Annex F Questionnaire (one per chemical)

Chemical name (as used by the POPS Review Committee (POPRC))

Hexabromobiphenyl (HBB)
CAS = Hexabromo -1,1'-biphenyl
CAS number = 36355-01-8 (see CAS numbers for other isomers in POPRC risk profile for HBB)
Common trade names: FireMaster(R) BP-6, FireMaster(R) FF-1

Explanatory note:
1. This chemical is undergoing a risk management evaluation. It has already satisfied the screening criteria set out in paragraph 4 (a) of Article 8 of the Convention. A risk profile has also been completed for this chemical in accordance with paragraph 6 of Article 8 and with Annex E to the Convention.

Introductory information

Name of the submitting Party/observer

NGO Observer: Environmental Health Fund on behalf of the International POPs Elimination Network (IPEN)

Contact details (name, telephone, e-mail) of the submitting Party/observer)

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Date of submission

8 February 2007

Additional Annex E information

(i) Production data, including quantity and location

(ii) Uses

This study examined contaminant levels of plastic fractions of European waste electrical and electronic equipment. “With respect to contaminants, our data indicate an effective phase-out of PBB, but still high levels of PBDE and PBDD/F are found. Sources and implications for the material recycling and thermal recovery approaches are discussed in detail.”
Schlummer M, Gruber L, Maurer A, Wolz G, van Eldik R. Department Product Safety and Analysis, Fraunhofer-Institute for Process Engineering and Packaging, Giggenhauser Str. 35, 85354 Freising, Germany. Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management. Chemosphere. 2007 Jan 4

(iii) Releases, such as discharges, losses and emissions

This study measured the concentrations of PBBs, PBDDs, and PBDFs in commercial PBDE mixtures. "Commercial PBDE mixtures tested in the present study contained both PBBs and PBDFs, as impurities, at concentrations in the range of several tens to several thousands of nanograms per gram. Concentrations of total PBDFs were greater than those of total PBBs in DE-79 and DE-83 mixtures. PBDDs were not detected at levels above the limit of detection. Profiles of PBB and PBDF congeners varied with the degree of bromination of the commercial PBDE mixtures (i.e., more highly brominated mixtures of PBDEs contained heavily brominated homologues of PBBs and PBDFs). On the basis of the production/ usage of commercial PBDE mixtures in 2001, potential global annual emissions of PBBs and PBDFs were calculated to be 40 and 2300 kg, respectively. Results of our study suggest that PBDFs can also be formed during the production of commercial PBDE mixtures, in addition to their formation during pyrolysis of brominated flame retardants."

Hanari N, Kannan K, Miyake Y, Okazawa T, Kodavanti PR, Aldous KM, Yamashita N. National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. Occurrence of polybrominated biphenyls, polybrominated dibenzo-p-dioxins, and polybrominated dibenzofurans as impurities in commercial polybrominated diphenyl ether mixtures. Environ Sci Technol. 2006 Jul 15;40(14):4400-5.

Explanatory note:

2. This information was requested for preparation of the risk profile in accordance with Annex E of the Convention. The POPRC would like to collect more information on these items. If you have additional or updated information, kindly provide it.

A. Efficacy and efficiency of possible control measures in meeting risk reduction goals (provide summary information and relevant references):

(i) Describe possible control measures

HBB has already been widely subjected to the control measures similar to those outlined in Annex A of the Stockholm Convention: elimination of production, use, export, and import. The HBB Risk Profile indicates that worldwide production of polybrominated biphenyls ended in 2000.[1]

(ii) Technical feasibility

The essential phase-out of global production and use indicates that technically feasible alternatives have already been implemented.

[1] Risk profile on Hexabromobiphenyl UNDP/POPS/POPRC.2/17/Add.3, November 2006

(iii) Costs, including environmental and health costs

The considerable phase-out of HBB that has already occurred indicates that costs of alternatives have not inhibited their substitution. Important points to consider when evaluating the costs of alternatives for any product include[2]:

- Alternatives with a higher initial purchase cost may actually be more cost effective over the life of the product when durability and other factors are taken into account.
- Mass-production of alternatives can significantly lower their costs.
- The costs of initiatives to protect health and the environment are frequently overestimated in advance and later decline rapidly after the regulation is implemented.

In addition, there are inherent problems with using cost-benefit analysis to evaluate risk reduction and regulatory decisions.[3] A fundamental problem is the difficulty of estimating the benefits attributed to a particular control measure. There is no meaningful way of assigning a dollar figure to human and environmental health. Efforts to do so usually place market values over social values. As summarized in a recent overview of the topic, “A cost-benefit analysis requires a number for each cost and benefit, no matter what the level of uncertainty may be. There is enormous pressure, in effect, to ignore all uncertainty and develop a single best estimate based on what is known today.” Cost-benefit analysis is usually justified as a necessary screen in a world of competing priorities. However, as the authors point out, “…resources are of course ultimately limited, but there is no evidence that we have approached the limits of what is possible (or desirable) in health and environmental protection.” Regarding employment implications of health and environmental initiatives, the authors comment that, “…virtually no job losses can be traced to environmental regulations. On the average 999 out of every 1000 major layoffs are not due to environmental policies.” [4]

The POPRC has already concluded that HBB, due to the characteristics of its components, is likely, as a result of long-range environmental transport and demonstrated toxicity in a range of non-human species, to cause significant adverse effects on human health and the environment, such that global action is warranted.[5] This indicates that elimination of HBB production, use, export, and import with a listing in Annex A of the Stockholm Convention would benefit human health or the environment. No discernible negative impacts on society have been reported from prohibition or phase-out of HBB.

