATH slightly above 200 °C has been shown to form a heat- insulating barrier on the surface that prevents further fire propagation of the matrix material.

The major concern with ATH is the required high loading levels in order to obtain equivalent flame retardant properties as by other additives. These loads can be reduced with a correct choice of particle size, surface modification and proper dispersion in the matrix material (Swaraj 2001). Furthermore, recently developed coated filler products (e.g. ZHS-coated ATH) offer the possibility of equivalent or better flame retardancy and smoke suppression at significantly reduced incorporation levels.

6.1.2 Magnesium hydroxide

Magnesium hydroxide acts in general the same way as ATH, but it thermally decomposes at slightly higher temperatures around 325 °C. Combinations of ATH and magnesium hydroxide function as very efficient smoke suppressants in PVC.

6.1.3 Red phosphorous

Red phosphorous has been reported to be most efficient as a flame retardant in oxygen containing polymers such as polycarbonate, polyethylene terephatalate (PET), polyamide and phenolic resins. Flame retardancy takes place due to formation of phosphorous-oxygen bonds that reduces the ester cleavage into cross linking aromatic structures with lesser volatility. In addition the red phosphorous creates a heat shield on the polymer surface that result in flame retardant properties. Some drawbacks with the use of red phosphorus are the red colour that could lead to discoloration of polymers and the formation of toxic phosphine gas during combustion **and long-term storage**.

Comment [J15]: Anthony JS, Davis EA, Haley MV, McCaskey DA, Kristovich RL. Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD. Chemical Characterization of the Pyrotechnically Disseminated KM03 Red Phosphorus Floating Smoke Pot. Govt Reports Announcements & Index (GRA&I), Issue 24, 2006

6.1.4 Ammonium polyphosphate (APP)

APP is mainly used as an acid source in intumescent systems, which are described in more detail in chapter 6.4. APP alone as a flame retardant has been found effective in polyamides and similar polymers.

6.1.5 Antimony trioxide

Antimony trioxide does not function as a flame retardant, but in combination with halogenated flame retardants it functions as a synergist. 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. As a synergist, the main advantage by the addition of antimony trioxide is to reduce the amount of halogenated flame retardants applied to the polymer.

6.1.6 Zinc borate

Zinc borate (used mainly in PVC) cannot be used alone to achieve desired flame retardant properties in polymers, since it is used as synergist together with other flame retardants, often brominated compounds.

6.1.7 Zinc hydroxystannate (ZHS) and Zinc stannate (ZS)

ZHS and ZS have primarily found use as alternative non-toxic synergists to antimony trioxide in PVC and other halogen-containing polymer systems. However, they have recently found growing applications in halogen-free formulations, and are particularly effective as partial replacements for hydrated fillers such as ATH and magnesium hydroxide, either in the form of powdered mixtures or as coated fillers (Cusack 2005).

6.2 Organophosphorous flame-retardants

6.2.1 Triethyl phosphate

Triethyl phosphate is either used alone or together with a bromine synergist, such as antimony trioxide, for unsaturated polyester resins. Less volatile types of flame retardants include trialkyl phosphates with longer alkyl chains such as tributyl, trioctyl or tris-butoxyethylphoshates. Several high alkylated phosphorous products are commercially available, which is required in lower added concentrations in the polymer.

6.2.2 Aryl phosphates

This large group of organophosphorous flame retardants include triphenyl, isopropyl – and t-butylsubstituted triaryl and cresyl phosphates. Phosphates with larger substitution carbon chains (therefore less volatile) are commercially available beside those mentioned above.

Aryl phosphates are used as flame retardants for phthalate plasticized PVC. It has been shown that although PVC does not require any flame retardancy as a polymer, the addition of phthalate plasticizers makes PVC flammable. Triaryl phosphates are more efficient flame retardants than the alkylated triaryl phosphates. However, the alkylated triaryl phoshates is shown to be more efficient plasticizers than triaryl phosphates.

6.2.3 Halogen containing phosphorous flame retardants

Several halogen containing phosphates, such as chloro and bromophosphates, are commercially available as shown in table 5 below.

Table 5 Commercial phosphorous organic flame-retardant chemical formulations (UNEP/POPS/POPRC.3/INF/23),(Supresta 2008).

