Annex F Questionnaire (one per chemical)

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

Commercial octabromodiphenyl ether (c-OctaBDE) IUPAC Name: Diphenyl ether, octabromo derivative (octabromodiphenyl ether, OctaBDE) Synonyms: octabromobiphenyl oxide; octabromodiphenyl oxide; octabromo phenoxybenzene and benzene; 1,1' oxybis-, octabromo derivative CAS Number: 32536-52-0

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)

Joseph DiGangi, PhD Environmental Health Fund +001-312-566-0985 digangi AT environmentalhealthfund.org

Date of submission

5 February 2008

Additional Annex E information

(i) Production data, including quantity and location

- (ii) Uses
- (iii) Releases, such as discharges, losses and emissions

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

C-OctaBDE should be recommended for listing in Annex A and Annex C without exemptions.

Annex A listing: C-OctaBDE has 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.^{1 2 3}

Annex C listing: The components of c-OctaBDE are unintentionally formed through debromination of higher substituted congeners, including commercial decabromodiphenyl ether (c-DecaBDE) which also has the potential for long range transport.⁴ This requires an Annex C listing of c-OctaBDE with control measures that address c-DecaBDE to prevent further formation of c-OctaBDE and other BDE congeners in the environment.

The question of the suitability of Annex C to control substances that degrade to POPs emerged during the discussion of PFOS at the Third Meeting of the POPRC. The Committee discussed whether PFOS could be listed in Annex C in accordance with the terms of the annex and Article 5. The legal advisor of the Secretariat responded that Article 5 refers to anthropogenic sources and that since PFOS sources were anthropogenic substances, PFOS could potentially be listed in Annex C with due amendments to the annex.⁵ In a like manner to the PFOS precursors, c-DecaBDE is an anthropogenic substance which degrades to form components of c-OctaBDE. Therefore, c-OctaBDE can potentially be listed in Annex C with due amendments to the annex.

The proposal for an Annex C listing will raise questions about the degree of BDE debromination in the environment. When debromination of BDEs was first reported, many disregarded it as an in vitro phenomenon and not relevant to environmental conditions. However, the Committee has agreed that debromination is occurring in aquatic organisms, mammals, and birds and that components of c-OctaBDE are produced in the environment by debromination of c-DecaBDE.⁶ Recent studies indicate the following:

http://www.pops.int/documents/meetings/poprc/POPRC3/POPRC3_Report_e/POPRC3_Report_e.pdf

¹ UNECE Convention on Long-range Transboundary Air Pollution, Protocol on Persistent Organic Pollutants, Risk profile and summary report for octabromodiphenyl ether (octaBDE), August 2005 ² Environment Canada, Regulatory Impact Analysis Statement for proposed Polybrominated Diphenyl Ether Regulations, 2006 <u>http://www.ec.gc.ca/CEPARegistry/regulations/detailReg.cfm?intReg=108</u>

³ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁴ Risk profile on commercial octabromodiphenyl ether UNEP/POPS/POPRC.3/20/Add.6

⁵ Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting, UNEP/POPS/POPRC.3/20, 17 December 2007

⁶ Risk profile on commercial octabromodiphenyl ether UNEP/POPS/POPRC.3/20/Add.6

- C-DecaBDE was found to debrominate under normal environmental conditions in house dust forming three c-nonaBDE congeners and several c-OctaBDE congeners⁷
- Fish collected near a wastewater treatment plant outfall contained c-DecaBDE breakdown products that are not present in commercial BDE mixtures; debromination occurred in the aquatic environment under realistic conditions⁸
- Debromination of c-DecaBDE occurred in Wistar rats; three c-nonaBDE congeners and one c-OctaBDE congener were found; the study found that c-DecaBDE and its breakdown products can cross the placental barrier⁹
- Debromination in rats occurred to produce three c-NonaBDEs and four c-OctaBDEs; only 5% of the parent c-DecaBDE was present in the rats after 21 days¹⁰
- Debromination of BDE-28, 47, 99, 100, 153, and 183 occurred in hexane under UV light in the sunlight region; the longest half-life was 6.5 hours¹¹
- Potential debromination products of c-DecaBDE were found in the egg yolk and plasma of male and female glaucous gulls¹²
- The occurrence of BDE-209 in aquatic species from South China suggests that BDE-209 appears to be more bioavailable than previously thought¹³

⁷ Stapleton H, Dodder N. Photodegradation of Decabromodiphenyl Ether in House Dust by Natural Sunlight. Environ Sci Technol 41, Oct, 2007

⁸ LaGuardia MJ, Hale RC, Harvey E. Department of Environmental and Aquatic Animal Health, Virginia Institute of Marine Science, The College of William & Mary, Gloucester Point, Virginia 23062, USA. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. Environ Sci Technol 41:6663 – 6670, 2007

⁹ Rui A, Cravedi JP, Debrauwer L, Garcia A, Canlet C, Jouanin I, Zalko D. Institut National de la Recherche Agronomique, Unité Mixte de Recherche 1089 Xénobiotiques, 180 chemin de Tournefeuille, BP3, 31931 Toulouse cedex 9, France. Disposition and metabolic profiling of [(14)C]-Decabromodiphenyl ether in pregnant Wistar rats. Environ Int, May, 2007

¹⁰ Huwe JK, Smith DJ. Biosciences Research Laboratory, ARS, USDA, P.O. Box 5674, University Station, Fargo, North Dakota 58105-5647, USA. Accumulation, whole-body depletion, and debromination of decabromodiphenyl ether in male sprague-dawley rats following dietary exposure. Environ Sci Technol 41:2371 – 2377, 2007

¹¹ Fang L, Huang J, Yu G, Wang L. POPs Research Centre, Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, PR China. Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane, Chemosphere, Nov 3, 2007

¹² Verreault J, Gebbink WA, Gauthier LT, Gabrielsen GW, Letcher RJ. Norwegian Polar Institute, Tromsø NO-9296, Norway. Brominated flame retardants in glaucous gulls from the Norwegian Arctic: more than just an issue of polybrominated diphenyl ethers. Environ Sci Technol 41:4925 – 4931, 2007

¹³ Guo JY, Wu FC, Mai BX, Luo XJ, Zeng EY. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.

- Workers exposed occupationally to c-DecaBDE contain heptaBDE and octaBDE congeners that are not present in the commercial c-DecaBDE mixture or in reference groups; a follow up study found that reduced exposure decreased the decaBDE concentrations but increased the heptaBDE and octaBDE concentrations suggesting that debromination was occurring in humans¹⁴
- In a study of PBDEs in humans, BDE47 was the predominant congener in serum samples (maternal, paternal, umbilical cord) while BDE209 (deca) was the predominant congener in placenta and breast milk samples¹⁵
- BDE47, -99, -100, and -209 (deca) were the dominant congeners measured in the high Arctic in the Bohai Sea¹⁶

In addition, there is a sizeable body of data on the properties of c-DecaBDE that should raise concerns about its debromination to form components of c-OctaBDE:

C-DecaBDE is found in biota

• BDE 209 is found in fish, birds, grizzly bears, and other animals at high concentrations, demonstrating that deca-BDE can be absorbed by biological systems.^{17 18 19}

Polybrominated diphenyl ethers in seafood products of south China. J Agric Food Chem 55:9152 – 9158, 2007

¹⁴ Thuresson K, Bergman A, Jakobsson K. Department of Environmental Chemistry, Stockholm University, Stockholm, Sweden. Occupational exposure to commercial decabromodiphenyl ether in workers manufacturing or handling flame-retarded rubber. Environ Sci Technol 39:1980 – 1986, 2005 Thuresson K, Hoglund P, Hagmar L, Sjodin A, Bergman A, Jakobsson K. Department of Environmental Chemistry, Stockholm University, Stockholm, Sweden. Apparent half-lives of hepta- to decabrominated diphenyl ethers in human serum as determined in occupationally exposed workers. Environ Health Perspect 114:176 – 181, 2006

¹⁵ Gomara B, Herrero L, Ramos JJ, Mateo JR, Fernandez MA, Garcia JF, Gonzalez MJ. Department of Instrumental Analysis and Environmental Chemistry, Institute of General Organic Chemistry, CSIC, Juan de la Cierva, 3, 28006-Madrid, Spain. Distribution of polybrominated diphenyl ethers in human umbilical cord serum, paternal serum, maternal serum, placentas, and breast milk from Madrid population, Spain. Environ Sci Technol 41(20):6961-6968, 2007

¹⁶ Wang XM, Ding X, Mai BX, Xie ZQ, Xiang CH, Sun LG, Sheng GY, Fu JM, Zeng EY. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China. Polybrominated diphenyl ethers in airborne particulates collected during a research expedition from the Bohai Sea to the Arctic. Environ Sci Technol 39:7803 – 7809, 2005

¹⁷ Johnson-Restrepo B, Kannan K, Addink R, Adams DH, Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. Environmental Science & Technology 2005, 39, (21), 8243-8250

¹⁸ Bixian M, Song J, Suin Q, Zeng E, Hale RC. Polybrominated Diphenyl Ethers in Birds of Prey Collected from Northern China, SETAC, Montreal, Quebec, 2006; Montreal, Quebec, 2006

