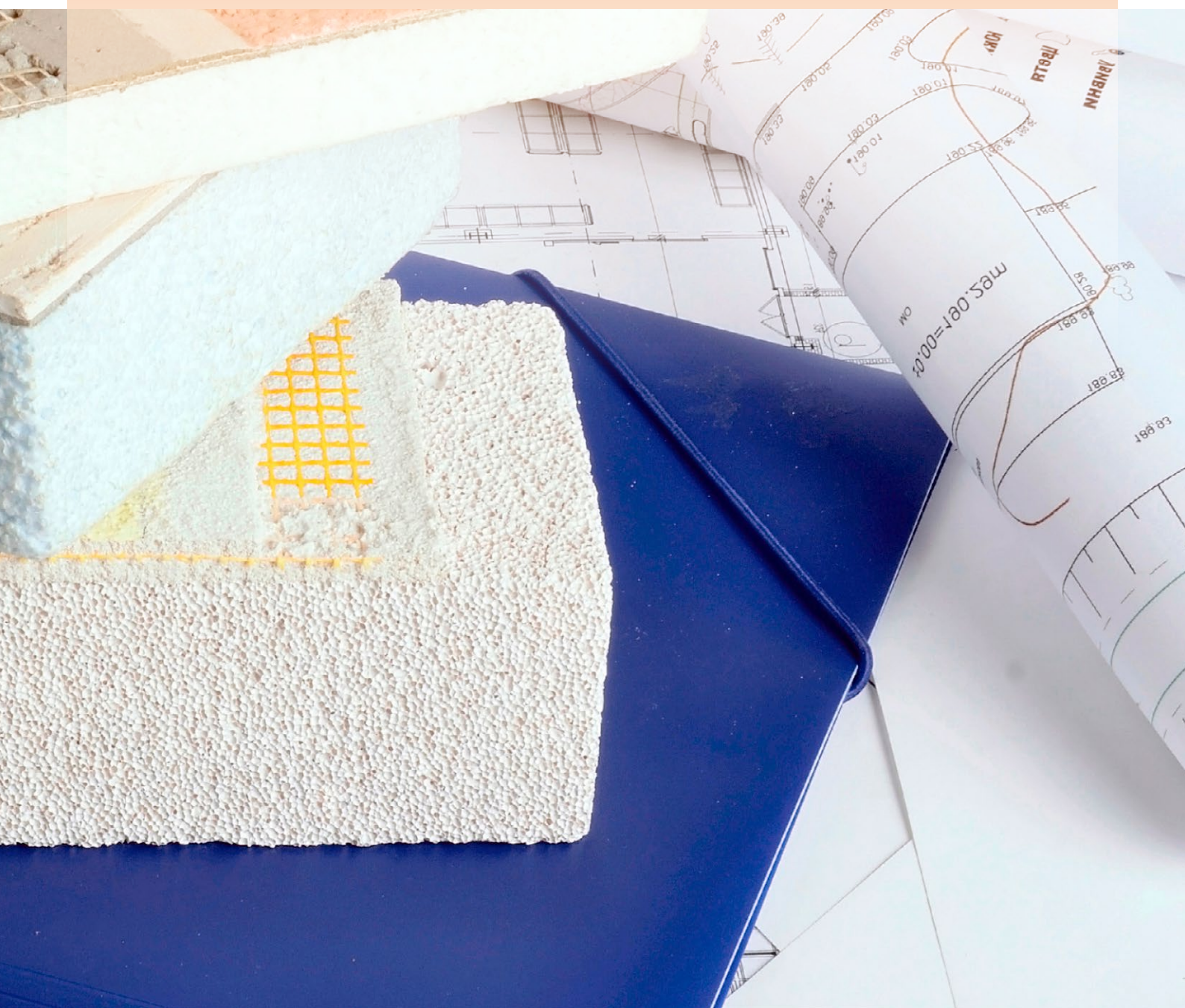


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STOCKHOLM CONVENTION

GUIDANCE ON ALTERNATIVES TO
HEXABROMOCYCLODODECANE (HBCD)

2021



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ABBREVIATIONS AND ACRONYMS

BFR	brominated flame retardant
c-Penta-BDE	commercial pentabromodiphenylether (tetra-BDE and penta-BDE)
c-Octa-BDE	commercial octabromodiphenyl ether (hexa-BDE and hepta-BDE)
CEN	European Committee for Standardization
COP	Conference of Parties
Deca-BDE	decabromodiphenyl ether
ECHA	European Chemicals Agency
EPS	expanded polystyrene
EU	European Union
HBCD	hexabromocyclododecane
HIPS	high impact polystyrene
ISO	International Organization for Standardization
POPs	persistent organic pollutants
POPRC	Persistent Organic Pollutants Review Committee
PPE	polyphenylene ether
PPO	polyphenylene oxide
PIR	polyisocyanurate rigid foam
PUR	polyurethane rigid foam
SCCP	short chain chlorinated paraffins
UL	Underwriters Laboratories
USEPA	United States Environmental Protection Agency
USDOE	United States Department of Energy
XPS	extruded polystyrene

1. INTRODUCTION

Following the listing in Annex A to the Stockholm Convention the production and use of hexabromocyclododecane (HBCD) must be eliminated. To facilitate transition into safer alternatives, Persistent Organic Pollutants Review Committee (POPRC) of the Stockholm Convention has developed General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals (UNEP/POPS/POPRC.5/10/Add.1, UNEP, 2007). In the Convention, and in the present document, the term “alternative” is used to denote a chemical, material, product, product design, system, production process or strategy that can replace listed persistent organic pollutants or candidate chemicals, or materials, products, product designs, systems, production processes or strategies that rely on listed persistent organic pollutants or candidate chemicals, while maintaining an acceptable level of efficacy.

