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Pierre Hennebert. THE SUBSTITUTION OF REGULATED BROMINATED FLAME RETARDANTS IN PLASTIC PRODUCTS AND WASTE AND THE DECLARED PROPERTIES OF THE SUBSTITUTES IN REACH. *Detritus*, 2021, 16, pp.16-25. 10.31025/2611-4135/2021.15122 . ineris-03500967

HAL Id: ineris-03500967

<https://hal-ineris.archives-ouvertes.fr/ineris-03500967>

Submitted on 25 Nov 2022

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THE SUBSTITUTION OF REGULATED BROMINATED FLAME RETARDANTS IN PLASTIC PRODUCTS AND WASTE AND THE DECLARED PROPERTIES OF THE SUBSTITUTES IN REACH

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Article Info:

Received:
26 February 2021
Revised:
9 July 2021
Accepted:
23 August 2021
Available online:
30 September 2021

Keywords:

Total bromine
Brominated flame retardants
Substitution
Classification
Registration

ABSTRACT

Plastics containing brominated flame retardants (BFR) currently contain both “legacy” regulated and non-regulated BFR (R-BFRs and NR-BFRs), as evidenced by the increasingly lower correspondence over time between total bromine and R-BFRs content. The portion of substitutive NR-BFR present in the plastics and their toxicity and ecotoxicity properties are documented. Data relating to plastics and foam present in electrical and electronic equipment (EEE), waste EEE, vehicles, textiles and upholstery, toys, leisure and sports equipment show how 88% of plastic waste contains bromine from NR-BFRs. BFR substances mentioned in the catalogs of the three main producers (Albemarle, ICL, Lanxess) and BFR on the official used list of 418 plastic additives in the EU were gathered and the toxic and ecotoxic properties of these compounds as listed in their ECHA registration dossier were compiled. Fifty-five preparations using 34 NR-BFRs substances, including polymers and blends, were found. Seventeen of these substances featured an incomplete dossier, 12 were equipped with a complete dossier, whilst 11 substances (including 2 ill-defined blends) should be reassessed. Eight substances have been notified for assessment by the ECHA as persistent, bioaccumulative and toxic, or as endocrine disruptors, including decabromodiphenylethane; 3 substances display functional concentrations (the concentration of additives that retards flame) exceeding the concentration limits classifying a waste as hazardous but are “reactive” (they bind to the polymer). The technical limit of 2 000 mg total Br/kg indicated for further recycling (EN 50625-3-1) relates to all brominated substances and is relevant in the sorting of all poorly classified new substances.

1. INTRODUCTION

Some plastic constituents of products include flame retardant compounds to protect the users against fire: electrical and electronic equipment, automotive and transport vehicles, construction piping and insulating material, furniture foams and upholstery, professional textiles, and many others. They are used in functional concentrations ranging from 3 to 15% w/w, with up to 30% tetrabromobisphenol A in epoxy resins (Haarman et al. 2020). Animals and people are exposed. For instance, Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and polybrominated biphenyls (PBBs) were found in children’s toys purchased from South China, but it accounts for a small proportion of their daily BFR exposure (Cheng SJ et al. 2009). Lower use of flame retardants with the same fire protection are considered (Charbonnet et al. 2020). While many of the toxic FRs

have been eliminated and replaced by other FRs, existing products containing toxic or potentially toxic chemical FRs will remain in use for decades, and new products containing these and similar chemicals will permeate the environment. When such products reach the end of their useful life, proper disposal methods are needed to avoid health and ecological risks (Lucas et al., 2018).

Low concentrations of bromine and (regulated R- or non-regulated NR-) brominated flame retardants (ineffective for flame retardancy) are also found in plastics due to improper recycling, showing that a circular economy must be controlled to avoid looping unwanted substances (Hennebert 2020).

Brominated flame retardants (BFRs) are numerous. So far, the regulated BFRs (R-BFRs), according to the Regulations 2004/850/EC on Persistent Organic Pollutants (POPs) and 2008/98/EC, are:

- Polybromobiphenyls (PBBs – hexabromobiphenyl 50

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mg/kg);

- Polybromodiphenylethers (PBDEs - mainly decabromodiphenylether decaBDE – sum 4-, 5-, 6-, 7-, 10-BDE 1 000 mg/kg);
- Hexabromocyclododecane (HBCDD 1 000 mg/kg) and
- Tetrabromobisphenol A (TBBPA 2 500 mg/kg).

Currently, PBBs are no longer found in plastic waste. For some years, PBDEs were largely replaced by decabromodiphenylethane: the substitution is now complete since the inclusion of decaBDE in the POPs list in 2019. DecaBDE still has exemption in the Stockholm Convention including certain EEE and is still produced and used. TBBPA is used in polyester and polycarbonate resins, typically for electrical and electronic equipment, and HBCDD was used up to 2014 in Europe but is still produced in China and is found only in expanded or extruded polystyrene. Most of HBCDD containing insulation used in construction the last 40 years is still in use and will end the next 50 or even 100 years in construction and demolition waste polymers.

