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# Deliverable report

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| **Coordinator:** | FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V. |
| **Project Website:** | www.creatorproject.eu |

## CREATOR CONSORTIUM

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|---|---|---|
| 1 | ICT | Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung – Institut für Chemische Technologie |
| 2 | VLB | Volbas S.A. |
| 3 | MOS | Machinefabriek Otto Schouten BV |
| 4 | CLR | Coolrec BV |
| 5 | REL | Treee SRL |
| 6 | GKR | Fundacion Gaiker |
| 7 | TCK | Transfercenter fur Kunststofftechnik GmbH |
| 8 | RMA | Erema Engineering Recycling Maschinen und Anlagen Ges.m.b.H |
| 9 | CTB | Centre Scientifique & Technique De L'industrie Textile Belge |
| 10 | MAI | Maier S. Coop. |
| 11 | DAW | DAW SE |
| 12 | CYC | Cyclefibre S.L. |
| 13 | CID | Fundacion Cidaut |
| 14 | KLU | Kuhne Logistics University GmbH |
| 15 | OVM | Openbare Vlaamse Afvalstoffenmaatschappij |
| 16 | RWE | RWEnergia Robert Wudarczyk |
| 17 | ITB | ITRB Group LTD |

# DOCUMENT HISTORY AND CONTRIBUTION OF THE PARTNERS

| VERSION | REVISER | CONTENT |
| --- | --- | --- |
| V0 | ICT | First draft |
| V1 | OVAM | Revision |
| V2 | ICT | Revision |
| V3 | ICT | Submission |

| PARTNER | SHORT NAME | CONTRIBUTION TO THE DELIVERABLE |
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| Fraunhofer ICT | ICT | Author and reviewer |
| OVAM | OVM | Reviewer |

# LIST OF ABBREVIATIONS

| ABBREVIATION | DESCRIPTION |
|---|---|
| ABS | Acrylonitrile butadiene styrene |
| BDE | Bromodiphenylether |
| Br | Bromine |
| CAS number | Chemical Abstracts Service number |
| C&DW | Construction and demolition waste |
| $CO_2$ | Carbon dioxide |
| DBDPE | 1,2-bis(pentabromophenyl)ethane |
| DecaBDE | Decabromodiphenylether |
| EC number | Enzyme Commission number |
| EDC | Endocrine disrupting chemicals |
| EPS | Expanded polystyrene foam |
| EU | European Union |
| GHS | Globally Harmonized System of Classification and Labelling of Chemicals |
| HBCD | 1,2,5,6,9,10-hexabromocylododecane |
| HeptaBDE | Heptabromodiphenylether |
| HexaBDE | Hexabromodiphenylether |
| HIPS | High-impact polystyrene |
| LC | Lethal concentration |
| LCA | Life-cycle analysis |

| | |
|---|---|
| LCC | Life-cycle cost |
| LD | Lethal dose |
| MSDS | Material safety data sheets |
| NADES | Natural deep eutectic solvents |
| NonaBDE | Nonabromodiphenyl |
| OctaBDE | Octabromodiphenylether |
| PBT | Persistent, bioaccumulative and toxic substances |
| PEC | Predicted environmental concentration |
| PentaBDE | Pentabromodiphenylether |
| PNEC | Predicted non-effect concentration |
| POP | Persistent organic pollutants |
| PPE | Personal protective equipment |
| PPM | Parts per million |
| PS | Polystyrene |
| TBBPA | Tetrabrombisphenol A |
| vPvB | Very persistent and very bioaccumulative |
| WEEE | Waste of electrical and electronic equipment |
| XPS | Extruded polystyrene foam |

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# 1 INTRODUCTION AND OBJECTIVES

The EU-funded project CREAToR focusses on process development and demonstration to remove hazardous, already banned bromine-containing flame-retardants from thermoplastic material waste streams. The project investigates the use of a continuous purification technology: extractive extrusion with supercritical $CO_2$ and natural deep eutectic solvents (NADES) as extractive media.

The project covers the whole value chain, from collecting thermoplastic waste streams from construction and building, and from the electrical and electronic equipment sectors, to 2$^{nd}$ generation use of the materials. Supporting developments spanning the secondary raw material value chain are a more accurate sorting of waste fractions in terms of their bromine content, the re-additivisation of purified materials with non-hazardous flame retardants, an integrated logistics concept and a harmonised material purity classification concept. These will create a closed-loop solution, transforming waste streams that are currently incinerated at a cost into value-bringing secondary raw materials.

The economic viability of CREAToR will be validated through material benchmarking and LCA/LCC assessment for the whole value chain, resulting in two 2$^{nd}$ generation materials: polystyrene (PS) for use in insulation foams for construction and building, and acrylonitrile butadiene styrene (ABS) in aesthetically decorated interior parts for the automotive sector. The strong industrial/recycler presence in the consortium will ensure the market relevance of the developments and the rapid commercialisation of the results after the end of the project.

Ecotoxic substances are defined as substances which cause damage either to animals, humans or nature by the release of toxic chemicals into the environment.

The purification process developed for the removal of the hazardous bromine-based flame retardants in CREAToR does not implement any new hazardous materials but rather uses non-toxic chemicals, such as well-known $CO_2$ or biocompatible and biodegradable NADES[1][2]. Besides using the lowest quantities possible, these materials will be used in a closed loop, and recycled for reuse after the extraction.

In summary, no new hazardous materials are introduced into the material processing chain or later into the environment. At the same time, the process handles all well-known and analysed hazardous materials contained in the waste stream which is purified.

This deliverable “D6.6 Eco-toxicity Roadmap” focusses on the risks to workers operating the process, that result from the handling of these known legacy flame-retardant materials. Hazards in the new process are identified and protective measures are recommended. Furthermore, we also consider the various additives in the waste stream materials - such as modifiers, pigments or UV-stabilisiers - and identify the stream in which they remain after the extraction.

