United States Environmental Protection Agency

FLAME RETARDANT ALTERNATIVES FOR HEXABROMOCYCLODODECANE (HBCD)

Executive Summary

FINAL REPORT

June 2014

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This report provides information on hexabromocyclododecane (HBCD; CASRN 25637-99-4; 3194-55-6) used as a flame retardant in polystyrene building insulation, possible substitutes, and alternative materials. The report was developed by the U.S. Environmental Protection Agency (EPA) with input from a partnership of stakeholders from business, government, academia, and environmental organizations. According to technical experts on the Partnership, between 2011 and 2014 there were only three viable flame retardant alternatives to HBCD for use in expanded and extruded polystyrene foam (EPS and XPS) insulation under current manufacturing processes. Alternative materials are also available as substitutes to HBCD-containing insulation. These alternatives may require additive flame retardants or other treatment to meet fire safety requirements. This report:

1) Identifies viable and non-viable flame retardant alternatives for HBCD in polystyrene building insulation foam;
2) Describes uses and provides an overview of end-of-life scenarios and exposure to HBCD;
3) Provides hazard profiles for HBCD and the three chemical alternatives; and
4) Provides an overview of relevant alternative materials.

Based on DfE AA criteria and guidance, the hazard profile of the butadiene styrene brominated copolymer (CASRN 1195978-93-8) shows that this chemical is anticipated to be safer than HBCD for multiple endpoints. Due to its large size, lack of low molecular weight (MW) components, and un-reactive functional groups, human health and ecotoxicity hazard for this polymer are measured or predicted to be low, although experimental data were not available for all endpoints. In general the exposure potential to the butadiene styrene brominated copolymer is expected to be lower than the other chemicals in this assessment because it is a large polymer and is unlikely to be released from the polystyrene. However, this alternative is inherently persistent and its long-term behavior in the environment is not currently known. Chemical suppliers have commercialized this polymer, and polystyrene manufacturers are testing it in their products to ensure that the polystyrene will meet all performance standards. The hazard designations for this alternative are based upon high MW formulations of the polymer, where all components have a MW >1,000. The polymer is regulated with a Significant New Use Rule that was finalized in June 2013. Manufacture (or import) of the polymer requires notification to EPA except in these cases: (1) the MW of the polymer is in the range of 1,000 to 10,000 daltons, or (2) the MW of the polymer is ≥10,000 daltons and less than 5 percent of the particles are in the respirable range of 10 microns or less (U.S. EPA 2013).

The hazard profiles of the tetrabromobisphenol A (TBBPA)-bis brominated ether derivative (CASRN 97416-84-7) and TBBPA bis(2,3-dibromopropyl) ether (CASRN 21850-44-2) show that these chemicals have limited data sets for human health endpoints and hazard designations show a potential for toxicity. These two chemicals are also anticipated to have High potential for bioaccumulation.

Background

In August 2010, EPA released the HBCD Action Plan. The Action Plan summarized hazard, exposure, and use information regarding environmental and health risks associated with HBCD.

HBCD is a flame retardant that has been found to have persistent, bioaccumulative, and toxic (PBT) characteristics. HBCD use as a flame retardant in EPS and XPS accounts for more than 95% of HBCD applications. EPS and XPS are used as rigid foam insulation in the building and construction industry. A small volume of HBCD is used in textiles and high-impact polystyrene (HIPS).

As part of the Agency's efforts to manage chemical risks, the Action Plan called upon the Design for the Environment (DfE) Program to conduct an alternatives assessment for HBCD. A DfE Alternatives Assessment identifies and compares potential alternatives that can be used as substitutes to replace chemicals that the Agency has designated for action. DfE alternatives assessments provide information on functional class, intrinsic hazard, exposure properties, and environmental fate for chemical alternatives. The information in DfE alternatives assessments can influence the selection of safer, more sustainable alternatives when combined with other information that is not the focus of DfE Alternatives Assessments, such as performance and cost.

