# Brominated flame retardants in end-of-life management not problematic regarding formation of brominated dioxins/furans (PBDD/F).

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## Introduction

Bromine is used as the building block for some of the most effective flame retarding agents available to the plastics industry today. They are used to protect against the risk of accidental fires in a wide range of products. Brominated flame retardants (BFRs), as all flame retardants, act to decrease the risk of fire by increasing the fire resistance of the materials in which they are applied. There is a perception that BFRs affect adversely the end-of-life management of plastics through formation of brominated dioxins and furans (PBDD/F). In fact, there exists a wide range of data and practical experience demonstrating that the end-of-life management of plastics containing BFRs are fully compliant with legislation setting the strictest limit values for PBDD/F and is fully compatible with an integrated waste management concept [1, 2]. Furthermore, all existing EU Risk Assessments on BFRs according to the European Existing Substance Regulations include an assessment of the potential formation of dioxins and furans [3, 4, 5, 6, 7]. All assessments conclude that the risks along the life-cycle of the chemicals for human health and the environment associated with the potential formation of PBDD/F are negligible. Moreover, two recent Swedish studies found, that consumer products with BFRs emit less pollutants than the same products without any FRs [8, 9].

## Results and Discussion

This paper summarises available studies and presents the latest results regarding potential formation of brominated dioxins and furans in end-of-life management of plastics containing brominated flame retardants. Additionally, before BFR products enter the market they are tested for PBDD/F according to the "*German Dioxin Ordinance*"[10]. Depending on the substitution pattern the limit values for PBDD/F are set at <1µg/kg (ppb) respectively <5 µg/kg (ppb).

**Mechanical Recycling**

Several recycling studies have shown that plastics containing specific BFRs can be mechanically recycled and have also demonstrated that the strict PBDD/F limit values of the German "*Dioxin Ordinance*" can be met if recycling is done properly[11, 12, 16]. New plastics containing BFRs have been successfully recycled up to five times whilst still meeting required fire safety and performance standards. For historical plastic waste and especially small parts, mechanical recycling is not recommended because it will not be economical to separate Penta- and OctaBDE containing plastics as required in a new EU Directive, which restricts the use of both substances by August 2004[13]. Table 1 gives an overview of selected BFR-polymer systems which were tested on PBDD/F concentrations after multiple recycling processes.

Furthermore, it was demonstrated that brominated dioxin/furan (PBDD/F) exposure at the workplace during recycling [14, 17] or recovery[15] is of no concern. The results of a further study[18] came to comparable conclusions regarding the processing of plastics containing specific BFRs.

**Table 1:** PBDF/D congeners determined in recycled HIPS and ABS plastics[2] in comparison to the "German Dioxin Ordinance".

| PBDD/F Species | HIPS/DecaBDE 5 x recycled | ABS/BEO 4 x recycled | ABS/TBBPA 4 x recycled | Limit value |
|---|---|---|---|---|
| **Dimensions** | µg/kg | µg/kg | µg/kg | µg/kg |
| Sect. 4 2,3,7,8-TetraBDD . | n.d. | n.d. | n.d. | |
| 1 1,2,3,78-PentaBDD | n.d. | n.d. | n.d. | |
| 2,3,7,8-TetraBDF | n.d. | n.d. | n.d. | |
| 2,3,4,7,8-PentaBDF | n.d. | n.d. | n.d. | |
| **Sum of the 4 PBDD/F** | 0.06 | n.d. (< 0.06) | n.d. (< 0.09) | 1 |
| 1,2,3,4,7,8-/1,2,3,6,7,8HexaBDDb | n.d. | n.d. | n.d. | |
| 1,2,3,7,8,9-HexaBDD | n.d. | n.d. | n.d. | |
| 1,2,3,7,8-PentaBDF | 0.06 | n.d. | n.d. | |
| **Sum of the 8 PBDD/F** | 0.12 | 0.16 | 0.23 | 5 |

In a study by the University of Erlangen comparing the situation at the workplace for extrusion and injection molding during recycling runs, no significant increase in the concentrations between first and second recycling pass are observed[17]. The values for injection molding are slightly lower during the second recycling pass. Also the concentrations in the exhaust gases (sampling point 3 and 6) decrease in the second recycling run. This may be due to the loss of volatile compounds during the first recycling pass. Even the exhaust gases are meeting the workplace exposure limits. Table 2 shows that the limit value of 50pg ITE /$m^3$ is not exceeded at any sampling point by any compound, even if the full limit of detection is included in the calculation.

