Stockholm Convention on
Persistent Organic Pollutants (POPs)

GUIDANCE

on feasible flame-retardant alternatives to commercial pentabromodiphenyl ether

2009 (UNEP/POPS/COP.4/INF24)

POPs Review
Committee

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Preface

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

Furthermore, the document has been revised by the intersessional working group on alternatives and substitution during the intersessional period between the fourth and the fifth meeting of the POPRC.

Disclaimer

The present document is a status report based on available knowledge on health and environmental effects of flame retardants. It is important to note that there are currently toxicological and ecotoxicological data gaps on the potential alternatives to c-PentaBDE. Nevertheless, based on the available data, there are alternatives that are considered to be less harmful than c-PentaBDE. The data presented in the document are just suggestive, and it is important to search for further health and environmental data to get a better understanding of toxicological and ecotoxicological effects of the alternatives presented. The document furthermore reflects the specific concerns of the Stockholm Convention and does not concern issues other than POPs issues.

SFT, Oslo, February 2009

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Summary

Flame retardants represent a large group of chemicals that consist mainly of inorganic and organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides. Flame retardant properties can also be achieved by other means than flame retardant chemicals through materials design and barrier technologies (intumescent systems). Chemical 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 molecular 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 bonded to the polymer. They may therefore, in contrast to reactive flame retardants, be released from the polymer and thereby also discharged to the environment.

In contrast to most additives, reactive 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 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 effective for the market.

Halogenated flame retardants are primarily based on chlorine and bromine. A large group of additive flame retardants 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 millennium. 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, which is also the case for Israel and Eastern European countries outside EU.

PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 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 thermosetting polyesters (UPE), rubber, paints and lacquers, textiles and hydraulic oils. The quantities used for each specific application are not publicly available.

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 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 flame retardants that are less hazardous than c-PentaBDE. It is important to search for further health and environmental data on a sound scientific basis for potential alternative flame retardants and non chemical flame retardant technologies and avoid those flame retardants that may pose an unacceptable risk to health and the environment.

Introduction

1.1 Flame retardants

With the increasing use of thermoplastics and thermosetting polymers 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 consist mainly of inorganic and organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides. Today, these flame retardant systems fulfil the multiple flammability requirements developed for the above-mentioned applications (EHC, 192-1997). More recently, a variety of non-chemical techniques for flame retardation have been developed and implemented.

Chemical 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 molecular structure compared to the original polymer molecule. This enables the polymer to keep the flame retardant properties intact over time with very low emissions to the environment (Danish EPA, 1999). Reactive flame retardants are used mainly in thermosets, especially polyester, epoxy resins and polyurethanes (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 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 the 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 flame retardants
- Organophosphorus flame retardants
- Nitrogen-based flame retardants
- Halogenated flame retardants
- Barrier technologies i.e. intumescent systems

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 phosphorus. 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 terms of volume the biggest flame retardant category in use on the market.

Organophosphorus 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 organophosphorus flame retardants in particular, triaryl phosphates (with three benzene rings attached to a phosphorus-containing group) are used as alternatives to brominated flame retardants. Organophosphorus 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 melamines 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 technologies have a wide 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 fibres used in furniture and mattresses and high performance synthetic materials used in fire-fighter uniforms and space suits.

2. Requirements for feasible flame retardants

2.1 Fire requirements

Tighter legislation and tougher fire requirements are the major forces that have driven forward development towards functionally better and more effective and improved technologies for fire protection. 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. Customers' 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.***

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 manufacturer's 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 of fire retarded materials

In contrast to most additives, reactive 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 requirements. In addition to fulfilling the appropriate mandatory fire requirements and rules, an effective 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

- Not significantly alter the mechanical properties of the polymer
- Be easy to incorporate into the host polymer
- Be compatible with the host polymer
- Be easy to extract/remove for recyclability of the 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 environmental properties

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

Commercial viability

- Be commercially available and cost effective

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.

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´-tribromodiphenylether (BDE-28) are also present in c-PentaBDE. Both BDE-17 and BDE-28 are synthetic precursors in the formation of major congeners in c-PentaBDE such as BDE-47.

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).

Table 1: Composition of c-PentaBDE

Categories of PBDEs	Tribromodiphenyl ethers		Tetrabromodi-phenyl ether	Pentabromodi-phenyl ethers		Hexabromodi-phenyl ether	Heptabromodi-phenyl ether
Congeners	BDE-17	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154
Content	Traces	Traces	Major	Major	Minor	Minor	Traces

Components of c-pentaBDE are 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 c-PentaBDE components 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 (UNEP/POPS/POPRC.3/20/Add1 2007).