Albemarle Corporation	Ameribrom, Inc. (ICL Industrial Products)	Great Lakes Chemical Corporation (now Chemtura)	Supresta (Akzo Nobel)
SAYTEX® RX-8500 *Proprietary reactive brominated flame retardant, proprietary aryl phosphate, triphenyl phosphate* *CAS 115-86-6*	FR 513 *Tribromoneopentyl alcohol* *CAS 36483-57-5*	Firemaster® 550 *Proprietary halogenated aryl esters, proprietary triaryl phosphate isopropylated, triphenyl phosphate*	Fyrol® FR-2 *Trs(1,3-dichloro-2-propyl) phosphate* *CAS 13674-87-8*
SAYTEX® RZ-243 *Proprietary tetrabromophthalate, proprietary aryl phosphate, triphenyl phosphate*		Firemaster® 552 *Proprietary halogenated aryl esters, proprietary triaryl phosphate isopropylated, triphenyl phosphate*	AB053 *Tris(1,3-dichloro-2-propyl) phosphate*
ANTIBLAZE® 195 *Tris(1,3-dichloro-2-propyl) phosphate* *CAS 13674-87-8*			AC003 *Proprietary organic phosphate ester, triphenyl phosphate*
ANTIBLAZE ® 205 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			AC073 *Proprietary aryl phosphates, triphenyl phosphate*
ANTIBLAZE® 180 *Tris(1,3-dichloro-propyl) phosphate* *CAS 13674-87-8*			Fyrquel 150, Fyrquel 220, and Fyrquel 300 *Butylated triphenyl phosphate esters*
ANTIBLAZE® V-500 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			
ANTIBLAZE® 182 *Proprietary chloroalkyl phosphate, aryl phosphate and triphenyl phosphate*			
ANTIBLAZE®TL10ST (proprietary chlorophosphate) *CAS # propietary mixture*			

Chloro alkyl phosphates have been found effective in flexible polyurethane (PUR) foams, but since they are not stable during curing reactions of PUR, which is a strong exothermic reaction with heat generated, they render discolouring problems. Therefore a blend of PentaBDE and triaryl phosphates was, and may still be, used in flexible PUR to avoid this discoloration problem.

Brominated phosphates have been reported to be effective flame retardants without the use of antimony trioxide as synergist, for polyesters and other polymers, such as HIPS and other polystyrenes that may not be relevant for this report.

6.2.4 Reactive phosphorous flame retardants

Reactive phosphorous polyols, including phosphine oxide diol and triol, have also been reported as useful flame retardants in PUR, PET and epoxy resins. No specified information of their flame retardant effiency in these polymers has been found in this study.

6.3 Nitrogen based organic flame-retardants

Nitrogen containing polymers have been found to be synergetic with phosphorous compounds. For example, polymers containing amine and amide groups were synergistic whereas polymers containing nitrile have been found to be antagonistic. One common example of nitrogen based flame retardants is melamine, which is also a common constituent in intumescent systems.

6.4 Intumescent systems

Intumescent (or swelling) systems have existed since the 1940s, principally in paints. Several intumescent systems linked to textile applications have been on the market for about 20 years, and have successfully shown their great potential. Intumescent systems include use of expandable graphite impregnated foams, surface treatments and barrier technologies of polymer materials.

Almost all intumescent systems comprise, in general, of three basic components

- a dehydrating component, such as APP
- a charring component, such as pentaerythritol (PER)
- a gas source, often a nitrogen component such as melamine

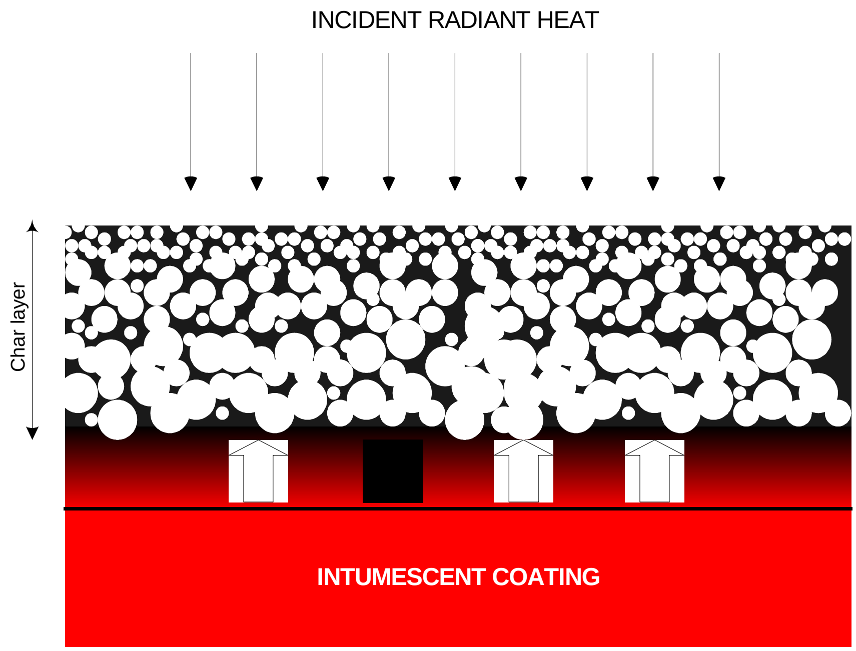

Figure 1 Mechanisms for intumescent systems.