**Table 2**: Workplace exposure during HIPS/DecaBDE processing (limit value=50 pg ITE/$m^3$)[17].

| Report Sample No. [1] | Air Volume [$m^3$] | Sampling site | ITE 8 PBDF/Ds excl. LOD [pg/$m^3$] | ITE 8 PBDF/Ds incl. 1/2 LOD [pg/$m^3$] | ITE 8 PBDF/Ds incl. LOD [pg/$m^3$] |
|---|---|---|---|---|---|
| R1 EX WP 2.1 | 26,24 | 1 | 0.25 | 0.33 | 0.40 |
| R1 EX WP 2.2 | 26,26 | 2 | 0.09 | 0.17 | 0.25 |
| R1 EX EG 3 | 9,82 | 3 | 4.95 | 4.95 | 4.95 |
| R1 IM WP 5.1 | 33,12 | 4 | 0.66 | 0.73 | 0.80 |
| R1 IM WP 5.2 | 33,08 | 5 | 0.83 | 0.90 | 0.98 |
| R1 IM EG 6 | 13,94 | 6 | 2.84 | 2.90 | 2.95 |
| R2 EX WP 8.1 | 27,28 | 1 | 0.44 | 0.56 | 0.67 |
| R2 EX WP 8.2 | 27,24 | 2 | 0.13 | 0.22 | 0.30 |
| R2 EX EG 9 | 11,4 | 3 | 0.72 | 1.14 | 1.55 |
| R2 IM WP 11.1 | 37,40 | 4 | 0.15 | 0.22 | 0.29 |
| R2 IM WP 11.2 | 37,40 | 5 | 0.07 | 0.14 | 0.21 |
| R2 EX EG 12 | 16,84 | 6 | 0.26 | 0.41 | 0.57 |

[1] R = Recycling run; EX = Extrusion; WP = Workplace air; EG = Exhaust gas; IM = Injection moulding

## Co-Combustion

The Forschungszentrum Karlsruhe and various industry partners (e.g. Association of Plastic Manufacturers in Europe, European Brominated Flame Retardants Industry Panel) have undertaken a number of research programs[19, 20]. The aim of these was to investigate the co-combustion of plastic waste streams together with municipal solid waste. Plastics containing brominated flame retardants were fed to the pilot plant, TAMARA, with 250 kg/h feed to simulate full scale incinerators. Different plastics such as those used in TV monitors and printed wiring boards were use as starting material. In one of these tests, in which the Br content of the fuel was increased to approximately 10 g/kg dry waste, results confirmed that up until a level of 3g, no detectable amounts of elementary $Br^2$ could be measured in the raw gas, post-incineration. Up to 22 wt-% of brominated flame-retarded WEEE was mixed with pre-treated municipal solid waste. Though the Br content of the incinerator was significantly increased there was no resulting increase in the formation of chlorinated dibenzo-p-dioxins and dibenzofurans. As with former tests an increased Br concentration in the feed correlated with an increase in Br containing homologues, with a trend towards the formation of dibenzofurans. Mixed halogenated dioxin/furans were also formed. The majority of the mixed halogenated congeners contained one Br atom per molecule. The contribution of compounds with two Br atoms could reach the same order of magnitude for high Br levels in the fuel. Species with three Br atoms were very rare. Purely brominated dioxin/furans could hardly be detected. The total amount of all halogen containing dibenzo-p-dioxins and dibenzofurans remained at an unaltered concentration. Only in tests where material with a high Br concentration was combusted mixed with material of high Cl concentration were concentrations found which exceeded the average almost by a factor of 2. These trials showed especially high concentrations of the chlorinated dibenzofurans. This incineration process is a dioxin sink to the extent that this study showed that > 98% of the brominated dioxins and furans had been destroyed during the controlled combustion process of WEEE (see figures 1 and 2). The incineration tests, pyrolysis and combustion studies have demonstrated that waste from E&E

equipment can be safely added to today s municipal solid waste (MSW) to generate in an environmentally sound manner useful energy when incinerating BFR-containing materials. PBDD/F formation is not altered by the presence of the bromine-containing waste, and remains well within emission standards in these processes.

