Brominated Diphenyl Ether Flame Retardants used in plastics

This case study aims to illustrate a chemical substitution process. It is based on publicly available information on company's experience as well as on substance hazards, alternatives to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1. Introduction

Flame retardants are a necessary component of many plastics used in electrical and electronic equipment. Brominated Diphenyl Ether flame retardants have been used to fulfill this purpose. However, due to their very persistent nature and the tendency to accumulate in biological organisms, the need to substitute BDEs have been raised. Now we are more concerned than ever, as we found out that BDEs in plastics are contaminating products including kid's toys, hindering the environmental friendly recycling practices.

Brominated diphenyl ethers (BDEs) are man-made chemicals found in plastics used in a variety of consumer products to make them difficult to burn. They have been widely used since the 1970s as flame retardants in electronics. BDEs are released from products when TVs or computers heat up or when the products degrade.

There are three important commercial BDE mixtures (i.e., penta-, octa-, and deca-bromodiphenyl ethers [BDEs]). DecaBDE's main use is for electronic enclosures, such as television cabinets. Deca accounts for 80 percent of the BDEs currently produced and is composed of around 97 percent pure brominated diphenyl ether. DecaBDE is used in Europe in a range of 10 000-100 000 tons a year. It is widely used as an additive flame retardant in many different industry sectors. Major uses are for plastics and textiles.

OctaBDE is largely used in plastics for personal computers and small appliances. PentaBDE is principally used in foam for cushioning in upholstery.

2. Hazards of Brominated Diphenyl Ethers

Brominated flame retardants are persistent and bioaccumulative industrial chemicals that cause numerous problems including cancer, thyroid problems, and neurodevelopmental effects. They are biomagnified toxic compounds, meaning they accumulate within food chains and they impair learning, memory, sexual development, and behavior.

DecaBDE has no harmonized classification according to CLP regulation. The classification provided by companies to ECHA in CLP notifications identifies that this substance causes serious eye irritation, is harmful if swallowed, is harmful in contact with skin, may cause long lasting harmful effects to aquatic life, is suspected of causing genetic defects and may cause damage to organs through prolonged or repeated exposure.

According to the harmonised classification and labelling approved by the European Union, octaBDE may damage the unborn child and is suspected of damaging fertility.

3. Regulatory status

According to EU restriction decaBDE shall not be manufactured or placed on the market as a substance on its own after 2 March 2019. EU restricts the use and marketing of decaBDE as a constituent in mixtures and articles, at a concentration equal to or greater than 0.1% by weight exempting the use for aircraft; motor vehicles; agricultural and forestry vehicles, electrical and electronic equipment (compliant with RoHS requirements).

DecaBDE is a substance of very high concern and included into candidate list for authorization.

The Stockholm Convention bans toxic chemicals on its persistent organic pollutants (POPs) list. This list includes some of the brominated diphenyl ether flame retardants (POP-BDEs) – decaBDE and hexaBDE, heptaBDE which are the main components of commercial octaBDE.

4. Effects of BDE flame retardants on plastics recycling

Life on earth as a sustainable form of production uses 100% recycling, as nothing is wasted or else life would eventually go extinct. Recycling practices are necessary for a sustainable economy, to be able to decrease the environmental impact of the industry by reducing waste produced and reducing the extraction of raw materials. Petroleum products are non-renewable, and their recycling makes sense from a resource depletion point of view as well. An industry that is producing non-biodegradable waste without any recycling practices is the opposite of being sustainable.

A 2016 study by World Economic Form concluded that in 2050 it is expected that there will be more plastics in the ocean than there is fish (WEF 2016).

Despite this, the contamination of recycled plastics with hazardous chemicals is hindering the recycling process. A study revealed that BDEs are contaminating many products including children's toys that uses recycled plastic materials which was previously contaminated with BDEs used as flame retardants. The effect of this is not only the risks caused by the BDEs, but also all the risks associated with a decrease in recycling practices.

22% of all the banned POP-BDE in Dutch electronic waste ends up in recycled plastics. 33% of all the banned POP-BDE in Dutch automotive plastic waste is reused or recycled.

4. Substitution

There are existing suggestions on the literature about the possible alternatives to BDE flame retardants used in electronics, and many major companies (Dell, HP, Compaq, Sony, IBM, Ericsson, Apple and Panasonic, etc.) reported that they have eliminated BDE flame retardants from their products, however the hazards or details of these alternatives are not certain and needs further investigation. The types of flame retardants used in products are generally considered confidential, but a typical replacement scheme would be to use copolymers together with halogen-free organo-phosphorous compounds for enclosures and other large parts. The large number of major companies that have phased out decaBDE in their products clearly indicates that decaBDE-free electronic components are available on the market, and that the requirement for "decaBDE-free" is not an obstacle to manufacturing any electrical and electronic equipment.