The recycling of the plastics must start with a separation of the plastic pieces/shreds with these R-BFRs that have a concentration above the concentration limit. Sorting of these plastics is performed by surrogate methods: atomic density (by X-ray transmission) or solid density (by flotation). A technical specification of the European standardization committee set the limit of 2,000 mg Br/kg as the maximum content for recycling (EN 50625-3-1). If legacy additives are removed and destructed safely, a recycling technology provides a method to manage such waste streams in an environmentally friendly and economically feasible manner. Therefore, it is important that either recyclers commit and adopt the concept of decontamination, by sorting or solvent based technologies (Wagner and Schlummer 2020).

Brominated plastics now contain both “legacy” regulated and non-regulated BFRs, as is evidenced by the increasingly lower correspondence, with time, between total bromine and R-BFRs content (Haarman et al. 2020). Therefore the question arise to what extent is the part of the substitutive BFR in plastics? And what are the toxicity and ecotoxicity properties of these substitutes? As substitution is going faster than classification and regulation, and as substances with similar structure are used (for instance decabromodiphenylethane replacing decabromodiphenylether), all these new BFRs should be investigated and their properties assessed and published to avoid regrettable substitutes (Fantke et al. 2015). This paper investigates the substitutes’ declared chemical properties on human health and the environment in ECHA registration dossier.

2. MATERIAL AND METHODS

2.1 Assessment on R-BFRs and NR-BFRs in WEEE plastic

The substituting NR-BFRs are not measured during routine quality control. Nevertheless, they can be assessed by the difference between total bromine and the bromine from regulated BFRs (R-BFRs), which are routinely measured. Sample preparation of plastic shreds is done according to

EN 15002. Total bromine is measured by ionic chromatography after combustion in an oxygen bomb. The R-BFRs are measure according to EN 62321-6.

Data from plastics and foam for electrical and electronic equipment (EEE), EEE waste, vehicles, textiles and upholstery, toys, leisure and sports equipment have been gathered, with detailed various origin (Hennebert 2020). Probably, the oldest wastes are cathode ray tubes (CRT), produced about 30 years ago. Some samples are individual particles or articles, and others are composite samples with or without “enough” particles to be representative of the waste lot to be characterized (Hennebert 2019, Hennebert and Beggio 2021, Beggio and Hennebert 2021). Here, the representativity of the laboratory sample is not a challenge, since only paired data (R-BFRs and Br) have been used, measured on the same particle/article or laboratory sample (after pre-treatment). The mean stoichiometric Br concentration in the different R-BFRs is 76% w/w. DecaBDE, by far the most present R-BFRs, has a mean Br concentration of 83% w/w. The corresponding reverse ratios R-BFRs/Br are 1.31 and 1.20, respectively.

2.2 Approach to compile the list of BFRs and source information on REACH properties

The BFR substances mentioned in the catalogs of the three main producers in industrial countries (Albemarle, ICL, Lanxess) were listed and their declared chemical properties on human health and the environment, as stated in their European ECHA registration dossier (<https://echa.europa.eu/information-on-chemicals>), were gathered. The large production in China (> 50% of all BFRs) has not been documented. The 9 brominated flame retardants from the list of the 418 “Plastic Additives Initiative” (a common list by ECHA and industry of additives used in quantity more than 100 tons per year in the EU) presently used in the EU (<https://echa.europa.eu/mapping-exercise-plastic-additives-initiative#table>) have also been used.

3. RESULTS AND DISCUSSION

3.1 Monitoring of the share of R-BFR and NR-BFRs in WEEE plastic

For clarity, all the measured R-BFRs are summed. As explained, in practice, PBBs are not found, decaBDE is dominant in the PBDEs (>90% R-BFRs), HBCDD is present in expanded EPS (and not mixed with the other R-BFRs), and TBBPA is sometimes present. In these data, not all the R-BFRs were measured for all the samples, but PBDEs and especially decaBDE have always been measured. Total bromine has been measured by XRF for particles or articles, or after shredding, combustion in an oxygen bomb and ionic chromatography for the composite samples. R-BFRs have been measured by standardized chromatographic methods (Figure 1, Table 1).

The stoichiometric ratio R-BFRs/Br is 1.31 for all R-BFRs, and for decaBDE it is 1.20. Considering sampling and analytical variability, this range can be extended [1;1.5] (vertical lines in Figure 2). Only 8% of the plastics have a concentration of R-BFRs between 1 and 1.5 times the concentration of bromine in this set of data. 88% of plastic waste contains bromine from BFR(s) other than the reg-