Explanatory notes:

[2] Ackerman F, Massey R. The Economics of Phasing Out PVC, Global Development and Environment Institute, Tufts University, USA, May 2006 http://www.ase.tufts.edu/gdae/Pubs/rp/Economics_of_PVC_revised.pdf

[3] Heinzerling L, Ackerman. Priceless: Human Health, the Environment and Limits of the Market. The New Press, 288 pages, 2004

[4] Heinzerling L, Ackerman. Priceless: Human Health, the Environment and Limits of the Market. The New Press, 288 pages, 2004

[5] Risk profile on Hexabromobiphenyl UNDP/POPS/POPRC.2/17/Add.3, November 2006

3. If relevant, provide information on uses for which there may be no suitable alternative or for which the analysis of socio-economic factors justify the inclusion of an exemption when considering listing decisions under the Convention. Detail the negative impacts on society that could result if no exemption were permitted.
4. "Risk reduction goals" could refer to targets or goals to reduce or eliminate releases from intentional production and use, unintentional production, stockpiles, wastes, and to reduce or avoid risks associated with long-range environment transport.
5. Provide the costs and benefits of implementing the control measure, including environmental and health costs and benefits.
6. Where relevant and possible "costs" should be expressed in US dollars per year.

B. Alternatives (products and processes) (provide summary information and relevant references):

(i) Describe alternatives

The HBB Risk Profile describes three principal commercial products that contained HBB in the USA and Canada: 1) acrylonitrile-butadiene-styrene (ABS) thermoplastics used for business machine housings and electrical products such as radio and TV; 2) as a fire retardant in cable coatings and lacquers, and 3) in polyurethane foam for auto upholstery.[6]

US EPA has described design changes and chemical substitutes that eliminate the use of brominated flame retardants such as PentaBDE or HBB in polyurethane foam.[7] The Danish Environmental Protection Agency has described alternative halogen-free flame retardants for a variety of uses including epoxy, phenolic resins, rigid and soft polyurethane foam, textiles, and a variety of plastics including ABS.[8] Both drop-in chemical substitutes and alternative materials are listed. Finally, the German Federal Ministry of Environment has reported on alternatives for flame retardants used in electronics, upholstery, and other sectors.[9]

ABS alternatives

The Danish report does not describe chemical alternatives for ABS. Instead, the report lists PC/ABS blends with or without phosphorous compounds as an alternative for use in ABS and notes that there are no requirements for flame retardancy in expanded styrene in Denmark.

Organic phosphorous compounds that can serve as alternatives are available as halogenated or non-halogenated substances.

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[6] Risk profile on Hexabromobiphenyl UNDP/POPS/POPRC.2/17/Add.3, November 2006
[7] USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam http://www.ecy.wa.gov/biblio/0507048.html
[8] Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999
[9] Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

The halogenated organic phosphorous compounds contain properties that argue against commercial use. The German report lists several halogenated organophosphorous compounds including tris-chloropropyl-phosphate, tris-chloroethyl-phosphate, and tris dichloropropyl phosphate.[10] The WHO review of tris dichloropropyl phosphate notes the formation of kidney, testicular, and brain tumors at all exposure levels (5-80 mg/kg) and additional adverse effects on bone marrow, spleen, testis, liver and kidney.[11] In the same review, WHO assessed tris-chloropropyl-phosphate and described it as "not readily degraded" in sewage sludge and present in peaches, pears, and fish. The US EPA Design for Environment report discussed above at the beginning of this submission describes tris dichloropropyl phosphate as having moderate concern for carcinogenicity, reproductive toxicity, developmental toxicity, systemic toxicity, genotoxicity, acute and chronic ecotoxicity, and persistence.[12] A study of tri-chloroethyl phosphate revealed dose-, sex-, and species-dependent lesions in the hippocampal region of the brain following subchronic oral administration to F344 rats.[13] Significant effects of tri-chloroethyl phosphate on murine reproduction including fewer and smaller litters were observed in another study.[14] Another study revealed toxic effects of chronic exposure to tri-chloroethyl phosphate on the brain and kidney.[15]

Non-halogenated organic phosphorous compounds are listed as alternatives for HIPS and PC plastics in the Danish report. Included in this class are commonly used non-halogenated substances such as triphenyl phosphate (TPP), tricresyl phosphate (TCP), resorcinol bis(diphenylphosphate) (RDP), and phosphonic acid (2-((hydroxymethyl) carbamyl)ethyl)-, dimethyl ester (Pyrovatex®).