At the time of the listing, information on available alternatives to HBCD was included in the Draft risk management evaluation on hexabromocyclododecane (UNEP/POPS/POPRC.7/5, UNEP 2011). POPRC also developed an update on the alternatives as an addendum to the Risk management evaluation (UNEP/POPS/POPRC.8/16/Add.3, UNEP, 2012) on chemical alternatives to hexabromocyclododecane, especially in expanded polystyrene or extruded polystyrene foam applications, in terms of their availability, cost, efficacy, efficiency and health and environmental impact, especially with regard to their persistent organic pollutant properties (UNEP, 2012).

The Environment Protection Agency of the United States (US EPA) carried out a comprehensive study on alternatives to HBCD in 2014 (USEPA, 2014a). In addition the European industry consortium seeking authorization for continued use of HBCD in buildings submitted a review of potential alternatives to European Chemicals Agency ECHA (Assessment of Alternatives, no date). This information has been included in the review of alternatives in Annexes A and B.

Information on HBCD alternatives has also been collected in a living document *Publication on POPs in Articles and Phasing-Out Opportunities* (<http://poppub.bcrc.cn/>), developed by the Stockholm Convention Regional Centre for Capacity-building and the Transfer of Technology in Asia and the Pacific and Basel, Rotterdam and Stockholm Secretariat in 2014.

The present document provides an update on the information previously published on chemical and non-chemical alternatives to HBCD in Guidance on alternatives in Guidance for the inventory, identification and substitution of Hexabromocyclododecane (HBCD) (UNEP, 2015a) and Draft guidance on best available techniques and best environmental practices for the production and use of hexabromocyclododecane listed with specific exemptions under the Stockholm Convention (UNEP, 2017).

2. PHASING OUT A CHEMICAL

The aim of a risk reduction strategy for HBCD should be to reduce and eliminate emissions and releases taking into consideration the indicative list in Annex F of the Stockholm Convention including technical feasibility of possible control measures and alternatives, the risk and benefits of the substances and their continued production and use. In considering any strategy for a reduction of such risks, it is important to consider the availability of substitutes in the sectors of concern. In this regard, the replacement of HBCD by another chemical or non-chemical alternative needs to take account of factors such as (UNEP, 2011):

- Technical feasibility (practicability of applying an alternative technology that currently exists or is expected to be developed in the foreseeable future);
- Costs, including environmental and health costs;
- Risk (safety of the alternatives);
- Availability and accessibility of substitutes in the sectors of concern.

There is a range of approaches available to substitute the use of HBCD in all applications. These approaches can be grouped into three categories (UNEP, 2011):

- Flame Retardant Substitution;
- Resin/Material Substitution; and,
- Product Redesign.

The first two approaches have been discussed below. No general guidance is available for product redesign.

3. FLAME RETARDANT SUBSTITUTION

The main uses of HBCD globally have been in flame-retardant expanded (EPS) and extruded (XPS) polystyrene foam for insulation and construction (more than 90% of the HBCD use), while the uses in the production of flame-retardant textile applications and in the production of high impact polystyrene (HIPS) for electric and electronic appliances casings were of a smaller scale (UNEP, 2012). Typical concentrations of HBCD in these uses are presented in Table 1.

Table 1: Typical concentrations of HBCD in different materials (UNEP, 2015b).

Flame-retardant materials	HBCD content (in mg/kg)
Expanded polystyrene (EPS)	5,000-10,000 ¹
Extruded polystyrene (XPS)	8,000-25,000 ²
Textile back-coatings	60,000-150,000 ³
Textiles	22,000-43,000 ⁴
High-impact polystyrene (HIPS)	10,000-70,000 ⁵

Fire performance of a material depends on flammability, which is also affected by fillers, coatings, laminates, pigments, dyes, and other compounding agents. The fire performance criteria in countries' regulations for a specific use are normally specified in general and relative terms, and they do not require the use of specific flame retardants. To demonstrate that the requirements are met, there are prescribed verifiable criteria, which standardization bodies such as ISO, CEN and UL often have helped to develop (KEMI, 2006).

According to the POPRC guidance on alternatives (UNEP, 2007), a "safer alternative" is an alternative that either reduces the potential for harm to human health or the environment or that has not been shown to meet the Annex D screening criteria for listing a chemical under the Convention as a persistent organic pollutant. The health and safety information available for some of the alternatives below is very limited.

Little information is available on costs of alternatives and the costs related to the transition. Accurate cost estimations must be company-specific; the impact of substituting chemicals on complex product formulations can only be analyzed in-house and a company must determine for itself how changes will impact market share or other business factors (USEPA, 2014a).

3.1 ALTERNATIVES TO HBCD IN THE PRODUCTION OF EPS AND XPS

Until 2011 there were no commercially or technically viable drop-in chemical alternatives to HBCD as a flame retardant in XPS production and the most common 'one-step'⁶ EPS manufacturing process, which is used at least in Europe and generally in North America. In March, 2011, an alternative for HBCD in EPS/XPS (polymeric flame-retardant) was announced, and has in many cases replaced HBCD as a drop-in substitute to HBCD. In the production of EPS raw material process, the flame retardant is incorporated into the ready-made bead. -HBCD (or any other FR used in EPS) does not penetrate the beads after polymerization: styrene is polymerized into polystyrene in a suspension in the presence of the FR and other ingredients. Flame retardants for EPS and XPS foam must allow the material to comply with fire safety codes while not compromising the performance of the foam.

¹ Submissions by Canada and PlasticsEurope/Exiba to the Stockholm Convention, 2011 (UNEP, 2011).

² BFRIP 2005, XPSA and CPIA, PlasticsEurope/Exiba submissions to the Stockholm Convention, 2011 (UNEP, 2011).