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[1] *Yang Liu, J. Brent Friesen, et al., Natural Deep Eutectic Solvents: Properties, Applications, and Perspectives, Journal of Natural Products 2018 81 (3), 679-690, DOI: 10.1021/acs.jnatprod.7b00945*

[2] *Alexandre Paiva, Rita Craveiro, et al., Natural Deep Eutectic Solvents – Solvents for the 21st Century, ACS Sustainable Chemistry & Engineering 2014 2 (5), 1063-1071, DOI: 10.1021/sc500096j*

# 2 HUMAN EXPOSURE AND HEALTH

The exposure of humans to any emission can be assessed by investigating the pathway and duration of exposure.

Humans are exposed to materials in their environment though different pathways. The most common ot these are oral uptake, inhalation and dermal uptake (Figure 1). In order to analyse the exposure, these pathways need to be identified and quantified. Protective actions may need to be implemented, such as substitutive materials, personal protective equipment (PPE), local exhaust ventilation or limitation of the exposure time. Furthermore, the workers need to be trained concerning the possible risks of emissions in their working environment.

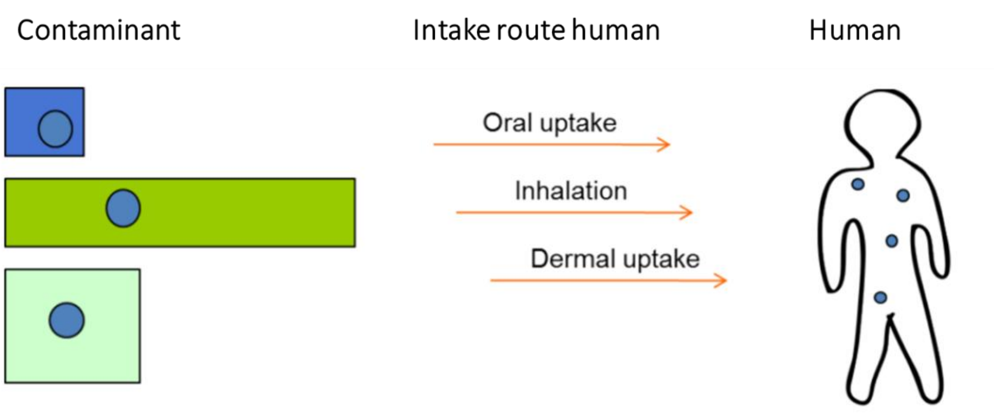


*Figure 1: Human intake routes of contaminants (modified from 3)*

In the development of new chemicals and processes, a safety analysis is therefore always obligatory. The CREAToR partner organisations follow established procedures to ensure safe working conditions for their employees.

However, as it aims for technology transfer and commercialisation of the materials and processes after the project, CREAToR will furthermore design a guideline summarising all steps needed to implement the process. This will be reported later in the deliverable D3.8 Qualification of CREAToR purification technology (3) in March 2023.

The current deliverable focusses on the identification of possible points of release of hazardous materials during the process, the nature of the released chemicals and their toxicity to humans. All materials used are analysed concerning their safety, via an evaluation of the corresponding safety data sheets (MSDS). These MSDS compile all relevant information and furthermore include best practice handling instructions.

[3] *https://emeritus.setg.ethz.ch/research/human-exposure-analysis.html*

# 3 THE CREATOR RECYCLING PROCESS

The process chain considered in the CREAToR project is shown in Figure 2.

The process starts with the collection and sorting of the input streams. Next, the bromine-contaminated waste stream is transferred to the purification step. After purification the material is supplied to the next application as a secondary raw material. The waste fraction is deposited as requested by the POP regulation[4] and the $CO_2$, the NADES liquid and the solvent are recycled for reuse in a closed loop.


*Figure 2: Process chain and material stream in CREAToR*

As the extractive purification is a new step in the current extrusion process, the exposure resulting from this stream is considered in this analysis (Figure 3 and Figure 4 ). Furthermore, hazardous deposits and their disposal are evaluated.

The extractive extrusion process is an advanced extrusion process specifically developed to extract substances from the polymer melt for its purification. In the CREAToR project this process is set up to continuously remove the bromine-containing flame retardant from a polymer melt.

The polymer granules (polystyrene or acrylonitrile butadiene styrene) from the sorting process, the co-solvent acetone and the $CO_2$ are gravimetrically fed into the extruder. A gravimetric gas dosing station is used for the $CO_2$ dosing, whereas a gravimetric HPLC-pump is used for the acetone injection as shown in

[4] *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32019R1021*

Figure 4. On the right side of the diagram, the contaminated polymer is fed into the extruder via the hopper. The polymer is then melted in the melting zone and further transported into the "mixing and conveying" zone. The "mixing and conveying zone" is characterized by two melt seals which allow a pressure build-up. Within this zone supercritical $CO_2$ (sc-$CO_2$) and the NADES is fed via the gas dosing system. Supercritical $CO_2$ is reached at a pressure level >73.75 bar and T>30.98 °C. During the mixing of the polymer melt and sc-$CO_2$ the bromine-containing flame retardant is dissolved and extracted together with the sc-$CO_2$. After the extraction, the sc-$CO_2$, the NADES and the contaminant are captured in a phase-separator and separated into a bromine and a $CO_2$/NADES fraction. The bromine fraction is disposed of and the $CO_2$/NADES fraction is recovered and reused in the process. At the extruder end the purified polymer melt is degassed before leaving the extruder die.

