

10.19

Lizenziert für Marketing Pro Wärmedämmung GmbH (MPW GmbH).
Die Inhalte sind urheberrechtlich geschützt.

Müll und Abfall

Fachzeitschrift
für Abfall-
und
Ressourcen-
wirtschaft*

51. Jahrgang
Oktober 2019
Seite 481-524

www.MUELLundABFALL.de

* Trade journal for waste
and resource management



Straßenreinigung und Winterdienst in der kommunalen Praxis

Von Dr. Manfred Wichmann

8., neu bearbeitete und erweiterte Auflage 2018, 823 Seiten,
fester Einband, € (D) 104,-, ISBN 978-3-503-17643-4

Online informieren und bestellen:  www.ESV.info/17643

ESV ERICH
SCHMIDT
VERLAG

Flame Retardant for the Effective Recycling of Expanded Polystyrene (EPS)

Dr. Christian Sinn, Dr. Christoph Semisch, Prof. Dr. Michael Braungart, and Dr. Peter Möhle



Abstract

Expanded polystyrene, abbreviated as EPS (also generally known as Styropor), has been used worldwide for many decades as an insulation material in building construction. As this material, like all other organic insulation material, is flammable, the addition of a flame retardant is mandatory for this application. Hexabromocyclododecane (HBCD) was used as the main flame retardant until 2016. Based on new findings at the time, however, it was classified as a PBT substance (PBT: persistent, bioaccumulative, toxic), no longer allowed to be utilized, and even turned used EPS insulation boards into "hazardous waste" – a regulation that was later withdrawn by the legislature.

So, better alternatives had to be found. In the present study, we have therefore investigated and evaluated two other brominated flame retardants with respect to their environmental and health impact as a flame retardant in EPS insulation materials. These are Polymeric FR and a TBBPA derivative.

Polymeric FR, a new brominated polymer, is neither toxic nor bioaccumulative. Combustion of Polymeric FR leads to the formation of hydrogen bromide, which is responsible for its flame-retardant effect. Traces of toxic organic compounds may additionally be formed under certain conditions.

In contrast, the second flame retardant that was investigated, a tetrabromobisphenol A (TBBPA) derivative, is very hazardous. This substance is endocrine disruptive in vitro, bioaccumulative, and persistent. Detection of the substance in environmental samples indicates that it can disperse and accumulate in the environment. Its hazardous effects are currently being investigated as part of an EU programme (CoRAP). The use of the substance may be prohibited in the foreseeable future.

Like Polymeric FR, the TBBPA derivative forms hydrogen bromide during combustion. It is slowly degraded under anaerobic conditions to the even more hazardous TBBPA, which is suspected to be carcinogenic and endocrine disruptive and is also being studied in the CoRAP programme. From the Cradle to Cradle perspective it is recommended to no longer use the TBBPA derivative due to its hazardous nature. Since the brominated polymer is neither toxic nor bioaccumulative, it is clearly superior to the TBBPA derivative with respect to its environmental and health impact. Its use even allows the mechanical recycling of used EPS and therefore contributes both to a reduction in the use of fossil resources and to a fall in carbon dioxide emissions.



Christian Sinn and Christoph Semisch are scientific supervisors at EPEA GmbH – Part of Drees & Sommer. Michael Braungart is managing director of BRAUNGART EPEA Internationale Umweltforschung GmbH. Peter Möhle is managing director of EPEA GmbH – Part of Drees & Sommer.

1. Introduction – Climate Change, Insulation, Insulation Materials, Recycling

Rising energy costs and climate change caused primarily by the emission of carbon dioxide together with its serious consequences call for improved thermal insulation of buildings, for example, through the increased use of insulation materials. At the same time, the growing resource shortages as well as the bottlenecks in the incineration of used products require the recycling of insulation materials after their use phase.

Despite numerous competing insulation materials available in Germany, the issue of insulation material recycling has not yet been taken sufficiently into account. However, the recycling of insulation materials only makes sense if ecological as well as economical minimum requirements are met. This is typically the case when a large proportion of the materials used for the manufacture of the insulation material system can be recycled at a high standard of quality and with minimum effort while being cost-effective. The process must not pose any risk to the environment or to health. A commercially usable method for the recycling of old EPS (expanded polystyrene) containing HBCD is not yet available. However, the PSLoop initiative is currently working on the further development of a solvent procedure with which even polystyrene can be recycled from HBCD-containing old insulation boards in the future (see Chapter 10).

The objective of this report, however, is not to compare the recyclability of different insulation material systems. Instead, an example will be used to demon-



Insulation material range, copyright BASF.

strate the potential impact of a new flame retardant on the recycling of EPS.

2. Flame Retardants in General

Almost all organic insulation materials, whether made of renewable or synthetic raw materials, are flammable. For obvious reasons, this property may be problematic in facade insulation. EPS is also flammable.

However, the flammability of EPS can be reduced by the addition of a flame retardant to such a degree that its use in buildings becomes possible.

The three most important groups of flame retardants in terms of quantity are as follows [1]:

Inorganic flame retardants, e.g. aluminium and magnesium hydroxide: They extract heat from the combustion process by eliminating and evaporating chemically bound water, thereby slowing the process down.

Brominated and chlorinated flame retardants: These substances readily lose halogen halide (e.g. hydrogen bromide, HBr) when heated. The hydrogen halide has a blocking effect on the individual stages of combustion via a multistage mechanism: it dissociates into halogen radicals that capture other radicals formed during combustion and thus stops the combustion chain reaction.