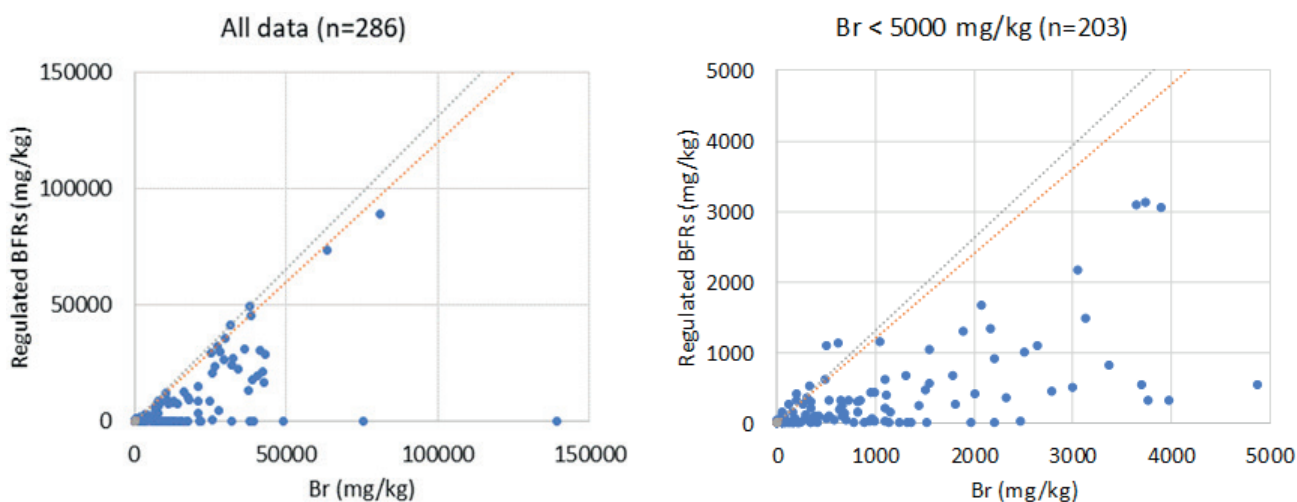


FIGURE 1: Regulated brominated flame retardants (R-BFRs) as a function of total bromine content (left) and the same data with Br ≤ 5,000 mg/kg (right), with stoichiometric ratio R-BFRs/Br of 1.20 w/w (orange line) and 1.31 w/w (grey line).

ulated ones. Only 4% of the data have a concentration of R-BFRs greater than 1.5 times the concentration of Br (with maximum R-BFRs = 1 135 mg/kg). This discrepancy is due mainly to sample preparation (i.e. the test portions of 1 gram that is used for Br and for R-BFRs measurement do not have the same composition), and secondarily to analytical variability (CVanalysis of R-BFRs = 13%, Hennebert 2019).

3.2 REACH evaluation status and hazard information of NR-BFRs substitutes

55 preparations using 34 BFR substances (other than the regulated ones) can be found in the catalogs of the three main producers, consulted in November 2019, and in the list of 418 additives. A summary is presented in Table 2 and Figure 3 and will be discussed first. Detailed results per substance are presented in Table 3.

The 2 R-BFRs and 7 NR-BFRs declared in the list of 418 additives actually used in the EU is presented in Table 4. It is not explained on the ECHA site why the two R-BFRs HBCDD and DecaBDE are included. The initiative started in 2016 and the excel file was published in 2019. The 7 NR-BFRs are included in Group 3 or Group 4 of the list established from the producer's catalog (Table 3). The correspondence is presented in the second column of Table 4.

Some substances (frequently proprietary) have no CAS number and hence no dossier can be found in the ECHA site (called here Group 1). Three of these substances are declared as not registered for sale in Europe. Another group of substances has a CAS number but has not been

declared to ECHA and has no dossier (Group 2). Another group of substances has a CAS number and a dossier, but no hazard statement codes (HSC) (Group 3). Most of their registration dossier items are just filled in as "information non available – n.a.". A fourth group of substances has a CAS number, a more complete dossier, and a HSC (Group 4). The groups are the following (Table 3):

- **Group 1:** 10 substances have no CAS number and no dossier in ECHA, among which 3 substances are not registered for sale in Europe and thus logically without

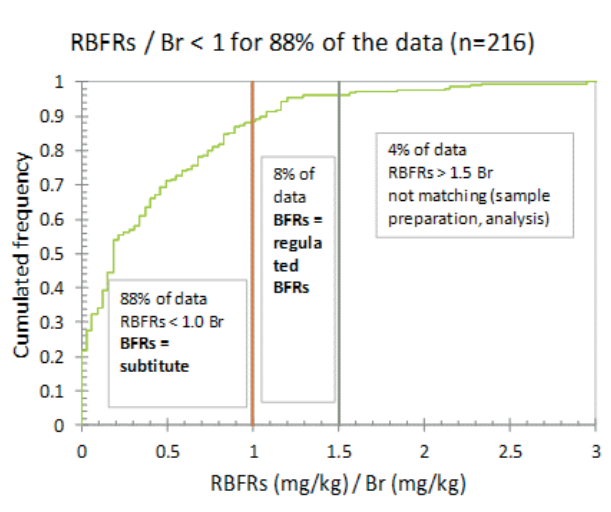


FIGURE 2: Distribution of individual R-BFRs/Br ratio (only data > LOQ) with practical R-BFRs/Br ratio including sampling and an analysis variability of 1 (orange) and 1.5 (grey)..

TABLE 1: Distributions of Br, R-BFRs and R-BFRs / Br ratio (CV coefficient of variation = relative standard deviation = standard deviation/mean).

Parameter	Unit	n	Minimum	Median	Mean	Maximum	Standard deviation	CV
Br	mg/kg	286	<10	596	7196	139000	14962	2.08
Sum R-FBRs	mg/kg	286	<10	18	3483	89200	10258	2.95
R-BFRs / Br	-	216	0.00	0.20	0.41	2.97	0.50	1.21

TABLE 2: Summary of the classification of substitutes of regulated brominated flame retardants (R-BFRs) in the REACH registration dossiers (PBT list = PBT evaluation list, ED list = ED evaluation list).