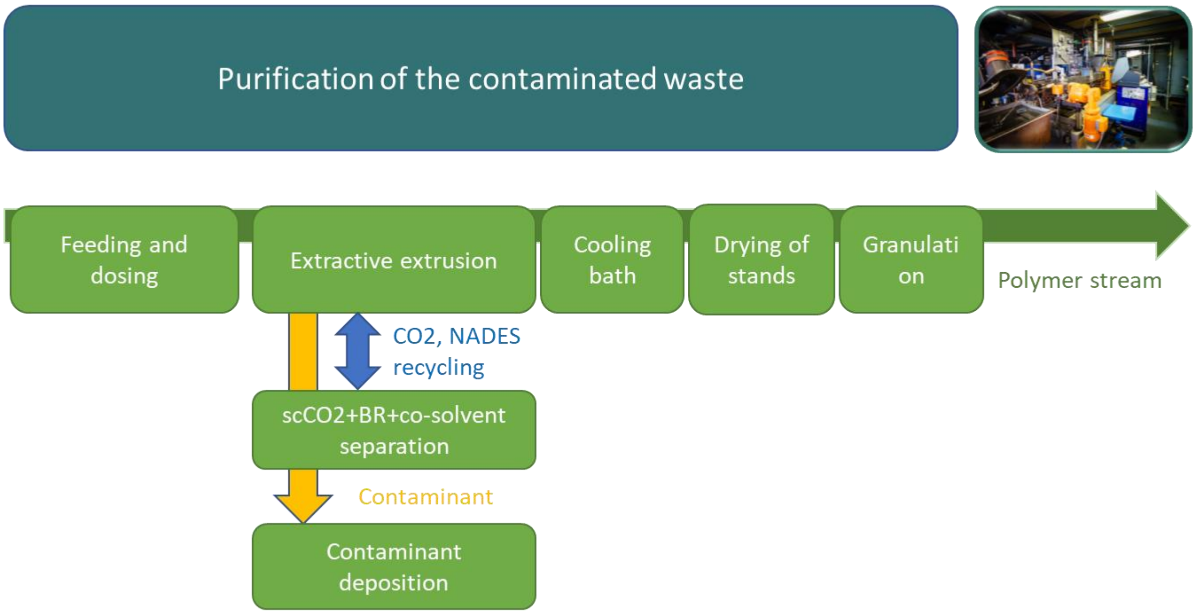


*Figure 3: CREAToR purification process*

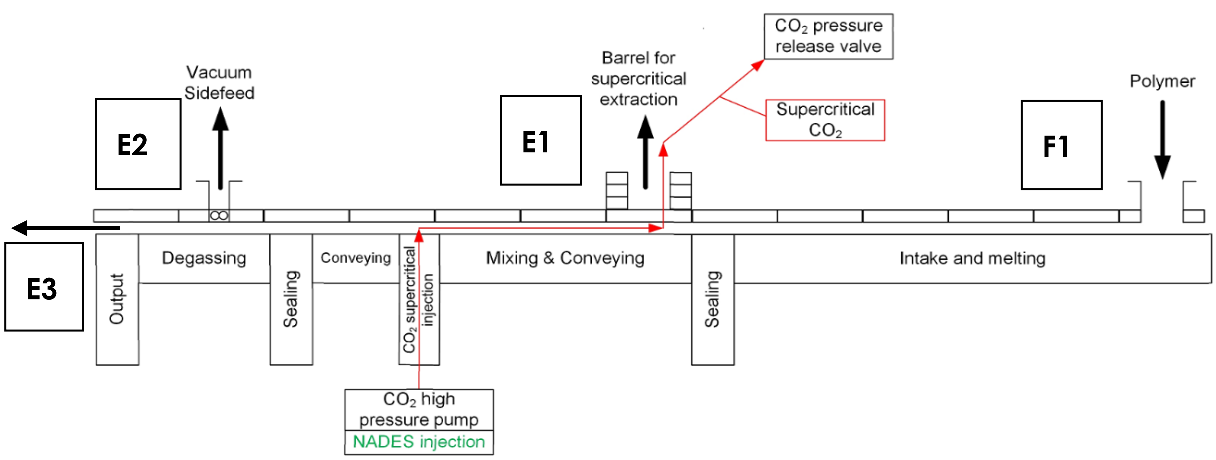


*Figure 4: CREAToR purification process*

This process description makes the sources of exposure clear. The material has one entry point to the extrusion line in the feeding and dosing step (F1) and three exit points either at the release valve (E1), the vacuum sidefeed (E2) or the die output (E3).

During the project duration the removal of 1,2,5,6,9,10-hexabromocylododecane (HBCD) from PS and tetrabrombisphenol A (TBBPA)from ABS was studied.

The evaluated waste streams - PS from C&DW and ABS from WEEE - also contain various other additives, such as mineral fillers or stabilisers.

The next chapter summarises all brominated flame retardants which are known to be legacy additives in WEEE and C&DW. Furthermore chapter 5 analyses the feed and exit materials at each point of the process. Additionally other additives contained in the polymer waste are identified and their exit fractions are determined.

# 4 HAZARDOUS MATERIALS IN THE PROCESS

Based on these regulations, chemicals of particular concern were identified. Table 1 presents the list of ten eco-toxic flame-retardant substances which occur in the CREAToR process, stating their EC and CAS descriptors.

As can be seen, all these flame retardants contain bromine. They have all been intensively studied to analyse their applicability and restrictions. In the project, the extraction of #1 and #2 (marked in bold) was studied.