Flame retardants based on phosphorus, e.g. organic and inorganic phosphates: These substances produce low volatile and incombustible compounds in the event of fire, e.g. phosphoric acid, which cover the surface of the plastic and prevent further oxidation.



Insulation material installation, copyright BASF

3. Flame Retardants for EPS

The choice of the flame retardant for a specific application depends on several factors. First, the flame retardant must generally be suitable for the material, meaning that it must be miscible with the material to be protected, show the required effect in an appropriate concentration, and not have a significant impact on the material properties. Second, it should not significantly increase material costs. And finally, the use of the flame retardant must not give rise to any additional risk to health or the environment. These criteria alone are often difficult to meet at the same time. It has been shown that only brominated organic compounds can be considered for the flame retardancy of expanded polystyrene used in building insulation.

These chemical substances belong to the class of so-called “organohalogen compounds”.

However, experience has also shown that organohalogen compounds are often more persistent than other compounds (i.e. not or only very slightly degradable), bioaccumulative (i.e. they can accumulate in fat tissue or in the food chain, for example), and toxic (i.e. poisonous) and therefore do not always meet the environmental and health impact criteria. This is why they are the focus of special attention. In particular, hexabromocyclododecane (common abbreviation: HBCD), which has been used for decades as a flame retardant in EPS, has turned out to be a hazardous substance over time: it is highly toxic to aquatic organisms, potentially reprotoxic, chemically very stable, and may accumulate in the food chain – which often ends with humans. HBCD was therefore listed as a persistent organic pollutant (POP) and has not been used in the production of new insulation materials in the EU since 2016 [2]. In addition to the strict regulation of the handling of EPS that results from the dismantling of old buildings, which is still flame retardant with HBCD [3], the question of an alternative flame retardant arose. After several years of intensive research by the EPS industry, only three brominated chemical compounds are currently available as flame retardants for EPS. They are a brominated polymer and two substances derived from tetrabromobisphenol A (TBBPA):

- ◆ Brominated butadiene-styrene copolymer (referred to in the following as Polymeric FR [4]), CAS # 1195978-93-8
- ◆ TBBPA bis(2,3-dibromopropyl)ether (referred to in the following as TBBPA ether), CAS # 21850-44-2
- ◆ TBBPA bis(2,3-dibromomethylpropyl)ether, CAS # 97416-84-7

These three substances were compared with each other with respect to their hazardousness as part of a project conducted by BASF SE and EPEA GmbH – Part of Drees & Sommer [5]. Because the second and third chemical compounds are very similar not only with respect to their structure but also their hazardousness, the comparison is reduced to the following two substances, namely the brominated polymer and the TBBPA bis(2,3-dibromopropyl)ether. For better legibility, only the names “Polymeric FR” and “TBBPA ether” will be used in the following sections.

4. Cradle to Cradle Assessment/Method

There are various approaches to assessing the hazards posed to the environment and health by chemical substances, materials, and ultimately products, but these approaches are essentially similar. In the above-mentioned project, the assessment was performed on the basis of the Cradle to Cradle method [6]. This method consists of a risk-based approach that takes into account not only the specific hazardousness (= poisonousness or toxicity) of a substance but also its application context, resulting in a semi-quantitative risk assessment. The risk assessment method for flame retardants is discussed in detail in Section 6.

The major advantage of the Cradle to Cradle method is that with relatively little effort it makes it possible

to rapidly identify the flaws of a product with respect to the environmental and health impact and therefore retain sufficient resources for the more important process of actual product optimisation.

The following 19 criteria were chosen for the assessment of the hazardousness of the two brominated flame retardants:

Health impact criteria

- ◆ Carcinogenicity
- ◆ Endocrine-disruptive potency
- ◆ Mutagenicity
- ◆ Reprotoxicity
- ◆ Oral toxicity
- ◆ Dermal toxicity
- ◆ Inhalation toxicity
- ◆ Neurotoxicity
- ◆ Skin and eye irritation potential
- ◆ Sensitisation potential

Environmental impact criteria

- ◆ Fish toxicity
- ◆ Daphnia toxicity
- ◆ Algae toxicity
- ◆ Soil toxicity
- ◆ Persistence
- ◆ Bioaccumulation potential
- ◆ Climatic relevance

Life cycle criteria

- ◆ Hazardousness of the combustion products
- ◆ Hazardousness of the biological degradation products

For each of the 19 criteria there is an exact definition as well as a scale for the classification of the toxicological study results from “non-hazardous” to “hazardous” [7].

The first 17 criteria (health and environmental impact) are chosen consistently in most methods for the toxicological assessment of substances. The persistence and bioaccumulation potential are not toxicities per se. However, they play an important role in the assessment of the hazardousness and are therefore always taken into account.

The Cradle to Cradle approach selected here also considers the derived products, because a non-hazardous product often forms hazardous substances only after thermal or biological degradation.

The result of the hazard assessment is indicated by a colour (traffic light code) and the risk by a letter “a”, “b”, “c”, or “x” and additionally by a colour. The colour grey indicates that no data is available. The coding key is shown in Figure 1:

a or b	optimal or recommended for use
c	minor hazardousness; recommended for the time being
x	hazardous; phase-out required
grey	unassessable due to lack of data

Figure 1
Colour code for the risk assessment of a substance or material (“phase-out” means that a substance should no longer be used).