As noted above, US EPA 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.[16] Bioconcentration factors in several fish species vary from 6 – 18,900.[17] In addition, triphenyl phosphate TPP is considered environmentally

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

[11] WHO Environmental Health Criteria 209: Flame retardants: tris(chloropropyl) phosphate and tris)2-chloroethyl) phosphate, 1998 http://www.who.int/ipcs/publications/ehc/who_ehc_209.pdf

[12] USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam http://www.ecy.wa.gov/biblio/0507048.html

[13] Burka LT, Sanders JM, Herr DW, Matthews HB. Experimental Toxicology Branch, National Institutes of Environmental Health Sciences, Research Triangle Park, NC 27709. Metabolism of tris(2-chloroethyl) phosphate in rats and mice. Drug Metab Dispos. 1991 Mar-Apr; 19(2)443-7

[14] National Toxicology Program, Tris(2-chloroethyl) phosphate Robert Chapin project officer, Dushyant Gulati and Leta Barnes, Environmental Health Research and Testing July 1991 http://www.ehponline.org/members/1997/Suppl-1/dfa968.html

[15] Matthews HB, Eustic SL, Haseman J. National Institute of Environmental Health Science, Research Triangle Park, North Carolina 27709. Toxicity and carcinogenicity of chronic exposure to tris(2-chloroethyl)phosphate. Fundam Appl Toxicol. 1993 May; 20(4): 477-85

[16] US Occupational Safety and Health Administration, Chemical Sampling Information, 19 January 1999 http://www.osha.gov/dts/chemicalsampling/data/CH_274400.html

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

hazardous in Germany due to its toxicity to aquatic organisms.[18] RDP is usually used in combination with TPP. Both the German and Danish reports comment on the insufficiency of human and environmental toxicity data for RDP.

Tricresyl phosphate toxicity apparently differs according to isomer: the ortho isomer is very toxic and potentially bioaccumulative and efforts are made to exclude it from commercial products.[19] [20] The mixture of isomers depends on the production method, particularly the cresols used as the starting material. Estimates indicate that current mixtures of tricresyl phosphate should contain less than 1% of the ortho isomer.[21]

Pyrovatex is not well-characterized though the Danish report notes that it is a weak inhibitor of acetyl choline esterase and the microsomal enzyme system and that high concentrations induced chromosome aberrations and reverse mutations.[22] The German alternatives report notes that the Pyrovatex easily separates formaldehyde and often is used together with ethylene carbamide to help trap released formaldehyde.[23] Due to the absence of toxicity information and its possible transmission to humans from use of consumer products, the report concludes that the data insufficient to be able to make a recommendation.

Alternatives in coatings and lacquers

The Danish report estimates 1 – 5 tonnes of PBB and 1 – 5 tonnes of PBDE were used in rubber cables in Denmark in 1997. The report (from 1999) states that, “There is a wide range of cables marketed as halogen-free and a pronounced trend away from halogen-containing flame retardants.” Halogen-free rubber cables can contain aluminum trihydroxide and zinc borate as flame retardant alternatives and incorporate the ethylene vinyl acetate polymer as well.

Aluminum trihydroxide is commonly used, effective, and also suppresses smoke.[24] Its functional disadvantage is that large amounts are required (up to 50%) which can affect

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

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

[20] WHO, Environmental Health Criteria 110; Tricresyl phosphate 1990 http://www.inchem.org/documents/ehc/ehc/ehc110.htm

[21] Danish Environmental Protection Agency, Toxicological evaluation and limit values for nonylphenol, nonylphenol ethoxylates, tricresyl, phosphates and benzoic acid, 1999 http://www2.mst.dk/common/Udgivramme/Frame.asp?pg=http://www2.mst.dk/Udgiv/publications/1999/87-7909-566-6/html/tric/kap01.htm

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

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

[24] Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999 http://www2.mst.dk/common/Udgivramme/Frame.asp?pg=http://www2.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/kap08_eng.htm

the properties of the material. The Danish Alternatives report summarizes the toxicity of the substance as very low except when there are high exposure levels or unusual routes of exposure and estimates that it would be extremely unlikely for its use in consumer products to cause adverse effects. Another review reports mitogenicity and cytotoxicity along with teratogenic effects only in combination with aluminum lactate or lactic acid.[25] Accumulation of the substance in food chains is not detectable. The German alternatives report describes the use of aluminum trihydroxide as a flame retardant as "unproblematic."

Zinc borate is often combined with aluminum trihydroxide and used to substitute for antimony trioxide. The German Federal Ministry of Environment report on flame retardant alternatives describes the teratogenicity of boron along with its ability to irritate the eyes, respiratory organs, and skin at high levels.[26] The German report describes the daily intake of boron from food at 1.6 – 4.5 mg/person per day and assumes that its use as a flame retardant will not result in significant additional concentrations for humans. However, it would be important to measure the ability for boron to be released in dust before its wide use in consumer products in homes.