Preparations and substances	n	CAS #	n	Classification (by notifiers)	n	Classified for HP of waste (CL = concentration limit for hazardous waste)	Notifications (by ECHA)	n	Group name in this paper
Preparations (3 main producers)	55								
Substances	34	No	10*						1
		Yes	24	No dossier in ECHA site	2				2
				Dossier in ECHA site, no Hazard Statement in the dossier	10		PBT list, PBT and ED list, ED list	3+1+2***	3
				Classified with HSC	12	CL 0.1%: 2 substances** CL 0.25%: 2 substances** CL 10%: 1 substance CL 20%: 4 substances CL 25%: 2 substances no HP: 1 substance	PBT list, PBT list and ED list	1+1****	4

* Including 3 proprietary substances not registered for sale in Europe

** The 3 substances with a concentration limit for hazardous waste below the functional concentration are a reactive intermediate for high molecular weight flame retardants and will normally not be found as separate substances in plastics but are linked to the polymer matrix: dibromo neopentyl glycol (CAS 36483-57-5), tribromo neopentyl alcohol (same CAS 36483-57-5) for PU foam, and 2,4,6-tribromophenol (CAS 118-79-6) for epoxides, respectively.

*** PBT list: 2,4,6-Tris (2,4,6-tribromophenoxy) -1,3,5 triazine (CAS 25713-60-4); brominated flame retardant, aromatic, combined with an imide structure (CAS 32588-76-4); decabromodiphenyl ethane (CAS 84852-53-9). The PBT and ED list: 1,3-dibromo-5-(2-[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propan-2-yl)-2-(2,3-dibromopropoxy)benzene (CAS 21850-44-2), ED list: 1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene] (CAS 97416-84-7), 2,2-bis(bromomethyl)propane-1,3-diol (CAS 3296-90-0)

**** PBT list: 2,4,6-tribromophenol (CAS 118-79-6), PBT+ED list: 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol (CAS 79-94-7)

CAS number = Chemical Abstracts Service number

HP = hazard property of waste

HSC = hazard statement code

PBT list = "under evaluation as persistent, bioaccumulative and toxic" by ECHA

ED list = "being assessed as an endocrine disruptor" by ECHA.

a dossier, 4 substances are declared as polymeric or an end-capped polymer (that have not been declared in the REACH system) and one substance is in pellet form (decabromodiphenylethane, the classical substitute

of banned decabromodiphenylether, which has a CAS number and a dossier, and is further detailed in Group 3). The remaining 2 substances are "Blend brominated flame retardant, diol, phosphate ester" and "Blend brominated flame retardant, halogen, phosphorus". Mixtures have not been declared, but their substances have. It is not known if the unnamed individual substances of these blends are registered;

- **Group 2:** 2 substances that have a CAS number but no dossier. These substances are polymers or building blocks for a polymer, that have not been declared in the REACH system;
- **Group 3:** 10 substances that have a CAS number and a dossier but without hazard statements and therefore not classified. The ECHA has, however, placed 6 of these substances on the PBT and/or ED list ("under evaluation as persistent, bioaccumulative and toxic" and "being assessed as an endocrine disruptor"). The most common result of these re-evaluations is that the substances are assessed as hazardous, and that the registration dossier must be modified. 3 other substances are polymers or building blocks for a polymer;
- **Group 4:** 12 substances among which 2 polymers, 2 salts of bromide Br- (potassium and ammonium), 4 tetrabromo phthalic derivatives, 2 brominated pentyl alcohols (5 carbons) and 1 bromophenol (6 carbons). The ECHA has, however, placed 2 of these substances (decabromodiphenylethane: PBT evaluation list; 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol: PBT evaluation list + ED evaluation list).

Registration of BFRs other than POP-regulated BFRs (55 preparations, 34 substances)

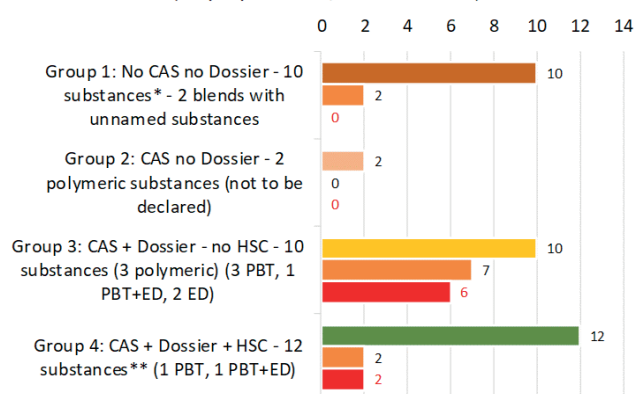


FIGURE 3: Classification of substitutes of regulated brominated flame retardants (R-BFRs) in the REACH registration dossier of ECHA. For each group: first bar: total number of substances; second bar: number of substances to assess or re-assess; third bar: number of substances under assessment by ECHA. (CAS = CAS number, Dossier = dossier in ECHA site, HSC = presence of hazard statement code of the substance, PBT = "under evaluation as persistent, bioaccumulative and toxic" by ECHA, ED = "being assessed as an endocrine disruptor" by ECHA). Notes: *3 substances not for sale in Europe, 4 polymeric, 1 physical form; ** 3 substances with functional concentration > hazardous concentration for waste.