Based on the information in the risk profile, c-PentaBDE, due to the characteristics of some 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 and the environment, such that global action is warranted (UNEP/POPS/POPRC.2/17/Add.1 - Risk profile on commercial pentabromodiphenyl ether and decision POPRC-2/1: Commercial pentabromodiphenyl ether).

4. Commercial use and production of c-PentaBDE

4.1 Historic production of c-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**
c-Penta-mix PBDE formulation	7100	150	150	100	7500	4

C-PentaBDE has been produced in Israel, Japan, US and the EU. China may have produced for their market as well. Since 2004, c-PentaBDE is no longer produced by at least BSEF member companies[1]. Today there is no production in Japan and c-PentaBDE was voluntarily withdrawn from the Japanese market in 1990 (UNECE, 2007). There is no official information available from the Israeli government of any present production or use of c-PentaBDE. However, as BSEF members do not make or supply c-PentaBDE and Israel Chemicals Ltd is a BSEF member, it is unlikely to be made or used there[2].

Since the late 1990s it is believed to have been produced primarily in the US, although there are some indications of present use. The sole producer of c-PentaBDE in the US, the Great Lakes Chemical Corporation (now Chemtura), voluntarily ended their production of c-PentaBDE by 1st of January 2005[3]. Before the phase-out in the US, the majority of c-PentaBDE formulation produced globally was used in North America (>97%). At the end of 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 declined during the second half of the 1990s and was estimated to be 300 metric tonnes in 2000, used solely for PUR production (EU, 2000). The use of c-PentaBDE was banned in the EU in 2004 through the Council directive 2003/11/EC relating to restrictions on the marketing and use of certain dangerous substances. From 1st of July 2006, c-PentaBDE was restricted in electrical and electronic appliances through the RoHS (**R**estriction **o**f the use of certain **H**azardous **S**ubstances in electrical and electronic equipment) – 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).

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[1] BSEF, personal communication (2009)

[2] BSEF, personal communication (2009)

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

Investigations through direct contacts with industry and studies of relevant sources of 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 regarding such activities was found. According to BSEF, there is no production in the Eastern European countries outside EU, at least by member companies to BSEF[4].

4.2 Historic use of c-PentaBDE

PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 to 30% by weight. The quantities used for each specific application are not publicly available (USEPA (Dfe), 2004).

Table 3: Historic use of c-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 (Thermosetting) polyesters (UPE)	Circuit boards, coatings	Electrical equipment, 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 public buildings, aircraft, public transport
Hydraulic oils	Drilling oils, hydraulic fluids	Off shore, coal mining

More than 95% of the US production of PentaBDE in the years leading up to the voluntary withdrawal of production and sales during 2004 was consumed in the US, for the manufacture of flexible polyurethane foam to produce cushioning and other products. There is no data available on the proportions of use of c-PentaBDE for the different applications identified in table 3.

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[4] BSEF, personal communication (2009)

4.3 Present use and trends in production of c-PentaBDE

Since there should be no current production of c-PentaBDE in Europe, Japan, Canada, Australia and the US, the remaining production would be located in other parts of the world. Besides Europe, Japan and North America, the bromine industry has worldwide representation. Despite direct personal contacts with the bromine industry, no information was provided of any production or use of c-PentaBDE in Africa, nor any Asian countries other than China, and South and Latin America[5, 6].

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

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 regarding any possible production of c-PentaBDE in China[7]. However, China has its own RoHS since 2006, where the use of PBDEs in electronics was banned (SJ/T, 11363-2006).

5. Alternative flame retardants and alternative technical solutions to c-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. As mentioned earlier, different flame retardants 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 an on-the-spot account and cannot be exhaustive, 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 is no single universal solution for fire protection of materials and applications.

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[5] Dr. Didier, M Trimbos, Eurobrom, personal communication (2008)

[6] Baker A, Dead Sea bromine Ltd, personal communication (2008)

[7] 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**	**Phosphorus/nitrogen organic alternatives to PentaBDE**	**Halogen organic alternatives to PentaBDE**	**Alternative flame retardant materials**	**Applications**	**Commercial commodities for the applications**
Epoxy resins	Aluminium hydroxide (ATH) Magnesium hydroxide Ammonium poly phosphate Red phosphorus Zinc hydroxystannate (ZHS), Zinc stannate (ZS) & ZHS/ZS-coated ATH	Metallic phosphinates Reactive nitrogen and phosphorus constituents (unspecified) DOPO[8]	Tetrabromobis phenol A (reactive) Etylenebis (tetrabromo) phtalimid	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 phosphorus	Melamine (nitrogen based) Dimethyl propyl phosphonate (DMPP) Reofos (non-halogen flame retardant)	Bromoalkyl phosphates Tetrabromophtalic anhydride Tris(chloroethyl) phosphate (TCPP) (together with brominated polyols or red phosphorus)	Intumescent systems	Cushioning materials, packaging, padding	Furniture, sound insulation packaging, padding panels, wood imitations, transportation