Alternatives for polyurethane foams

Design changes

The US EPA has described design changes that eliminate the use of PentaBDE and other brominated flame retardants such as HBB in polyurethane foam. [27] Currently available alternatives include barrier technologies and graphite impregnated foam. Barrier technologies have the widest immediate commercial applicability and involve layers of materials that provide fire resistance. These include boric acid-treated cotton materials used in mattresses; blends of natural and synthetic fibers used in furniture and mattresses (VISIL, Basofil, Polybenzimidazole, KEVLAR, NOMEX and fiberglass); and high performance synthetic materials used in firefighter uniforms and space suits. The manufacturing processes of the synthetic materials should be evaluated for use of toxic chemicals and preference given to those with the least hazardous synthetic pathway. Graphite impregnated foam is flame resistant and used in aircraft seating. Finally, some manufacturers have re-designed products to even eliminate the use of filling material such as Herman Miller.[28]

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

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

[27] USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam http://www.ecy.wa.gov/biblio/0507048.html

[28] Lowell Center for Sustainable Production, Prepared by Pure Strategies, University of Massachusetts Lowell, Lowell MA 01854, Decabromodiphenylether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. April 2005

Barrier technologies that use cotton and boric acid appear to offer a flame retardant system that is commercially available and affordable. The German Federal Ministry of Environment report on flame retardant alternatives describes the teratogenicity of boron along with its ability to irritate the eyes, respiratory organs, and skin at high levels.[29] The German report describes the daily intake of boron from food at 1.6 – 4.5 mg/person per day and assumes that its use as a flame retardant will not result in significant additional concentrations for humans. However, it would be important to measure the ability for boron to be released in dust before its wide use in consumer products in homes.

Chemical substitutes

Chemical substitutes for HBB or PentaBDE are also commercially available and described in the US EPA Design for Environment report on flame retardant alternatives.[30] Table 4-1 in the report shows the toxicological properties of 30 substances from twelve products. Unfortunately, 12 of these substances have a moderate or high concern for persistence or would produce persistent degradation products (see table below). An additional 6 substances have a moderate concern for the ability to bioaccumulate. Substitution of these products for HBB or PentaBDE would substitute one persistent, bioaccumulative substance for another. For this reason, these products would not be appropriate substitutes.

An examination of the remaining products/substances shows that many utilize triphenyl phosphate which raises moderate concerns for systemic toxicity and high acute and chronic ecotoxicity (see below).

Tribromoneopentyl alcohol used in Ameribrom FR513 shows moderate concerns for carcinogenicity, reproductive, developmental, neurotoxicity along with moderate acute and chronic ecotoxicity. The proprietary aryl phosphates used in the Supresta products display moderate systemic toxicity with one also having moderate genotoxicity and high chronic ecotoxicity (see table below). These products should be actually tested to yield empirical evidence of their toxicity characteristics before being considered for use in commerce.

The drop-in chemical substitutes for HBB or PentaBDE in polyurethane foam described above either possess persistence and bioaccumulation properties or display ecotoxicity, systemic toxicity, and other characteristics of concern. As noted above, further characterization of the Supresta ACO73 components might reveal the full potential toxicity of this product. Unfortunately, the commercial product still contains triphenyl phosphate which causes high acute and chronic ecotoxicity.

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

[30] USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam http://www.ecy.wa.gov/biblio/0507048.html

Persistent and bioaccumulative alternatives for use in polyurethane foam described by US EPA

Persistence (moderate, high, or persistent degradation products expected)	Albemarle Antiblaze 180 and 195 Tris (1,3-dichloro-2-propyl) phosphate CAS 13674-87-8 Albemarle Antiblaze 182 and 205 Proprietary A chloroalkyl phosphate Albemarle Antiblaze V500 Proprietary C chloroakyl phosphate Albemarle Saytex RX-8500 Proprietary D reactive brominated flame retardant [b] Albemarle Saytex RZ-243 Proprietary E tetrabromophthalate diol diester [b] Great Lakes Firemaster 550 Proprietary F Halogenated aryl ester [b] Great Lakes Firemaster 550 Proprietary H halogenated aryl ester [b] Great Lakes Firemaster 552 Proprietary F halogenated aryl ester [b] Great Lakes Firemaster 552 Proprietary H halogenated aryl ester [b] Supresta AB053 Tris (1,3-dichloro-2-propyl) phosphate CAS 13674-87-8 Supresta AC003 Propietary I organic phosphate ester Supresta Fyrol FR-2 Tris (1,3-dichloro-2-propyl) phosphate CAS 13674-87-8
Bioaccumulation (moderate)	Albemarle Antiblaze 182 and 205 Proprietary B aryl phosphate [a] Albemarle Antiblaze V500 Proprietary B aryl phosphate [a] Albemarle Saytex RX-8500 Proprietary B Aryl phosphate [a] Albemarle Saytex RZ-243 Proprietary B Aryl phosphate [a] Great Lakes Firemaster 550 Proprietary G triaryl phosphate CAS 115-86-6 [a] Great Lakes Firemaster 552 Proprietary G triaryl phosphate isopropylated [a]