TABLE 3: Substitutes of regulated brominated flame retardants (R-BFRs) as found in the catalogs of the three main producers, CAS number, formula, and their classification in ECHA REACH registration dossiers by the notifiers, ECHA notifications, presence of a Brief Profile (BP), hazard statement codes, corresponding concentration limit for classification as hazardous waste, lowest concentration limit and hazard property of the lowest concentration limit (HP 4 = irritant, HP 5 = toxic, HP 7 = carcinogenic, HP 11 = mutagenic, HP 14 = ecotoxic). Substances to re-evaluate are red coloured cells.

Group and Substances	Name/Note	CAS No	Formula	ECHA (Classification)	ECHA Notifications	BP	Hazard Statement Code, Concentration Limit (Waste Hazard Property)	Lowest CL	HP of lowest CL
GROUP 1 Substances: No CAS (10)									
Decabromodiphenyl ethane pellet form		No		ND					
Brominated Epoxy Polymer		No	-	ND					
Brominated polymeric flame retardant	-	No	-	ND					
End Capped Brominated Epoxy 1		No	-	ND					
Tetrabromobenzoate ester composition	(not registered for sale in Europe)	No	-	ND					
Tetrabromophthalate diol blend	(not registered for sale in Europe)	No	-	ND					
Tetrabromophthalic anhydride derivative	(not registered for sale in Europe)	No	-	ND					
Blend of brominated polystyrene and polyester		No		ND					
Blend brominated flame retardant, diol, phosphate ester		No		ND					
Blend brominated flame retardant, halogen, phosphorus		No		ND					
GROUP 2 Substances: No dossier (2)									
Brominated Butadiene/Styrene Block Copolymer		1195978-93-8	-	ND					
Poly pentabromobenzyl acrylate		59447-57-3	-	ND					
GROUP 3 Substances: No Hazard Statement (10)									
2,4,6-Tris (2,4,6-tribromophenoxy) -1,3,5 triazine		25713-60-4	C ₂₁ H ₆ Br ₉ N ₃ O ₃	No HSC	PBT list	Yes			
Brominated flame retardant, aromatic, combined with an imide structure		32588-76-4	C ₁₈ H ₆ Br ₆ N ₂ O ₄	No HSC	PBT list	Yes			
Decabromodiphenyl ethane	Ethylene-1,2-bis(pentabromophenyl); 1,1'-(ethane-1,2-diyl)bis[pentabromobenzene]	84852-53-9	C ₁₄ H ₄ Br ₁₀	No HSC	PBT list	Yes			
1,3-dibromo-5-(2-[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propan-2-yl)-2-(2,3-dibromopropoxy)benzene		21850-44-2	C ₂₁ H ₂₀ Br ₈ O ₂	No HSC	PBT list. ED list.	Yes			
Brominated epoxy flame retardant	Pratherm EC 20	135229-48-0	-	No HSC					
Tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate		19186-97-1	C ₁₅ H ₂₄ Br ₉ O ₄ P	No HSC		Yes			
Carbonic dichloride, polymer with 4,4'-(1-methylethylidene) bis[2,6-dibromophenol], bis(2,4,6-tribromophenyl) ester	Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	71342-77-3	-	No HSC					
Carbonic dichloride, polymer with 4,4'-(1-methylethylidene) bis[2,6-dibromophenol] and phenol	Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	94334-64-2	-	No HSC					
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]	Group 3; hot in catalog but in additives list	97416-84-7	C ₂₃ H ₂₄ Br ₈ O ₂	No HSC	ED list	Yes			