Goal of the Partnership and Report

DfE convened a multi-stakeholder partnership to assess the potential human health and environmental hazards of HBCD and its alternatives for use in EPS and XPS foam. The information presented in this report is based on the Partnership's knowledge and the DfE Program's research. Chapter 1 of the report provides background information on HBCD and defines the report's purpose and scope. Chapter 2 discusses the uses, end-of-life scenarios, and exposure potential of HBCD. Chapter 3 offers background information on flame retardants and outlines which flame retardants are and are not included in the alternatives assessment. Chapter 4 explains the hazard evaluation methodology and includes the hazard profiles for HBCD and the three identified alternatives. Chapter 5 summarizes the results of the assessment, discusses considerations for selecting flame retardants and includes an overview of alternative materials. Since the primary use for HBCD is in EPS and XPS foam insulation, the project scope does not include alternatives to HBCD for its minor uses in textiles and HIPS. Alternatives to HBCD for these uses are included in a separate DfE Alternatives Assessment for decabromodiphenyl ether (decaBDE). Flame retardant performance and costs of HBCD and the three alternatives were not assessed in-depth in this report.

Results

Members of the Partnership identified many chemicals as potential alternatives; however, only three chemicals were identified as viable alternatives to HBCD in EPS and XPS foam: a butadiene styrene brominated copolymer (CASRN 1195978-93-8), a TBBPA-bis brominated ether derivative (CASRN 97416-84-7), and TBBPA bis(2,3-dibromopropyl) ether (CASRN 21850-44-2). Only three alternatives were identified for evaluation in this report because flame retardants for EPS and XPS foam must allow the material to comply with fire safety codes while not compromising the performance of the foam. All three alternatives are brominated. No non-brominated flame retardants are known to be compatible in polystyrene manufacturing and associated flame tests. Figure ES-1 summarizes the hazard information for HBCD and the three alternatives assessed. Few measured experimental data were available for the TBBPA-bis brominated ether derivative; therefore, estimated hazard designations were determined using TBBPA bis(2,3-dibromopropyl ether) (CASRN 21850-44-2) as an analog.

The human health endpoints evaluated in DfE alternatives assessments include acute toxicity, carcinogenicity, genotoxicity, reproductive toxicity, developmental toxicity, neurotoxicity, repeated dose toxicity, skin sensitization, respiratory sensitization, eye irritation, and dermal irritation. HBCD has been assigned a High hazard designation for developmental neurotoxicity, a Moderate hazard designation for reproductive toxicity and repeated dose toxicity, and an estimated Moderate hazard designation for carcinogenicity and neurotoxicity; other health endpoints have Low or Very Low hazard designations. The butadiene styrene brominated copolymer has Low hazard designations (either measured or estimated) for most human health endpoints due to its high MW and limited potential for absorption; there is one Moderate hazard designation for the eye irritation endpoint based on experimental data. The TBBPA-bis brominated ether derivative and TBBPA bis(2,3-dibromopropyl) ether have a Moderate hazard designation for carcinogenicity, mutagenicity, reproductive toxicity, developmental toxicity, and repeated dose toxicity based on potential alkylating properties. Low hazard designations have been assigned to these similar substances for acute toxicity, neurotoxicity, skin sensitization and irritation.

The ecotoxicity endpoints evaluated in DfE alternatives assessments include acute and chronic aquatic toxicities. HBCD is aquatically toxic and has Very High hazard designations for both acute and chronic aquatic toxicity. Aquatic toxicity for the three alternatives is Low, driven by their lack of appreciable water solubility leading to “no effects at saturation” (NES). Ecotoxicity data for terrestrial species was limited, and thus the potential for impacts on high trophic level and terrestrial wildlife from HBCD and its alternatives or associated degradation products is unclear.

The environmental fate of HBCD and the three alternatives is described primarily in terms of persistence and bioaccumulation potential. All three chemicals have High or Very High persistence designations, a quality typical for the majority of flame retardants. Long-term fate of the three alternatives in the environment is not well understood. The butadiene styrene brominated copolymer is estimated to have Low bioaccumulation potential due to its size (average MW >1,000 daltons) and lack of low MW components, while HBCD, the TBBPA-bis brominated derivative, and TBBPA bis(2,3-dibromopropyl) ether have Very High, High, and High potential for bioaccumulation.

Under conditions where fire or incineration occurs, a halogenated substance may: contribute to halogenated dibenzodioxin and dibenzofuran formation, increase the generation of PAHs, and impact fire parameters such as smoke and carbon monoxide (Sidhu, Morgan et al. 2013). However, combustion reactions are complex and variable and make inclusion of combustion by-products in hazard assessment challenging. Both halogenated and non-halogenated flame retardants may yield other toxic by-products that would need to be compared, not only halogenated dioxins and furans. For these reasons, the pyrolysis transformation products are not assessed in this report.

