

## Experiences from a large scale warehouse fire with bromine-containing polybutylene terephthalate forming almost no polybrominated dibenzodioxins and dibenzofurans

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### Introduction

On July 10, 1991 a large scale fire occurred in an external intermediate store of our plastics production plant in Krefeld-Uerdingen, fortunately without bodily injury but causing a property damage of about 8 to 10 millions DM. During the fire accident a large warehouse was mostly destroyed and 400 t polycarbonate (PC) and 390 t polybutylene terephthalate (PBT) pellets stored in it were burnt.

About 180 t of these PBT products had been flame retarded grades containing brominated flame retardants and antimony trioxide. Due to that the competent authorities immediately started the question if partly or completely burnt plastics residues and the surroundings of the warehouse could possibly be contaminated by polybrominated dibenzodioxins and dibenzofurans (PBDD/PBDF).

Therefore experts of the Regional Institute for Immission Control (LIS) in Essen and of our company collected several representative samples from the fire site which were analyzed for their PBDD/PBDF content independently by the Society for Work Place and Environmental Analysis (GfA), Münster-Roxel, and by our specialized laboratory. The results were to give guidance to the authority involved in their decision on industrial hygiene measures, disposal of burnt residues and clearing of debris.

Afterwards the question arose if apart from PBDD/PBDF traces on the fire site and its immediate environs additional amounts could possibly have been transported via the air path and deposited in a larger distance. Therefore a few months later soil samples were collected in a residential district, situated in the main wind and fire smoke direction at a distance of 1300 to 1800 m from the warehouse and were analyzed as well.

### Experimental section

#### Sampling of fire residues

The LIS specialists took three partly burnt plastics samples, identified as

P 1, "Pocan" (our PBT trade name), "white"

P 2, "lightblue pellet"

P 3, "coloured pellet mixture".

We took five different samples on July 11, 1991:

No. 1 through 4: partly up to mostly burnt PBT material (identified by its residual bromine content and by the aluminium foil left after the fire from the alu/paper laminate packaging bags for PBT pellets)

No. 5: ash/slag mixed sample from different locations in the warehouse

### Soil sampling

All sampling areas were situated within a narrow angle around the main wind and smoke direction. Soil was sampled at a depth of 0 - 10 cm, if necessary after removal of plants and grass.

No. A: fallow ground; distance from warehouse 1460 m

No. B: children's play ground; distance 1340 m

No. C: ground near a cross roads; distance 1740 m.

### Sample extraction and clean up (as performed in our laboratory)

Samples were spiked with isotope labelled standards ( $^{13}\text{C}_{12}$ -2,3,7,8-Tc-traBDD,  $^{13}\text{C}_{12}$ -1,2,3,7,8-PentaBDD,  $^{13}\text{C}_{12}$ -2,3,7,8-TetraBDF and  $^{13}\text{C}_{12}$ -1,2,3,7,8-PentaBDF) and soxhlet-extracted with dichloromethane for 8 hours. PBDD/PBDF were isolated as described previously [ 1 ].

### Quantitation of PBDD/PBDF

The fire residue samples No. 1 through 5 were analyzed using gas chromatography and low resolution mass spectrometry. Conditions have been published in [ 1 ].

PBDD/PBDF traces in the soil samples were determined by gas chromatography and high resolution mass spectrometry (Finnigan MAT 95 at a resolution of 5000). The internal standards spiked into the original sample were used for the quantitation by isotope dilution technique.

The cleaned extract was spiked with  $^{13}\text{C}_{12}$ -1,2,3,4,7,8-hexachloroDD prior to the GC/HRMS quantitation, taking this standard to establish the recovery of the surrogates added to the original samples.

### Gaschromatography conditions

Column: 25 m x 0,32 mm; 0,17  $\mu\text{m}$  film Ultra 2 capillary (Hewlett Packard, no. 19091 A 012), directly coupled to the ion source (transfer line at 270  $^{\circ}\text{C}$ ).