¹⁹ Christensen JR, Macduffee M, Macdonald RW, Whiticar M, Ross PS. Persistent organic pollutants in British Columbia grizzly bears: Consequence of divergent diets. Environmental Science & Technology 2005, 39, (18), 6952-6960

- Deca-BDE can be absorbed by dietary intake in carp, lake trout and rats ^{20 21 22 23}
- Given that animal uptake rates are usually in the range of 1 3 % of a given dose of decaBDE²⁴, high concentrations in terrestrial animals^{25 26} suggest that decaBDE can bioaccumulate²⁷

C-DecaBDE debrominates in biological systems

• Carp debrominate decaBDE to penta-, hexa-, hepta- and octaBDE²⁸

C-DecaBDE debrominates by photolysis

- DecaBDE dissolved in organic solvents breaks down within minutes while decaBDE adsorbed onto wet sand or soil breaks down within hours or days^{29 30 31}
- DecaBDE dissolved in water or organic solvents breaks down into tri-, tetra-, and pentaBDE congeners^{32 33 34}

²³ Morck A, Hakk H, Orn U, Wehler EK. Decabromodiphenyl ether in the rat: Absorption, distribution, metabolism, and excretion. Drug Metabolism and Disposition 2003, 31, (7), 900-907

³³ Eriksson J, Green, N, Marsh G, Bergman, A. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. Environmental Science & Technology 2004, 38, (11), 3119-3125

²⁰ Kierkegaard A, Balk L, Tjarnlund U, De Wit CA, Jansson B. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (Oncorhynchus mykiss). Environmental Science & Technology 1999, 33, (10), 1612-1617

²¹ Stapleton HM, Alaee M, Letcher RJ, Baker JE. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (Cyprinus carpio) following dietary exposure. Environmental Science & Technology 2004, 38, (1), 112-119

 ²² Tomy GT, Palace VP, Halldorson T, Braekevelt, E, Danell R, Wautier K, Evans B, Brinkworth L, Fisk AT. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in juvenile lake trout (Salvelinus namaycush). Environmental Science & Technology 2004, 38, (5), 1496-1504

²⁴ Stapleton, H. Brominated Flame Retardants: Assessing DecaBDE Debromination in the Environment. Health and Environment Alliance, <u>www.env-health.org</u>, May 2006

²⁵ Christensen JR, Macduffee M, Macdonald RW, Whiticar M, Ross PS. Persistent organic pollutants in British Columbia grizzly bears: Consequence of divergent diets. Environmental Science & Technology 2005, 39, (18), 6952-6960

²⁶ Voorspoels S, Covaci A, Lepom P, Escutenaire S, Schepens P. Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (Vulpes vulpes). Environmental Science & Technology 2006, 40, (9), 2937-2943

²⁷ Stapleton H. Summary of Scientific Studies on Accumulation and Debromination of DecaBDE. Health and Environment Alliance, <u>www.env-health.org</u>, December 2006

²⁸ Stapleton HM, Alaee M, Letcher RJ, Baker JE. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (Cyprinus carpio) following dietary exposure. Environmental Science & Technology 2004, 38, (1), 112-119

²⁹ Ahn MY, Filley TR, Jafvert CT, Nies L, Hua I, Bezares-Cruz, J. Photodegradation of decabromodiphenyl ether adsorbed onto clay minerals, metal oxides, and sediment. Environmental Science & Technology 2006, 40, (1), 215-220

³⁰ Eriksson J, Green, N, Marsh G, Bergman, A. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. Environmental Science & Technology 2004, 38, (11), 3119-3125

³¹ Soderstrom, G, Sellstrom U, De Wit CA, Tysklind M. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environmental Science & Technology 2004, 38, (1), 127-132

³² Soderstrom, G, Sellstrom U, De Wit CA, Tysklind M. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environmental Science & Technology 2004, 38, (1), 127-132

Bacteria debrominate c-DecaBDE in sewage sludge

• Debromination of decaBDE can occur as a result of metabolysis by bacteria in sewage sludge^{35 36}

DecaBDE is present and breaks down in humans

- Levels of PBDEs in the human population have been rising steadily for the past thirty years and concentrations are doubling approximately every five years³⁷
- DecaBDE levels are rising along with the levels of other PBDEs in the general population³⁸
- DecaBDE has been measured in human blood and breast milk^{39 40} and at high levels in electronics recycling workers⁴¹

These studies indicate the need for the Committee to seriously take up the question of an Annex C listing for c-OctaBDE. Evaluations of this type carry various uncertainties due to availability of data, however, the Convention reminds the POPRC in Article 8 para 7a that, "Lack of full scientific certainty shall not prevent the proposal from proceeding." This statement codifies the Convention commitment to use available information in protecting public health from the harms caused by POPs.

(ii) Technical feasibility

The wide availability of alternatives for c-OctaBDE and c-DecaBDE make their substitution technically feasible for many uses. Alternatives are available and have already been implemented for the most common historical use of c-OctaBDE, acrylonitrile – butadiene – styrene (ABS) plastic in office equipment and business machines.^{42 43} Please see the analysis of alternatives below for both congeners and the Technical Feasibility section of the Alternatives section below for a list of prominent

⁴¹ Jakobsson K, Thuresson K, Rylander L, Sjodin A, Hagmar L, Bergman A. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. Chemosphere. 2002 Feb;46(5):709-16

³⁴ Bezares-Cruz J, Jafvert CT, Hua I. Solar Photodecomposition of Decabromodiphenyl Ether: Products and Quantum Yield. Environ. Sci. Technol., 38 (15), 4149 -4156, 2004

³⁵ H e JZ, Robrock KR, Alvarez-Cohen L. Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). Environmental Science & Technology 2006, 40, (14), 4429-4434

³⁶ Gerecke AC, Hartmann PC, Heeb NV, Kohler HPE, Giger W, Schmid P, Zennegg M, Kohler M. Anaerobic degradation of decabromodiphenyl ether. Environmental Science & Technology 2005, 39, (4), 1078-1083

³⁷ Hites R. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. Environ. Sci. Technol. 38 (4): 945-56

³⁸ Hites, R. op cit.; WWF UK ContamiNATION: National Biomonitoring Survey 2003 <u>http://www.wwf.org.uk/filelibrary/pdf/biomonitoringresults.pdf</u>

³⁹ Schecter A, Vuk MP, Papke O, Ryan, JJ, Birnbaum L, Rosen, R. Polybrominated diphenyl ethers (PBDEs) in US mothers' milk. Environmental Health Perspectives 2003, 111, (14), 1723-1729

⁴⁰ Schecter A, Papke O, Harris, TR, Tung, KC. Partitioning of polybrominated diphenyl ether (PBDE) congeners in human blood and milk. Toxicological & Environmental Chemistry 2006, 88, (2), 319-324

⁴² Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

⁴³ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

companies that have already implemented alternatives to both c-OctaBDE and c-DecaBDE.

(iii) Costs, including environmental and health costs

The considerable phase-out of c-OctaBDE and c-DecaBDE that has already occurred indicates that costs of alternatives have not inhibited their substitution. Please see the Technical Feasibility section of the Alternatives section below for a list of prominent companies that have already implemented alternatives to both c-OctaBDE and c-DecaBDE.

Important points to consider when evaluating the costs of alternatives for any product include⁴⁴:

- Alternatives with a higher initial purchase cost may actually be cheaper 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.

Clariant, the Swiss chemical manufacturer notes that, "...offering a more environmentally friendly product is often not sufficient for market success, even if the price and technical properties are comparable to established flame retardants. Therefore, legally binding requirements together with market pull – manufacturers and consumers of end use products demanding more environmentally friendly solutions – will encourage the development of alternative non-halogen flame retardants."⁴⁵

In addition, there are inherent problems with using cost-benefit analysis to evaluate risk reduction and regulatory decisions.⁴⁶ 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." Costbenefit 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,

⁴⁴ 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

⁴⁵ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007

http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

⁴⁶ Heinzerling L, Ackerman. Priceless: Human Health, the Environment and Limits of the Market. The New Press, 288 pages, 2004

"...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."

The POPRC has already concluded that the hexa, hepta, octa, and nonaBDE components of the commercial octabromodiphenyl ether are likely, as a result of long-range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted. ⁴⁷ For the octa and nonaBDE components the decision included consideration of debromination and the precautionary approach. This indicates that elimination of c-OctaBDE 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 c-OctaBDE.⁴⁸

Explanatory notes:

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):

In general, alternatives to POPs that use, contain, or lead to the formation (through degradation, metabolism, or combustion) of substances that are persistent and bioaccumulative are inappropriate. Alternatives should be assessed to avoid replacing POPs with other potential persistent and bioaccumulative substances.