*Table 1: Hazardous substances handled in the CREAToR process*

| NR | TOXIC SUBSTANCE | EC NUMBER | CAS NUMBER |
|---|---|---|---|
| **1** | **1,2,5,6,9,10-Hexabromocylododecane (HBCD)** | **221-695-9** | **3194-55-6** |
| **2** | **Tetrabrombisphenol A (TBBPA)** | **201-236-9** | **79-94-7** |
| Bromodiphenylethers: | | | |
| 3 | Pentabromodiphenylether (PentaBDE) | 251-084-2 | 32534-81-9 |
| 4 | Octabromodiphenylether (OctaBDE) | 251-087-9 | 32536-52-0 |
| 5 | Decabromodiphenylether (DecaBDE) | 214-604-9 | 1163-19-5 |
| 6 | Hexabromodiphenylether (HexaBDE) | 253-058-6 | 36483-60-0 |
| 7 | Heptabromodiphenylether (HeptaBDE) | 273-031-2 | 68928-80-3 |
| 8 | Nonabromodiphenyl (NonaBDE) | 264-565-7 | 63936-56-1 |
| 9 | 1,2-bis(pentabromophenyl)ethane (DBDPE) | 284-366-9 | 84852-53-9 |

The removal of further additives in the waste stream was not considered during the extraction. However, it is well known that the polymers do contain various additives.

Polystyrene as a foamed EPS and XPS from C&DW contains only few addtives compared to various plastics in the WEEE.

The main additives besides the flame retardant in EPS/XPS are

- nucleation agent, e.g. talc, 0,1-0,25 % wt-%
- colour/heat transport agent graphite 2 wt-%
- depending on the application, stabililsatiors and antistatic additives in low amounts

The main additives in WEEE plastics are

- fillers, such as calcium carbonate, glass fibres, talc
- colours
- stabilisers, like titanium dioxide

- other flame retardants like magnesium hydroxide or aluminium trihydroxide

These lists of additional ingredients will always be specific for one application. As soon as the process is introduced to a higher technical readiness level for a certain waste stream, a deeper analysis needs to be carried out.

For each of the flame-retardant substances, information on the degree of hazard was collected. Table 2 shows a summary of the substances and their ecotoxicity data. The complete information gathered can be found for each substance in the Annex.

The following classifications of the flame retardants, as given in the literature, were investigated. These always refer to a specific exposure model and can only give advice on the degree of hazard of the material.

- Predicted environmental concentration (PEC) is a calculated value of a chemical in the environment based on an exposure model.
- Predicted non-effect concentration (PNEC) of a chemical identifies the limit below which no adverse effects of exposure in an ecosystem are measured.

LD50 (lethal dose) and LC50 (lethal concentration) are used to determine the toxicity on animals. The LD50 is a median lethal dose, while LC50 is a median lethal concentration that kills half of the test population.

Table 2: Toxicity of the substances used

| NR | TOXIC SUBSTANCE | CONTENT IN POLYMER | ENVIRONMENTAL FATE AND BEHAVIOUR GHS[5] | PEC/PNEC | LC50, LD50 |
|---|---|---|---|---|---|
| 1 | **1,2,5,6,9,10-hexabromocylo dodecane (HBCD)[12,6]** | 7.000-15.000 ppm[7] in PS based insulation boards in C&DW<br><br>Highly concentrated slurry in the deposit | Bioaccumulative persistent, lipophile<br><br>GHS:<br>H361, H362, H410<br>P201, P260, P263, P273, P308, P313, P391 | PEC: 0.0004-0.006 mg/l (pelagic organism); 0.33-46.2 mg/kg dw (benthic organisms); 0.15-0.3 mg/kg soil dw (soil organisms); 4.51 mg/kg ww (wildlife consumers)<br>PNEC: 0.00056 mg/l (pelagic organisms; 6.5 mg/kg sediment dw (benthic organisms); 10.9 mg/kg soil dw (soil organisms); 39.8 mg/kg food ww (wildlife consumers) | LD50 oral - rat - >20.000 mg/kg |
| 2 | **Tetrabrombisphe nol A (TBBPA)[8, 9]** | 50 000 ppm in ABS from WEEE[7]<br><br>Highly concentrated slurry in the deposit | Controversial statements, evidence of multifaceted effects in cells and animals,<br><br>GHS:<br>H410<br>P273, P510 | PEC/PNEC<br>Compounding water 3.7<br>Sediment 2.8<br>Conversion water 0.92<br>Sediment 0.66 | Oncorhyn chus mykiss 0.40 mg/l for 96 hr |
| <br>3<br><br><br>4<br><br><br>5<br><br><br>6<br><br><br>7<br><br><br>8 | BDEs[10,11]<br>Pentabromodip henylether (PentaBDE)<br>Octabromodiph enylether (OctaBDE)<br>Decabromodip henylether (DecaBDE)<br>Hexabromodiph enylether (HexaBDE)<br>Heptabromodip henylether (HeptaBDE)<br>Nonabromodip henyl (NonaBDE) | 20.000-40.000 ppm in WEEE | Terrestial: expected to be immobile in soil<br>Aquatic: expected to be adsorbed by suspended solids and sediment<br>Volatilisation from water surfaces is not expected bioconcentration in aquatic organisms is high to very high<br><br>GHS:<br>H302, H312, H319, H225, H304, H315, H319, H332, H335, H336, H341, H373, H360, H362, H410, H413<br>P201, P202, P210, P260, P261, P264, P270, P271, P273, P280, P281, P301, P302, P304, P305, P308, P312, P313, P314, P331, P322, | No PNECs have been calculated in literature, as the risks of PBT/vPvB substances cannot in general be assessed quantitatively. | Deca is the most hazardo us of these: acute: inhalatio n dust LC50 > 48.2 mg/l, 1 hour<br>Hexa orl-rat LD: >500 mg/kg |

| | | | | |
|---|---|---|---|---|
| | | | P330, P337, P338, P340, P351, P352, P405, P501, P363 | |
| 9 | 1,2-Bis(pentabromophenyl)ethane (DBDPE) | 1 501 ppm in HIPS in WEEE | Persistent, bioaccumulative and toxic<br><br>GHS:<br>H302, H315, H319, H335<br>P261- P305, P351, P338 | PNEC terrestial: 156 mg/kg |