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[8] DOPO=Dihydrooxaphosphaphenanthrene oxide

Materials/polymers /resins	**Inorganic alternatives to PentaBDE**	**Phosphorus/ nitrogen organic alternatives to PentaBDE**	**Halogen organic alternatives to PentaBDE**	**Alternative flame retardant 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 propyl phosphonate (DMPP)	Dibromostyrene Tetrabromophtalic anhydride based diol Tetrabromophtalic anhydride Bis (tribromophenoxy) ethane	Intumescent systems	Circuit boards, coatings	Electrical equipment, coatings for chemical processing plants mouldings, military and marine applications: construction panels
Rubber	N/A	Alkyl diaryl phosphates (nitril rubber)	N/A	Intumescent systems	Transportation	Conveyor belts, foamed pipes for insulation
Paints/lacquers	N/A	Triaryl phosphates (unspecified)	Tetrabromo phthalate diol Tetrabromophtalic 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 hydroxymethyl 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 public buildings, aircraft, underground

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

N/A : not available or not applicable

6. Present manufacture and use of alternative flame retardants to c-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 1960s 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 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 phosphorus

Red phosphorus has been reported to be most efficient as a flame retardant in oxygen containing polymers such as polycarbonates, polyethylene terephtalate (PET), polyamide and phenolic resins. Flame retardancy takes place due to formation of phosphorus-oxygen bonds that reduces the ester linkages into cross linking aromatic structures with lesser volatility. In addition, the red phosphorus creates a heat shield on the polymer surface that results 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 (Davis et. al, 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 section 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 realised 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 a 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 Organophosphorus 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 highly alkylated phosphorus products are commercially available, which is required in lower added concentrations in the polymer.

6.2.2 Aryl phosphates

This large group of organophosphorus flame retardants include triphenyl-, isopropyl-, and t-butyl-substituted triaryl and cresyl phosphates. Phosphates with higher 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 phosphates are shown to be more efficient plasticizers than triaryl phosphates.

6.2.3 Halogen containing phosphorus flame retardants

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

Table 5: Commercial phosphorus 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 *Tris(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 # proprietary 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 highly exothermic reaction (with heat generated), they cause 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 phosphorus flame retardants

Reactive phosphorus 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 efficiency 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 phosphorus 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 Barrier technologies - 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, 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

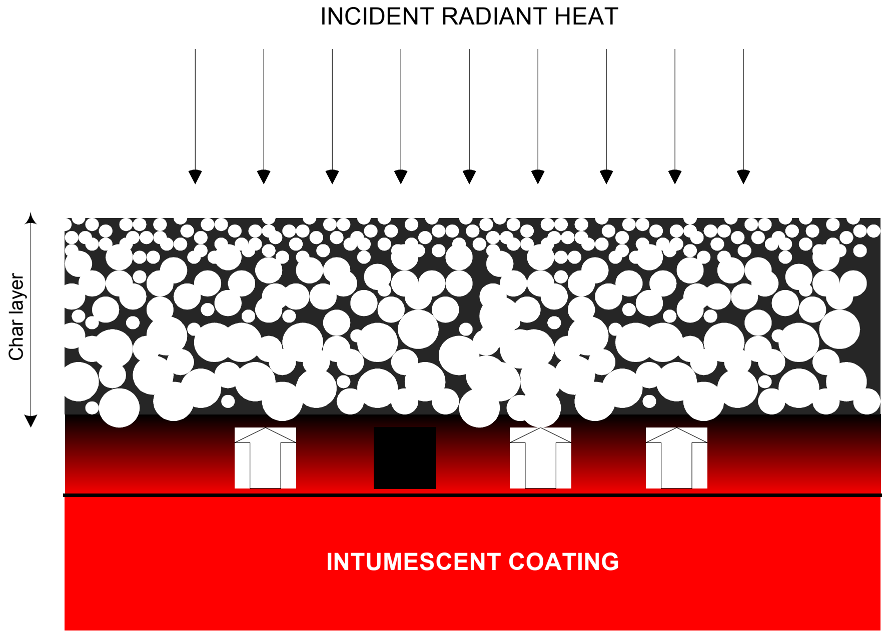

Figure 1: Mechanisms for intumescent systems

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 in the research phase and awaiting to be commercialised (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 intumescent~~s~~ 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 fumes/gases (Swaraj, 2001; Posner, 2004).