The assessment of the risk posed by a chemical comprises the following steps:

- ◆ Determination of the hazardousness (substance-specific variable).
- ◆ Definition of the exposure scenario (context-dependent variable).

- ◆ Analysis of the individual risks by the combination of hazardousness and exposure as well as their specification by a letter “a”, “b”, “c”, or “x”. Individual risk refers in this case to the hazard encountered in a specific situation and by a single hazard characteristic, e.g. sensitisation by touching the EPS (a risk, however, that is equal to zero and therefore does not exist).
- ◆ If required, determination of the total risk by aggregating the individual risks.

The colour coding has proven to be beneficial for the rapid identification of risks. This becomes particularly clear when displaying a larger number of individual results (see also Chapter 8).

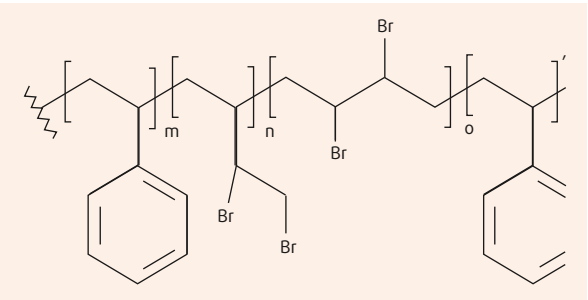
5. Cradle to Cradle Assessment/ Toxicological Profiles of the Brominated Flame Retardants for EPS

In this section, the toxicological profiles of the two brominated flame retardants Polymeric FR and TBBPA ether are introduced as a result of the Cradle to Cradle assessment. The detailed establishment of the profiles is deliberately omitted in this section due to its extent. Instead, the results are presented in a summarised form and explained, and specific characteristics are indicated.

5.1 Polymeric FR

Properties:

- ◆ Name: Brominated butadiene-styrene copolymer
- ◆ Molecular weight: 60,000–160,000 g/mol
- ◆ Registration number according to CAS: 1195978-93-8
- ◆ Status: Non-toxic polymer
- ◆ Trade names: Emerald Innovation 3000; FR-122P; GreenCrest C



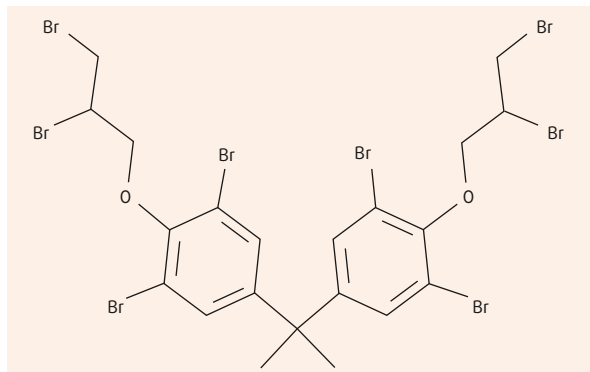
What is special about Polymeric FR compared with TBPA ether is that Polymeric FR is a polymer – i.e. a very large molecule. Because of its size, the molecule cannot pass through the cell membrane. This inevitably means that Polymeric FR is neither toxic nor bioaccumulative. This is also confirmed without exception by all performed toxicity tests. [1] Only the formation of toxic substances during the combustion of Polymeric FR is conceivable. Like most synthetic polymers, Polymeric FR is not biologically degradable. This is why the field for persistence is red. Persistence (longevity, durability) on its own, however, is not a problematic property: it is even a desired property in insulation applications in which flame retardancy must last for decades.

New Brominated Flame Retardants for EPS

5.2 TBBPA Ether

Properties:

- ◆ Name: Tetrabromobisphenol A bis (2,3-dibromopropyl)ether
- ◆ Molecular formula: $C_{21}H_{20}Br_8O_2$
- ◆ Molecular weight: 944 g/mol
- ◆ Registration number according to CAS: 21850-44-2
- ◆ Status: Currently in the CoRAP process (Community Rolling Action Plan)
- ◆ Trade names: SR-720, FR-720, and others



The hazard profile in Figure 3 shows that TBBPA ether is not only endocrine (i.e. hormonal) disruptive [8, 9], but also persistent [10, 11] and bioaccumulative [12]. This means, for example, that the substance can be dispersed in the environment (e.g. in rivers or in the ocean) over great distances at very low and therefore non-hazardous concentration and can then reaccumulate in organisms or the food chain to dangerous concentrations.

A well-known example of this is the pesticide DDT, which was used worldwide in agriculture and later re-discovered in the fat tissue of polar bears in the Arctic. These types of substances are considered very hazardous chemicals because of this property. This “dispersion effect” has also been experimentally proven for TBBPA ether. The substance was detected, for example, in the eggs of herring gulls in the Great Lakes in the USA and in the tissues of fish and penguins in Antarctica [13, 14].

Both hazard profiles determined by the Cradle to Cradle method completely agree factually with the profiles published by the United States Environmental Protection Agency (EPA) in 2014 [15].

Furthermore, the parent substance TBBPA is also formed during the – very slow – biological degradation of TBBPA ether. TBBPA itself is even more hazardous than TBBPA ether. It is, for example, suspected to be carcinogenic [16]. In this case, we are therefore also talking about a toxification of the original substance by biological degradation. Incomplete incineration of TBBPA ether is also likely to give rise to the formation of additional toxic substances, for example, brominated phenols [17].