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[5] *https://pubchem.ncbi.nlm.nih.gov/ghs/*

*6 https://ec.europa.eu/health/ph_risk/committees/04_scher/docs/scher_o_093.pdf*

[7] *Content measured in CREAToR input material using HPLC-MS*

*8 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.001.125; https://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/4th_Consultation/TBBPA_RoHS_Dossier_V2_final_20191204.pdf; https://pubchem.ncbi.nlm.nih.gov/compound/Tetrabromobisphenol-A#section=Ecotoxicity-Values*

*9 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.001.125; https://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/4th_Consultation/TBBPA_RoHS_Dossier_V2_final_20191204.pdf; https://pubchem.ncbi.nlm.nih.gov/compound/Tetrabromobisphenol-A#section=Ecotoxicity-Values*

*10 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.013.277; https://echa.europa.eu/documents/10162/a3f810b8-511d-4fd0-8d78-8a8a7ea363bc; http://cdn.chemservice.com/product/msdsnew/External/English/S-15886J0%20English%20SDS%20US.pdf; https://echa.europa.eu/documents/10162/13641/annex_xvi_consultant_report_decabde_en.pdf/337cc41c-0964-41a3-8d97-40b785f22fad*

*11 https://pubchem.ncbi.nlm.nih.gov/compound/Hexabromodiphenyl-ethers#section=Environmental-Fate*

# 5 EXPOSURE OF CHEMICALS DURING THE CREATOR RECYCLING PROCESS

As described in chapter 3, the material stream has one place of input (into the process) and three outlets (exiting the process). In the following section we will analyse which material is expected to exit the process at which exiting point during regular processing and in the event of a failure.

Feed

At the entry point F1 the following materials are dosed:

- Waste stream, hazardous flame retardant and additives integrated into the polymer matrix
- $CO_2$
- NADES

Exit

At the exit points the following materials can be emitted.

E1 removal of extractant
- $CO_2$ and NADES, hazardous flame retardant dissolved in the stream, $CO_2$- and NADES-soluble, unipolar additives such as plasticisers and UV stabilisers

E2 degassing of the polymer
- $CO_2$ with hazardous flame retardant, $CO_2$, $CO_2$-soluble, unipolar additives such as plasticisers and UV stabilisers
- Water, which may be dissolved in the waste stream

E3 polymer outlet
- Polymer with mineral fillers, such as colours, $TiO_2$, antimontrioxid (not $CO_2$- and NADES-soluble) and residual hazardous flame retardant. The main content of fillers in the polymers is mineral fillers remaining in the polymer matrix of the purified material.

As can be seen, at all outlets the material can contain hazardous materials. These exiting materials are treated as following:

E1+E2 must be fed into a solvent recovery process to reuse the $CO_2$ and NADES and to remove the hazardous material. In the project this stream was treated in a phase separator, in which the hazardous material content and the NADES were separated from the $CO_2$. At higher TRL a distillation step and a $CO_2$ scrubber installation is required to ensure reuse of the solvent stream ($CO_2$+NADES) and enable the recovery of the hazardous substance(s) for disposal or reuse in a different process.

In the case of E3, the purified polymer must undergo analysis to ensure that it fulfills the current regulations concerning its content. If hazardous materials are still in this stream, they are safely integrated into the polymer matrix for their handling.

The bromine deposit remaining in the phase separator must be disposed of as a toxic, bioaccumulative solvent. At higher TRL the removal would be achieved using a closed vessel which is remotely emptied into another closed vessel for disposal.

Based on this analysis and the toxic potential of the material, during the project trials the use of a face mask and gloves was mandatory. Furthermore, in case of any leaks during processing, the extractive extrusion line for purification was placed under a suction device. At higher TRL the personal protective equipment would stay the same.

# 5 CONCLUSION

The CREAToR process does not introduce any new hazardous materials into the recycling process, but rather uses the environmentally friendly solvents $CO_2$ and NADES.

However, as the waste stream contains the hazardous flame retardant, the process requires a safe environment for the workers. Additionally, the released material streams need to be disposed of as defined by national/EU regulations.

The largest quantity of additives in the polymer waste materials will be mineral fillers retained in the purified polymer. However, the input waste stream and the exit streams from the purification need always to be analysed for the specific operating environment to ensure safe operation.

We recommend that face masks and gloves be mandatory for the workers. Furthermore, the processing site must be operated under a suction device in case of gas leakages.

The deposit of the hazardous bromine and brominated flame retardants must be disposed of as a toxic bioaccumulative, carciogenic substance. At high TRL a closed removal should be installed to avoid any contact of the material with humans or nature.