6.5 Halogenated flame retardants

Several types of halogenated flame retardants, mainly the brominated ones, 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. Within this broad class of PBDE chemicals, the use of commercial Octabromdiphenylether and commercial Pentabromdiphenylether is restricted in all applications in Europe. The use of Decabromdiphenylether has restrictions in some countries. The potential adverse effects of several of the halogenated flame retardants are under international scientific review.

7. Historic, present and future consumption of alternative flame retardants to c-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 have 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 take into account 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 worldwide.

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 the 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 plastics in electronic enclosures is growing at around 5% per year (SRI Consulting, 2005). With no de-selection, substitution or regulatory prohibition, a conservative estimate on the growth of the use of BFRs could be 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 Asian countries**	**Total volume [1000 metric tonnes]**	**Value [million USD]**
Aluminium hydroxide	315	235	47	48	645	424
Organo phosphorus 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	**563**	**490**	**160**	**269**	**1481**	**2865**

The estimated growth of around 63% in demand of BFRs till 2017 would lead to a total demand for BFRs averaging 500-600,000 metric tonnes per year, primarily as the predominant brominated flame retardant substances on the international market today, namely decabromodiphenylether and TBBP-A[9].

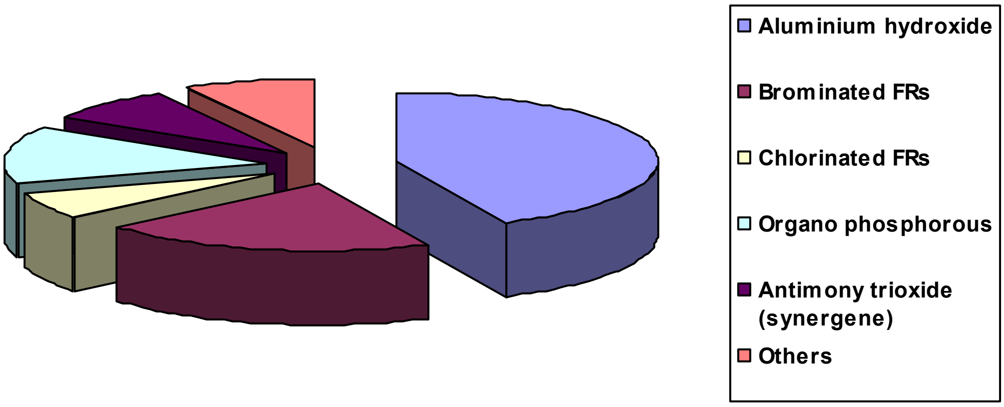

Figure 2: The global market share of groups of flame retardants (SRI Consulting, 2005)

With an innovative approach, there will be an introduction of new and innovative specific formulations of less hazardous flame retardant systems, including non-

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[9] Kirschner M, personal communication (2008)

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 a current picture of the hazard characteristics as comparable as possible, as shown 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).

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	Little ecotoxic data available
Magnesium hydroxide	Low concern	Low concern	Toxic and ecotoxic: little data available
Red phosphorus	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 toxic and ecotoxic 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 toxic and ecotoxic data available
Antimony trioxide	Ranked as possible carcinogen by IARC[10] and EU	Low concern	May produce toxic or irritating vapours during combustion conditions

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[10] IARC – International Agency for Research on Cancer

Chemical	**Toxicological properties**	**Ecotoxicological properties**	**Comments**
Zinc hydroxystannate & Zinc stannate	Low concern	Low concern	Very low acute toxicity. Very low aqueous solubility
Organophosphorus flame retardants			
Triethylphosphate	No data available	No data available	
Aryl phosphates	Low concern	A few compounds show high acute aquatic toxicity	
Halogen containing phosphorus 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)	High concern	Low concern	Subject to risk assessment in the EU under the 4th Priority List Will be transferred to REACH
Reactive phosphorus	No data available	No data available	
Nitrogen based organic flame retardants			
Melamine	Low concern	Low concern	Allergic dermatitis has been reported among workers

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.