³ European Commission, 2008; Environment Canada and Health Canada, 2011 (UNEP, 2011).

⁴ Kajiwara *et al.*, 2009.

⁵ ECHA, 2009 (UNEP, 2011).

⁶ In 'one-step' production process all additives are mixed in the styrene solution prior to polymerisation. This process is the most energy and resource efficient (in terms of water use) way to make EPS and is universally employed in Europe. In 'two-step' process the beads are polymerized in the first step without the flame-retardant additive and pentane; the possible flame retardant and pentane are added in the second step. This gives potentially wider possibilities of possible alternatives in the two-step process because there is less potential for the flame retardant molecule to interfere with polymerization of the styrene to polystyrene (Assessment of Alternatives).

A butadiene-styrene brominated copolymer (Bluedge™) appears to be the main chemical substitute in EPS and XPS production for one-step process. It is produced in the USA, Israel, and the Netherlands by Lanxess and ICL and sold under different tradenames (Emerald Innovation™ 3000, FR122P, and GreenCrest®). According to the flame retardant industry, the EPS industry has already replaced HBCD with the Bluedge™ in many countries, and the production capacity is considered adequate to meet the global demand currently and into the future⁷. In addition, there are two tetrabromobisphenol A (TBBPA) derivatives, which have been identified as viable alternative by US EPA (2014a) and the EU industry consortium seeking authorization for HBCDD (Assessment of Alternatives, see also ICL-IP, 2014). No nonbrominated flame retardants were identified that would be compatible in polystyrene foam manufacturing and associated flame tests.

More detailed information on the known alternatives to HBCD in XPS and EPS production is in Annex A. In addition to the polymeric flame-retardant, TBBPA derivatives appear to be another major chemical substitute to HBCD (ICL-IP, 2014), although there have been concerns about the supply (Assessment of Alternatives).

3.2 ALTERNATIVES TO HBCD IN TEXTILES

A variety of flame retardants has been used in the production of flame-retardant textiles.

For textile backcoating, chemical alternatives to HBCD include TexFron 4002, deca-BDE, decabromodiphenylethane (DBDPE), ethylene bis(tetrabromophthalimide), chlorinated paraffins and ammonium polyphosphates (ECHA, 2009; KLIF, 2011, ICL-IP, 2019b). Deca-BDE was listed in the Stockholm Convention Annex A in 2017 and cannot be considered an acceptable substitute.

Decabromodiphenylethane (DBDPE) has replaced BDE-209 in many applications. DBDPE is, however, relatively persistent and may accumulate significantly in fish. DBDPE is commonly found in environmental samples. Short chain chlorinated paraffins have also been used in the production of flame retardant textiles. Short chain chlorinated paraffins (SCCP) were listed in Stockholm Convention Annex A in 2015 and cannot be considered as safe alternatives to HBCD. Long chain chlorinated paraffins are reproductive toxicants to humans, show chronic toxicity with effects on liver and kidneys, and are potential carcinogens (ECHA, 2009).

Polymeric TexFron 4002 flame retardant is Oeko-Tex® certified and is also used for adhesives and coatings.

Out of the identified technically viable and commercially available substitutes to HBCD, ammonium polyphosphate is widely used. In Canada the chemical is categorized as Persistent and inherently Toxic.

More detailed information on the known alternatives to HBCD in the production of textiles are in Annex B.

3.3 ALTERNATIVES TO HBCD IN HIPS

A variety of flame retardants in addition to HBCD has been used in the production of flame-retardant HIPS.

One of the common flame-retardants used in HIPS was deca-BDE (decabromodiphenylether, i.e. BDE-209). Since it was listed in the Stockholm Convention Annex A in 2017, it cannot be considered an acceptable substitute. Assessments made on alternatives to deca-BDE (USEPA, 2014b, UNEP/POPS/POPRC.11/10/Add.1) are directly applicable for this application of HBCD as well. USEPA (2014b) identifies ten alternative flame-retardants that are possible alternatives for deca-BDE in HIPS (not including HBCD).

More detailed information on the known alternatives to HBCD in the production of HIPS are in Annex B.

⁷ Personal communication with ICL-IP, 3 February 2019. Personal communication with DOW, 8 February 2019.

4. NON-CHEMICAL ALTERNATIVES TO HBCD

The materials that can be used in a specific application is dependent on the country's fire safety regulations and other requirements set for a material. Non-flame retardant EPS boards are used in some countries in combination with other construction materials which protect the EPS from catching fire. EPS without flame retardant is widely applied as ground or floor insulation below a concrete layer, but it is also used in walls and other open constructions if thermal barriers are applied.

Replacing EPS/XPS insulation with other materials can furthermore affect overall product cost and performance, and may additionally require a different approach during building and construction. Alternative insulation materials to EPS/ XPS are available for all uses, with the exception of some demanding XPS use in moist or freeze/thaw sensitive applications in North America (UNEP, 2011). In terms of market volumes the major insulation materials apart from the EPS/EXS are mineral wool, fibre glass wool and polyurethane rigid foams. The alternative insulation materials/techniques may have characteristics that are different from XPS and EPS and that are more or less appropriate for some specific use scenarios (such as resistance to water absorption, resistance to mechanical loadings (high compression strength) and structural integrity for service life) (ECHA, 2009; USDOE, 2010).

Use of alternative insulation materials/techniques may also incorporate different environmental issues such as increased energy costs during transportation, and may come with their own unique set of health and/or environmental risks which in most instances are not too well known. When release to the outer environment is not considered, the health effects of any given insulation material is primarily of importance in the work environment, since the insulation material is built inside the wall, foundation and ceilings. Exposure to alternative insulation materials during building repair, refurbishment and demolition must also be considered.