# 6 ANNEX

Material data for the hazardous substances

| #1 1,2,5,6,9,10-HEXABROMOCYLODODECANE (HBCD) IN ITS ALPHA (A), BETA (B), GAMMA (G) AND DELTA (D) FORMATION, EC NR 221-695-9, CAS NR 3194-55-6 | |
|---|---|
| **MOLECULAR FORMULA** | $C_{12}H_{18}Br_6$ |
| **MOLECULAR WEIGHT** (g/mol) | 641.7 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | 188 |
| $T_{BOILING}$ (°C) | > 190 |
| **VAPOUR PRESSURE** (Pa) | n.a. |
| **WATER SOLUBILITY** | α-HBCD 48.8 µg/l, β-HBCD: 14.7 µg/l and γ-HBCD: 2.1 µg/l[12] |
| **AVERAGE AMOUNT IN INSULATION BOARD** | 0.7 – 1.5 wt-% |
| **GLOBALLY HARMONISED SYSTEM (GHS) HAZARD STATEMANTS** | H361, H362, H410<br>P201, P260, P263, P273, P308, P313, P391 |
| **DANGEROUS SUBSTANCES DIRECTIVE / DANGEROUS PRODUCTS DIRECTIVE** | serious health hazard, toxic for reproduction |
| **EDC, PBT/VPVB ASSESSMENT** | PBT |
| **ENVIRONMENTAL FATE AND BEHAVIOUR** | bioaccumulative |
| **PEC** | 0.0004-0.006 mg/l (pelagic organism); 0.33-46.2 mg/kg dw (benthic organisms); 0.15-0.3 mg/kg soil dw (soil organisms); 4.51 mg/kg ww (wildlife consumers) |
| **PNEC** | 0.00056 mg/l (pelagic organisms; 6.5 mg/kg sediment dw (benthic organisms); 10.9 mg/kg soil dw (soil organisms); 39.8 mg/kg food ww (wildlife consumers) |
| **LC50** | LD50 oral - rat - >2 0.000 mg/kg |

[12] *Hunziker, R W, Friederich, U, MacGregor, J A, Desjardins, D, Ariano, J, & Gonsior, S. Fate and effect of hexabromocyclododecane in the environment. Germany.*

#### #2 Tetrabrombisphenol A, EC NR 201-236-9, CAS NR 79-94-7[13]

| | |
|---|---|
| **MOLECULAR FORMULA** | $C_{15}H_{12}Br_4O_2$ |
| **MOLECULAR WEIGHT** (g/mol) | 543.88 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | 178 |
| $T_{BOILING}$ (°C) | >250 (decomposition) |
| **WATER SOLUBILITY** (mg/l) | very insoluble; ~0.24 |
| **AVERAGE CONTENT IN ABS FROM WEEE** | up to 20 wt-% |
| **GLOBALLY HARMONISED SYSTEM (GHS)[2] HAZARD STATEMENTS** | H410<br>P273, P510 |
| **DANGEROUS SUBSTANCES DIRECTIVE / DANGEROUS PRODUCTS DIRECTIVE** | hazard to environment |
| **EDC, PBT/VPVB ASSESSMENT IF APPLICABLE** | PBT, EDC |

[13] *https://echa.europa.eu/de/substance-information/-/substanceinfo/100.001.125; https://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/4th_Consultation/TBBPA_RoHS_Dossier_V2_final_20191204.pdf; https://pubchem.ncbi.nlm.nih.gov/compound/Tetrabromobisphenol-A#section=Ecotoxicity-Values*

| | |
|---|---|
| **PEC/PEC** | (tables below) |

| Scenario | Step | PEC/PNEC ratio water | PEC/PNEC ratio sediment |
|---|---|---|---|
| Reactive flame retardant use | Manufacture of epoxy and/or polycarbonate resins | 0.092 | 0.067 |
| | Processing of epoxy resins | $1.4\times10^{-3}$ | $1.0\times10^{-3}$ |
| | Processing of polycarbonate resins | $1.4\times10^{-3}$ | $1.0\times10^{-3}$ |
| Additive flame retardant use - ABS | Compounding | **3.7** | **2.8** |
| | Conversion | 0.92 | 0.66 |

| Fact | Compartment | PNEC value ECHA Registered Substances Database 2018 |
|---|---|---|
| Hazard for Aquatic Organisms | Freshwater | 16 µg/l |
| | Marine water | 0.34 µg/l |
| | Sewage treatment plant (STP) | 1.5 mg/l |
| | Sediment (freshwater) | 9 mg/kg sediment dw |
| | Sediment (marine water) | 1.8 mg/kg sediment dw |
| Hazard for Air | Air | No hazard identified |
| Hazard for Terrestrial Organism | Soil | 0.031 mg/kg soil dw |
| Hazard for Predators | Secondary poisoning | 222.22 mg/kg food |

| | |
|---|---|
| **LC50** | Oncorhynchus mykiss 0.40 mg/l for 96 hr ; Daphnia magna /(water flea)/; Conditions: static; Concentration: 0.96 mg/l for 48 hr |

### #3 PENTABROMODIPHENYLETHER (PENTA-BDE), EC NR 251-084-2, CAS NR 32534-81-9

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}H_5Br_5O$ |
| **MOLECULAR WEIGHT** (g/mol) | 564.7 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | -7 |
| $T_{BOILING}$ (°C) | >200 (decomposition) |
| **VAPOUR PRESSURE** (Pa) | 4.13*10-6 |
| **WATER SOLUBILITY** (mg/l) | very insoluble |
| **GLOBALLY HARMONISED SYSTEM (GHS) HAZARD STATEMANTS** | H373, H362, H410 |
| **DANGEROUS SUBSTANCES DIRECTIVE / DANGEROUS PRODUCTS DIRECTIVE** | serious health hazard, hazardous to the environment |

#### #4 Octabromodiphenylether (Octa-BDE), EC NR 251-087-9, CAS NR 32536-52-0

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}H_2Br_8O$ |
| **MOLECULAR WEIGHT** (g/mol) | 801.4 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | depends on formulation |
| $T_{BOILING}$ (°C) | decomposition |
| **VAPOUR PRESSURE** (Pa) | 1.6998*10-7 |
| **WATER SOLUBILITY** (mg/l) | < 0.1 |
| **GLOBALLY HARMONISED SYSTEM (GHS) HAZARD STATEMANTS** | H360<br>P201, P202, P281, P308, P313, P405, P501 |
| **DANGEROUS SUBSTANCES DIRECTIVE / DANGEROUS PRODUCTS DIRECTIVE** | health hazard |