9. Example of costs related to substitution of c-PentaBDE 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 organophosphorus substances. For the feasibility of flame retardant systems, technical and environmental properties are important, but they must also be commercially available and cost effective. Table 8 illustrates an example of a market cost comparison for flame retarded flexible PUR-foam that contain c-PentaBDE in combination with organophosphorus substances and another flexible PUR foam that contain tris (2-chloro-1-methylethyl) phosphate (TCPP).

Table 8: Comparison of flame retarded PUR- flexible foam[11]

Application	**Content of FRs**	**Cost of flame retarded PUR per kg**	**Comments**
Flexible PUR foam	10% PentaBDE in addition to approx 2% inexpensive organophosphorus 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 shows that flexible PUR foam that contains TCPP is more cost effective than the use of c-PentaBDE together with inexpensive organophosphorus 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 non-chemical 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.

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

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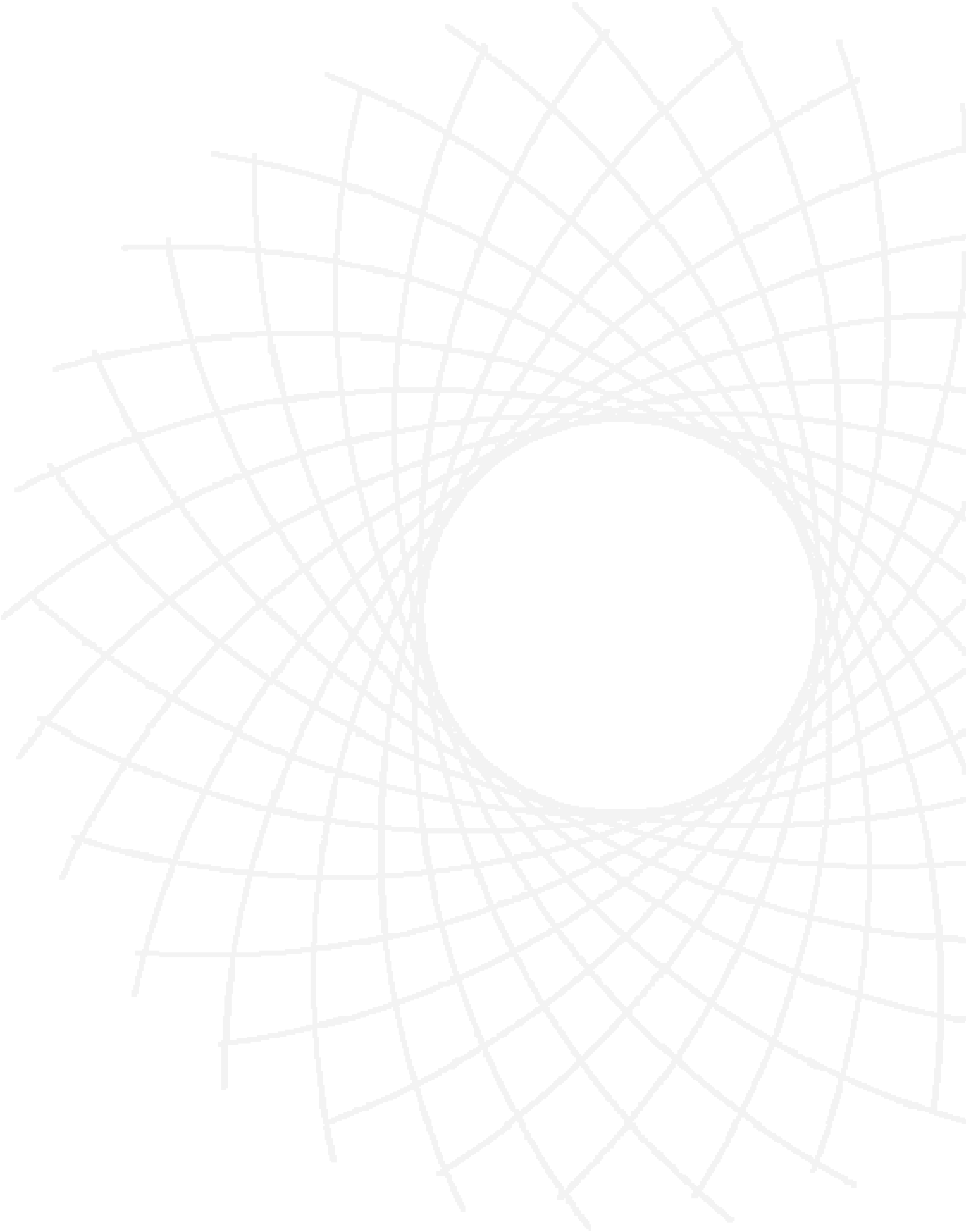

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