Injection: 1  $\mu\text{l}$  (split/splitless injector, 280  $^{\circ}\text{C}$ )

### Temperature program:

$T_1 = 70^{\circ}\text{C}$  (1 min)  $T_1 / T_2$  heating rate 10  $^{\circ}\text{C}/\text{min}$

$T_2 = 150^{\circ}\text{C}$  (8 min)  $T_2 / T_3$  heating rate 5  $^{\circ}\text{C}/\text{min}$

$T_3 = 325^{\circ}\text{C}$  (10 min)

### Mass spectrometry conditions

The mass spectrometer was operated in the electron impact mode (70 eV); ion source temperature 270  $^{\circ}\text{C}$ . The two most intense signals of the molecular ion cluster were monitored.

### Identification of PBDD/PBDF

The confirmation criteria for PBDD/PBDF are given in [ 2 ]. Identification of isomers was accomplished by comparison of the retention times of sample peaks and the corresponding peaks of the standard solution. As the retention behaviour of all single isomers cannot be established, this way of isomer characterisation cannot exclude false positive results.

### Results and discussion

The results are summarized in table 1. The conformity of results on burnt PBT samples, obtained by the LIS contract laboratory and by ours, is quite satisfying when taking into account the present, still not fully developed status of PBDD/PBDF methodology, the ultra trace range to be determined, the massive matrix interferences in the burnt samples and the fact that non-identical samples were analyzed.

For the purpose of the authorities' decision on work place protection measures and disposal of residues, the figures were evaluated in respect to future PBDD/PBDF limits which can only be estimated from the different German Federal Environment Ministries' drafts for a supplemented Hazardous Substances Ordinance, cf. table 1, second column.

The comparison of results vs. probable limits shows that the burnt material in our view does not require special workers protection; only one single sample, No. 2, exceeds the limit for the sum of the first four isomers by a factor of 1,6 which is within experimental error.

The authorities involved also came to this conclusion and regulated that during the removal of burnt material and the clearing of debris only normal dust masks should be worn by workers and the burnt plastics residues could be deposited in our companies controlled waste landfill sites as had been offered by us.

It is obvious to also compare the data of burnt PBT out of this "real life fire testing" with laboratory pyrolysis results on the PBT grades involved which had been obtained in our previous investigation programme [ 3 ]. Before doing so, one has to consider that under lab pyrolysis conditions any PBDD/PBDF quantities formed are collected within the pyrolysis tube and the quartz wool trap and thus determined, whereas in the case of the burnt plastics samples only their content is analyzed. The question of PBDD/ PBDF traces emitted and distributed by the fire smoke can only indirectly be resolved by looking into the results of the soil samples, cf. table 2.

Only in case of soil sample No. A the figures show quantities of up to 1 ppt for the penta- and hexa-congeners, whereas any other isomers in all samples are not detectable at a detection limit of 0,5 ppt. When recalculated into TEQ quantities only minute amounts result, being even far below the average background PChloroDD/PChloroDF burden of soils in non-industrialized areas [ 4 ].

Thus one cannot distinguish between soil contamination caused by the fire accident and the background level from other sources.

### Conclusions

Flame retarded plastics containing polybrominated diphenylethers had been observed very critically because of their suspected PBDD/PBDF formation potential for a couple of years. As a voluntary measure, German plasticsmanufacturers have completely stopped using this class of flame retardants since more then two years.

The need for plastics grades meeting severe fire safety standards especially in the electro/electronics industry has even increased; it could be - partly - fulfilled by bromine-free products in the range of polycarbonates and blends of polycarbonate with acrylonitrile/butadiene/styrene copolymers (PC + ABS), meanwhile introduced into the market.

On the other hand, the ABS matrix alone as well as PBT need brominated compounds and antimony trioxide in their flame retarded formulations. We use tetrabromobisphenol A or its polymeric derivatives as bromine carrier in our present materials, after having thoroughly investigated the PBDD/ PBDF content in the pellets, their formation during compounding, processing, during typical use of finished parts, e.g. an ABS television housing, as well as during recycling.

As mentioned earlier, the products were also tested by simulating smouldering combustion conditions, and by chance we now have the results from a large scale fire described in this paper.