6. Risk Assessment/Method

The risk posed by a substance to health and the environment is determined by two factors: the hazardousness of the substance and the exposure to the sub-

Hazardousness (category)	Carcinogenicity	Endocrine-disruptive Potential	Mutagenicity	Reprotoxicity	Oral Toxicity	Dermal Toxicity	Inhalation Toxicity	Neurotoxicity	Irritation Potential	Sensitisation Potential	Fish Toxicity	Daphnia Toxicity	Algae Toxicity	Soil Toxicity	Persistence	Bioaccumulation Potential	Climatic Relevance	Combustion Products	Biological Degradation Products
Assessment																			

Figure 2
Cradle to Cradle® hazard profile for Polymeric FR.

Hazardousness (category)	Carcinogenicity	Endocrine-disruptive Potential	Mutagenicity	Reprotoxicity	Oral Toxicity	Dermal Toxicity	Inhalation Toxicity	Neurotoxicity	Irritation Potential	Sensitisation Potential	Fish Toxicity	Daphnia Toxicity	Algae Toxicity	Soil Toxicity	Persistence	Bioaccumulation Potential	Climatic Relevance	Combustion Products	Biological Degradation Products
Assessment																			

Figure 3
Cradle to Cradle® hazard profile for TBBPA ether.

stance. While the hazardousness is a substance-specific property, the exposure describes the potential interaction of the hazardous substance with its surroundings, for example, contact via the human skin, oral ingestion, or release into the environment. For example, the exposure of a person to a substance in a skin cream or to an inhaled substance is naturally very high. Risk and hazardousness are interconnected via the following equation:

$$\text{risk} = \text{hazard} \times \text{exposure}$$

This indicates, for example, that a very toxic substances (i.e. a very hazardous substance) contained in a sturdy and sealed bottle (i.e. absolutely no exposure) does not pose a risk.

Despite the simple structure of the equation, the quantitative calculation of a risk is often complex, because it requires many assumptions and a large amount of data, which is not always available.

An alternative method is the qualitative risk analysis. This is a combination of the hazard assessment and the complex quantitative risk analysis. The qual-

Figure 4
Derivation of the Cradle to Cradle risks of brominated flame retardants in EPS.

		Hazardousness			
		GREEN	YELLOW	RED	GREY
Exposure level	no exposure				
	low				
	low in the case of high persistence and high bio-accumulation potential				
	medium/high				

itative risk analysis is a simple tool that permits the rapid identification of risks. It is a customised linkage between the hazardousness of a substance and the qualitative description of the exposure. The table in Figure 4 shows for brominated flame retardants the various combinations of hazardousness and exposure level as well as the resulting risks.

7. Risk Assessment/Exposure Scenarios

Following the analysis of the hazardousness of the flame retardants and the introduction of a method for qualitative risk analysis, this section presents all possible scenarios for the two flame retardants that may occur during the life cycle phases production, logistics, processing, installation, service life, and post-service life. The exposures occurring in the scenarios are determined qualitatively. This means that the magnitude of the exposure is based on established estimations. These are in detail 17 possible scenarios, but they are only partially described in the following. Particular attention is paid to these scenarios:

- ◆ Production of the flame retardant
- ◆ Service life
- ◆ Recycling
- ◆ Incineration

However, all 17 scenarios are included in the risk calculation result tables (Figure 6).

7.1 Production

The flame retardants are manufactured in a chemical plant under the usual strict safety regulation standards. It is assumed that the occupational safety standards are at this high level and the workers are protected from exposure. However, small amounts of the flame retardant are permanently introduced into the environment via the waste water, e.g. during cleaning operations.

Exposure level: Low, only relevant to the environment

7.2 Service Life

The insulation material normally remains unchanged for many years without contact with humans or the environment in or on the building.

Exposure level: None

Exceptional case of building fire

In the event of a fire, EPS is destroyed. In this case, the environment is highly exposed to the flame retardant and its combustion products for a short period of time. Because the burning of the exterior insulation material EPS occurs on the outside of the building, which usually is not in direct proximity to people, there is virtually no exposure to humans.

Exposure level: Briefly high

7.3 Recycling

There are various options for recycling used EPS. EPS is a thermoplastic. It can be recycled mechanically or chemically. This report will discuss only the mechanical recycling because it is currently common practice. In this process, the polymeric structure of EPS is not

destroyed, i.e. the EPS is not chemically altered. Recycling only involves melting down and re-extruding the polystyrene. In these processes, temperature-dependent minor thermal decomposition of both flame retardants is conceivable and, in the case of the low-molecular TBBPA ethers, an additional uncontrolled release of the flame retardant present in the EPS. However, at this point it must be noted that analytical studies would be required for the quantification of these assumptions. Because of the uncertainties, a worst-case assumption is made for the exposure level in this case.

Irrespective of quantification, however, it is plausible that more volatile flame retardants such as TBBPA ether are clearly less suitable for recycling of used EPS.

Exposure level: Medium

7.4 Incineration

If the EPS is not recycled, it can generally be landfilled or incinerated. However, because the landfilling of waste with a loss on ignition of more than 5% is prohibited in Germany [18], it will not be discussed in detail here.