4.1 NON FLAME RETARDANT EPS AND XPS IN COMBINATION WITH THERMAL BARRIERS

Non-flame retarded EPS and XPS insulation foams in combination with other construction materials are used in several countries to protect the EPS and XPS from catching fire. For example, in Sweden and Norway, national regulations allow the use of non-flame retarded insulation materials, provided the total building element meets fire safety requirements. In these countries, use of EPS in combination with thermal barriers reduces the need for flame retarded EPS without compromising fire safety performance in constructions (KLIF, 2011). By covering EPS and XPS insulation foams with concrete on all sides, the building element as a whole could be classified as non-combustible and used in construction. EPS insulation boards can also be covered with a layer on non-combustible insulation material such as mineral wool. This is particularly suitable for flat roofs. In all solutions involving non-flame retarded EPS and XPS, the layer of non-combustible material will have to fully cover the insulation material on all sides and precautions have to be taken to avoid openings and penetrations in the construction such as around windows (KLIF, 2011).

The use of flame resistant barriers - coating, laminate, foil laminate, foil – as back coatings may not work with polystyrene foam because they will interfere with the ability of the foam to recede away from the fire. Additionally, the coating levels necessary to pass flammability tests are not economical. (USEPA, 2014a).

4.2 MINERAL WOOLS

Stone wool insulation is made from volcanic rock, typically basalt or dolomite, an increasing proportion of which is recycled material in the form of briquettes. Slag wool is made from blast furnace slag (waste). The stone wool is a subgroup of the mineral wool together with glass wool. Over the last decade, glass wool, rock (stone) wool and slag wool have together met just over half of the world demand for insulation.

The structure and density of the product can be adapted to its precise final usage. Inorganic rock or slag is the main components (typically 98%) of stone wool. The remaining 2% organic content is generally a thermosetting resin binder (an adhesive), usually phenol formaldehyde and a little mineral oil.

For glass wool the raw materials are sand, limestone and soda ash, as well as recycled off cuts from the production process. Small quantities of binding agents are added to the fibres. Glass wool products usually contain 95% to 96% inorganic material (Eurima, 2011).

4.3 PHENOLIC FOAMS

Phenolic foam insulation is made by combining phenol-formaldehyde resin with a foaming agent. When hardener is added to the mix and rapidly stirred, the exothermic reaction of the resin, in combination with the action of the foaming agent, causes foaming of the resin. This is followed by rapid setting of the foamed material (Greenspec, 2011). In the process phenol is polymerized by substituting formaldehyde on the phenol's aromatic ring via a condensation reaction and a rigid thermoset material is formed. Compared to the EPS/XPS and PUR/PIR, the market share of the phenolic foams seems to be small due to higher prices.

4.4 NATURAL FIBRE-BASED INSULATION MATERIALS

Various modern insulation materials are based on natural fibres, primarily plant fibres, but also sheep wool. Some of these have been known for centuries but have got a renaissance over the last decades with the growing interest for environment friendly building techniques. They are available as loose insulation fill, as insulation batts or/and as rolls.

4.5 SPECIALTY AND EMERGING ALTERNATIVE MATERIALS

The insulation materials presented below may be functional alternatives to EPS and XPS, but are not currently considered to be viable for large scale building applications, and are constrained to specialty applications or limited geographic areas. Specific insulation products are generally not suitable for all applications.

Aerogel is available as a rigid board, roll, or loose-fill; and is used to insulate underfloors, rainscreens, roofing, cathedral ceilings, and interior walls (Madonik, 2011). It is made from silica gel, polyethylene terephthalate (PET), fiberglass, and magnesium hydroxide (KLIF, 2011b). Aerogel is lightweight and has a very high R-value of 10, but is costly.

Carbon foam is a type of rigid board foam made from calcined coke. It is manufactured in limited quantities and is used primarily as a specialty insulation in the aeronautic, marine, and energy industries (Madonik, 2011).

Foamglas is a rigid board insulation made from sand, limestone, and soda ash that is primarily used for high-temperature industrial applications where extreme heat resistance is required but can be used to as insulation in roofs, walls, and below-grade.

Reflective insulation is a foil-faced insulation material that incorporates a radiant barrier (normally highly reflective aluminum) with a kraft paper, plastic film, polyethylene bubble, or cardboard backing (USDOE, 2019). Reflective insulation is used to reduce radiant heat flow across an open space, most usefully for downward radiant heat flow, and is typically used between roof rafters, floor joists (or reflective insulation), and wall studs. Reflective insulation is not an alternative for EPS and XPS, but rather works best in complement with other forms of insulation.

Agrifiber insulation is manufactured from agricultural waste (e.g., rice hulls, fungal mycelia, wheat or rice straw) and is available as board insulation (Wilson 2011). Agrifiber typically uses borate as a flame retardant (Sustainable Sources, 2019). New agrifiber insulations under development using mycelium as a binder are reported to have obtained a Class 1 fire rating without use of added chemical flame retardants (Wilson, 2011).

5. ALTERNATIVES TO FLAME-RETARDANTS IN TEXTILE BACK-COATING

Flame retardant use in textiles can be avoided if the material itself is non-flammable or has low flammability. Some natural materials such as wool may therefore be used as barrier materials in furniture (UNEP, 2011). Other inherently flame retardant materials include rayon with a phosphorus additive, polyester fibers, and aramids (Weil & Levchik, 2009).

Intumescent systems for textile back-coating have been on the market for about 20 years (Posner *et al.* 2010). They are based on the formation of expanded coal tar, which partly acts as an insulating barrier against heat and as a smoke-fume trap. Intumescent systems for textile back coating require special handling in application to ensure that the systems work as intended. It is important that the best conditions and combinations of the 3 different components of the systems are in an evenly and well distributed dispersion in the textile application for the desired flame protection to be achieved (Posner 2004). Intumescent systems may not be applicable to the same sets of textiles as flame retardant-based back-coatings.