The main function of APP is to catalyse the dehydration reaction of other components in the intumescent system. It has been shown that in spite of the fact that APP functions as a catalyst it has been used in rather large concentrations partly due to its participation in the formation of a char structure. In polyolefin polymers it has been shown that melamine and PER act as synergists to APP.

Other intumescent systems have been applied in polymers such as expandable graphite and silica based and metal hydroxide compounds, some of them incorporated as nanocomposites. Recent research describes extended nanoparticles of clay as promising char-forming fillers for good fire protection. These applications are however still on a research level and wait to become commercial. (Kashiwagi et al. 2005).

Metal complexes such as zinc-molybdenum compounds together with phosphate esters and ATH have been used to effectively increase the char formation for PVC.

Whatever the detailed mechanisms for intumescents systems are, the formation of a thick char layer, high carbon concentration, high viscosity of pyrolyzing melt and low penetration capability for propagation of heat, makes intumescent systems efficient to reduce flammability and the exposure of fume gases (Swaraj 2001), (Posner 2004).

6.5 Halogenated flame retardants

Several types of halogenated flame retardants, mainly brominated flame retardants, are described in the literature which includes compounds belonging to families of polybrominated diphenylethers (PBDEs), where congeners of PentaBDE are a part, tetrabromobisphenol-A (TBBPA), tribromophenol (TBP) and brominated phthalic anhydride. Such use of flame retardant additives depends mainly on the type of polymer to be applied for flame retardancy. Although the use of brominated flame retardants is still growing by around 5% per year, their use is strongly questioned due to their potentially harmful environmental and health characteristics. A number of brominated flame retardants are already restricted in several countries worldwide **and many prominent manufacturers have phased out their use**. Due to further restrictions and public concern against health and environmentally hazardous chemicals, brominated flame retardants have ~~no~~ **a time-limited** future.

7. Historic, present and future consumption of alternative flame retardants to PentaBDE

In general it is very hard to forecast the international market for flame retardants since there are so many market driving forces involved, such as environmental, health and safety regulations, consumer awareness etc., that has a tendency to change rapidly over a limited period of time.

This means that the assumptions made in this chapter are either conservative, meaning that there is a linear approach to the development of the present flame retardants markets, or an innovative approach, meaning that there are incentives to introduce less hazardous flame retardants systems as a result of more stringent regulations and awareness from the public world wide.

Around 90% of the world's production of flame retardants ends up in electronics and plastics, while the remaining 10% ends up in coated fabrics and upholstery furniture and bedding products. In 2004, the production of halogenated flame retardants was equivalent to around 27% of total global production. By then the brominated flame retardants (BFR) constituted around 21% of the total production and use of flame retardants world wide. A further consideration is that the market for plastic in electronic enclosures is growing at around 5% per year (SRI Consulting 2005). With **no deselection, substitution, or regulatory prohibition** ~~a conservative approach~~ the use of BFRs **c**~~w~~ould then grow by around 63% over a 10 year period**.**~~.~~

Table 6 Global consumption of flame retardants and their geographical distribution (SRI Consulting 2005).

Category	United States	Europe	Japan	Other Asia	Total volume [1000 metric tonnes]	Value [million USD]
Aluminium hydroxide	315	235	47	48	645	424
Organo phosphorous FRs	65	95	30	14	205	645
Brominated FRs	66	56	50	139	311	930
Antimony trioxide	33	22	17	44	115	523
Chlorinated FRs	33	35	5	10	82	146
Other FRs	51	47	11	14	123	197
TOTAL	**564**	**489**	**160**	**269**	**1481**	**2865**

The ~~conservative~~ estimated growth of around 63% in demand of BFRs till 2017 w**ould**~~ill~~ lead to a total demand for BFRs round 500-600.000 metric tonnes per year, primilary as the predominant brominated flame retardant substances on the international market today, namely decabromodiphenylether and TBBP-A[7]. **This estimate assumes these substances**