The effect of increasing levels of bromine on the combustion process was investigated as well. In addition to analyzing dioxin/furan emissions, the positive effect of bromine on metal volatilization and the reuse of slag for road construction and the potential for recovering and recycling the bromine were evaluated. In line with earlier studies it was shown that the volatilization of heavy metals, such as Cu, Zn, Sb, Sn, is increased substantially by the presence of chlorine and bromine. The metals are transferred out of the fuel bed to the fly ashes, where they can be recovered. The slag is being cleaned up from metals and can be re-used in road construction. The heavy metals are being concentrated in the fly ashes and can be disposed of properly. Using suitable wet scrubbing systems, it is technically feasible to recycle the bromine contained in WEEE from the combustion gases. If the bromine is recovered, it can then be used to produce different types of commercial bromine-based products such as bromine itself, hydrogen bromide, or sodium bromide.

**Figure 1**: Halogenated dioxins and furans in the raw gas versus Br inventory in the fuel[20].

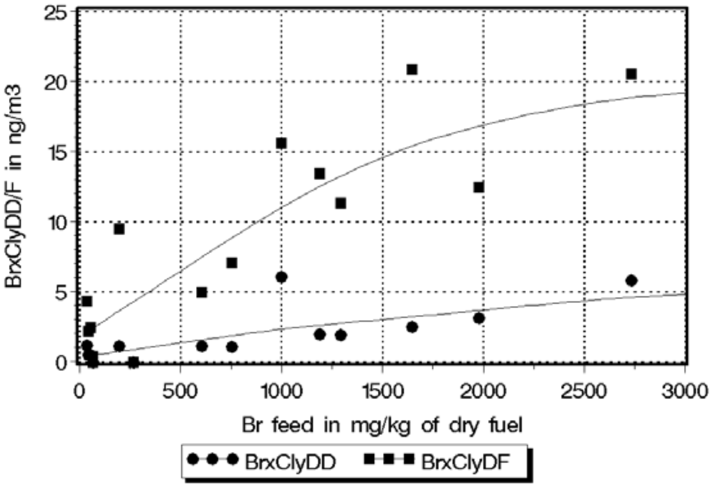
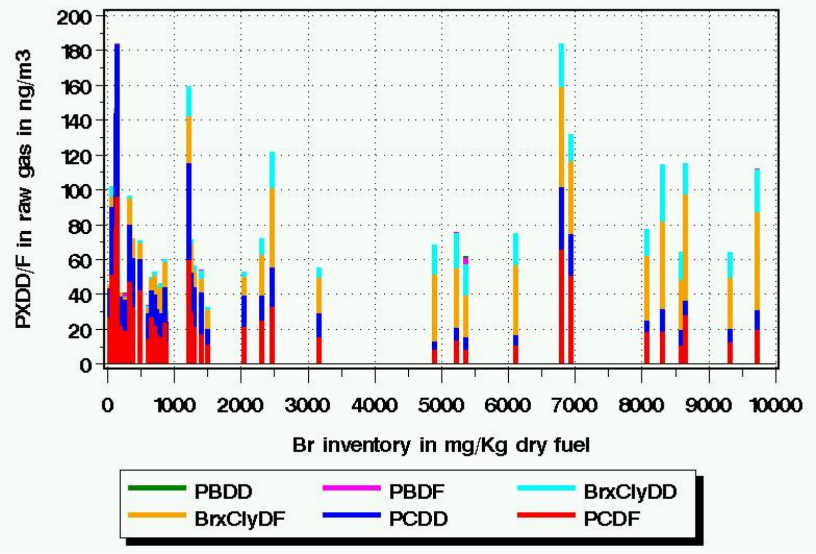


**Figure 2**: Halogenated dioxins and furans in the raw gas versus Br inventory in the fuel[20].




## Smelters

Several metal smelters developed recycling process for electrical and electronic equipment waste, to recover the metals and the energy. The plastics provide energy to the smelting process and also acts as reducing agent. BFR containing plastics have been tested in this process and fully meet the smelter requirements. Neither the PBDD/F emission limits nor the workplace exposure limits were exceeded.

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