Group and Substances	Name/Note	CAS No	Formula	ECHA (Classification)	ECHA Notifications	BP	Hazard Statement Code, Concentration Limit (Waste Hazard Property)	Lowest CL	HP of lowest CL
2,2-bis(bromomethyl)propane-1,3-diol	Group 3; not in catalog but in additives list	3296-90-0	C ₂₃ H ₂₄ Br ₈ O ₂	No HSC	ED list	Yes			
GROUP 4 Substances: with Hazard Statement Code(s) (12)									
Dibromo neopentyl glycol		36483-57-5	C ₅ H ₁₀ Br ₂ O ₂	H302 H315 H319 H335 H340 1B H341 H350 1B H351 H373 H413		Yes	H302 25% (HP 6) H315 H319 20% (HP 4) H335 20% (HP 5) H340 0.1% (HP 11) H341 1% (HP 11) H350 0.1% (HP 7) H351 1% (HP 7) H373 - (no HP) H413 25% (HP 14)	0.10%	HP 7 HP 11
Tribromo neopentyl alcohol	2,2-dimethylpropane-1-ol, tribromo derivative	36483-57-5	C ₅ H ₉ Br ₃ O	H302 H319 H340 1B H341 H350 1B H412		Yes	H302 25% (HP 6) H315 H319 20% (HP 4) H340 0.1% (HP 11) H341 1% (HP 11) H350 0.1% (HP 7) H412 25% (HP 14)	0.10%	HP 7 HP 11
2,4,6-tribromophenol		118-79-6	C ₆ H ₃ Br ₃ O	H301 H302 H312 H315 H317 H319 H332 H335 H400 H410 H411	PBT list	Yes	H301 5% (HP 6) H302 25% (HP 6) H312 55% (HP 6) H315 H319 20% (HP 4) H332 22.5% (HP 6) H335 20% (HP 5) H400 25% (HP 14) H410 0.25% (HP 14) H411 25% (HP 14)	0.25%	HP 14 (H410)
Potassium bromide		7758-02-3	BrK	H315 H318 H319 H335 H336 H373 H412		Yes	H315+H319 20% (HP 4) H318 10% (HP 4) H335 20% (HP 5) H336 - (no HP) H373 10% (HP 5) H412 25% (HP 14)	10%	HP 4 HP 5
Ammonium bromide		12124-97-9	BrH ₄ N	H315 H319 H335		Yes	H315+H319 20% (HP 4) H335 20% (HP 5)	20%	HP 4 HP 5
Bis(2-ethylhexyl) tetrabromophthalate	Tetrabromophthalate ester	26040-51-7	C ₂₄ H ₃₄ Br ₄ O ₄	H319			H315+H319 20% (HP 4)	20%	HP 4
Brominated Epoxy Oligomery	Tetrabromobisphenol A diglycidyl ether, Brominated Epoxy Polymer	68928-70-1	-	H315 H319			H315+H319 20% (HP 4)	20%	HP 4
Brominated Polystyrene, acrylate copolymer	Benzene, ethenyl-, homopolymer, brominated	88497-56-7	-	H319			H315+H319 20% (HP 4)	20%	HP 4
2-(2-hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate	Tetrabromophthalate diol, Tetrabromophthalate diol	20566-35-2	C ₁₅ H ₁₆ Br ₄ O ₇	H412		Yes	H412 25% (HP 14)	25%	HP 14 (H412)
Reaction products of tetrabromophthalic anhydride with 2,2'-oxydiethanol and methyloxirane		77098-07-8	-	H412		Yes	H412 25% (HP 14)	25%	HP 14 (H412)
Tetrabromophthalic anhydride		632-79-1	C ₈ Br ₄ O ₃	H317		Yes	H317 - (no HP)	no CL	no HP
2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol	Group 4; not in catalog	79-94-7	C ₁₅ H ₁₂ Br ₄ O ₂	H400 H410	PBT list, ED list, ED	Yes	H400 25% (HP 14) H410 0.25% (HP 14)	0.25%	HP 14 (H410)

BP = Brief Profile on ECHA site (a summary document on properties and classification of the substance)

ED list = "Under assessment as Endocrine Disrupting"

HSC = hazard statement code

ND = no dossier

PBT list = "Under assessment as Persistent, Bioaccumulative and Toxic"

(HP 14 calculated without multiplying "M-factors")

TABLE 4: Brominated flame retardants (BFRs) declared in the list of 418 plastic additives actually used in the EU.

Group and Substances	Name/Note	CAS No	Formula	ECHA (Classification)	ECHA Notifications	BP	Hazard Statement Code, Concentration Limit (Waste Hazard Property)	Lowest CL	HP of lowest CL
Hexabromocyclododecane	Not in the scope of this paper	25637-99-4			POP+others	Yes			
Bis(pentabromophenyl) ether	Not in the scope of this paper	1163-19-5			POP+others	Yes			
2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine	Group 3; in catalog	426-040-2 (No CAS number in the file)	C ₂₁ H ₆ Br ₉ N ₃ O ₃	No HSC	PBT	Yes			
1,1'-(ethane-1,2-diyl)bis[pentabromobenzene]	Group 3; in catalog	84852-53-9	C ₁₄ H ₄ Br ₁₀	No HSC	PBT	Yes			
N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	Group 3; in catalog	32588-76-4	C ₁₈ H ₄ Br ₈ N ₂ O ₄	No HSC	PBT	Yes			
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene]	Group 3; in catalog	21850-44-2	C ₂₁ H ₂₀ Br ₈ O ₂	No HSC	PBT, ED	Yes			
1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene]	Group 3; not in catalog	97416-84-7	C ₂₃ H ₂₄ Br ₈ O ₂	No HSC	ED	Yes			
2,2-bis(bromomethyl)propane-1,3-diol	Group 3; not in catalog	3296-90-0	C ₂₃ H ₂₄ Br ₈ O ₂	No HSC	ED	Yes			
2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol	Group 4; not in catalog	79-94-7	C ₁₅ H ₁₂ Br ₄ O ₂	H400 H410	PBT, ED	Yes	H400 25% (HP 14) H410 0.25% (HP 14)	0.25%	HP 14 (H410)

BP = Brief Profile on ECHA site (a summary document on properties and classification of the substance)

ED list = "Under assessment as Endocrine Disrupting"

HSC = hazard statement code

PBT list = "Under assessment as Persistent, Bioaccumulative and Toxic"

(HP 14 calculated without multiplying "M-factors")

The substances for which the dossier must be completed, or which are reassessed (according to the REACH regulation), are: the substances of 2 blends of Group 1, 7 substances (6 with ECHA notification) of Group 3, and 2 substances (with ECHA notification) of Group 4. Since there are mixtures, the total substances used that have to be assessed is 11 (or more depending on the composition of the 2 blends) out of 34, of which 8 are notified by the ECHA.