6. ALTERNATIVES TO HIGH IMPACT POLYSTYRENE (HIPS) WITH HBCD

Polyphenylene Oxides (PPO) or polyphenylene ether (PPE) resins are used as alloys with polystyrene for applications like computer housings, and internal components as well as telecommunication equipment. It is possible to use non-halogenated flame retardants with these alloys. The PPO component is a good char former and therefore, only a moderate amount of a fire retardant can provide required flame retardancy (Murashko *et al.*, 1998).

European manufactures of television sets appear to be using alloys including PPE/HIPS with non-halogenated flame retardant. This is an indication that alloys of PPE/HIPS with non-halogenated flame retardant also perform to required industry standards. Alloys of PPE/HIPS are known to have relatively higher inherent resistance to burning and spreading fire because they form an insulating char foam surface when heated. They also have higher impact strength and give similar design opportunities for parts with fine structural details. In addition, alloys of PPE/HIPS require fewer changes to the expensive molds and tooling used in the molding process (Maag *et al.*, 2010). PC/ABS alloys are widely used for the very same applications. Non-halogenated flame retardants are available for both PPO/HIPS and PC/ABS under the tradename Fyrolflex® (ICL-IP, 2019a).

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ANNEX A. CHEMICAL ALTERNATIVES TO HBCD IN EPS/XPS. ADAPTED FROM UNEP (2012)

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Benzene, ethenyl-, polymer with 1,3-butadiene, brominated (brominated copolymer of styrene and butadiene) Synonym: Polymeric FR CAS No: 1195978-93-8	Blueedge™ Emerald Innovation™ 3000 FR122P GreenCrest® Polymeric FR™	EPS via onestep process, likely also suitable in two-step process XPS	Commercially available. Originally developed by Dow Chemicals Company as a polymeric, high molecular weight flame retardant alternative to HBCD. Exclusive rights for the production, sales and marketing of the pFR have been granted by Dow to three flame retardant manufacturers worldwide: ICL-IP, Chemtura (now LANXESS) and Albemarle. Estimated 50% of the global demand of HBCD substituted in 2017 ⁸ Production capacity in the US: 14 000 MT (LANXESS) Production capacity in Israel: 10 000 MT (ICL-Industrial Products) According to ICL-IP (pers. comm. 2019), total installed capacity of polymeric FR of Blueedge™ technology licensed producers is more than adequate to meet global demand today and into the future.	Based on USEPA (2014A) evaluation, the chemical is anticipated to be safer than HBCD for multiple endpoints. Due to its large size, lack of low molecular weight (MW) components, and un-reactive functional groups, human health and ecotoxicity hazard for this polymer are measured or predicted to be low, although experimental data were not available for all endpoints. In general the exposure potential to the butadiene-styrene brominated copolymer is expected to be lower than the other chemicals in this assessment because it is a large polymer and is unlikely to be released from the polystyrene. This alternative is inherently persistent and its long-term behavior in the environment is not currently known.	Diverging information received (see UNEP, 2012). According to ICL-IP cost data from 2014, FR-122P was expected to be more expensive compared to HBCD. This is due to higher costs of raw materials and production process. The overall extra cost of the final EPS article is estimated to be higher by 2% to 3% compared to the present cost of HBCD based final EPS article. This calculation is based on a 0.7% - 1% concentration of FR-122P in the EPS final article (ICL-IP, 2014). Separately to any cost differences between the FRs are the costs to re-certify flame retarded EPS resins/products for all of the foam applications. Canada has estimated this at a few million dollars.	Pilot tests conducted by customers of one of the manufacturers have reportedly confirmed that FR122P delivers the required level of fire safety to their products. Polymeric FR is reported to have essentially equivalent flame-retardant efficiency to HBCD when used at equivalent bromine content. Substitution rate of HBCD by the pFR is 1:1.2. According to Great Lakes Solutions, 1.7% of polymeric FR is required to pass the EN Class E flammability test. The required load is thus comparable to that of HBCD (0.5-2.5% HBCD w/w) in PS foams. Good thermal stability and compatibility with PS. In higher temperature processing conditions Polymeric FR needs to be stabilized, similar to HBCD. According to DOW (pers. comm. 2019), substituting HBCD with Blueedge™ is straightforward maintaining the PS foam properties.

⁸ <https://lanxess.com/en/corporate/media/press-releases/2017-00049e/> Accessed 23 January, 2019