(i) Describe alternatives

Alternatives to c-OctaBDE

Alternatives to C-OctaBDE include substitute chemicals and alternative techniques including non-chemical alternatives such as design changes. These are described in several governmental reports.^{49 50 51 52 53}

⁴⁷ Risk profile on commercial octabromodiphenyl ether UNEP/POPS/POPRC.3/20/Add.6

⁴⁸ Environment Canada, Regulatory Impact Analysis Statement for proposed Polybrominated Diphenyl Ether Regulations, 2006 <u>http://www.ec.gc.ca/CEPARegistry/regulations/detailReg.cfm?intReg=108</u>

⁴⁹ Environment Canada, Regulatory Impact Analysis Statement for proposed Polybrominated Diphenyl Ether Regulations, 2006 <u>http://www.ec.gc.ca/CEPARegistry/regulations/detailReg.cfm?intReg=108</u>

⁵⁰ Leisewitz, A., H. Kruse and E. Schramm. 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

⁵¹ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

Design changes to address c-OctaBDE

Design changes can eliminate the need for flame retardants by using alternatives materials or designs that eliminate the need for chemical flame retardants. These include shielding the plastic outer casing of components with metal or making the entire case of metal.^{54 55} Other options described in the RPA report⁵⁶ include maintaining certain distances between high voltage parts and the outer casings and using polymers with low rates of combustion such as amino-, phenol-, fluoro-, and silicone-based polymers.

In some cases design changes can occur by utilizing plastics or blends of polymers that contain different substances for flame retardation.⁵⁷ The RPA report mentions use of polycarbonate / ABS blends (PC/ABS) and polypropylene / polystyrene (PPE/PS) blends.

Two flame retardants used in the polymer blends are triphenyl phosphate (TPP) and bis (diphenylphosphate) (RDP). US EPA reports moderate systemic toxicity and high acute and chronic ecotoxicity of TPP as two characteristics of concern. ⁵⁸ The US Occupational Safety and Health Administration (OSHA) reports inhibition of cholinesterase as a health effect of triphenyl phosphate exposure.⁵⁹ Bioconcentration factors for TPP in several fish species vary from 6 - 18,900.⁶⁰ In addition, triphenyl phosphate is considered environmentally hazardous in Germany due to its toxicity to aquatic organisms.⁶¹ RDP also appears to be harmful to aquatic organizations and estimates on losses from products to the environment is lacking.⁶² While TPP and RDP have hazardous properties that must be addressed across their lifecycle, neither is persistent and RDP does not appear to be bioaccumulative.

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⁵² Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁵³ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁵⁴ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁵⁵ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁵⁶ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁵⁷ Risk and Policy Analysis of advantages and transport for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002 ⁵⁸ USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives

Polyurethane Foam <u>http://www.epa.gov/dfe/pubs/index.htm#ffr</u>

⁵⁹ US Occupational Safety and Health Administration, Chemical Sampling Information, 19 January 1999 http://www.osha.gov/dts/chemicalsampling/data/CH_274400.html

⁶⁰ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁶¹ 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

⁶² Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

Chemical substitutes for c-OctaBDE in ABS plastic

Chemical substitutes for c-OctaBDE in ABS plastic are commercially available and described in several reports. These include tetrabromobisphenol A (TBBPA), triaryl phosphate, triaryl phosphates butylated, bisphosphate, bis (tribromophenoxy) ethane, and phenoxy-terminated carbonate oligomer of tetrabromobisphenol A (a brominated phenoxy oligomer or BEO).

In ABS, TBBPA and brominated epoxy oligomers are used as additive flame retardants meaning that they are not bound to the polymer and therefore have a greater tendency to be released to the environment. TBBPA is a cytotoxicant, immunotoxicant, and thyroid hormone agonist with the potential to disrupt estrogen signaling.⁶³ TBBPA is classified as very toxic to aquatic organisms and is on the OSPAR Commission's List of Chemicals for Priority Action due to its persistence and toxicity.^{64 65} To avoid their use in ABS applications, poly (phenylene oxide) / high impact polystyrene (PPO / HIPS) blends flame retarded with resorcinol diphosphate (RDP) have been proposed.⁶⁶

Bisphosphate and its derivatives include RDP and are used in "Blue Angel" printers and PCs with PC / ABS casings.⁶⁷ The US EPA DfE report lists triaryl phosphate and an isopropylated derivative as having moderate bioaccumulation properties based on structure activity relationships.⁶⁸ Bis (tribromophenoxy) ethane is poorly characterized. Studies by its manufacturer indicate low toxicity, but the substance tends to persist and bioaccumulate.⁶⁹

Chemical substitutes for c-OctaBDE in synthetic textiles

Chemical substitutes for c-OctaBDE in textiles include reactive phosphorous constituents and hexabromocyclododecane.

Tetrabromobisphenol-A OSPAR Commission Update, 2005

⁶³ Birnbaum LS, Staskal DF. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Experimental Toxicology Division, Research Triangle Park, North Carolina, USA; and University of North Carolina, Curriculum in Toxicology, Chapel Hill, North Carolina, USA, Brominated flame retardants: Cause for concern? Environ Health Perspect 112: 9 – 17, 2004

http://www.ehponline.org/members/2003/6559/6559.html

 ⁶⁴ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002
⁶⁵ OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic,

http://www.ospar.org/documents/dbase/publications/p00202_BD%20on%20TBBPA.pdf

⁶⁶ Morose G. An overview of alternatives to tetrabromobisphenol A (TBBPA) and

hexabromocyclododecane (HBCD), Lowell Center for Sustainable Production, University of Massachusetts – Lowell, March 2006 <u>http://sustainableproduction.org/downloads/AternativestoTBBPAandHBCD.pdf</u>

⁶⁷ 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

⁶⁸ USEPA, Environmental Profiles of Chemical Flame-Retardant Alternatives Polyurethane Foam <u>http://www.epa.gov/dfe/pubs/index.htm#ffr</u>

⁶⁹ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

Specific reactive phosphorous constituents 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).⁷⁰ Methyl phosphonic acid has attracted the attention of those working on chemical weapons since it is a degradation product of VX, sarin, and soman.⁷¹ 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." ⁷² However, methyl phosphonic acid does not appear to be bioaccumulative.⁷³ Other types of toxicity information are minimal but note that the substance reacts violently with water.⁷⁴ The phosphonic acid family also includes amino-methyl phosphonic acid, a degradation product of the herbicide, glyphosate (also known as [carboxymethylamino] methyl phosphonic acid.)

Hexabromocyclododecane (HBCD) is used as an additive flame retardant indicating that it is not bound to the polymer and therefore has a greater tendency to be released to the environment. HBCD is bioaccumulative, persistent, and causes neurobehavioral alterations in vitro.⁷⁵

Chemical substitutes for c-OctaBDE in thermoplastic elastomers

Chemical substitutes for c-OctaBDE in thermoplastic elastomers include bis (tribromophenoxy) ethane and tribromophenyl allyl ether.⁷⁶ Bis (tribromophenoxy) ethane is discussed above under alternatives for c-OctaBDE in ABS plastic. Very little information was available for tribromophenyl allyl ether, though it is on a list of flame retardants considered "deferred" for testing by the interagency testing committee of US EPA.⁷⁷

http://yosemite.epa.gov/oswer/ceppoehs.nsf/Profiles/676-97-1?OpenDocument

⁷⁵ Birnbaum LS, Staskal DF. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Experimental Toxicology Division, Research Triangle Park, North Carolina, USA; and University of North Carolina, Curriculum in

⁷⁰ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁷¹ OPCW Declarations Branch, Some Scheduled Chemicals, 2006

http://www.opcw.org/docs/publications/some%20scheduled%20chemicals.pdf

⁷² 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

⁷³ Munro NB, Talmage SS, Griffin GD, Waters LC, Watson AP, King JF, Hauschild V. The sources, fate, and toxicity of chemical warfare agent degradation. Environ Health Perspect 107:933-974, 1999 http://www.ehponline.org/docs/1999/107p933-974munro/munro.pdf

http://www.ehponline.org/docs/1999/107p933-974munro/munro.pdf ⁷⁴ US EPA Chemical Profile: methyl phosphonic dichloride. Extremely hazardous substances, section 302 of EPCRA, Chemical Emergency Preparedness and Prevention, 1985

Toxicology, Chapel Hill, North Carolina, USA, Brominated flame retardants: Cause for concern? Environ Health Perspect 112: 9 – 17, 2004

⁷⁶ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁷⁷ IPCS Environmental Health Criteria 192. Flame retardants: A general introduction 1997 http://www.inchem.org/documents/ehc/ehc192.htm

Chemical substitutes for c-OctaBDE in polyolefins

Chemical substitutes for c-OctaBDE in polyolefins include polypropylenedibromostyrene, dibromostyrene, and tetrabromobisphenol A (TBBPA).⁷⁸ Tetrabromobisphenol A is described above in chemical substitute alternatives for c-OctaBDE in ABS plastic. Few data are available for dibromostyrene and polypropylenedibromostyrene. For dibromostyrene, an EU assessment found insufficient information on toxicity, no bioaccumulation based on a low BCF value, and overall persistence of 49 days based on modeling.⁷⁹

Assessing c-OctaBDE alternatives

The RPA report summarizes the alternatives for c-OctaBDE by noting the lack of comprehensive data available for the chemical alternatives and pointing out the viability of non-chemical alternatives such as shielding the plastic outer casing of components with metal or making the entire case of metal, maintaining certain distances between high voltage parts and the outer casings, and using polymers with low rates of combustion such as amino-, phenol-, fluoro-, and silicone-based polymers.^{80 81}

In general, chemical alternatives that exhibit properties such as persistence and bioaccumulation are inappropriate as replacements for a POP with these same properties. Two chemical substitutes are both persistent and bioaccumulative: bis (tribromophenoxy) ethane and hexabromocyclododecane. In addition, dibromostyrene was somewhat persistent and not bioaccumulative based on a low BCF value.