#### #5 Decabromodiphenylether (Deca-BDE), EC NR 214-604-9, CAS NR 1163-19-5[14]

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}Br_{10}O$ |
| **MOLECULAR WEIGHT** (g/mol) | 959.2 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | 304-307 |
| $T_{BOILING}$ (°C) | 425 (decomposition) |
| **VAPOUR PRESSURE** (Pa) | 4.63*10-6 |
| **WATER SOLUBILITY** (mg/l) | < 0.1 |
| **GLOBALLY HARMONISED SYSTEM (GHS) HAZARD STATEMANTS** | H302, H312, H319, H332, H341, H373, H413<br>P201, P202, P260, P261, P264, P270, P271, P273, P280, P281, P301, P302, P304, P305, P308, P312, P313, P314, P322, P330, P337, P338, P340, P351, P352, P405, P501, P363 |
| **EDC, PBT/VPVB ASSESSMENT IF APPLICABLE** | PBT/vPvB |
| **ENVIRONMENTAL FATE AND BEHAVIOUR** | Canadian data on degradation in lake sediments are referred to in the SVHC, but only as preliminary results. These data are currently under peer review for publication (Orihel et al., in press) and describe the formation of small amounts of nona- and octaBDEs from 13C-labelled decaBDE over a period of 30 days in intact lake sediment cores held in situ to simulate natural conditions. Slow debromination of decaBDE was observed with the formation of all nona-BDEs and 4 to 5 octa-BDEs and trace amounts of hepta-BDE, hexa-BDE, penta-BDE, and di-BDE.<br>The mechanisms associated with the observations (abiotic or microbial degradation) are not identified. |
| **PEC/PNEC** | No PNECs have been calculated, as the risks of PBT/vPvB substances cannot, in general, be assessed quantitatively |
| **LC50** | Acute: inhalation dust LC50 > 48.2 mg/l, 1 hour |

[14] *https://echa.europa.eu/de/substance-information/-/substanceinfo/100.013.277; https://echa.europa.eu/documents/10162/a3f810b8-511d-4fd0-8d78-8a8a7ea363bc; http://cdn.chemservice.com/product/msdsnew/External/English/S-15886J0%20English%20SDS%20US.pdf; https://echa.europa.eu/documents/10162/13641/annex_xvi_consultant_report_decabde_en.pdf/337cc41c-0964-41a3-8d97-40b785f22fad*

### #6 HexaBDE, EC NR 253-058-6, CAS NR 36483-60-0[15]

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}H_4Br_6O$ |
| **MOLECULAR WEIGHT** (g/mol) | 643.62 |
| **STATE OF AGGREGATION AT ROOM TEMPERATURE** | solid |
| $T_{MELT}$ (°C) | 148-151°C |
| $T_{BOILING}$ (°C) | 454.4°C (@ 760 mmHg) |
| **VAPOUR PRESSURE** (mm Hg) | 5.13E-08 |
| **WATER SOLUBILITY** (mg/l) | 4.08X10-3 mg/l at 25 °C (calculated value) |
| **TOTAL AMOUNT USED** | 2 720 ppm in HIPS and 1 230 ppm in ABS |
| **GLOBALLY HARMONISED SYSTEM (GHS)[2] HAZARD STATEMANTS** | H225-H304-H315-H336-H410<br>P210-P261-P273-P301+P310-P331-P501 |
| **EDC, PBT/VPVB ASSESSMENT IF APPLICABLE** | 1A or 1B carcinogenicity, mutagenicity, or reproductive toxicity |
| **ENVIRONMENTAL FATE AND BEHAVIOUR** | Terrestrial fate: Based on a classification scheme, an estimated Koc value of 35,000(SRC), determined from a structure estimation method, indicates that hexabromodiphenyl ether is expected to be immobile in soil (SRC). Aquatic fate: Based on a classification scheme, an estimated Koc value of 35,000 (SRC), determined from a structure estimation method, indicates that hexabromodiphenyl ether is expected to be adsorbed by suspended solids and sediment (SRC). Volatilisation from water surfaces is not expected based on an estimated Henry's Law constant of 4.7X10-7 atm-cu m/mole (SRC), developed using a fragment constant estimation method. According to a classification scheme, BCFs of 216-1310 and 527-1490 in carp suggest the bioconcentration in aquatic organisms is high to very high (SRC). Hexabromodiphenyl ether is not expected to undergo hydrolysis in the environment due to the lack of functional groups that hydrolyse under environmental conditions. Utilising the Japanese MITI test, 15 % of the Theoretical BOD was reached in 4 weeks. Based on this test, hexabromodiphenyl ether is not readily biodegradable. |
| **LC50** | orl-rat LD: >500 mg/kg |

[15] *https://pubchem.ncbi.nlm.nih.gov/compound/Hexabromodiphenyl-ethers#section=Environmental-Fate*