The incineration of used EPS in plants without flue gas cleaning is not permitted in Germany. However, the utilisation of used plastics as household fuel is quite common in certain areas of the world. Incineration in such circumstances would lead to the destruction of the flame retardant, the release of corrosive and toxic hydrogen bromide, and the formation of hazardous organic compounds, which, in the case of TBBPA ether, may be highly toxic (see Section 5.2).

Exposure level: High

In contrast, incineration in plants equipped with flue gas cleaning that is state of the art (i.e. pursuant to the 17th German Federal Immission Protection Act (BImSchV) [19]) almost completely prevents the release of hydrogen bromide and organobromine compounds. Experimental data for this scenario is available [20], but not extensive.

Exposure level: None

The results lead in the next section to the risks.

8. Risk Assessment/Results

After compiling the hazard characteristics and estimating the exposure levels, the qualitative risk assessment is performed. This is accomplished by linking each hazard characteristic from Section 5.2 with each exposure level from Section 7 according to the algorithm from Section 6, Figure 4, for each flame retardant. In each case, the outcome is a risk matrix of $17 \times 19 = 323$ individual risks. The results are shown in the two following tables [5]. How are the tables to be read? This can be shown by means of the following example. The individual risks associated with a fire in a building insulated with TBBPA ether flame-retardant EPS can be obtained from line 9 in Figure 6: the exposure is high due to the extensive release of the hazardous substance in a fire. This poses a direct risk to health and the environment due to the endocrine-disruptive effect of the substance. Furthermore, the substance may be hazardous even in distant locations due to its combination of persistence and bioaccumulative properties. Additional toxic com-

New Brominated Flame Retardants for EPS

bustion products are also formed. Moreover, hazardous substances may be created through biological decomposition at a later point in time and elsewhere.

In summary, this means the following for the two flame retardants:

Flame retardant 1 (Polymeric FR)

The risk assessment of Polymeric FR does not provide any indication of any risk associated with the use of Polymeric FR as a flame retardant in EPS – except for the formation of hazardous combustion products in the four scenarios “traffic accident and fire during transportation”, “insulation material on fire in a building fire”, “EPS on fire in a landfill site”, and “in-

cineration in a plant without flue gas cleaning”. In these cases, primarily corrosive and acutely toxic hydrogen bromide is formed. Traces of other toxic compounds may also occur.

When considering these four cases, it must be taken into account that traffic accidents involving a cargo fire during transportation of flame retardants are very rare occurrences. Because the landfilling of flame-retardant EPS and its incineration in plants without flue gas cleaning is prohibited in Germany, these two scenarios are also virtually excluded. Only in the event of a fire in an insulated building is there a high probability that hazardous gases will be released. However, even building fires are rare events.

Hazardousness (category) >			Carcinogenicity	Endocrine-disruptive Potency	Mutagenicity	Reprotoxicity	Oral Toxicity	Dermal Toxicity	Inhalation Toxicity	Neurotoxicity	Irritation Potential	Sensitization Potential	Fish Toxicity	Daphnia Toxicity	Algae Toxicity	Terrestrial Toxicity	Persistence	Bioaccumulation	Climatic Relevance	Combustion Products	Biological Degradation Products
Hazard assessment >																					
#	Life cycle phase	Exposure																			
1	Production (flame retardant synthesis)	low, only relevant to the environment																			
2	Logistics (transportation of flame retardant)	none																			
3	Logistics (accident during transportation of flame retardant)	high																			
4	Production (admixture of flame retardant to EPS)	low, only relevant to the environment																			
5	Logistics (transportation of the ready-for-sale EPS)	none																			
6	Logistics (accident during transportation of the ready-for-sale EPS)	none																			
7	Installation of insulation material in the building	none																			
8	Service life – standard scenario (no fire)	none																			
9	Service life – building fire	high																			
10	Post-service life – dismantling	low, only relevant to the environment																			
11	Post-service life – transportation of used EPS	none																			
12	Post-service life – mechanical recycling (re-extrusion)	medium																			
13	Post-service life – mechanical recycling (PSLoop)	low, only relevant to the environment																			
14	Post-service life – chemical recycling (pyrolysis)	low, only relevant to the environment																			
15	Post-service life – landfill	medium																			
16	Post-service life – incineration (without flue gas cleaning)	high (flue gas only)																			
17	Post-service life – incineration (with flue gas cleaning)	none																			

Figure 5
Overview of the qualitative assessment of individual risks for Polymeric FR in EPS.

Overall, Polymeric FR must be therefore be classified as a relatively “non-hazardous flame retardant”.

Flame retardant 2 (TBBPA ether)

The risk assessment of TBBPA ether differs greatly from that of Polymeric FR. First, toxicity studies indicate an endocrine-disruptive potency of this compound. Second, TBBPA ether is persistent and bioaccumulative.

The combination of these properties means that any release of TBBPA ether may result in long-term environmental damage. Furthermore, the compound can be degraded in the environment to even more hazardous substances.

The risk analysis also shows an additional important result: exposure is low during use as the flame retardants are enclosed in the polymer matrix and can barely be released. Exposure occurs only in exceptional cases. However, exposure may also occur in the manufacture of TBBPA ether (and during the recycling of EPS containing TBBPA ether additive, if performed). Although this exposure is low, it is permanent instead and therefore much more extensive. Here, too, the risk matrix result is confirmed by an experimental finding: the above-mentioned discovery of TBBPA ether in the eggs of herring gulls in the Great Lakes in the USA were made in the proximity of a plant that manufactures flame retardants [22].