[a] assigned using estimated values and structure activity relationships
[b] persistent degradation products expected

Toxicity properties of concern in alternatives to PBDE in polyurethane foams described by US EPA

Substance	Properties of concern
Albemarle Antiblaze 182 and 205 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Albemarle Antiblaze V500 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Albemarle Saytex RX-8500 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Albemarle Saytex RZ-243 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Ameribrom FR513 Tribromoneopentyl alcohol CAS 36483-57-5	Moderate cancer, reproductive, developmental, and neurological hazard[a]; Moderate acute and chronic [a] ecotoxicity
Great Lakes Firemaster 550 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Great Lakes Firemaster 552 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Supresta AC003 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Supresta AC073 Triphenyl phosphate CAS 115-86-6	Moderate systemic toxicity; High acute and chronic[a] ecotoxicity
Supresta AC073 Proprietary J Aryl phosphate	Moderate systemic and genotoxicity; High chronic[a] ecotoxicity
Supresta AC073 Proprietary K Aryl phosphate	Moderate systemic toxicity[a]
Supresta AC073 Proprietary L Aryl phosphate	Moderate systemic toxicity[a]

[a] assigned using estimated values and structure activity relationships

The Danish report lists ammonium polyphosphate and red phosphorous as alternatives for rigid polyurethane foam and ammonium polyphosphate, melamine, and reactive phosphorous polyols as alternatives for soft polyurethane foam.

Ammonium polyphosphate is often used in combination with aluminum trihydroxide. The substance metabolizes into ammonia and phosphate and is not thought to cause acute toxicity in humans.[31] However, there are no analyses of long-term toxicity, teratogenicity, mutagenicity, or carcinogenicity. Ammonium polyphosphate breaks down rapidly and does not accumulate in the food chain. The German alternatives report concludes that skin irritation is possible due to the formation of phosphoric acids but that the substance appears to be "unproblematic".

Red phosphorous is easily ignited and poorly characterized toxicologically. The German Flame Retardant study reports that there is no data available for red phosphorous on ecotoxicity, carcinogenicity, mutagenicity, long-term toxicity, or toxicokinetics.[32] In addition, the report notes that no data exists on concentrations of red phosphorous in indoor or outdoor air (from sewage sludge) as a consequence of incorporating red phosphorous into products. Eye and mucous membrane irritation can result due to the formation of phosphoric acid. Ecosystem accumulation is thought to be unlikely. A 1990 US government report examined the behavioral and physiological effects of red phosphorous/butyl rubber smoke inhalation on black-tailed prairie dogs (Cynomys ludovicianus) and rock doves (Columbia livia) but this report was not available.[33] Other US government researchers have noted that high levels of toxic phosphine were observed during long-term storage of red phosphorous.[34] The Danish report describes its risk factors as "…including flammability and autoignition, and disproportionation will give toxic phosphine" and suggests that "…smaller producers of plastic products avoid the use of red phosphorous."[35]

Melamine and its derivatives display several toxic effects. These include changed electrolyte compositions of urine, teratogenic effects in fertilized rainbow trout eggs, and

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

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

[33] Sterner RT, Shumake SA, Thompson RD, Johns BE. Animal and Plant Health Inspection Service, Denver, CO. Denver Wildlife Research Center**.** Behavioral-Physiological Effects of Red Phosphorus Smoke Inhalation on Two Wildlife Species. Govt Reports Announcements & Index (GRA&I), Issue 23, 1990

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

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

reproductive effects in snails and houseflies.[36] In addition, melamine caused chronic injury to the male rat bladder due to stones formed during exposure which correlated strongly with carcinoma.[37] In a fire, melamine cyanurate will release toxic fumes such as hydrocyanic acid and isocyanate.[38] The Danish report notes that there is no data on emission from products and that melamine appears to have low acute and chronic toxicity. The report concludes that, "…no adverse effects are envisaged from the level of exposure expected from the use of melamine as a flame retardant. At the level of exposure precipitation in the renal tubulus and in the bladder should not be a significant risk." [39] In contrast, the German report describes the lack of data, presence in environmental samples and moderate organ toxicity of melamine and concludes it is a "…problematic substance."[40]

Specific reactive phosphorous polyols were not identified in the Danish report though polyglycol esters of methyl phosphonic acid (CAS 676-97-1) have been used for flame retardants in polyurethane foam (e.g. CAS 294675-51-7).[41] Methyl phosphonic acid has attracted the attention of those working on chemical weapons since it is a degradation product of VX, sarin, and soman.[42] Researchers at the Oak Ridge National Laboratory in the US describe methyl phosphonic acid as one of degradation products of chemical weapons with "significant persistence." [43] Other types of toxicity information are minimal but note that the substance reacts violently with water.[44] The phosphonic acid family also includes amino-methyl phosphonic acid, a degradation product of the herbicide, glyphosate (also known as [carboxymethylamino] methyl phosphonic acid.)