In addition to the chemical hazard assessment of HBCD and its alternatives, Chapter 5 of the report includes general information about alternative insulation materials. These technologies include rigid board alternatives (e.g., similar to EPS and XPS), alternatives for certain functional uses (e.g., blanket insulation, foamed-in-place insulation), and specialty and emerging alternative materials (e.g., aerogel, carbon foam). The report does not assess these materials, does not compare them to EPS or XPS, and does not assess flame retardancy needs for each of these materials.

How to Use This Report

The intended audience for the report includes, but is not limited to, chemical manufacturers, product manufacturers, retailers, consumers, non-governmental organizations (NGOs), consultants, and state and federal regulators. Three possible uses of this report include: identification of potential substitutes; selection of alternative chemicals based on comparative hazard assessment; and use of hazard information for further analysis and decision-making.

This report allows stakeholders interested in chemical substitution to identify functional substitutes for HBCD in EPS and XPS foam. The list of potential alternatives introduced in Chapter 3 includes chemicals identified by stakeholders as viable, functional alternatives, as well as chemicals that are not considered functional alternatives. Decision-makers can understand and compare the hazard concerns associated with the four chemicals using the profiles in Chapter 4. The inclusion of a chemical in this assessment does not indicate environmental- or health-based preferability. Manufacturers considering the potential functional alternatives in this report will likely also conduct performance testing to confirm an alternative's performance in their product. Although outside of the report scope, decision makers should also consider the human health and environmental impacts of insulation's non-flame retardant additives (e.g., synergists and stabilizers) discussed in Chapter 2 of the report.

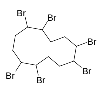
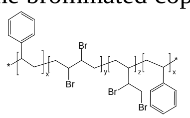
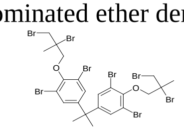
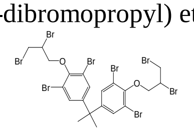
Chapter 4 describes the hazard criteria, data interpretation, and information used to assign hazard values in each category. The chapter provides a human health and environmental profile for each chemical that is based on empirical data, and enhanced with modeling and expert judgment to fill data gaps. Where toxicity is estimated in the absence of measured data, DfE encourages users to be conservative in the interpretation of the hazard profiles. Chemicals used at high volumes, or likely to be in the future, should be of high priority for further empirical testing.

The information in this report can be used to inform or supplement further analyses such as risk assessments or life-cycle assessments (LCAs) on preferred alternative chemicals. The criteria used to develop the hazard assessments in this report can also be used to inform green chemistry design, if availability of safer alternatives is limited.

ES-1 Hazard Summary for HBCD and Alternatives

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H,* and *VH)* were assigned using values from predictive models and/or professional judgment.
This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion by-products are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

d This hazard designation would be assigned MODERATE for a potential for lung overloading if >5% of the particles are in the respirable range as a result of dust forming operations.
§ Based on analogy to experimental data for a structurally similar compound.
¥ Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

Chemical For full chemical name and relevant trade names see the hazard profiles in Section 4.8	**CASRN**	**Human Health Effects**											**Aquatic Toxicity**		**Environmental Fate**	
		Acute Toxicity	**Carcinogenicity**	**Genotoxicity**	**Reproductive**	**Developmental**	**Neurological**	**Repeated Dose**	**Skin Sensitization**	**Respiratory Sensitization**[1]	**Eye Irritation**	**Dermal Irritation**	**Acute**	**Chronic**	**Persistence**	**Bioaccumulation**
Hexabromocyclododecane (HBCD) 	25637-99-4; 3194-55-6	L	*M*	L	M	H	*M*	M	L		VL	VL	VH	VH	H	VH
Butadiene styrene brominated copolymer¥ 	1195978-93-8	L	*L*	L	L	L	*L*	L[d]	L		M	L	*L*	*L*	*VH*	*L*
TBBPA-bis brominated ether derivative¥ 	97416-84-7	*L*§	*M*§	*M*§	*M*§	*M*§	*L*	*M*§	*L*§		*L*	*L*	*L*	*L*	*H*	*H*
TBBPA bis(2,3-dibromopropyl) ether¥ 	21850-44-2	L	*M*	M	*M*	*M*	*L*	*M*	L		L	L	L	*L*	VH	*H*

[1] At this time, there are no standard test methods for respiratory sensitization and no test data; as a result there was no designation for this endpoint.