Hazardousness			Carcinogenicity	Endocrine-disruptive Potential	Mutagenicity	Reprotoxicity	Oral Toxicity	Dermal Toxicity	Inhalation Toxicity	Neurotoxicity	Irritation Potential	Sensitization Potential	Fish Toxicity	Daphnia Toxicity	Algae Toxicity	Terrestrial Toxicity	Persistence	Bioaccumulation	Climatic Relevance	Combustion Products	Biological Degradation Products
Hazard assessment >																					
#	Life cycle	Exposur																			
1	Production (flame retardant synthesis)	low, only relevant to the environment																			
2	Logistics (transportation of flame retardant)	non																			
3	Logistics (accident during transportation of flame retardant)	high																			
4	Production (admixture of flame retardant to EPS)	low, only relevant to the environment																			
5	Logistics (transportation of the ready-for-sale EPS)	non																			
6	Logistics (accident during transportation of the ready-for-sale EPS)	non																			
7	Installation of insulation material in the building	non																			
8	Service life – standard scenario (no fire)	non																			
9	Service life – building fire	high																			
10	Post-service life – dismantling	low, only relevant to the environment																			
11	Post-service life – transportation of used	non																			
12	Post-service life – mechanical recycling (re-extrusion)	medi																			
13	Post-service life – mechanical recycling (PSLoop)	low, only relevant to the environment																			
14	Post-service life – chemical recycling	low, only relevant to the environment																			
15	Post-service life – landfill	mittel																			
16	Post-service life – incineration (without flue gas cleaning)	high (flue gas)																			
17	Post-service life – incineration (with flue gas cleaning)	non																			

Figure 6
Overview of the qualitative assessment of individual risks for TBBPA ether in EPS.

This indicates that the greatest risk to health and the environment when using TBBPA ether in EPS does not arise from the service life phase, but from the manufacture of the flame retardant and from recycling, if performed.

9. Discussion and Recommendations

Polymeric FR, a brominated polymer, is neither toxic nor bioaccumulative. During combustion, Polymeric FR leads to the formation of hydrogen bromide (HBr), which is responsible for its flame-retardant effect. Traces of toxic organic compounds may additionally be formed under certain conditions. Of central importance, however, is the high molecular weight that imparts the properties of a plastic to Polymeric FR, which is mixed with the polystyrene and therefore cannot migrate. In this respect, it is therefore to be considered to be equivalent to reactive flame retardants that are covalently bonded to the plastic matrix.

In contrast to this, the second flame retardant that was investigated, a TBBPA derivative, is very hazardous. This substance is endocrine disruptive in vitro, bioaccumulative, and persistent. Detection of the substance in environmental samples proves that it can disperse and accumulate in the environment. Its hazardous effects are currently being investigated as part of the CoRAP programme. The use of the substance may be prohibited in the foreseeable future.

Like Polymeric FR, the TBBPA derivative forms hydrogen bromide during combustion. It is slowly degraded under anaerobic conditions to the even more hazardous TBBPA, which is suspected to be carcinogenic and endocrine disruptive and is also being studied in the CoRAP programme. From the Cradle to Cradle perspective it is recommended to no longer use the TBBPA derivative due to its hazardous nature.

The greatest risk arises probably not from its use, but from the manufacture and potentially problematic post-service life scenarios of this flame retardant.

Since the brominated polymer is neither toxic nor bioaccumulative, it is clearly superior to the TBBPA derivative with respect to its environmental and health impact.

10. Significance for the Recyclability of Flame-retardant EPS

The ecotoxicological assessment of the flame retardants used so far in EPS clearly shows the important role that flame retardants play in the future recyclability of EPS insulation material waste.

The use of a flame retardant that is largely non-hazardous even if released into the environment and that is not destroyed during recycling is one of the requirements for effective recycling of used EPS. Consequently, the recycling of EPS boards that contain the flame retardant Polymeric FR is already possible today and increasingly being employed by the German EPS industry, provided these are clean EPS sections.

A solution is even in sight for the recyclability of "old" EPS insulation boards that still contain the flame retardant HBCD. Because of the long life expectancy of

EPS (more than 50 years or until building demolition), the disposal of this "old" insulation material will gain in importance in the next 100 years due to the increase in building demolitions and renovations. Manufacturers are forecasting a continuous increase in annual polystyrene building waste to around 85,000 tonnes by 2050. Consequently, the EPS industry is currently working on a pilot project to set up a demonstration facility for the processing and recycling of polystyrene from soiled insulation material waste that contains HBCD as part of the PolyStyrene Loop initiative [23]. In the future, it will be important to ensure that the disposal of EPS waste in accordance with the waste hierarchy (reuse prior to recycling prior to incineration with energy recovery prior to landfilling) is not only environmentally sound for all parties involved – i.e. industry, waste disposal companies, craftsmen, and authorities – but also economically and practically feasible.