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
<p>Benzene, 1,1'-(1-methylethylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)]</p> <p>Synonym: TBBPA-bis brominated ether derivative</p> <p>CAS No: 97416-84-7</p>	<p>Pyrogard SR-130</p> <p>SR-130</p> <p>FR-130</p> <p>AP 1300 S</p>	<p>EPS</p> <p>XPS</p> <p>HIPS</p> <p>Limited testing in the Plastics Europe testing programme and not known to be technically feasible for use in EPS in Europe (Assessment of Alternatives).</p>	<p>Commercially available, but unlikely to be available in sufficient quantities to replace HBCD in the EU in 2014 (Assessment of Alternatives).</p> <p>Japan was expected to replace HBCD with FR130 and polymeric FR (ICL-IP, 2014).</p> <p>Several producers in Europe and China.</p>	<p>According to the EU EPS industry, not likely to be suitable due to expected similar environmental fate and behavior to HBCD (Analysis of Alternatives).</p> <p>The hazard profile show that these chemicals have limited data sets for human health endpoints and hazard designations show a potential for toxicity. Anticipated to have high potential for bioaccumulation. (USEPA, 2014a)</p> <p>The substance fulfils the screening criteria for persistence and bioaccumulation as defined in REACH Annex XIII section 3.1 and is therefore considered to be a potential PBT/vPvB substance (Baua, 2017). Final assessment not yet completed in January 2019.</p>		<p>Widely used.</p>
<p>Tetrabromobisphenol A bis (allyl ether)</p> <p>CAS No: 25327-89-3</p>	<p>BE 51, FG 3200, Fire Guard 3200, Flame Cut 122K, Pyrogard SR 319, SR 319</p> <p>EcoFlameRetardant B-51</p>	<p>Two-step EPS process</p>	<p>Used in the two-step EPS process only</p>	<p>Substance is a derivative of TBBPA (ECB 2006).</p> <p>The hazard profile show that these chemicals have limited data sets for human health endpoints and hazard designations show a potential for toxicity. Anticipated to have high potential for bioaccumulation. (USEPA, 2014a).</p> <p>Little information is available on HSE properties. According to the information reviewed in KLIF (2009) it can be characterised with low toxicity, potential immunotoxin, not easily hydrolysed, may be resistant to environmental degradation (see KLIF 2009 for details and Assessment of Alternatives).</p>		<p>This flame retardant is recommended in patents as a potential alternative, but in general only has limited use and availability. It does not work well in XPS manufacturing processes, and for EPS is only viable in the less-economic two-step manufactured process. The lower brominated content and mixture of aliphatic and aromatic bromine affects the efficiency of the material (USEPA, 2014a).</p>

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
1,2,5,6-tetrabromocyclo-octane (TBCO) CAS No: 3194-57-8	Saytex BC-48 (Albemarle Corporation)	Two-step EPS process	Used in the two-step process only. Its thermal stability does not meet operating temperature requirements for the manufacture of XPS foam (USEPA, 2014a). This substance may no longer be commercially available. No information is available on production volumes in the US or in the EU. TBCO is also on the Canadian Non-Domestic Substances List with as much as 10 tons/year reported as being imported into Canada.	A report by the UK Environment Agency (Fisk <i>et al.</i> 2003) indicates that TBCO is hazardous to the aquatic environment (i.e. chronic NOEC < 0.1 mg/l or acute L(E)C50s < 10 mg/l), and potentially PBT/vPvB. Due to poor availability of HSE information further analysis could not be carried out.		
2,4,6-tribromophenyl allyl ether CAS No: 3278-89-5	Pyroguard FR 100, Great Lakes PHE-65, Bromkal 643AE	Two-step EPS process		Proposed as one of the 120 HPV chemicals structurally similar to known Arctic contaminants (Brown & Wania 2008). Likely bioaccumulative and subject to long range transport since the substance is found in Arctic seals in both blubber and brain (Von der Recke & Vetter 2007).		

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE), CAS No: 21850-44-2 with dicumene for XPS and dicumyl peroxide for EPS, as usual synergists	STARFLAME PS SAM 54: masterbatch for XPS STARFLAME PO SAM 55: masterbatch for XPS GC SAM 55 E: powder blend for EPS	EPS XPS	For XPS the alternative is already in use in commercial scale. For EPS only laboratory scale experience, not yet in wide use. All raw materials, however, are worldwide commodities and thus GC SAM 55 E is reported to be immediately available for up-scaling on a commercial scale.	According to the KLIF (2009) review, TBBPA-DBPE has low toxicity. No endocrine effects have been observed, but it has a high potential to inhibit estradiol sulfotransferase and have a moderate competition with the thyroxine for the binding to the plasma protein transthyretin. TBBPA-DBPE is poorly absorbed through the gastrointestinal tract in rats, but the absorbed quantities accumulate in liver and slowly metabolize. The available information does not allow assessing the environmental persistence (Washington State 2006). According to KLIF (2009) and the information from the manufacturer, TBBPA-DBPE has low biodegradability but appears to be susceptible to hydrolysis. Contradicting conclusions on bioaccumulation are reported in Washington State (2006) and KLIF (2009). According to the manufacturer bioaccumulation is not expected. The National Toxicology Program (NTP) believes that the substance might have a carcinogenic potential. Positive for mutagenic activity with and without metabolic activation in Salmonella typhimurium strains (NIEHS 2002). bis(α,α-dimethylbenzyl) peroxide is classified as + R51/53 : Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. It is also classified as + R36/38 : Irritating to eyes and skin (Assessment of Alternatives)	According to the manufacturer, comparable to HBCD solution in EPS (costs around 6.5 €/kg). Slightly more expensive than HBCD in XPS.	Flame retardant properties, 20-30% less than HBCD. Reportedly good thermal stability, easily dispersible and compatible with polystyrene, insoluble in water and soluble in Toluene and Xylene.

ANNEX B. ALTERNATIVES TO HBCD IN HIPS AND TEXTILES. ADAPTED FROM UNEP (2012)