The remaining chemical alternatives, while not both persistent and bioaccumulative, still have characteristics that raise some concerns about human health and the environment. The core substance of the reactive phosphorous constituent, methyl phosphonic acid, is persistent. Triphenyl phosphate is bioaccumulative since bioconcentration factors in several fish species vary from 6 - 18,900.⁸² Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms.^{83 84 85}

⁷⁸ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁷⁹ Pakalin S, Cole T, Steinkellner, Nicolas R, Tissier C, Munn S, Eisenreich S. Review on production processes of decabromodiphenyl ether (decaBDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to decaBDE. European Commission, Directorate General Joint Research Center, European Chemicals Bureau, January 2007 http://ecb.jrc.it/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf

⁸⁰ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁸¹ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁸² Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

⁸³ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

⁸⁴ 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 <u>http://cleanproduction.org/Green.Greenscreen.php</u>

Information is sparse for three substitutes: triaryl phosphates butylated, bisphosphate, and tribromophenyl allyl ether.

Identifying 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".⁸⁶ 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. According to Green Screen criteria in examining alternatives to c-DecaBDE, only resorcinol bis (diphenylphosphate) passed the first benchmark to land in benchmark 2: Use – but search for safer substitutes, making it the preferred chemical substitute.

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."⁸⁷ 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.

Alternatives to c-DecaBDE

C-DecaBDE is used as an additive flame retardant often together with antimony trioxide in plastics (~80%) and textiles (~20%) with the predominate uses including TV enclosures made of high impact polystyrene (HIPS), coated wire, electrical parts, mattresses, draperies, commercial upholstered furniture, cars, airplanes, tents, awnings, and other fabric applications.⁸⁸ According to the industry, decaBDE is the highest use brominated flame retardant in the Americas and global volume estimates put use at more 56,400 metric tons in 2003 as opposed to negligible use of octaBDE.⁸⁹A number of

⁸⁵ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

⁸⁶ 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://cleanproduction.org/Green.Greenscreen.php

⁸⁷ 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

⁸⁸ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

⁸⁹ Minnesota Pollution Control Agency, Decabromodiphenyl ether (Deca-BDE), A report to the Minnesota legislature, January 15, 2008 <u>http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf</u>

reports address non-chemical and chemical alternatives for c-DecaBDE in these uses.^{90 91} 92 93 94 95 96

Design changes to address c-DecaBDE

A general substitution for uses in electrical equipment is using a metal sheet to cover plastic in contact with electrical parts.⁹⁷ In TV design, manufacturers have been able to achieve UL standards by separating the voltage supply from ignitable plastics though this does not flame retard them from external sources of ignition.⁹⁸ Other strategies include reducing operating voltage and removing the power supply from the product (used in printers and phones). Redesign of mattresses includes eliminating flammable foam (implemented by Herman Miller furniture), utilizing inherently fire-resistant fabrics (used in fire fighter apparel), and use of barrier layers with boric acid (used in mattresses, upholstered furniture, and draperies; see below).⁹⁹

⁹⁰ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 2006

http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

⁹¹ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

⁹² Pakalin S, Cole T, Steinkellner J, Nicolas R, Tissier C, Munn S, Eisenreich S. European Chemicals Bureau, Review on production processes of decabromodiphenyl ether (DecaBDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to DecaBDE, European Commission Directorate General Joint Research Center, January 2007 http://ecb.jrc.it/documents/Existing-Chemicals/Review on production process of decaBDE.pdf

⁹³ Illinois Environmental Protection Agency, Report on alternatives to the flame retardant decaBDE: Evaluation of toxicity, availability, affordability, and fire safety issues. A report to the Governor and State Assembly. March 2007 <u>http://www.epa.state.il.us/reports/decabde-study/</u>

⁹⁴ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005 <u>http://www.ecy.wa.gov/pubs/0507048.pdf</u>

⁹⁵ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007 http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

⁹⁶ Stuer-Lauridsen F, Cohr KH, Andersen TT, DHI Water & Environment, Health and environmental

assessment of alternatives to deca-BDE in electrical and electronic equipment, Danish Ministry of the Environment, No. 1142, 2007

http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-351-6/pdf/978-87-7052-352-3.pdf

⁹⁷ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 2006

⁹⁸ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

⁹⁹ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

Chemical substitutes for c-DecaBDE in HIPS

Non-halogenated alternatives for this application include blends of polycarbonate and ABS (PC / ABS), polycarbonate (PC), blends of HIPS and polyphenylene oxide (HIPS / PPO), and polylactide (PLA).¹⁰⁰

The PC / ABS blends use a flame retardant and polytetrafluoroethylene (PTFE) indicating that they are not halogen-free. Two common flame retardants are resorcinol bis diphenyl phosphate (RDP) and bisphenol a diphosphate (BPADP). Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms.^{101 102 103} BDADP has a high potential for persistence and includes triphenyl phosphate as a degradation product.¹⁰⁴ BDADP also includes Bisphenol A as a contaminant and degradation product which displays endocrine disruption, developmental and reproductive toxicity, and other toxic effects.¹⁰⁵ PC may be compounded similarly.

The PPO in the HIPS / PPO blends provide increased flame retardancy and the blends often utilize resorcinol bis diphenyl phosphate (see paragraph above.) These blends have a higher heat tolerance and mechanical strength than HIPS retarded with c-DecaBDE.¹⁰⁶

Polylactide needs modification for product applications due to its low melting point and brittleness. However, NEC has made a PLA resin with metal hydroxide flame retardants and kenaf fibers for improved strength making it as heat resistant, easy to process, and strong as PC.¹⁰⁷ JVC, Sony, and Mitsubishi are actively developing PLA materials with aluminum hydroxide flame retardants. The Danish Alternatives report summarizes the toxicity of aluminum hydroxide 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

 ¹⁰⁰ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>
¹⁰¹ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final

¹⁰¹ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

¹⁰² 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://cleanproduction.org/Green.Greenscreen.php

¹⁰³ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

¹⁰⁴ 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://cleanproduction.org/Green.Greenscreen.php

¹⁰⁵ 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://cleanproduction.org/Green.Greenscreen.php

¹⁰⁶ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

¹⁰⁷ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

in consumer products to cause adverse effects.¹⁰⁸ The German Alternatives report describes the use of aluminum trihydroxide as a flame retardant as "unproblematic."¹⁰⁹

Chemical substitutes for c-DecaBDE in polypropylene

Non-brominated flame retardants for use in polypropylene or polypropylene ether coated wire and cable include ammonium polyphosphate, magnesium hydroxide, and melamine phosphate.¹¹⁰

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.¹¹¹ 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".¹¹²

Magnesium hydroxide is commonly ingested as an antacid and forms the active ingredient in milk of magnesia. Surprisingly, there is very little toxicological information on magnesium hydroxide. One possible problem with the its use as a flame retardant is that large amounts of (~50%) are required for effective flame retardancy and this may change the properties of the material.

Melamine and its derivatives display several toxic effects. These include changed electrolyte compositions of urine, teratogenic effects in fertilized rainbow trout eggs, and reproductive effects in snails and houseflies.¹¹³ In addition, melamine caused chronic injury to the male rat bladder due to stones formed during exposure which correlated strongly with carcinoma.¹¹⁴ In a fire, melamine cyanurate will release toxic fumes such as hydrocyanic acid and isocyanate.¹¹⁵ The Danish report notes that there is no data on

¹⁰⁸ 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

¹⁰⁹ 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

¹¹⁰ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007 http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

¹¹¹ 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

¹¹² 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

¹¹³ Daugherty ML. Chemical hazard information profile draft report: Melamine, CAS No. 108-78-1, Office of Toxic Substances, US EPA, 1982.

¹¹⁴ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

¹¹⁵ Leisewitz A, Kruse H, Schramm E, German Federal Ministry of the Environment, Nature Conservation,

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." ¹¹⁶ 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."¹¹⁷ Melamine and its derivatives are not both persistent and bioaccumulative.