Assessing alternatives

The Danish alternatives report makes the following conclusions in its assessment:
1) Substitutes are available for most applications at relatively low extra cost;

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[36] Daugherty ML. Chemical hazard information profile draft report: Melamine, CAS No. 108-78-1, Office of Toxic Substances, US EPA, 1982.
[37] Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999
[38] Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000
[39] Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999
[40] Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000
[41] OPCW Declarations Branch, Some Scheduled Chemicals, 2006 http://www.opcw.org/docs/publications/some%20scheduled%20chemicals.pdf
[42] Munro NB, Talmage SS, Griffin GD, Waters LC, Watson AP, King JF, Hauschild V. Life Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA**.** The sources, fate, and toxicity of chemical warfare agent degradation products. Environ. Health Perspect. 107 (12): 933-974. 1999
[43] Munro NB, Talmage SS, Griffin GD, Waters LC, Watson AP, King JF, Hauschild V. Life Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA**.** The sources, fate, and toxicity of chemical warfare agent degradation products. Environ. Health Perspect. 107 (12): 933-974. 1999
[44] US EPA Chemical Profile: methyl phosphonic dichloride. Extremely hazardous substances, section 302 of EPCRA, Chemical Emergency Preparedness and Prevention, 1985 http://yosemite.epa.gov/oswer/ceppoehs.nsf/Profiles/676-97-1?OpenDocument

2) Criteria for developing functional flame retardants should include non-hazardous synthetic pathway, minimum human and environmental toxicity, minimum release during product use, minimum formation of hazardous substances during incineration or burning, recyclable, degradable, and decompose into a non-hazardous substance;
3) Organophosphorous compounds can be released from products in significant amounts;
4) Inorganic phosphorous compounds are more positive than organophosphorous ones though a more comprehensive assessment is needed;
5) Aluminum hydroxide has desirable minimal toxicity characteristics presumable shared by magnesium hydroxide though no assessment is currently available;
6) High loading may be a disadvantage
7) Zinc borate and melamine may be desirable but require a more comprehensive assessment

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

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

One screening guide focuses on evaluating environmentally preferable flame retardants for TV enclosures by developing and using a "Green Screen".[45] The criteria used by the Green Screen include: hazard endpoints with categories of high, medium, and low; criteria for determining each level of chemical concern; and consideration of degradation products and metabolites. The Screen places a substance into one of four categories: Avoid – very high concern, Use – but search for safer substitutes, Use – but still opportunity for improvement, and Prefer – green chemical.

For an overarching approach to the topic of alternatives assessment, the Lowell Center for Sustainable Production has developed an Alternatives Assessment Framework with the goal of, "Creating an open source framework for the relatively quick assessment of safer and more socially just alternatives to chemicals, materials, and products of concern." [46] The Framework discusses goals, guiding principles, decision making rules, comparative and design assessment, and types of evaluation. Since the Framework is designed to be an open source tool, the Lowell Center encourages companies, NGOs, and governments to use, adapt, and expand on it.

[45] Rossi M, Heine L. Clean Production Action, Green Blue, The Green Screen for Safer Chemicals – Version1.0: Evaluating environmentally preferable flame retardants for TV enclosures, 2007 http://www.cleanproduction.org/Home.php
[46] Rossi M, Tickner J, Geiser K. Alternatives Assessment Framework, Lowell Center for Sustainable Production, Version 1.0, July 2006 http://www.chemicalspolicy.org/downloads/FinalAltsAssess06_000.pdf

(ii) Technical feasibility

All the alternatives described above are technically feasible and have been used in commercial applications.

(iii) Costs, including environmental and health costs

The Danish Alternatives Report describes costs of alternatives to brominated flame retardants in general as follows: “The prices of the alternatives are in general not higher than the BFRs but higher loading is often necessary. This is in particular true with respect to the inorganic compounds aluminum trihydroxide and magnesium hydroxide. Due to the low price of aluminum trihydroxide alternative materials may not be more expensive than BFR containing materials, but magnesium containing materials will usually be significantly more expensive.” [47] US EPA describes the boric acid-treated cotton alternatives used as barriers as, “…the least expensive flame-retardant barrier materials available.” [48]

(iv) Efficacy

The alternatives described above meet US federal and state regulatory requirements along with standards bodies such as ASTM and UL.

(v) Availability

The alternatives described here are available since many are already in commercial use.

(vi) Accessibility

The alternatives described here are accessible since many are already in commercial use.