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Ethylenebis (tetrabromophthalimide) (EBTPI) CAS No: 32588-76-4	BT93, BT93W, BT93WFG, Citex BT 93, Saytex BT93, Saytex BT93W	HIPS	Commercially available and used extensively. It is mostly used in HIPS, polyethylene, polypropylene, thermoplastic polyesters, polyamide, EPDM, rubbers, polycarbonate, ethylene co-polymers, ionomer resins, and textiles.	Very high hazard for persistence and high hazard for bioaccumulation. For detailed information see USEPA (2014b). The available data is insufficient for a comprehensive environmental assessment of EBTPI. The few studies reported indicate that EBTPI is not readily biodegradable, does not bioaccumulate and has a low aquatic toxicity (Danish EPA 2007). Indications are that EBTPI is of low mammalian toxicity (KLIF 2009). The EU Technical Committee of New and Existing Chemicals Substances (TCNES) considered EBTPI very persistent. However, the bioaccumulation criterion was not met based on molecular properties of the substance and EBTPI was not listed as a vPvB substance. The only available study of the aquatic toxicity of EBTPI indicates that acute toxic effects occur at levels much higher than the estimated water solubility. Long-term NOEC values are not found in the literature. More ecotoxicology data are required for assessment of the toxicity (T) criterion. (Pakalin <i>et al.</i> 2007).	Higher price compared to deca-BDE (ECHA, 2014).	Technically feasible and used extensively
Benzene, 1,1'-(1-methylethylidene) bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)] Synonym: TBBPA-bis brominated ether derivative CAS No: 97416-84-7	Pyroguard SR-130 SR-130 FR-130 AP 1300 S	EPS XPS HIPS	Commercially available. Japan was expected to replace HBCD with FR130 and polymeric FR (ICL-IP, 2014). Several producers in Europe and China.	The hazard profile show that these chemicals have limited data sets for human health endpoints and hazard designations show a potential for toxicity. Anticipated to have high potential for bioaccumulation. (USEPA, 2014a) The substance fulfils the screening criteria for persistence and bioaccumulation as defined in REACH Annex XIII section 3.1 and is therefore considered to be a potential PBT/vPvB substance (Baua, 2017). Final assessment not yet completed in January 2019.		Widely used.
Decabromodiphenyl ether (DecaBDE) CAS No: 11663-19-5	SAYTEX 102E FR-1210 DE-83R	HIPS Textiles	Commercially available and used extensively. Many manufacturers have phased use out since the early 2000's.	DecaBDE is a POP listed in Annex A to the Stockholm Convention in 2017 with specific exemptions.		Technically feasible and used extensively

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Decabromodiphenylethane (DBDPE) CAS No: 84852-53-9	SAYTEX 8010 Firemaster 2100 Planelon BDE S8010 FR-1410	HIPS Textiles Additive FR	Commercially available and used extensively. DBDPE was introduced in the mid-1980s and became commercially important as an alternative to DecaBDE formulations in the early 1990s. Europe does not produce DBDPE, but imports in 2001 were estimated to be between 1000 and 5000 tons, primarily to Germany. DBDPE is the second highest current use additive BFR in China with production increasing at 80% per year (http://www.polymer.cn/). It is produced by at least two Chinese companies: The production volume of DBDPE in China in 2006 was 12,000 tons (Xiao, 2006). In Japan, there has been a clear shift in consumption away from DecaBDE to DBDPE.	Very high hazard for persistence and high hazard for bioaccumulation and human developmental toxicity (based on analogy to experimental data for a structurally similar compound). For detailed information see USEPA (2014b). Available evidence indicates decabromodiphenylethane (DBDPE) is potentially persistent. It is not susceptible to abiotic degradation (e.g., hydrolysis) and is not readily biodegradable under aerobic conditions in the aquatic environment (viz: 2% according to OECD 301C). Persistence is linked to low water solubility (0.72 µg/L). (Environment Agency 2007, Pakalin et al. 2007). DBDPE has a relatively low hazard potential to aquatic organisms due to its low water solubility. It is also of low toxicity to mammals (Environment Agency 2007). DBDPE alters gene expression in chicken embryos (Egloff et al. 2011), is acutely toxic to <i>Daphnia magna</i> , reduces the hatching rates of zebra-fish eggs, and significantly raises the mortality of hatched larvae (Nakari & Huhtala 2010). In the risk assessment made by the UK, conclusions on bioaccumulation were not possible in the absence of reliable data (Environment Agency 2007). Recent information shows that in fish DBDPE bioaccumulates one order of magnitude higher than DecaBDE which indicates it can significantly accumulate in fish (He et al. 2012). DBDPE is found in predator avian species such as falcons and their eggs (Guerra et al. 2012) and in piscivorous water birds (Luo et al. 2009). In a Lake Winnipeg food web DBDPE was found to biomagnify (Law et al. 2009). DBDPE is widely detected in environmental samples; sewage sludge, air, sediments, fish and birds, as well as in house and office dust (La Guardia et al. 2012). In a recent Nordic screening study (NCM 2011), DBDPE was found in 100% of air, 50% of sediment, 100% of sludge and 70% of biota samples. The concentrations were often comparable with BDE-47 and BDE-209 levels found. DBDPE has also been found in house dust in the US (Stapleton et al. 2008), Belgium, UK (Ali et al. 2011) and Sweden (Karlsson et al. 2007). The chemical is the main BFR in human hair in non-e-waste recycling areas in China. Significant correlations were found between hair levels and dust levels (Zheng et al. 2011) suggesting endogenous pathways to hair.	According to one Party, DBDPE is commonly used in HIPS and textiles, with better effect than HBCD and approximately equal price as HBCD, and basically replaced HBCD in 2011 in this application in China. Higher price than deca-BDE (ECHA, 2014)	Technically feasible and used extensively