The classification of product plastics incorporating these additives (according to the CLP) is beyond the scope of this study. For the simpler waste classification, the functional concentration of the additives in the plastics (recommended in the technical specifications) can be compared to the concentration that renders a waste hazardous (according to the waste regulations of EU 2014 and EU 2017).

In detail for the 12 classified substances (Table 3, Group 4), the number of substances, the concentration limits and the hazardous properties (for waste) are:

- 2 with 0.1% (for HP 7 'Carcinogenic' and HP 11 'Toxic for reproduction');
- 2 with 0.25% (HP 14 'Ecotoxic' chronic "high level");
- 1 with 10% (HP 4 'Irritant' and HP 5 'Toxic');
- with 20% (HP 4 and / or HP 5), and
- 3 with 25% (HP 14 'Ecotoxic' acute).

The two substances with a concentration limit of 0.1% are neopentyl tribromo alcohol [H350 0.1% (HP 7), H340 0.1% (HP 11), H341 1% (HP 11)] and dibromo neopentyl

glycol [H350 0.1% (HP 7), H351 1% (HP 7), H341 1% (HP 11)]. The substances with a concentration limit of 0.25% are 2,4,6 tribromophenol and 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol [0.25% H410 (HP 14)]. According to their producer, the first three substances are used as a reactive intermediate for high molecular weight flame retardants, especially for rigid and flexible PU foam (the first two) and for the capping of brominated epoxides (the latter) (Table 5). These substances should normally not be found as separate substances in plastics but linked to the polymer matrix.

The 5 substances from the producer's catalog with ECHA notifications of assessment are presented in Table 6 with the information from their producer. Four substances are declared "additive" (they are miscible with the polymer but remain extractable and quantifiable) and they have 14 to 21 carbons. One substance (tribromophenol) is "reactive" (it will bind to the polymer and will not be found as a separate substance in a laboratory analysis) and has 6 carbons. Decabromodiphenylethane, the substitute of decabromodiphenylether, present in the catalog of the three producers, and widely used today, is declared without hazard statement codes, but is under assessment in the PBT evaluation list of the ECHA.

To conclude, out of a total of 34 substances, 2 blends do not have a CAS number and dossier (Group 1), 7 substances have a CAS number and a dossier but are without any hazard statement (Group 3), among which 6 are under assessment by the ECHA, and 12 have a CAS number, a dossier and a hazard statement (Group 4), among which

TABLE 5: Producer information on NR-BFRs with functional concentration greater than the concentration limit that renders a waste hazardous.

Substance	Name	Abbreviation / Brand Name	Brand Name 2 - Note	CAS No	Formula	Category
Dibromoneopentyl glycol		FR-522	FR-522, is a reactive, dibromoneopentyl glycol, flame retardant, containing 60% aliphatic bromine. Thermosetting polyester resins formulated with FR-522 have high chemical and flame resistance, minimal thermal discoloration and excellent light stability. The high bromine content of FR-522 and its ready reaction into polyurethanes make it suitable for use in rigid polyurethane foams...	36483-57-5	C ₅ H ₁₀ Br ₂ O ₂	Reactive
Tribromoneopentyl alcohol	2,2-dimethylpropan-1-ol, tribromo derivative	FR-513	FR-513 is a reactive flame retardant containing 73% aliphatic bromine. As tribromoneopentyl alcohol it combines a high bromine content with exceptional stability, and is particularly suitable where thermal, hydrolytic and light stability are required. FR-513 high solubility in polyurethane systems increases effectiveness as a reactive flame retardant for polyurethanes...	36483-57-5	C ₅ H ₃ Br ₃ O	Reactive
2,4,6-tribromophenol		FR-613	FR-613 is a reactive flame retardant with a high content of aromatic bromine, used mainly as an intermediate for high molecular weight flame retardants. It is also an effective fungicide and wood preservative. ...	118-79-6	C ₆ H ₃ Br ₃ O	Reactive

2 are under assessment by the ECHA. Eleven substances or more (due to the use of two blends) are re-assessed or could be re-evaluated in the future, and eventually restricted. The 7 non-POP NR-BFRs on the official list of plastic additives are currently being re-evaluated by the ECHA (3 PBT, 2 ED, 2 PBT + ED) (Table 4).

4. CONCLUSIONS

The regulated R-BFRs have been logically substituted by other non-regulated NR-BFRs. In this numerous data set, 88% of the product and waste samples contain BFR(s) other than the regulated ones.