Chemical substitutes for c-DecaBDE in polybutylene terephthalate (PBT) and polyamide (PA)

Alternatives to brominated flame retardants in this use for electrical parts include magnesium hydroxide, melamine cyanurate, and melamine polyphosphate in polyamide and phosphinic acid in polybutylene terephthalate.¹¹⁸ See the section above for reviews of magnesium hydroxide and melamine compounds. Phosphinic acid is not well characterized, though the Danish EPA report notes that it is considered to be very persistent.¹¹⁹

Chemical substitutes for c-DecaBDE in mattresses, upholstery, and draperies

The choice and feasibility of c-DecaBDE substitutes in textiles can be affected by the fabric which is used since the flame retardancy of various fabrics varies from those that easily burn with a vigorous flame (cotton) to those that burn slowly (wool and silk), to very slowly (modacrylic and saran), and even some that do not burn (aramid, novoloid, and melamine.)¹²⁰ Note that modacrylic synthesis utilizes highly toxic substances such as acrylonitrile and vinyl bromide.¹²¹ ¹²² ¹²³ ¹²⁴

¹¹⁸ Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007 http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

¹¹⁹ Stuer-Lauridsen F, Cohr KH, Andersen TT, DHI Water & Environment, Health and environmental assessment of alternatives to deca-BDE in electrical and electronic equipment, Danish Ministry of the Environment, No. 1142, 2007

¹²⁰ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts -Lowell, 2005 http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf ¹²¹ http://www.britannica.com/eb/article-9053135/modacrylic

¹²² National Toxicology Program, Report on carcinogens background document for vinyl bromide. http://ntp.niehs.nih.gov/ntp/newhomeroc/roc10/VB.pdf

¹²³ http://www.atsdr.cdc.gov/tfacts125.html

and Nuclear Safety, Substituting Environmentally relevant flame retardants: Assessment Fundamentals, Research Report 204 08 642 or 207 44 542, 2000

¹¹⁶ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

¹¹⁷ 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

¹²⁴ World Intellectual Property Organization, WO/2005/111289, Fire blocker fiber composition, high loft web structures, and articles made therefrom, undated http://www.wipo.int/pctdb/en/wo.jsp?IA=WO2005111289&DISPLAY=DESC

Mattresses can utilize a phosphate-based flame retardant as a coating for mattress fabrics (see above) or fire barriers that place a fire-resistant material in the cushioning or between the exterior cover fabric and the first layer of cushioning.¹²⁵ The latter method is commonly used commercially and thought to be applicable to upholstered furniture as well. Draperies can be flame retarded with phosphonate type substances or made using inherently flame-resistant fabrics.¹²⁶

According to industry sources cited in the Pure Strategies report, "…chemical flame retardants are not necessary in 99% of cases for panel and upholstery fabrics to meet the fire codes for residential upholstered furniture."

Assessing c-DecaBDE alternatives

Given the range of alternative flame retardants and techniques available, a wise course of action would be to examine the toxicity of the substance, its breakdown products, manufacturing processes, and the use of synthetic materials, and give preference to those that pose least risk. As noted in the Danish EPA report, "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."¹²⁷

In general, chemical alternatives that exhibit properties such as persistence and bioaccumulation seem inappropriate as replacements for a POP with these same properties. Two chemical substitutes are persistent: bis (tribromophenoxy) bisphenol a diphosphate (BPADP) and phosphinic acid. Resorcinol bis (diphenylphosphate) is neither persistent nor bioaccumulative, however its triphenyl phosphate degradation product has moderate concern for bioaccumulation and it is harmful to aquatic organisms.¹²⁸ ¹²⁹ ¹³⁰ Melamine is not persistent or bioaccumulative but displays several toxic effects which the German report describes as "problematic".¹³¹ The metal hydroxides are approved by both

¹²⁵ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

¹²⁶ Pure Strategies, Decabromodiphenyl ether: An investigation of non-halogen substitutes in electronic enclosure and textile applications. Lowell Center for Sustainable Production, University of Massachusetts – Lowell, 2005 <u>http://sustainableproduction.org/downloads/DecaBDESubstitutesFinal4-15-05.pdf</u>

¹²⁷ Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

¹²⁸ Washington State, USA. Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Draft Final Plan, December 1, 2005

¹²⁹ 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://cleanproduction.org/Green.Greenscreen.php

¹³⁰ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

¹³¹ 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 Danish EPA and German reports through they note that more information is needed.^{132 133}

Please see the descriptions of the various options above and the use of the Green Screen and the Alternative Assessments Framework described in the c-OctaBDE assessment section to assess choices in alternatives.^{134 135}

(ii) Technical feasibility

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

The EU RPA concluded that, "Based on consultation with industry, it is evident that most companies have already replaced octabromodiphenyl ether in their products with other flame retardants and some companies utilise design measures, rather than flame retardants, for certain types of products. Overall, there does not appear to be any major technical obstacle to replacement of the substance, although some of the flame retardant/polymer combinations considered in this section may have inferior technical performance in certain applications."¹³⁶

For c-DecaBDE, the Danish EPA report concluded that, "This study has not identified any application of Deca-BDE in electrical and electronic equipment for which substitution is not possible, from the scientific or technical point of view. For all EEE materials and components presently using Deca-BDE, technically acceptable alternatives are available on the market. The widespread use of alternatives, and availability of EEE components without Deca-BDE, is indicated by the fact that a large number of the world's major manufacturers of EEE have phased out the use of Deca-BDE in their products."¹³⁷

Many high profile companies have already implemented alternatives to both c-OctaBDE and c-DecaBDE. For example, Dell (#1 in US PC sales) eliminated all halogenated flame-retardants in all desktop, notebook and server chassis plastic parts in 2004 and has

¹³² Danish Environmental Protection Agency, Brominated flame retardants: Substance flow analysis and assessment of alternatives, June 1999

¹³³ 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

¹³⁴ 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://cleanproduction.org/Green.Greenscreen.php

¹³⁵ 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

¹³⁶ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

¹³⁷ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 200 http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

recently expanded these restrictions to include all products designed after June 2006.¹³⁸ HP (#2 in US PC sales) has a policy banning use of c-DecaBDE in its products.¹³⁹ Toshiba (#4 in US PC sales) does not use c-DecaBDE in their products.¹⁴⁰ Lenovo (#6 in US PC sales) has eliminated PBDEs including c-OctaBDE and c-DecaBDE in all of their products.¹⁴¹ Samsung (#3 in US TV sales), Sony (#1 in US TV sales), Panasonic (#6 in US TV sales), and Philips (#6 in US TV sales) have eliminated c-DecaBDE from their televisions.^{142 143 144} LG Electronics (#8 in US TV sales) plans to eliminate all c-DecaBDE and all other brominated flame retardants by 2010.¹⁴⁵ A comparison of computer, TV, and game manufacturers on their BFR phase-out timelines and BFR-free products has also been assembled by Greenpeace and is updated every three months.¹⁴⁶

Additional companies that have phased out c-DecaBDE and other PBDEs in all their products include: IBM, Ericsson, Apple, Matsushita (including Panasonic), Intel, and B&O.¹⁴⁷

Norway has announced a ban on new products containing decaBDE beginning in April 2008.¹⁴⁸ The pre-existing ban on the use of decaBDE in electronic and electrical products will be extended to textiles, furniture filling and cables leaving the transport sector as the only exemption.

(iii) Costs, including environmental and health costs

In general, the wide scale implementation of alternatives to c-OctaBDE and c-DecaBDE indicates their cost competitiveness and market viability. The EU RPA report notes that most of the c-OctaBDE alternatives would be more costly but also states that some cost

¹⁴¹ Pierce, Mike (Lenovo Corporation, Global Environmental Affairs). 2006. Lenovo Engineering Specification 41A7731: Baseline Environmental Requirements for Materials, Parts, and Products for Lenovo Hardware Products.

http://www.pc.ibm.com/ww/lenovo/procurement/Guidelines/41A7731.J83906N.R0.WORD.SRC.doc

¹⁴² Personal communication from Michael Moss, Environmental Senior Manager, QA Lab, Samsung Electronics America to Alexandra McPherson, Clean Production Action, November 17, 2006 as cited in http://cleanproduction.org/library/Electronics%20BFR%20Fact%20Sheet.pdf ¹⁴³ http://www.sony.net/SonyInfo/procurementinfo/ss00259/

¹⁴⁴ As cited in http://www.cleanproduction.org/library/CPA-HealthyBusiness-1.pdf

¹⁴⁵ As cited in <u>http://www.cleanproduction.org/library/CPA-HealthyBusiness-1.pdf</u> ¹⁴⁶ Greenpeace International Guide to Greener Electronics, December 2007

Update: http://www.greenpeace.org/electronics

http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

¹³⁸ Greiner T, Rossi M, Thorpe B, Kerr B, Healthy Business Strategies for Transforming the Toxic Chemical Economy, Clean Production Action, June 2006, http://www.cleanproduction.org/library/CPA-HealthyBusiness-1.pdf

http://www.hp.com/hpinfo/newsroom/press/2005/051101a.html

¹⁴⁰ Personal communication from Peter Leone, Manager, Product Safety & Standards Compliance, Toshiba America Information Systems, Inc. to Alexandra McPherson, Clean Production Action, March 30, 2006 as cited in http://cleanproduction.org/library/Electronics%20BFR%20Fact%20Sheet.pdf

Lassen C, Havelund S, Leisewitz A, Maxson P, COWI A/S, Denmark: Oko-Recherche BmbH, Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 200

¹⁴⁸ END Europe Daily 2465, Norwegians virtually extinguish deca-BDE, 18 January 2008

reduction may be achieved, if plastics without flame retardants were used since they tend to be more expensive than the plastics in which they are used.¹⁴⁹ For c-DecaBDE, the Danish EPA report estimates that, "The prices of the copolymers with organophosphorous flame retardants (FRs) are about 60-70% higher than HIPS with Deca-BDE, corresponding to a price increase of the raw materials of an average TV-set with CRT technology (27.5-inch screen) of about $5 \in$ "¹⁵⁰

The State of Illinois (USA) concluded that there no significant affordability issues for alternatives to c-DecaBDE in consumer electronics, other electrical applications and electronic products, and most uses of textiles and foams.¹⁵¹ Illinois did indicate that there were moderate affordability issues in medical and transportation uses due to the performance / safety testing and associated laboratory work required in those industries before a new design may be brought to market. The report noted that, "…many users of DecaBDE are in the process of phasing it out or intend to phase it out as soon as reasonably possible."