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Triphenyl phosphate CAS No: 115-86-6		HIPS	Commercially available and used extensively	<p>According to the classification provided by companies in the EU to ECHA in REACH registrations this substance is very toxic to aquatic life and is toxic to aquatic life with long lasting effects (ECHA brief profile, 2019).</p> <p>According to a review published by the Danish EPA (2007), TPP is highly toxic to algae, invertebrates and fish with typical LC50 values <1 mg/L. Two studies of the chronic toxicity in fish report NOEC values in the range 0.014-0.23 mg/L, however, the validity of the studies are questionable. BCF values >100 have been reported in several long-term studies with different species of fish, and TPP is considered to be potentially bioaccumulative. This is supported by the log Kow value for TPP (range 4.58-4.67). TPP is inherently biodegradable, and is furthermore found to biodegrade under both aerobic and anaerobic conditions in water/sediment and soil systems under various conditions. The log Kow and log Koc values indicate that the availability and the mobility of TPP in the environment is limited.</p> <p>No data was found with respect to acute or repeated human exposure. The only parameter affected in the Danish review in subacute and subchronic dietary studies in rats was retardation in weight gain (Danish EPA 2007). US EPA (2005) reports moderate systemic toxicity and high acute and chronic ecotoxicity of TPP as two characteristics of concern. The US Occupational Safety and Health Administration (OSHA) reports inhibition of cholinesterase as a health effect of triphenyl phosphate exposure (US OSHA 1999).</p> <p>Danish EPA (2007) concluded that triphenyl phosphate (TPP) does not meet the persistency and bioaccumulation criteria in the PBT assessment.</p> <p>Triphenyl phosphate is considered environmentally hazardous in Germany due to its toxicity to aquatic organisms (Leisewitz <i>et al.</i> 2000).</p> <p>In a recent study, triphenyl phosphate was associated with a substantial 19% decrease in sperm concentration in men (Meeker & Stapleton 2010).</p> <p>Very high hazard for acute and chronic aquatic toxicity. For detailed information see USEPA (2014b).</p>	Higher price than deca-BDE (ECHA, 2014)	Technically feasible and used extensively

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Bisphenol A bis (biphenyl phosphate) (BDP) CAS No: 5945-33-5	Fyrolflex BDP	HIPS Additive FR	Commercially available and used extensively	<p>According to the classification provided by companies to ECHA in REACH registrations this substance may cause long lasting harmful effects to aquatic life (ECHA brief profile, 2019).</p> <p>Bisphenol A bis (biphenyl phosphate) (BDP) is a phosphoric trichloride reaction product with bisphenol A and phenol. It may contain bisphenol A as an impurity.</p> <p>According to Washington State (2006) the results of the industry toxicity studies indicate low toxicity concern for humans, and low to medium toxicity concern for aquatic organisms. There are no animal cancer studies available for this chemical and no information on potential human exposures. The chemical does show a tendency to persist in the environment. Bioaccumulation could not be assessed.</p> <p>One of the BDP degradation products is bisphenol A (Washington State 2006), a substance declared by Canada to meet the criteria for persistence and toxicity concerns regarding permanent alterations in hormonal, developmental or reproductive capacity (Environment Canada 2008).</p> <p>Bisphenol A is classified in the EU as a substance that has toxic effects on reproduction. It was identified as an endocrine disruptor for human health and environment and listed in the EU Candidate List of substances of very high concern (SVHCs) due to its toxic for reproduction properties in January 2017. (ECHA, 2019a).</p>	Lower price than deca-BDE (ECHA, 2014)	Technically feasible and used extensively. Loading for HIPS 10-20% (ICL-IP, 2019a)
Diphenyl cresyl phosphate CAS No: 26444-49-5		HIPS	Commercially available and used extensively	<p>According to the classification provided by companies to ECHA in CLP notifications this substance is very toxic to aquatic life with long lasting effects, is very toxic to aquatic life and is harmful if swallowed. (ECHA brief profile, 2019).</p> <p>Diphenyl cresyl phosphate is poorly characterized but appears to be toxic to aquatic organisms and not readily biodegradable (OECD SIDS).</p> <p>According to the classification provided by companies to ECHA in CLP notifications this substance is very toxic to aquatic life with long lasting effects, is very toxic to aquatic life and is harmful if swallowed (ECHA, 2019b).</p> <p>According to Washington State (2006) half-life in water is 4.86 years, BCF 980 and it has moderate aquatic toxicity, has developmental and reproductive toxicity but is not mutagenic and has low oral toxicity.</p>		Technically feasible and used extensively

Chemical	Trade names	Claimed suitability	Availability	HSE properties	Costs	Efficacy
Chlorinated paraffins (C10-13) -CAS No: 85535-84-8		Textiles	Available and used extensively	Short-chain chlorinated paraffins (Alkanes, C10-13, chloro) with greater than 48% chlorination have been listed as a POP under the Stockholm Convention and cannot be considered as safe alternatives to HBCD. Because of the complex nature of CPs, it is not always possible to separate SCCPs from other CPs in chemical references. SCCP commercial products consist of mixtures of isomers and congeners, and the Cl % of a product does not allow for identification of compounds present in the mixture.	Used extensively	Technically feasible and used extensively
Ammonium polyphosphate - CAS RN 68333-79-9		Textiles	Available and used extensively	According to the classification provided by companies to ECHA in REACH registrations this substance is harmful if swallowed and causes serious eye irritation. (ECHA brief profile, 2019) Little data is available on properties. There is no data on bioaccumulation. In Canada the chemical is categorized as Persistent and Inherently Toxic.	Used extensively	Technically feasible and used extensively
Resorcinol bis (biphenyl phosphate) - CAS RN 57583-54-7				Available data on the toxicity of RDP for human health are limited, and are essentially toxicokinetic studies, repeated dose toxicity studies, neurotoxicity studies and developmental and reproductive toxicity studies conducted with the commercial product RDP. These data showed a possible neurotoxic effect on several species (3 studies in rat and hen), an increase in weight of the adrenal glands, and a possible developmental effect in the rat (a single 2G study available showing a delay in preputial separation and vaginal opening and an increase in weight of the adrenal glands). Only one toxicity study was conducted with pure RDP. It shows that the exposure of pregnant rabbits by oral gavage from GD6 to GD28 shows fetal malformations at 1000 mg/kg/d. (France, 2018)		Resorcinol bis (biphenyl phosphate) shows moderate fire retardant activity in HIPS, whereas in PPO/HIPS alloy it is an efficient fire retardant additive (Murashko <i>et al.</i> , 1998).

www.pops.int

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