Hewlett-Packard Company reports that:

"Examples of flame retardants that we use instead of halogens are mainly different types of organic phosphate esters, see below:

Substance	*CAS number*
DEEP, diethylethylphosphonate	*78-38-6*
DPK, diphenylcresylphosphate	*247-693-8*
RDP, resorcinol bis (diphenylphosphate)	*57583-54-7*
TEP, triethylphosphate	*78-40-0*
TCP, tricresylphosphate	*1330-78-5*
TPP, triphenylphosphate	*115-86-6*

Source: Danish study (2006) on decaBDE alternatives for electrical and electronic equipment

4.1. Hazard assessment

(Environmental/human health/physical) of some alternatives (GS Benchmark Score: 1 being the worst, 4 being the best)

Table 6.2: Green Screen (Version 1.0) Levels of Concern for Nine Flame Retardants

Screening Level Toxicology Hazard Summary

Chemical	CAS #	Human Health Effects									Aquatic Toxicity		Fate		Physical		GS Benchmark Score (Chemical)
		Carcinogenicity	Mutagenicity	Reproductive/ Developmental	Endocrine Disruption	Neurotoxicity	Acute Toxicity	Skin/Eye Corrosion/Irritation	Dermal/Respiratory Sensitization	Systemic Toxicity/ Repeated Dose	Acute Aquatic	Chronic Aquatic	Persistence	Bioaccumulation	Explosivity	Flammability	
Decabromodiphenyl Ether	1163-19-5	M	L	M	M	M	L	M	L	M	H	H	vH	M	nd	L	1
Aluminum Trihydroxide	21645-51-2	L	L	L	nd	M	L	M	L	M	L	M	vH	L	L	L	2
Ammonium Polyphosphate	68333-79-9	L	L	L	nd	nd	L	L	L	L	L	L	L	L	L	L	4
Ethylenediamine Phosphate	14852-17-6	L	M	M	nd	nd	M	H	H	M	L	H	M	L	L	L	2
Magnesium Hydroxide	1309-42-8	L	L	L	nd	L	L	M	L	M	L	L	vH	L	L	L	2
Magnesium Stearate	557-04-0	L	L	L	nd	nd	L	M	L	M	L	M	H	L	M	H	2
Melamine Polyphosphate	218768-84-4	M	M	L	nd	nd	L	L	L	H	L	L	M	L	L	L	2
Red Phosphorus	7723-14-0	L	L	L	nd	H	H	H	L	H	L	M	M	L	H	H	1
Zinc Borate	1332-07-6	L	L	M	M	nd	L	M	L	M	H	nd	nd	L	L	L	2

nd=not determined/unknown

L=Low Hazard M=Moderate Hazard H=High Hazard vH=very High Hazard-Endpoints in colored text (**L, M, and H**) were assigned based on experimental data.

Endpoints in black italics (*L, M, and H*) were assigned using estimated values and professional judgment (Structure Activity Relationships)

Source: Decabromodiphenyl Ether Flame Retardant in Plastic Pallets (2012)

Further hazard assessment for the alternatives can be found in the 2014 final report named "AN ALTERNATIVES ASSESSMENT FOR THE FLAME RETARDANT DECABROMODIPHENYL ETHER (DecaBDE)" published by the US EPA.

4.2. Economic feasibility

The reporting on the economic cost of the alternatives compared to BDE varies throughout the literature, hence no conclusions can be made regarding the economic feasibility.

European Chemicals Agency concludes for decaBDE that "the proposed restriction is technically and economically feasible. Technically feasible alternatives are available for existing uses of decaBDE at low additional cost".

References:

AN ALTERNATIVES ASSESSMENT FOR THE FLAME RETARDANT DECABROMODIPHENYL ETHER (DecaBDE) (2014), link (Accessed 08.07.2017): https://www.epa.gov/sites/production/files/2014-05/documents/decabde_final.pdf

Danish study (2006) on Deca-BDE alternatives for electrical and electronic equipment, link (Accessed 08.07.2017): http://www2.mst.dk/udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

Decabromodiphenyl Ether Flame Retardant in Plastic Pallets (2012), link (Accessed 08.07.2017): http://www.subsport.eu/wp-content/uploads/2012/08/Decabromodiphenyl-Ether-Flame-Retardant-in-Plastic-Pallets-Final-Report21.pdf

ECHA.2012. Member State Committee Support Document For Identification Of Bis(Pentabromophenyl) Ether as aSubstance Of Very High Concern Because Of Its Pbt/Vpvb Properties. Link (Accessed 08.07.2017): http://echa.europa.eu/documents/10162/b41b5e85-68c6-4522-980f-75f3e0f7f21d

ECHA. 2013. Draft background document for Bis(pentabromophenyl)ether (decabromodiphenyl ether; decaBDE). Link (Accessed 08.07.2017): http://echa.europa.eu/documents/10162/041e5785-f8b6-44b7-86d4-c7b212c5373e

ECHA. 2014. List of existing substances subject to transitional measures, Bis(pentabromophenyl)ether (decaBDE) –Termination of evaluation. Link (Accessed 08.07.2017): http://echa.europa.eu/documents/10162/69918301-fad2-46a1-aee9-200c139da2a4

ECHA. 2016. Classification data base: C-L inventory. Link (Accessed 08.07.2017): http://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/131436

ECHA. 2016. Registration dossier information. Link (Accessed 08.07.2017): http://echa.europa.eu/registration-dossier/-/registered-dossier/14217/2/3

ECHA, RAC & SEAC. 2015. Background document to the Opinion on the Annex XV dossier proposing restrictions on Bis(pentabromophenyl) ether. Link (Accessed 08.07.2017): http://echa.europa.eu/documents/10162/13641/rac_seac_background_doc_decabde_en.pdf

Leslie et al. 2016, Propelling plastics into the circular economy — weeding out the toxics first. Link: http://dx.doi.org/10.1016/j.envint.2016.05.012

Subsport case story, link (Accessed 08.07.2017): http://www.subsport.eu/case-stories/363-en

Subsport case story, link (Accessed 08.07.2017): http://www.subsport.eu/case-stories/244-en

WEF 2016, link (Accessed 08.07.2017): http://www3.weforum.org/docs/WEF_The_New_Plastics_Economy.pdf

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