Bibliography

- [1] **US Environmental Protection Agency:** Flame Retardant Alternatives for Hexabromocyclododecane (HBCD). Final Report. (June 2014) EPA Publication 740R14001.
- [2] **Umweltbundesamt (UBA):** Häufig gestellte Fragen und Antworten zu Hexabromocyclododecan (HBCD). Antworten auf häufig gestellte Fragen. [Frequently asked questions and answers about Hexabromocyclododecane (HBCD). Answers to frequently asked questions]. Background paper. (December 2017) <https://www.umweltbundesamt.de/publikationen/haufig-gestellte-fragen-antworten-zu> (accessed April 2019).
- [3] **Kambeck, N. and Grunow, M.:** Recycling von HBCD-haltigen Dämmstoffen als Entsorgungsoption im Sinne der "Circular Economy" [Recycling of insulation materials containing HBCD as a disposal option in the sense of "circular economy"] StoffR 6 (2018) 245–248.
- [4] **"Polymeric FR" is the internal product name of Dow Chemical for the brominated polymer.**
- [5] **EPEA – Part of Drees & Sommer:** Comparison of Brominated Flame Retardants used in Expanded Polystyrene (EPS). (January 2019) Confidential report for BASF SE.
- [6] **Cradle to Cradle Products Innovation Institute (C2CPII):** <https://www.c2ccertified.org/>
- [7] **Cradle to Cradle Standard/Material Health Assessment:** https://www.c2ccertified.org/resources/detail/cradle_to_cradle_certified_product_standard
- [8] **Cantón, R.; Sanderson, J.; Nijmeijer, S.; et al.:** In Vitro Effects of Brominated Flame Retardants and Metabolites on CYP17 Catalytic Activity: A Novel Mechanism of Action? Toxicol. Appl. Pharmacol. (2006) 274:274–281.
- [9] **Hamers, T.; Kamstra, J.; Sonneveld, E.; et al.:** In Vitro Profiling of the Endocrine-disruptive Potency of Brominated Flame Retardants. Toxicol. Sci. (2006) 92(1):157–173.
- [10] **ECHA (2013):** 1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]. Registered substances. European Chemicals Agency. http://apps.echa.europa.eu/registered/data/dossiers/DISS-d6b26f7d-78a6-4269-e044-00144f67d031/DISS-d6b26f7d-78a6-4269-e044-00144f67d031_DISS-d6b26f7d-78a6-4269-e044-00144f67d031.html#1/4/2013.
- [11] **MITI (Japanese Ministry of International Trade and Industry):** Bio-degradation and bioaccumulation data of existing chemicals based on the CSCL Japan. Compiled under the supervision of Chemical Products Safety Division, Basic Industries Bureau, Ministry of 4-165 International Trade & Industry, Japan; Chemicals Inspection & Testing Institute, Japan. Ed.; Japan Chemical Industry Ecology – Toxicology & Information Center: 2007.
- [12] **EPI (EPIWIN/EPISUITE):** Estimation Program Interface for Windows, Version 4.0. U.S. Environmental Protection Agency: Washington D.C. <http://www.epa.gov/opptintr/exposure> – Letcher, R. and Chu, S.: High-Sensitivity Method for Determination of Tetrabromobisphenol-S and Tetrabromobisphenol-A Derivative Flame Retardants in Great Lakes Herring Gull Eggs by Liquid Chromatography Atmospheric Pressure Photoionization – Tandem Mass Spectroscopy. Environ. Sci. Technol. (2010) 44, 8615–8621.
- [13] **Wolschke, H., Meng, X. Xie, Z.; Ebinghaus, R.; and Cai, M.:** Novel Flame Retardants, Polybrominated Diphenyl Ethers and Dioxin-like Polychlorinated Biphenyls in Fish, Penguin, and Skua from King George Island, Antarctica. Marine Pollution Bulletin 96 (2015) 513–518.

[14] **US Environmental Protection Agency:** Flame Retardant Alternatives for Hexabromocyclododecane (HBCD). Final Report. (June 2014) EPA Publication 740R14001.

[15] **Justification for the Selection of a Substance for CoRAP Inclusion – Tetrabromobisphenol A:** <https://echa.europa.eu/documents/10162/743bdc88-bd85-486c-84a4-e685e9245a9c> (accessed on 15 December 2018).

[16] **Liu, A.; Zhao, Z.; Qu, G.; Shen, Z.; Shi, J.; and Jiang, G.:** Transformation/Degradation of Tetrabromobisphenol A and its Derivatives: A Review of the Metabolism and Metabolites. *Environmental Pollution* 243 (2018), 1141–1153.

[17] **Technische Anleitung zur Verwertung, Behandlung und sonstigen Entsorgung von Siedlungsabfällen [Technical guidance on the recovery, treatment, and other disposal of municipal waste] (TASi) (14 May 1993).**

[18] **17th German Federal Immission Protection Act (17. BImSchV) BGBl. (2003) I p. 1633:** https://www.bgbl.de/xaver/bgbl/start.xav?startbk=Bundesanzeiger_BGBl&jumpTo=bgbl103s1633.pdf#bgbl_103s1633.pdf%2F%2F%5B%40attr_id%3D%27bgbl103s1633.pdf%27%5D_1547568452851 (accessed on Dec 12, 2018).

[19] **Mark, F. E.; Vehlowl, J.; Dresch, H.; Dima, B.; Grüttner, W.; and Horn, J.:** Destruction of the Flame Retardant Hexabromocyclododecane in a Full-scale Municipal Solid Waste Incinerator. *Horn J. Waste Manag Res.* (Feb 2015) 33(2):165–74.