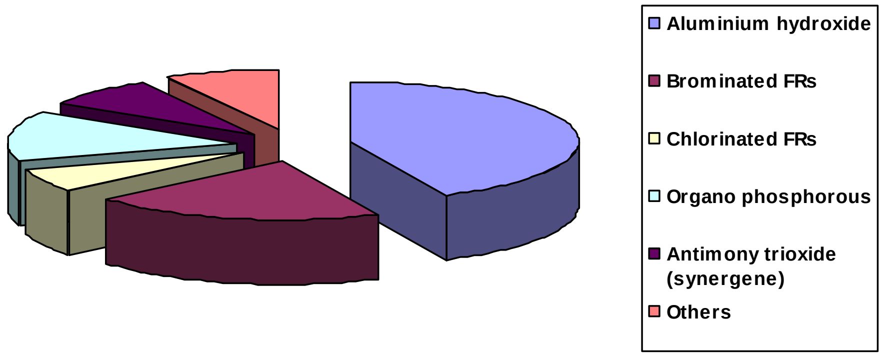

Figure 2 The global market share of groups of flame retardants (SRI Consulting 2005).

With the innovative approach, there will be an introduction of new and innovative specific formulations of less hazardous flame retardant systems **including non-chemical alternatives** that are (or will be) feasible from a commercial and technical point of view, i.e. intumescent systems. These and other less harmful commercial flame retardant systems will balance a conservative market growth of halogenated flame retardants consumption over the coming years.

8. Health and environmental properties of alternative flame retardants to PentaBDE

Since there is a lack of data on health and environmental properties, it is not always possible to perform a comprehensive comparison of all known flame retardant systems described in **the** literature in general and in this report in particular. However, in order to evaluate the toxicity and ecotoxicity of potential alternatives to PentaBDE, the ranking system in table 7 below can be applied.The intention in this report is to present an overall picture of the hazard characteristics as comparable as possible as done in table 7. The system has been used by some US authorities in their recent surveys on alternatives to PBDEs (Illinois EPA 2007), (US EPA 2004).

[7] Kirschner M, personal communication (2008)

Table 7 Health and environmental properties of a range of alternative flame retardants to C-PentaBDE.

Chemical	**Toxicological properties**	**Ecotoxicological properties**	**Comments**
Inorganic flame retardants and synergists			
Aluminium hydroxide	Low concern	Low concern	Ecotox: Few data available
Magnesium hydroxide	Low concern	Low concern	Tox and ecotox: few data available
Red phosphorous	Non toxic in pure form Low concern	Highly flammable and very toxic to aquatic organisms	May form toxic phosphine gas during combustion in combination with moisture
Ammonium poly phosphate	Insufficient data for assessments	Insufficient data for assessments	May be slightly irritating to skin
Zinc borate	High concern on zinc toxicity	High acute aquatic toxicity	Limited tox and ecotox data available
Boron compounds other than zinc borate, *(Borax and disodium tetra borate)*	Moderate concern due to 2-generation reproductive/developmental effects	Limited data available	Limited tox and ecotox data available
Antimony trioxide	Ranked as possible carcinogen by IARC[8] and EU	Low concern	May produce toxic or irritating vapours during combustion conditions
Zinc hydroxystannate & Zinc stannate	Low concern	Low concern	Very low acute toxicity. Very low aqueous solubility
Organophosphorous flame-retardants			
Triethylphosphate	No data available	No data available	
Aryl phosphates	Low concern	A few compounds show high acute aquatic toxicity	
Halogen containing phosphorous compounds	A few compounds show moderate reproductive toxic properties	A few compounds show moderate or high persistence and acute aquatic toxicity	
Tris (2-chloro-1-methylethyl) phosphate (TCPP or TMCP)	Concern	Low concern	Subject to risk assessment in the EU under the 4th Priority List Will be transferred to REACH
Reactive phosphorous	No data available	No data available	
Nitrogen based organic flame-retardants			
Melamine	Low concern	Low concern	Allergic dermatitis has been reported among workers

[8] IARC – **I**nternational **A**gency for **R**esearch on **C**ancer

There are toxicological and ecotoxicological data gaps for the potential alternatives to PentaBDE, but the data available clearly show that there are commercially available alternative flame retardants that are less hazardous than C-PentaBDE.