#### #7 HeptaBDE, EC NR 273-031-2, CAS NR 68928-80-3[16]

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}H_3Br_7O$ |
| **MOLECULAR WEIGHT** (g/mol) | 722.48 |
| $T_{MELT}$ (°C) | 70-150 °C (decomp) |
| $T_{BOILING}$ (°C) | 495.3°C (@ 760 mmHg) |
| **VAPOUR PRESSURE** (mm Hg) | 5.13E-08mmHg at 25°C |
| **WATER SOLUBILITY** (mg/l) | 4.08X10-3 mg/l at 25 °C (calculated value) |
| **TOTAL AMOUNT USED** | 10 800 ppm in HIPS and 8 930 ppm in ABS |
| **EDC, PBT/VPVB ASSESSMENT IF APPLICABLE** | 1A or 1B carcinogenicity, mutagenicity, or reproductive toxicity |
| **ENVIRONMENTAL FATE AND BEHAVIOUR** | Terrestrial fate: Based on a classification scheme, an estimated Koc value of 89,000 (SRC), determined from a structure estimation method, indicates that heptabromodiphenyl ether is expected to be immobile (SRC). Volatilisation of heptabromodiphenyl ether from moist soil surfaces is not expected to be an important fate process (SRC) given an estimated Henry's Law constant of 1.9X10-7 atm-cu m/mole (SRC), using a fragment constant estimation method. Heptabromodiphenyl ether is not expected to volatilise from dry soil surfaces (SRC) based on an estimated vapour pressure of 3.3X10-10 mm Hg (SRC), determined from a fragment constant method. Aquatic fate: Based on a classification scheme, an estimated Koc value of 89,000 (SRC), determined from a structure estimation method, indicates that heptabromodiphenyl ether is expected to be adsorbed by suspended solids and sediment (SRC). Volatilisation from water surfaces is not expected based on an estimated Henry's Law constant of 1.9X10-7 atm-cu m/mole (SRC), developed using a fragment constant estimation method. According to a classification scheme, an estimated BCF of 29 (SRC), from an estimated log Kow of 9.4 and a regression-derived equation, suggests the potential for bioconcentration in aquatic organisms is moderate (SRC). Atmospheric fate: According to a model of gas/particle partitioning of semivolatile organic compounds in the atmosphere, heptabromodiphenyl ether, which has an estimated vapour pressure of 3.3X10-10 mm Hg at 25 °C (SRC), determined from a fragment constant method, is expected to exist solely in the particulate phase in the ambient atmosphere (SRC). Particulate-phase heptabromodiphenyl ether may be removed from the air by wet and dry deposition (SRC). |
| **LC50** | orl-rat LD: >500 mg/kg |

[16] *https://pubchem.ncbi.nlm.nih.gov/compound/Heptabromodiphenyl-ether#section=Environmental-Fate*

#### #8 NonaBDE, EC NR 264-565-7, CAS NR 63936-56-1

| | |
|---|---|
| **CHEMICAL GROUP** | Brominated diphenylethers |
| **MOLECULAR FORMULA** | $C_{12}HBr_9O$ |
| **MOLECULAR WEIGHT** (g/mol) | 880.27 |
| $T_{BOILING}$ (°C) | 557.9°C (@ 760 mmHg) |
| **VAPOUR PRESSURE** (mm Hg) | 6.56E-12mmHg (@ 25°C) |
| **WATER SOLUBILITY** (mg/l) | 4.08X10-3 mg/l (@ 25 °C) |
| **TOTAL AMOUNT USED** | 1 790 ppm in HIPS and 930 ppm in ABS |
| **EDC, PBT/VPVB ASSESSMENT IF APPLICABLE** | 1A or 1B carcinogenicity, mutagenicity, or reproductive toxicity |

### #9 DBDPE, EC NR 284-366-9, CAS NR 84852-53-9

<table>
<tr><td>MOLECULAR FORMULA</td><td>$C_{14}H_4Br_{10}$</td></tr>
<tr><td>MOLECULAR WEIgGHT (g/mol)</td><td>971.2 g/mol</td></tr>
<tr><td>STATE OF AGGREGATION AT ROOM TEMPERATURE</td><td>Solid</td></tr>
<tr><td>$T_{MELT}$ (°C)</td><td>350</td></tr>
<tr><td>$T_{BOILING}$ (°C)</td><td>676.24° C (@ 760 mmHg)</td></tr>
<tr><td>VAPOUR PRESSURE (mm Hg)</td><td>< 0</td></tr>
<tr><td>WATER SOLUBILITY</td><td>0.72 µg/l</td></tr>
<tr><td>TOTAL AMOUNT USED</td><td>1 1 501 ppm in HIPS</td></tr>
<tr><td>GLOBALLY HARMONISED SYSTEM (GHS) HAZARD STATEMANTS</td><td>H302-H315, H319-H335<br><br>P261-P305. P351, P338</td></tr>
<tr><td>EDC, PBT/VPVB ASSESSMENT IF APPLICABLE</td><td>Under assessment as persistent, bioaccumulative and toxic</td></tr>
<tr><td>PNEC</td><td>The Predicted No-Effect Concentration (PNEC) value is the concentration of a substance below which adverse e when more than one summary is provided, PNEC values may refer to constituents of the substance and not to th dossiers.<br>
<table>
<tr><th colspan="2">Hazard for Aquatic Organisms</th><th>Hazard for Air</th></tr>
<tr><td>Freshwater</td><td>No hazard identified (1)</td><td>Air</td></tr>
<tr><td>Intermittent releases (freshwater)</td><td>No hazard identified (1)</td><td>Hazard for Terre</td></tr>
<tr><td>Marine water</td><td>No data: aquatic toxicity unlikely (1)</td><td>Soil</td></tr>
<tr><td>Intermittent releases (marine water)</td><td>No data: aquatic toxicity unlikely (1)</td><td></td></tr>
<tr><td>Sewage treatment plant (STP)</td><td>1 mg/L (1)</td><td>Hazard for Pred</td></tr>
<tr><td>Sediment (freshwater)</td><td>100 mg/kg sediment dw (1)</td><td>Secondary poisc</td></tr>
<tr><td>Sediment (marine water)</td><td>10 mg/kg sediment dw (1)</td><td></td></tr>
</table></td></tr>
<tr><td>LC50</td><td>LD50 5 000 mg/kg bw (rat)<br>NOEL (4.667 months) 88.1 mg/kg bw (birds)<br>Short-term toxicity to fish<br>NOELR (4 days) 110 mg/l</td></tr>
</table>