Explanatory notes:

7. Provide a brief description of the alternative product or process and, if appropriate, the sector(s), use(s) or user(s) for which it would be relevant.
8. If several alternatives could be envisaged for the chemical under consideration, including non-chemical alternatives, provide information under this section for each alternative.
9. Specify for each proposed alternative whether it has actually been implemented (and give details), whether it has only reached the trial stage (again, with details) or whether it is just a proposal.
10. The evaluation of the efficacy should include any information on the performance, benefits, costs, and limitations of potential alternatives.
11. Specify if the information provided is connected to the specific needs and circumstances of developing countries.
12. The evaluation of the risk of the alternative should include any information on whether the proposed alternative has been thoroughly tested or evaluated in order to avoid inadvertently increasing risks to human health and the environment. The evaluation should include any information on potential risks associated with untested alternatives and any increased risk over the life-cycle of the alternative, including manufacture, distribution, use, maintenance and disposal.
13. If the alternative has not been tried or tested, information on projected impacts may also be useful.
14.Information or comments on improving the availability and accessibility of alternatives may also be useful.

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

[48] USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam http://www.ecy.wa.gov/biblio/0507048.html

C. Positive and/or negative impacts on society of implementing possible control measures (provide summary information and relevant references):

(i) Health, including public, environmental and occupational health

Elimination of HBB production, use, export, and import through a listing in Annex A of the Stockholm Convention would positively impact human health and the environment by preventing use of a persistent toxic substance that warrants global action. As outlined in the Risk Profile, HBB displays toxic effects including induction of metabolizing enzymes, immunotoxicity, hepatotoxicity, reproductive toxicity, carcinogencity, and hyperthyroidism.[49] HBB is apparently not currently in use. A listing in Annex A would prevent future production and integration into products of a substance that 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.[50]

(ii) Agriculture, including aquaculture and forestry

(iii) Biota (biodiversity)

(iv) Economic aspects

Cost competitive alternatives that do not exhibit POPs characteristics have already been implemented by companies for all uses of HBB.

(v) Movement towards sustainable development

Reduction and elimination of HBB is consistent with sustainable development plans that seek to reduce emissions of toxic chemicals. A relevant global plan is the Strategic Approach to International Chemicals Management (SAICM) that emerged from the World Summit on Sustainable Development.[51] Over 100 health and environment ministers agreed to the SAICM which was adopted at a high-level meeting in Dubai in February 2006.[52] SAICM makes the essential link between chemical safety, sustainable development, and poverty reduction.[53] The Global Plan of Action of SAICM contains specific measures to support risk reduction that include prioritizing safe and effective alternatives for persistent, bioaccumulative, and toxic substances. The Overarching Policy Strategy of SAICM includes POPs as a class of chemicals to be prioritized for halting production and use and substitution with safer substitutes.

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[49] Risk profile on Hexabromobiphenyl UNDP/POPS/POPRC.2/17/Add.3, November 2006
[50] Risk profile on Hexabromobiphenyl UNDP/POPS/POPRC.2/17/Add.3, November 2006
[51] http://www.chem.unep.ch/saicm/
[52] UNEP Press Release, New Global Chemicals Strategy Given Green Light by Governments, 7 February 2006 http://www.chem.unep.ch/saicm/iccm_sec.htm
[53] http://www.chem.unep.ch/saicm/SAICM%20texts/SAICM%20documents.htm

(vi) Social costs

Since HBB has already been replaced with other substances, the impact of an Annex A listing on consumers should be invisible.

Explanatory notes:

15. Socio-economic considerations could include:

- Any information on the impact (if any), costs and benefits to the local, national and regional economy, including the manufacturing sector and industrial and other users (e.g., capital costs and benefits associated with the transition to the alternatives); and impacts on agriculture and forestry;
- Any information on the impact (if any) on the wider society, associated with the transition to alternatives, including the negative and positive impacts on public, environmental, and occupational health. Consideration should also be given to the positive and negative impacts on the natural environment and biodiversity.
- Information should be provided on how control measures fit within national sustainable development strategies and plans.

D. Waste and disposal implications (in particular, obsolete stocks of pesticides and clean-up of contaminated sites) (provide summary information and relevant references):

Since HBB has already been largely phased-out, the impact on municipal waste and disposal should be minimal. The Risk Profile outlines former consumer uses of HBB including ABS plastic used for business machine housings and electrical products such as radio and TV, cable coatings, and polyurethane foam. In addition there are concerns over export of electronic waste to developing countries leading to HBB releases during recycling operations. Finally, burning or incineration of HBB-containing waste could lead to formation and release of brominated dibenzo-*p*-dioxins and furans. A listing of HBB in Annex A would subject wastes products or articles containing the substance to Article 6 of the Stockholm Convention and require that they be disposed, "…in a safe, efficient and environmentally sound manner." [54]

(i) Technical feasibility

(ii) Costs

Explanatory note:

16. Specify if the information provided is connected to the specific needs and circumstances of developing countries.

E. Access to information and public education (provide summary information and relevant references):

Listing HBB in Annex A will involve control measures that are straight forward to communicate and therefore should be effective and suitable, even in countries that have limited chemical regulatory infrastructure.