[20] **Note 1:** Persistence and bioaccumulative potential are considered combined in the risk matrix because high persistence poses a risk only in combination with high bioaccumulation potential. If one of the two risks is “green” by itself, the combined risk is also “green”.
Note 2: If the exposure level is “low, only relevant to the environment”, the combustion products are not considered. – Letcher, R. and Chu, S., High-Sensitivity Method for Determination of Tetrabromobisphenol-S and Tetrabromobisphenol-A Derivative Flame Retardants in Great Lakes Herring Gull Eggs by Liquid Chromatography Atmospheric Pressure Photoionization – Tandem Mass Spectroscopy. *Environ. Sci. Technol.* (2010) 44, 8615–8621.

[21] **PolyStyrene Loop (PSLoop):** An industry-scale recycling process for HBCD containing PS foam. <https://polystyreneloop.org/> (accessed on July 15, 2019).

Authors’ addresses

Dr. Christian Sinn (corresponding author)
Dr. Christoph Semisch, Prof. Dr. Michael Braungart, Dr. Peter Mösele
EPEA GmbH – Part of Drees & Sommer
Trostbrücke 4, 20457 Hamburg, Germany

Die Ressource für Einsteiger



Umweltrecht Einführung

Von Prof. Dr. iur. Peter-Christoph Storm

11., völlig neu bearbeitete Auflage 2020, 428 Seiten,
mit zahlreichen Beispielen und Übersichten,
€ (D) 32,-, ISBN 978-3-503-19103-1

Auch als eBook erhältlich

Online informieren und bestellen:

 www.ESV.info/19103

Strukturiert und kompakt vermittelt das Buch Grundkenntnisse des deutschen Umweltrechts:

- ▶ Ziele und Maßnahmen
- ▶ Organisation und Verfahren
- ▶ Sanktionen und Rechtsschutz

Konzentriert auf die wichtigsten Umweltgesetze des Bundes verdeutlicht es auch die enge Verflechtung mit dem europäischen Umweltunionsrecht.

Jetzt neu in 11. Auflage

Das Buch ist jetzt wieder umfassend auf den aktuellen Stand gebracht und berücksichtigt gegenüber der Voraufgabe vor allem

- ▶ das Gesetz zur Modernisierung der Umweltverträglichkeitsprüfung (2017)
- ▶ die Änderungen des Erneuerbare-Energien-Gesetzes (EEG 2017)
- ▶ das Klimaschutzpaket der Bundesregierung (u.a. neues KSG und BEHG)

Fazit: Ein Standardwerk für alle, die an einer ersten und allgemein verständlichen Information über die rechtliche Seite des Schutzes und der Pflege der natürlichen Lebensgrundlagen interessiert sind!

»... ein fachlich wie konzeptionell reifes Werk, das wie ein guter Tropfen über die Jahrzehnte immer noch besser geworden ist.«

Prof. Dr. Wilfried Erbguth, Rostock, zur Voraufgabe in:
Deutsches Verwaltungsblatt (DVBl), 7/2016

ESV ERICH
SCHMIDT
VERLAG

Auf Wissen vertrauen

Bestellungen bitte an den Buchhandel oder: Erich Schmidt Verlag GmbH & Co. KG · Genthiner Str. 30 G · 10785 Berlin
Tel. (030) 25 00 85-265 · Fax (030) 25 00 85-275 · ESV@ESVmedien.de · www.ESV.info

Nicht von Pappe...

... und nachhaltig verwertbar.



Online informieren und bestellen:

 www.ESV.info/16536

ESV ERICH
SCHMIDT
VERLAG

Auf Wissen vertrauen

Vom Überblick zum Detail – kommentiert sind u. a.:

- ▶ Kreislaufwirtschaftsgesetz **KrWG**, zuletzt ausführlich §§ 39–41
- ▶ Anzeige- und Erlaubnisverordnung **AbfAEV**
- ▶ novellierte Abfallbeauftragtenverordnung **AbfBeauftrV**
- ▶ Altfahrzeugverordnung **AltfahrzeugV**
- ▶ novellierte Abfallverzeichnis-Verordnung **AVV**
- ▶ Deponieverordnung **DepV**
- ▶ novelliertes Elektro- und Elektronikgerätegesetz **ElektroG**
- ▶ novellierte Gewerbeabfallverordnung **GewAbfV**
- ▶ Nachweisverordnung **NachwV** und
- ▶ POP-Abfall-Überwachungs-Verordnung **POP-Abfall-ÜberwV**

Realitätsnah wird die Rechtslage aus zwei Perspektiven erläutert – dem Umweltrecht und dem Wirtschaftsordnungsrecht.

Recht der Abfall- und Kreislaufwirtschaft des Bundes, der Länder und der Europäischen Union

Kommentierungen der Abfallrahmenrichtlinie, des KrWG und weiterer abfallrechtlicher Gesetze und Verordnungen

Herausgegeben seit der 2. Auflage von Prof. Dr. jur. Heinrich Freiherr von Lersner, Dr. jur. Helge Wendenburg, Dr. jur. Olaf Kropp und Jörg Rüdiger

Loseblattwerk, 11.168 Seiten in 6 Ordnern, inkl. Online-Zugang zu Teilen einer umfangreichen, ständig aktualisierten umweltrechtlichen Vorschriftendatenbank, ISBN 978-3-503-16536-0

Bestellungen bitte an den Buchhandel oder:

Erich Schmidt Verlag GmbH & Co. KG · Genthiner Str. 30 G · 10785 Berlin
Tel. (030) 25 00 85-229 · Fax (030) 25 00 85-275 · ESV@ESVmedien.de · www.ESV.info