The European Chemical Agency (ECHA) dossiers of these substances show that:

- 12 substances have no dossier (including polymers that must not be declared, and 3 substances not for sale in Europe);
- 10 substances have a dossier without hazard statements and are therefore not classified: The ECHA has, however, placed 6 of these substances on the PBT evaluation list (“under evaluation as persistent, bioaccumulative and toxic”) and the ED evaluation list (“being assessed as an endocrine disruptor”);
- 12 substances have a dossier and hazard statements (including 3 polymeric substances); however, the ECHA has placed 2 of these substances on the PBT evaluation list and ED evaluation list;
- The 3 substances that have a functional concentration (the concentration of additives that retards flame) greater than the concentration limits classifying a waste as hazardous, are declared as “reactive”: they will bind to the polymer during their use and will not be independent substances anymore;
- The 7 non-POP NR-BFRs on the official list of plastic additives are currently being re-evaluated by ECHA (3 PBT, 2 ED, 2 PBT + ED).

As substitution is going faster than classification and regulation, and as homologous substances are used (for instance decabromodiphenylethane / decabromodipheny-

lether), all these new NR-BFRs should be investigated and their properties on human health and the environment assessed and published, as already done for some, with the European Chemicals Agency (ECHA).

Total bromine is a relevant surrogate indicator of the presence of total BFR(s) in plastic waste, even if the brominated substances are not known and the new substances are currently not monitored for most samples. The technical limit of 2,000 mg Br/kg as the maximum content for further recycling (EN 50625-3-1) takes into account all brominated substances regulated and not yet regulated, and therefore limits the recycling of BFRs that are not currently properly registered. Similar work should be done on phosphorus substitutes.

ACKNOWLEDGMENTS

This work has been supported by INERIS and by the Ministry for Ecologic Transition, France

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TABLE 6: Producer information on NR-BFRs with ECHA notifications.

Substance	Abbreviation / Brand Name	Brand Name 2 - Note	CAS No	Formula	ECHA Notifications	Category
2,4,6-Tris (2,4,6-tribromophenoxy) -1,3,5 triazine	FR-245	FR-245 is a proprietary, additive flame retardant. The combination of aromatic bromine and cyanurate provides high FR efficiency and good thermal stability. A major use of FR-245 is in ABS and HIPS. FR-245 combines good UV, impact and flow properties...	25713-60-4	C ₂₁ H ₆ Br ₉ N ₃ O ₃	PBT evaluation list	Additive
Brominated flame retardant, aromatic, combined with an imide structure	SAYTEX® BT-93 Bromine-based flame retardant for electronic enclosures, electrical components, films, and textiles that require the highest degree of UV stability (light yellow powder form). SAYTEX® BT-93W Bromine-based flame retardant for electronic enclosures, electrical components, films, and textiles that require outstanding thermal and UV stability (white powder form)	SAYTEX BT-93 flame retardant is a unique additive that combines stable, aromatic bromine with an imide structure. SAYTEX BT-93W flame retardant is a unique, white-colored additive that combines stable, aromatic bromine with an imide structure	32588-76-4	C ₁₈ H ₄ Br ₈ N ₂ O ₄	PBT evaluation list	Additive
Decabromodiphenyl ethane	Firemaster® 2100R		84852-53-9	C ₁₄ H ₄ Br ₁₀	PBT evaluation list	Additive
	SAYTEX® 8010 Bromine-based flame retardants for electronic enclosures, electronic and electrical components, insulation foams and textiles (powder form)	SAYTEX 8010 flame retardant is a non-diphenyl oxide-based product containing a high level of aromatic bromine				
	FR-1410	Decabromodiphenyl Ethane FR-1410 is an additive flame retardant containing 82% aromatic bromine. Its high bromine content coupled with its exceptional thermal stability makes it the material of choice for a large variety of applications. Major application areas include HIPS, Low and High Density Polyethylene, Polypropylene (Homopolymers and Copolymers), Elastomers, PBT, Polyamides, UPE and Epoxy...				
1,3-dibromo-5-(2-[3,5-dibromo-4-(2,3-dibromopropoxy)phenyl]propan-2-yl)-2-(2,3-dibromopropoxy) benzene	FR-720	FR-720 is an additive flame retardant containing both aromatic and aliphatic bromine. FR-720 is suitable for polyolefin and styrenic resins and it is especially recommended for UL-94 class V-2. It is also applicable in class V-0 polypropylene. FR-720 is cost efficient and maintains good physical properties of the compound...	21850-44-2	C ₂₁ H ₂₀ Br ₈ O ₂	PBT evaluation list, ED evaluation list	Additive
2,4,6-tribromophenol	PH-73FF™	PH-73FF™ is a reactive intermediate containing over 70% bromine recommended for phenol-based reactions in a free-flowing briquette form. PH-73FF™ by Lanxess is a free flowing, non-caking, low dusting, halogenated, flame retardant. It is a reactive intermediate containing over 70% bromine recommended for phenol-based reactions in a free-flowing briquette form. PH-73FF™ possesses uniform size & shape and high bulk density. It is also used as an antifungal agent (with FIFRA approval) or chemical intermediate.	118-79-6	C ₆ H ₃ Br ₃ O	PBT evaluation list	Reactive
	FR-613	FR-613 is a reactive flame retardant with a high content of aromatic bromine, used mainly as an intermediate for high molecular weight flame retardants. It is also an effective fungicide and wood preservative. ...				

PBT evaluation list: Under assessment as Persistent, Bioaccumulative and Toxic; ED evaluation list: Under assessment as Endocrine Disrupting

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