The State of Maine (USA) estimates 57% of the TVs in the state are already c-DecaBDEfree and concludes that, "... a shift to other plastics likely will lead to a small increase in the price of low-end TVs".¹⁵² With regard to electrical parts, the State notes that, "The fact that decaBDE is used in only about 10% of all electrical parts flame retarded with PBT and only about 6% of parts flame retarded with PA is further suggests that the cost of alternatives is not a significant barrier to use." For mattresses, the report notes that, "...there are safer, low-cost alternatives to decaBDE." In the area of transportation, the report states that the auto industry claims a need for five years to fully eliminate c-DecaBDE from cars and that the airplane industry might also require a long transition.

The State of Minnesota examined decaBDE alternatives and concluded that, "The cost to accomplish a phase out of Deca-BDE is concluded to be minor for the consumer electronics and textile industries."¹⁵³ The report goes on to say that cost of alternatives is more of a concern in medical devices and transportation primarily due to the highly regulated nature of the industries and the extensive product testing that is required.

See the discussion of individual alternatives for information regarding toxicity characteristics for a view of environmental and health costs.

http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

¹⁴⁹ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002 ¹⁵⁰ Lassen C, Havelund S, Leisewitz A, Maxson P. COWI A/S, Denmark; Oko-Recherche BmbH,

Germany; Concorde East/West Sprl, Belgium. Deca-BDE and alternatives in electrical and electronic equipment, Danish Ministry of the Environment, 200

¹⁵¹ Illinois Environmental Protection Agency, Report on alternatives to the flame retardant decaBDE: Evaluation of toxicity, availability, affordability, and fire safety issues. A report to the Governor and State Assembly. March 2007 <u>http://www.epa.state.il.us/reports/decabde-study/</u>

¹⁵² Maine Center for Disease Control and Prevention, Brominated flame retardants; Third report to the Maine Legislature, Maine Department of Environmental Protection (USA), 2007

¹⁵³ Minnesota Pollution Control Agency, Decabromodiphenyl ether (Deca-BDE), A report to the Minnesota legislature, January 15, 2008 <u>http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf</u>

(iv) Efficacy

The wide commercial use of alternatives described above that meet appropriate guidelines and laws indicate that alternatives to c-OctaBDE and c-DecaBDE are efficacious. The State of Minnesota concluded that, "A phase-out of Deca-BDE can be accomplished without affecting fire safety."¹⁵⁴

(v) Availability

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

(vi) Accessibility

The alternatives described here are accessible since most 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.

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 c-OctaBDE through listing in Annex A and Annex C would positively impact human health and the environment by decreasing emissions of a substance that warrants global action. As outlined in the Risk Profile, c-OctaBDE has widely contaminated the environment including humans and food. The c-OctaBDE Risk Profile describes the need for more information regarding toxicity and ecotoxicity of the component congeners but notes both immunotoxic and neurotoxic effects.¹⁵⁵ There is also

¹⁵⁴ Minnesota Pollution Control Agency, Decabromodiphenyl ether (Deca-BDE), A report to the Minnesota legislature, January 15, 2008 <u>http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf</u>

¹⁵⁵ Risk profile on commercial octabromodiphenyl ether UNEP/POPS/POPRC.3/20/Add.6

a risk to systemic, developmental, female fertility and local toxicity from workplace exposure.¹⁵⁶ Concerns for human health include the presence of c-OctaBDE in breast milk and its transfer to the infant along with prolonged exposure.¹⁵⁷ In addition, the elimination of c-OctaBDE and other brominated flame retardants will reduce the likelihood of emitting brominated dioxins and furans.¹⁵⁸ If c-OctaBDE production and use is not eliminated, then levels in the environment including humans and animals will continue to rise, even in locations distant from production and use.

(ii) Agriculture, including aquaculture and forestry

(iii) Biota (biodiversity)

(iv) Economic aspects

Cost competitive alternatives that do not exhibit persistence and/or bioaccumulation characteristics have already been implemented by companies for most uses of c-OctaBDE and c-DecaBDE.

Society may incur some specific costs when materials such as c-OctaBDE are removed from the market and when associated wastes and contaminated sites are addressed. The Polluter Pays principle¹⁵⁹, under which such costs should be internalized by the producer and/or the user, may be applied, but this is seldom done (at least without regulatory assistance). No good estimates are available of the potential cost recovery that can be achieved since the original 'polluter' often cannot be identified or is no longer in business. Nonetheless, the Polluter Pays Principle may be applied to legacy problems if the original 'polluter' can be identified and if a Party's regulatory framework permits.

(v) Movement towards sustainable development

Reduction and elimination of c-OctaBDE 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.¹⁶⁰ Over 100 health and environment ministers agreed to the SAICM which was adopted at a high-level meeting in Dubai in February 2006.¹⁶¹ SAICM makes the essential link between chemical safety, sustainable

 ¹⁵⁶ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002
¹⁵⁷ Risk and Policy Analysts Limited for Department for Environment, Food and Rural Affairs, UK. Risk

reduction strategy and analysis of advantages and drawbacks for octabromodiphenyl ether. 24 June 2002

¹⁵⁸ Leisewitz, A., H. Kruse and E. Schramm. 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

¹⁵⁹ Stockholm Convention Preamble: "Reaffirming Principle 16 of the Rio Declaration on Environment and Development which states that national authorities should endeavour to promote the internalization of environmental costs and the use of economic instruments, taking into account the approach that the polluter should, in principle, bear the cost of pollution, with due regard to the public interest and without distorting international trade and investment."

¹⁶⁰ <u>http://www.chem.unep.ch/saicm/</u>

¹⁶¹ UNEP Press Release, New Global Chemicals Strategy Given Green Light by Governments, 7 February 2006 <u>http://www.chem.unep.ch/saicm/iccm_sec.htm</u>

development, and poverty reduction.¹⁶² 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.

(vi) Social costs

The impact on business and consumer products associated with transition to c-OctaBDE and c-DecaBDE alternatives should be largely invisible and has largely already occurred. No difference in function exists in electronic equipment, mattresses etc with alternative flame retardants. The societal benefits will include a gradual decline in c-OctaBDE and c-DecaBDE levels as observed after banning PCBs.

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):

The use of c-OctaBDE in consumer and business office products creates implications for municipal waste and disposal along with attention to possible production stockpiles. The Risk Profile outlines uses of c-OctaBDE including office equipment and business machines. In addition there are concerns over export of electronic waste to developing countries leading to c-OctaBDE releases during recycling operations. Finally, burning or incineration of c-OctaBDE-containing waste could lead to formation and release of brominated dibenzo-*p*-dioxins and furans.¹⁶³ A listing of c-OctaBDE 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."

(i) Technical feasibility (ii) Costs

¹⁶² <u>http://www.chem.unep.ch/saicm/SAICM%20texts/SAICM%20documents.htm</u>

¹⁶³ Leisewitz, A., H. Kruse and E. Schramm. 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

¹⁶⁴ Stockholm Convention on Persistent Organic Pollutants, Article 6

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 c-OctaBDE 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.