All these experiences indicate that our bromine containing plastics can be safely processed, used and also recycled. The future PBDD/PBDD concentration limits of the present German draft dioxin ordinance, as well as the guide value for tolerable work place exposure to dioxin equivalents during processing, proposed by the competent German Federal Institute for Workers Protection, will be obeyed with these products.

And even at the circumstances of a whole warehouse burnt down nothing dramatical happens.

### Literature

- [ 1 ] Neupert M, Weis H, Thies J., Stock B. Analytical procedures in connection with acute animal toxicity-II. Pyrolysis products obtained from an ABS copolymer containing octabromo diphenyl ether as a flame retardant. *Chemosphere* 1989; 19, 219
- [ 2 ] Donnelly J R, Grange A H, Nunn N J, Sovocool G W, Brumley W C, Mitchum R K. Analysis of thermoplastic resins for brominated dibenzofurans. *Biomedical and environmental mass spectrometry* 1989; 18, 884-96
- [ 3 ] Thies J, Neupert M, Pump W. Tetrabromobisphenol A (TBBA) , its derivatives and flame retarded (FR) polymers - content of polybrominated dibenzo-p-dioxins (PBDD) and dibenzofurans (PBDF) - PBDD/F formation under processing and smouldering (worst case) conditions. *Chemosphere* 1990; 20, 1921-8
- [ 4 ] Report of the German Federal Ministry for Environment, Nature Protection and Nuclear Safety on Dioxins, August 21, 1991

### Annexes

Tables 1 and 2

Table 1. PBDD/PBDF content of burnt plastics and ash samples from the fire place

Sample	*	P 1 Pocan white	P 2 blue pellets	P 3 pellet mixture	No. 1 burnt PBT	No. 2 burnt PBT	No. 3 burnt PBT	No. 4 burnt PBT	No. 5 ash/slag mixture
Laboratory		LIS	LIS	LIS	Bayer	Bayer	Bayer	Bayer	Bayer
Dimension: ppb									
<b>PBDD/F isomers</b>									
2,3,7,8-Br4DD	$\Sigma < 2$	< 0,02	< 0,02	< 0,02	0,4	0,5	0,3	0,5	< 0,2
2,3,7,8-Br4DF		0,1	< 0,02	< 0,02	< 0,2	< 0,5	< 0,5	0,4	< 0,2
1,2,3,7,8-Br5DD		< 0,04	< 0,05	< 0,05	< 0,8	0,7	< 2	< 2	< 0,2
2,3,4,7,8-Br5DF		< 0,04	< 0,04	< 0,06	< 1	2	1	< 1	< 0,5
1,2,3,4,7,8-Br6DD and 1,2,3,6,7,8-Br6DD	$\Sigma < 5$	< 0,8	< 0,9	< 0,95	< 5	< 5	< 5	< 5	< 1
1,2,3,7,8,9-Br6DD		< 0,8	< 0,9	< 0,95	< 5	< 5	< 5	< 5	< 1
1,2,3,7,8-Br5DF		< 0,04	0,06	< 0,06	< 0,8	< 2	1	1	< 0,2

\* Limits requiring workers protection, as estimated from drafts for a supplement of the German Hazardous Substances Ordinance

Table 2. PBDD/PBDF content of ash particles and soil samples

Sample	A soil	B soil	C soil
Distance from fire	1460 m	1340 m	1740 m
Laboratory	Bayer	Bayer	Bayer
Dimension: ppt			
<b>PBDD/F isomers</b>			
2,3,7,8-Br4DD	< 0,5	< 0,5	< 0,5
2,3,7,8-Br4DF	< 0,5	< 0,5	< 0,5
1,2,3,7,8-Br5DD	< 0,5	< 0,5	< 0,5
2,3,4,7,8-Br5DF	1	< 0,5	< 0,5
1,2,3,4,7,8-Br6DD and 1,2,3,6,7,8-Br6DD	0,5	< 0,5	< 0,5
1,2,3,7,8,9-Br6DD	1	< 0,5	< 0,5
1,2,3,7,8-Br5DF	1	< 0,5	< 0,5