8bis Assessing alternatives

The Danish alternatives report makes the following conclusions in its assessment of PentaBDE alternatives:
1) Substitutes are available for most applications at relatively low extra cost;
2) Criteria for developing functional flame retardants should include non-hazardous synthetic pathway, minimum human and environmental toxicity, minimum release during product use, minimum formation of hazardous substances during incineration or burning, recyclable, degradable, and decompose into a non hazardous substance;
3) Organophosphorous compounds can be released from products in significant amounts;
4) Inorganic phosphorous compounds are preferable to organophosphorous ones though a more comprehensive assessment is needed;
5) Aluminum hydroxide has desirable minimal toxicity characteristics presumable shared by magnesium hydroxide though no assessment is currently available;
6) High loading may be a disadvantage
7) Zinc borate and melamine may be desirable but require a more comprehensive assessment

The German Alternatives report makes the following conclusions about the various alternatives described above:
1) More data is needed to assess non-halogen phosphoric esters;
2) Melamine is problematic; and
3) "Merely zinc borate, magnesium hydroxide and expandable graphite should not cause any problems when used."

The substitution of alternatives for POPs provokes a deeper question about methods to evaluate and compare the hazards of various substances.

One screening guide focuses on evaluating environmentally preferable flame retardants for TV enclosures by developing and using a "Green Screen". The criteria used by the Green Screen include: hazard endpoints with categories of high, medium, and low; criteria for determining each level of chemical concern; and consideration of degradation products and metabolites. The Screen places a substance into one of four categories: Avoid – very high concern, Use – but search for safer substitutes, Use – but still opportunity for improvement, and Prefer – green chemical.

For an overarching approach to the topic of alternatives assessment, the Lowell Center for Sustainable Production has developed an Alternatives Assessment Framework with the goal of, "Creating an open source framework for the relatively quick assessment of safer and more socially just alternatives to chemicals, materials, and products of concern." The Framework discusses goals, guiding principles, decision making rules, comparative and design assessment, and types of evaluation. Since the Framework is designed to be an open source tool, the Lowell Center encourages companies, NGOs, and governments to use, adapt, and expand on it.

Comment [J16]: I thnk it would be helpful for readers (governments and other stakeholders) of this document to receive some information about how to actually use the information or at least some considerations in how to make decisions about alternatives.

Comment [J17]: Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

Comment [J18]: Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

Comment [J19]: Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals – Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007 http://www.cleanproduction.org/Home.php

Comment [J20]: Rossi M, Tickner J, Geiser K. Alternatives Assessment Framework, Lowell Center for Sustainable Production, Version 1.0, July 2006 http://www.chemicalspolicy.org/downloads/FinalAltsAssess06_000.pdf

9. Example of costs related to substitution of C-PentaBCD in flexible PUR foam

As mentioned earlier, chloro alkyl phosphates are effective and frequently used as flame retardants in flexible polyurethane (PUR) foams as alternatives to C-PentaBDE in combination with organophosphorous substances. Not only the technical and environmental properties are important for feasibility of flame retardant systems, but also that they are commercially available and cost efficient. Table 8 illustrates an example of a market cost comparison for flame retarded flexible PUR-foam that contain C-PentaBDE in combination with organophosphorous substances and another flexible PUR foam that contain tris (2-chloro-1-methylethyl) phosphate (TCPP).

Comment [J21]: While this cost comparison is interesting, if possible, it might be useful to also include some other alternatives and maybe a non-chemical alternative. TCPP is identified in the German alternatives report as a "water polluting substance" and suspected carcinogen with the possibility of bioaccumulation and concludes that "substitution desirable".

Table 8 Comparison of flame retarded PUR- flexible foam[9]

Application	Content of FRs	Cost of flame retarded PUR per kg	Comments
Flexible PUR foam	10% PentaBDE in addition to approx 2% inexpensive organophosphorous substances	Approx 0,70 € per kg PUR	Price for PentaBDE was set to 6 € per kg, by 2005 when it was phased out in EU
Flexible PUR foam	20% TCPP	Approx 0,35 € per kg PUR	Present price of TCPP is 1,80 € per kg

This example in table 8 show that flexible PUR foam that contain TCPP is more cost efficient than the use of C-PentaBDE together with inexpensive organophosphorous substances.

10. Conclusion

The objective of this report has been to review possible alternatives to PentaBDE. The available data illustrate that there are alternative **chemical and nonchemical** flame retardants commercially available which are less hazardous than C-PentaBDE. It should be the overall target to replace harmful substances with safer options, but it is also important to point out that the alternative flame retardants presented need to be evaluated based on their range of application. A case by case assessment will be necessary to find the best suitable alternative for a specific use. The data presented in this report are just suggestive and not conclusive, and it is crucial to search for further health and environmental data to get a better understanding of toxicological and ecotoxicological effects of the alternatives presented.

[9] Beard A, Clariant, Personal communication (2008)

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