[54] Stockholm Convention on Persistent Organic Pollutants, Article 6

Explanatory note:
17. Please provide details here of access to information and public education with respect to both control measures and alternatives.

F. Status of control and monitoring capacity (provide summary information and relevant references):

Listing HBB in Annex A would be the most cost effective option in countries that lack the needed infrastructure to adequately monitor production and uses of HBB. Monitoring may require extensive resources and infrastructure that the country does not have.

Explanatory note:
18. With regard to control capacity, the information required is on legislative and institutional frameworks for the chemical under consideration and their enforcement. With regard to monitoring capacity, the information required is on the technical and institutional infrastructure for the environmental monitoring and biomonitoring of the chemical under consideration, not monitoring capacity for alternatives.

G. Any national or regional control actions already taken, including information on alternatives, and other relevant risk management information:

Explanatory notes:
19. Actions or measures taken could include prohibitions, phase-outs, restrictions, cleanup of contaminated sites, waste disposal, economic incentives, and other non-legally binding initiatives.
20. Information could include details on whether these control actions have been cost-effective in providing the desired benefits and have had a measurable impact on reducing levels in the environment and contributed to risk reduction.

H. Other relevant information for the risk management evaluation:

Explanatory notes:
21. The above list of items is only indicative. Any other relevant information for the risk management evaluation should also be provided.

I. Other information requested by the POPRC:

For hexabromobiphenyl (HBB)

When evaluating hexabromobiphenyl (HBB) against the criteria contained in Annex D and during the preparation of the risk profile as described in Annex E, it was considered that the risk profile would benefit from further data.Therefore, in addition to seeking information under the headings listed in Annex F, the Committee is seeking:

- Data related to the ecotoxicity of HBB in aquatic systems and under environmentally relevant conditions, including exposures via food in aquatic species
- Laboratory or field food-chain studies
- Additional mammalian toxicity data
- Critical body burdens
- Toxicokinetic information

Body burden

PBBs and PBDEs were measured in the adipose tissue of on women in southeastern Spain. “Among PBB congeners studied, PBB 153 presented the highest concentrations and contributed 79% of all PBBs. There are no published data on PBB congeners in adipose tissues of the Spanish population for comparison, but the levels found were similar to those described in other European countries.”
Fernandez MF, Araque P, Kiviranta H, Molina-Molina JM, Rantakokko P, Laine O, Vartiainen T, Olea N. Laboratory of Medical Investigations, Clinico University Hospital, University of Granada, 18071 Granada, Spain. PBDEs and PBBs in the adipose tissue of women from Spain. Chemosphere. 2007 Jan;66(2):377-83. 2006 Jun 12

Mammalian toxicity

“Polybrominated biphenyl (PBB) exposure in humans is known to cause immunotoxicity and disorders related to the central nervous system. Coplanar PBBs bind to the aryl hydrocarbon receptor (AHR) in vertebrates. We compared the coplanar PBB, 3,3',4,4',5,5'-hexabromobiphenyl (cHBB), with its stereoisomer, the non-coplanar PBB, 2,2',4,4'6,6'-hexabromobiphenyl (ncHBB), using C57BL/6J (B6) inbred mice (having the high-affinity AHR) and congenic B6.D2-Ahr d mice (having the low-affinity AHR in a >99.8% C57BL/6J genetic background). Pregnant dams were treated i.p. with vehicle alone, cHBB, or ncHBB on gestational day 5 (GD 5). Unexpectedly, neonatal lethality within the first 72 h postpartum was significant in cHBB-treated B6 mice at doses as low as 2.5 mg/kg, whereas no deaths were seen in B6 pups whose mother had received ncHBB 100 mg/kg or in either B6.D2-Ahr d or Ahr(-/-) knockout mice whose mother had received cHBB 100 mg/kg. Histological and gross anatomical analyses of a battery of tissues in the mother or fetus at GD 18, as well as 24 h postpartum, revealed no significant differences, except for decreased thymus and spleen weights in cHBB-treated B6 GD 18 fetuses. Cross-fostering and genetics experiments confirmed the association of neonatal deaths principally with in utero (rather than lactational) exposure to cHBB, and also no paternal effect. For the end points of mouse neonatal lethality and immunotoxicity, cHBB appears to act through the high-affinity AHR receptor. Although dioxin in utero is well known to cause AHR-dependent cleft palate and hydronephrosis, cHBB did not; thus, chronic activation of the AHR appears to be necessary but not sufficient for AHR-mediated teratogenicity.”
Curran CP, Miller KA, Dalton TP, Vorhees CV, Miller ML, Shertzer HG, Nebert DW. Department of Environmental Health, University of Cincinnati Medical Center, P.O. Box 670056, Cincinnati OH 45267-0056, USA. Genetic differences in lethality of newborn mice treated in utero with coplanar versus non-coplanar hexabromobiphenyl. Toxicol Sci. 2006 Feb;89(2):454-64. 2005 Nov 16