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 c-OctaBDE in Annex A would be the most cost effective option in countries that lack the needed infrastructure to adequately monitor production and uses of c-OctaBDE. 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:

Eleven States in the USA have enacted legislation to prohibit or severely limit production and use of octaBDE (and penta-BDE). These include the following: California¹⁶⁵, Hawaii¹⁶⁶, Illinois¹⁶⁷, Maine¹⁶⁸, Maryland¹⁶⁹, Michigan¹⁷⁰, Minnesota¹⁷¹, New York¹⁷²,

¹⁶⁵ AB302 Enacted 11 August 2003 <u>http://www.leginfo.ca.gov/pub/03-04/bill/asm/ab_0301-0350/ab_302_bill_20030811_chaptered.html</u>

¹⁶⁶ HB2013 Enacted June 2004 <u>http://www.capitol.hawaii.gov/session2004/bills/hb2013_cd1_.htm</u>

¹⁶⁷ HB2572 Enacted 1 July 2005 <u>http://www.ilga.gov/legislation/publicacts/fulltext.asp?Name=094-0100</u>

¹⁶⁸ LD1790 Enacted 14 April 2004 <u>http://janus.state.me.us/legis/ros/lom/lom121st/14pub601-650/pub601-650-33.htm http://mlis.state.md.us/2005rs/billfile/HB0083.htm</u>

¹⁶⁹ HB83 Enacted 26 May 2005

¹⁷⁰ HB4406 Enacted 3 January 2005 <u>http://www.legislature.mi.gov/documents/2003-</u>2004/publicact/pdf/2004-PA-0562.pdf

¹⁷¹ SF2096 <u>http://www.ncel.net/articles/MN-SF2096.PBDE.enacted.doc</u>

¹⁷² S7621 Enacted 17 August 2004

Oregon¹⁷³, Rhode Island¹⁷⁴, and Washington.¹⁷⁵ The combined population of these states is greater than 98 million, roughly one-third the population of the USA.¹⁷⁶

Seven States in the USA recently have enacted legislation that includes decaBDE either as prohibitions or seeking greater information about alternatives as a step toward regulation. These include the following: Illinois¹⁷⁷ (information report); Maine¹⁷⁸ (prohibitions); Maryland¹⁷⁹ (prohibitions), Minnesota¹⁸⁰ (information report); New York¹⁸¹ (information report); Rhode Island¹⁸² (information report); and Washington¹⁸³ (prohibitions). The combined population of these states is approximately 50 million, roughly one-sixth the population of the USA.¹⁸⁴ In addition, Hawaii's House passed Concurrent Resolution 84 in 2006 which called for a study of decaBDE since the Committee found that the substance, "...poses a health risk to consumers" and that "Research needs to be conducted into safer alternative flame retardants."¹⁸⁵

Sweden has banned decaBDE for uses outside the RoHS Directive.¹⁸⁶ Norway has announced that the existing ban on the use of decaBDE in electronic and electrical products will be extended to textiles, furniture filling, and cables.¹⁸⁷

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:

¹⁷³ SB962 Enaction 14 July 2005 http://www.leg.state.or.us/05reg/measures/sb0900.dir/sb0962.a.html ¹⁷⁴ HB7917A Enacted 2006 http://www.ncel.net/articles/RI-H7917A.2006.pdf

¹⁷⁵ State of Washington Executive Order 04-01 http://www.ncel.net/articles/WA-SB6090.2005.pdf

¹⁷⁶ http://www.50states.com/ http://www.census.gov/population/www/popclockus.html

¹⁷⁸ LD 1658, Public Law 296 http://www.ncel.net/articles/ME-LD%201658%20-

%20as%20amended%20in%20Committee.rtf

¹⁷⁷ HB2572 Enacted 1 July 2005 http://www.ilga.gov/legislation/publicacts/fulltext.asp?Name=094-0100

¹⁷⁹ HB83 http://www.ncel.net/articles/MD-HB83.2005.pdf

¹⁸⁰ SF2096 http://www.ncel.net/articles/MN-SF2096.PBDE.enacted.doc

¹⁸¹ SB7621 http://www.ncel.net/articles/NY-SB7621-2004.doc

¹⁸² HB7917A Enacted 2006 http://www.ncel.net/articles/RI-H7917A.2006.pdf

¹⁸³ Chapter 65, 2007 laws http://www.ncel.net/articles/WA-1024-S.SL.pdf

¹⁸⁴ <u>http://www.50states.com/ http://www.census.gov/population/www/popclockus.html</u>

¹⁸⁵ http://www.capitol.hawaii.gov/session2006/CommReports/HCR84_SSCR3692_.htm

¹⁸⁶ http://www.kemi.se/templates/News.aspx?id=4636

¹⁸⁷ ENDS Daily, Norwegians virtually extinguish deca-BDE, 18 January 2008

Information on octaBDE and nonaBDE related to risk estimation and bioaccumulation

Information on quantitative assessments of the role of debromination

A series of current research publications with associated references are described below.

"The photodegradation of six individual PBDE congeners (BDE-28, 47, 99, 100, 153, 183) in hexane was investigated under UV light in the sunlight region, employing a mercury lamp filtered with Pyrex glass. All photodegradation reactions followed the pseudo-first-order kinetics, with the half-lives ranging from 0.26h for BDE-183 to 6.46h for BDE-100. The photochemical reaction rates of PBDEs decreased with decreasing number of bromine substituents in the molecule, also in some cases were influenced by the PBDE substitution pattern. Principal photoproducts detected were less brominated PBDEs, and no PBDE-solvent adducts were found. Consecutive reductive debromination was confirmed as the main mechanism for the photodegradation of PBDEs in hexane. In general, debromination firstly occurred on the more substituted rings, when the numbers of bromine atoms on the two phenyl rings were unequal. For less brominated PBDEs, the photoreactivity of bromines at various positions of phenyl rings decreased in the order: ortho>para; while for higher brominated PBDEs, the difference became not significant." Fang L, Huang J, Yu G, Wang L. POPs Research Centre, Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, PR China. Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane, Chemosphere, Nov 3, 2007

"To examine whether debromination was likely in the field, PBDE congener profiles were tracked from a wastewater treatment plant (sludge) to receiving stream sediments and associated aquatic biota. BDE-209 and 23 additional PBDEs were detected. Sludge congener profiles resembled the commercial penta- and deca- formulations, suggesting minimal -209 debromination during wastewater treatment. Similar profiles were observed in surficial sediments at the outfall and downstream. However, sunfish (Lepomis gibbosus), creek chub (Semotilus atromaculatus), and crayfish (Cambarus puncticambarus sp. c) collected near the outfall contained tri- through deca-PBDEs, including congeners not detected in the commercial deca-mixture, sludges or sediments (BDE-179, -184, -188, -201, and -202). A previous in vivo laboratory study identified these as -209 debromination products. This supports the hypothesis that metabolic debromination of -209 does occur in the aquatic environment under realistic conditions. Hence assessments that assume no BDE-209 debromination may underestimate associated bioaccumulation and toxicity attributable to the less brominated congeners produced."

LaGuardia MJ, Hale RC, Harvey E. Department of Environmental and Aquatic Animal Health, Virginia Institute of Marine Science, The College of William & Mary, Gloucester Point, Virginia 23062, USA. Evidence of debromination of decabromodiphenyl ether

(BDE-209) in biota from a wastewater receiving stream. Environ Sci Technol 41:6663 – 6670, 2007

"Water, sediment, and aquatic species including plankton, fish, and turtles were collected from a small lake in Beijing, which receives effluent discharged from a large sewage treatment plant (STP). The samples were examined to investigate polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) releases from a STP and their distributions in the lake. The accumulations of sigma 12PBDEs and BDE-209 in the sediment were 62.3 and 1150 ng/cm2, respectively, while that of sigma PCBs was 99.3 ng/cm2. BDE-209 was detected in more than 50% of the aquatic species. A strong linear correlation (R2 = 0.92) was found between sigma 12PBDEs and sigma PCBs levels in aquatic species but not in sediments. The different PBDE congener profiles in sediments and biota samples suggest metabolic debromination in the sampled fish. Bioaccumulations of PBDEs and PCBs were found in aquatic species. The logarithm bioaccumulation factor (BAF) decreases with the number of bromines in PBDEs molecules, while the log BAF versus the number of chlorines in PCBs appears to be parabolic. Biomagnifications of these compounds were not obvious in the food web by analysis of the relationship between sigma 12PBDEs or sigma PCBs levels and the trophic level of aquatic biota species."

Wang Y, Li X, Li A, Wang T, Zhang Q, Wang P, Fu J, Jiang G. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. Effect of municipal sewage treatment plant effluent on bioaccumulation of polychlorinated biphenyls and polybrominated diphenyl ethers in the recipient water. Environ Sci Technol 41:6026 – 6032, 2007

"Photolytic degradation of decabromodiphenyl ether (BDE 209) has been observed in several matrices such as solvent/water mixtures, sediments and soil; however, no studies have investigated the degradation potential of BDE 209 in house dust. In this study, both a natural and a BDE 209 spiked dust material were exposed to sunlight for 200 cumulative hours. Degradation of BDE 209 was observed in both matrices, but was 35% greater in the spiked dust relative to the natural dust material. The pseudo first order degradation rates were 2.3 x 10-3 h -1 and 1.7 x 10-3 h -1 for the spiked and natural dust, respectively. During the 200 h exposure, as much as 38% of the original BDE 209 mass was degraded in the spiked dust, 25% of which could not be accounted for and was lost to unknown pathways and/or products. The remaining 13% was accounted for by the formation of lower brominated congeners. Debrominated products detected in the spiked dust included all three nonabrominated congeners (BDE 206, BDE 207 and BDE 208), and several octabrominated congeners (BDE 196, BDE 197, BDE 201, BDE 202, and BDE 203/200). In technical commercial OctaBDE mixtures, BDE 201 is a very small component (below detection limit to 0.8%) and BDE 202 is not detected. Therefore, the presence of these congeners in house dust may provide a marker of environmental debromination of BDE 209. The ratio of BDE 197:201 may also be indicative of BDE 209 degradation as the ratio of these two congeners appeared to reach a steady state value (about 1) in both exposure scenarios in this study."

Stapleton H, Dodder N. Photodegradation of Decabromodiphenyl Ether in House Dust by Natural Sunlight. Environ Sci Technol 41, Oct, 2007

"In this work, pregnant Wistar rats were force-fed with 99.8% pure [(14)C]-DBDE over 96 h at a late stage of gestation (days 16 to 19). More than 19% of the administered dose was recovered in tissues and carcasses, demonstrating efficient absorption of DBDE despite its high molecular weight and low solubility. The highest concentrations of DBDE residues were found in endocrine glands (adrenals, ovaries) and in the liver, with lower values recorded for fat. In all tissue extracts, most of the radioactivity was associated with unchanged DBDE. The use of high-grade purity [(14)C]-DBDE allowed quantification of several metabolites present both in maternal tissues and in foetuses. These biotransformation products accounted for 9-27% of the extractable radioactivity in tissues and 14% of that in foetuses. Three nona-BDEs and one octa-BDE were identified by LC-APPI/MS. The unequivocal characterisation of a hydroxylated octa-BDE isolated from liver was confirmed by NMR. In rat, the main metabolic pathways of DBDE are debromination and oxidation. DBDE, and very likely most of its metabolites, are able to cross the placental barrier in rat. Metabolic profiles, obtained in vivo for the first time, demonstrated the presence of DBDE and major biotransformation products in endocrine glands as well as in foetuses."

Rui A, Cravedi JP, Debrauwer L, Garcia A, Canlet C, Jouanin I, Zalko D. Institut National de la Recherche Agronomique, Unité Mixte de Recherche 1089 Xénobiotiques, 180 chemin de Tournefeuille, BP3, 31931 Toulouse cedex 9, France. Disposition and metabolic profiling of [(14)C]-Decabromodiphenyl ether in pregnant Wistar rats. Environ Int, May, 2007

"Decabromodiphenyl ether (BDE-209) is the major component in the flame-retardant formulation DecaBDE which is incorporated into numerous consumer goods ranging from upholsteries to electronics. Because of the high volume of DecaBDE produced, its presence in consumer products and the environment, and the finding of BDE-209 in the blood of exposed workers, the extent of bioavailability, persistence, and potential debromination are important issues. To measure the bioconcentration, distribution, reductive debromination, and whole-body half-lives of BDE-209 after multiple low doses in an animal model, we dosed rats with a commercial DecaBDE (0.3 microg/g of diet) for 21 days and measured tissue polybrominated diphenyl ether levels during a 21 day withdrawal period. BDE-209, three nona-BDEs, and four octa-BDEs accumulated in the rats and distributed proportionately throughout the body. Only 5% of the total BDE-209 dose was present as parent compound in the rats after 21 days of dosing and <4% in the feces, suggesting extensive metabolism. A nona-BDE (BDE-207) and two octa-BDEs (BDEs-201 and -197) appeared to form via meta-debromination(s) of BDE-209 to a minimal extent (1% of the total BDE-209 dose). The wholebody half-lives tended to increase with decreasing bromination; however, two octa-BDEs, presumably forming from debromination, increased in the rats after 21 days of withdrawal and demonstrated the potential for BDE-209 to form more persistent lipophilic compounds in vivo." Huwe JK, Smith DJ. Biosciences Research Laboratory, ARS, USDA, P.O. Box 5674, University Station, Fargo, North Dakota 58105-5647, USA. Accumulation, whole-body

depletion, and debromination of decabromodiphenyl ether in male sprague-dawley rats following dietary exposure. Environ Sci Technol 41:2371 – 2377, 2007

"...examined in egg yolk and plasma of male and female glaucous gulls (Larus hyperboreus) from the Norwegian Arctic. Also examined were BDE209 and 38 tri- to nona-BDE congeners and brominated biphenyl (BB) 101...Sum (sigma)38PBDE concentrations ranged from 2.49 to 54.5 ng/g wet wt in plasma and 81.2 to 321 ng/g wet wt in egg yolk. The BDE209 was virtually nondetectable, whereas six octa-BDEs (i.e., BDE196, 197, 201, 202, 203, and 205), as well as three nona-BDEs (i.e., BDE206, 207, and 208, and potential BDE209 debromination products) were found sporadically in plasma and egg yolk."

Verreault J, Gebbink WA, Gauthier LT, Gabrielsen GW, Letcher RJ. Norwegian Polar Institute, Tromsø NO-9296, Norway. Brominated flame retardants in glaucous gulls from the Norwegian Arctic: more than just an issue of polybrominated diphenyl ethers. Environ Sci Technol 41:4925 – 4931, 2007

"Congener patterns of PBDEs in seafood samples suggested that seafood products are prone to accumulating low-brominated congeners, and possible metabolic debromination of BDE-99 to BDE-47 could occur in certain organisms, such as crabs and mantis shrimp. Generally, the congener profile was dominated by BDE-209, and to a lesser extent by BDE-47 and BDE-99, which was consistent with the fact that Deca-BDE is mass-produced in China and with previous sediment results from the same area. The occurrence of BDE-209 in aquatic species from South China suggests that BDE-209 appears to be more bioavailable than previously thought, and the environmental fate and safety of BDE-209 require further investigation and call for a thorough reassessment." Guo JY, Wu FC, Mai BX, Luo XJ, Zeng EY. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. Polybrominated diphenyl ethers in seafood products of south China. J Agric Food Chem 55:9152 – 9158, 2007

"Based on previous findings in dietary studies with carp (Cyprinus carpio), we investigated the mechanism of 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) debromination to 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) using liver and intestinal components. In vitro aerobic and anaerobic experiments tested the ability of carp intestinal microflora to debrominate BDE-99. No debromination of BDE-99 to BDE-47 was observed in microfloral samples; therefore, carp enzymatic pathways were assessed for debromination ability. After sixty-min incubation, intestine and liver microsomes exhibited 83+/-34% and 106+/-18% conversions, respectively, of BDE-99 to BDE-47; with no significant (p>0.05) difference between organ debromination capabilities. Microsomal incubations with BDE-99, enzyme cofactors and competing substrates assessed the potential mechanisms of debromination. The presence of NADPH in the microsomal assay did not significantly (p>0.05) affect BDE-99 debromination, which suggest that cytochrome P450 enzymes are not the main debrominating pathway for BDE-99. Co-incubation of BDE-99 spiked microsomes with reverse thyronine (rT3) significantly (p<0.05) decreased the debromination capacity of intestinal microsomes indicating the potential of catalytic mediation via thyroid hormone deiodinases. The

significant findings of this study are that intestinal microflora are not responsible for BDE-99 debromination, however, it is an endogenous process which occurs with approximately equal activity in intestine and liver microsomes and it can be inhibited by rT3."

Benedict RT, Stapleton HM, Letcher RJ, MItchelmore CL. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, P.O. Box 38, Solomons, MD 20688, USA. Debromination of polybrominated diphenyl ether-99 (BDE-99) in carp (Cyprinus carpio) microflora and microsomes. Debromination of polybrominated diphenyl ether-99 (BDE-99) in carp (Cyprinus carpio) microflora and microsomes. Chemosphere 69:987 – 993, 2007

"To identify candidate metabolites, mouse plasma samples were collected after continuous oral and subcutaneous exposure to DE-71, a widely used commercial pentabromodiphenyl ether product, for 34 days. METHODS: Samples were extracted, separated into neutral and phenolic fractions, and analyzed by gas chromatographic mass spectrometry. RESULTS: In the plasma samples of orally treated animals, 2,2',4,4',5,5'hexabromodiphenyl ether (BDE-153) represented 52% of total measurable PBDEs, whereas it represented only 4.3% in the DE-71 mixture. This suggested that BDE-153 was more persistent than other congeners in mice. Several metabolites were detected and quantitated: 2,4-dibromophenol, 2,4,5-tribromophenol, and six hydroxylated PBDEs. The presence of the two phenols suggested cleavage of the ether bond of 2,2',4,4'tetrabromodiphenyl ether (BDE-47) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), respectively. The hydroxylated (HO)-PBDEs might come from hydroxylation or debromination/hydroxylation. Among the quantitated hydroxylated metabolites, the most abundant was 4-HO-2,2',3,4'-tetra-BDE, which suggested that there was a bromine shift during the hydroxylation process. para-HO-PBDEs have been proposed to behave as endocrine disruptors. CONCLUSIONS: THERE SEEM TO BE THREE METABOLIC PATHWAYS: cleavage of the diphenyl ether bond, hydroxylation, and debromination/hydroxylation. The cleavage of the diphenyl ether bond formed bromophenols, and the other two pathways formed hydroxylated PBDEs, of which para-HO-PBDEs are most likely formed from BDE-47. These metabolites may be the most thyroxine-like and/or estrogen-like congeners among the HO-PBDEs." Qui X, Mercado-Feliciano M, Bigsby RM, Hites RA. School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405, USA. Measurement of polybrominated diphenyl ethers and metabolites in mouse plasma after exposure to a commercial pentabromodiphenyl ether mixture. Environ Health Perspect 115:1052 - 1058, 2007

Toxicological and ecotoxicological information for the commercial mixture and its components