

Workplace Monitoring of Polybrominated Dibenzofurans (PBDFs) and -Dioxins (PBDDs), Part III. Extruder Production and Injection Molding of Bis - Tetrabromophthalimide Ethylene (TBPI)/Sb<sub>2</sub>O<sub>3</sub>-Blended Polybutylene-Terephthalate (PBTP).

Karl S. Brenner<sup>1)</sup>, H. Knies<sup>2)</sup>

<sup>1)</sup>ZAX/Analytik, Bldg. D 216, <sup>2)</sup>DUS/Sicherheit u. Arbeitsschutz, Bldg. M 940; BASF AG, Carl-Bosch-Strasse 38, D-67056 Ludwigshafen, Fed. Rep. of Germany

**Abstract**

Workplace air measurements are presented for PBDDs and PBDFs. These measurements were taken during extruder production and injection molding of a PBTP-polymer blended with glass fiber, Sb<sub>2</sub>O<sub>3</sub>, and bis-tetrabromophthalimide-ethylene (TBPI, Saytex BT 93). The extruder granulate, molded test articles, Saytex BT 93-powder and the used Saytex BT 93/PBTP-batch were also analyzed. No 2,3,7,8-isomer-substituted PBDDs and PBDFs could be detected using the methods described earlier, including an MSD. The values monitored for the other PBDD/F-isomers (di- to hexabromo-compounds) were in the region of 1 to 340 pg/m<sup>3</sup>. The values for the different products were in the region of 0.01 to 3.4 ppb(ng/g).

**Introduction, Sampling Techniques**

TBPI is a possible substitute for brominated diphenyl ethers. To check the assumed low potential for PBDD/PBDF-formation, workplace measurements were performed during extruder production and injection molding of TBPI-blended PBTP-polymer.

The same sampling trains (STs) and sampling technique were used as described for the experiments with TBBA (tetrabromobisphenol A carbonate oligomer) [1]. In all cases the combination rotation- and "5-jet"-impinger\*\* was used.

As in the former experiments, the **sampling plans** were designed in a way to obtain representative data about the possible average respiratory burden. Fig. 1 and 2 give the schemes for both experiments. During the **extruder blending experiment** 4 samples were taken with STs, namely at the extruder workplace (ST1A,WP); the granulator exhaust line (ST2A,GR); the extruder head and water bath exhaust line (ST3A,EH/WB); and in the granulate refilling station located in a separate room (ST4A,RS).

\*Saytex BT 93 is a Trade Mark of Great Lakes Chemical Corp., West Lafayette, Indiana 47906, USA, and of Ethyl Corporation, Baton Rouge, Louisiana 70898USA.

\*\*BASF Patents pending; distributor: Fa.K. Ziemer GmbH, Pommernstr. 96, D-68309 Mannheim, Germany

# SOU/FRM

At the **injection molding station** we monitored the workplace atmosphere; the exhaust line from the injection molding head and form and the storage hood, where the test articles were cooled to room temperature. Fig.1 u. 2 show the workplace situations.

**PBTP-samples**, blended with TBPI were taken statistically from the granulator. This batch of polymer (PBTP/TBPI(14%)/Sb<sub>2</sub>O<sub>3</sub>(7%)/glass fibre) was used for the injection molding experiment. The Saytex BT 93/PBTP-batch, used for the extruder blending was also sampled as was a 3-lot mixture from the original Saytex BT 93-powder. Test articles were taken every 2 hrs, 6 of them were tested. The **Analysis** of Sampling Trains and Products will be described later.

## Results and Discussion

The results for the **extruder experiment** and the **injection molding experiment** are summarized in Figures 3 to 6.

Using the high-vol-STs allowed us to detect and determine concentrations of PBDFs/Ds down to the 1 pg/m<sup>3</sup>-region. **No 2,3,7,8-isomer PBDFs and Ds** could be detected at **both workplaces**, as far as this analytical technique allows at the moment (lack of some standards, GC-separation power still too low, use of a MSD, etc.).

The high sampling rates and sample volumes taken enabled us to reach the detection limits preset by the planned biomonitoring for the workforce in the plant. The data collected allowed the toxicologists to set up a valid risk assessment for the workers and make the necessary occupational safety considerations. The detection limits were in the range of 1 pg isomer/m<sup>3</sup> to 240 pg isomer (octabromo-derivatives)/m<sup>3</sup>.

The values measured for the **extruder experiment** were in the low pg/m<sup>3</sup>-region for the  $\Sigma$ PBDDs and in the region from 20 to 300 pg/m<sup>3</sup> for the  $\Sigma$ PBDFs (Fig.3, 4).

The values from ST2A,GR and ST3A,EH/WB cannot be compared directly because of the different dilution effects of the exhausts but they can serve to estimate the PCDD/F-formation during production.

During the **injection molding experiment** the  $\Sigma$ s of Tri- to Penta-BDFs detected at ST2B/IH, were in the range from 12 to 2 pg/m<sup>3</sup> (Fig.5), a concentration almost ubiquitous during production of BFR-blended polymers; no PBDDs were detected. With these data the occupational safety considerations and risk assessments for the production workforce can be accomplished.

The measured PBDF-values for the **Polymer Blends, Test Articles, Saytex BT 93/PBTP-Batch** and the **Saytex BT 93-Powder (TBPI)** are listed in Fig. 6. Except for granulate B, which contained 3 ppb  $\Sigma$ TBDDs, no PBDDs were detected.

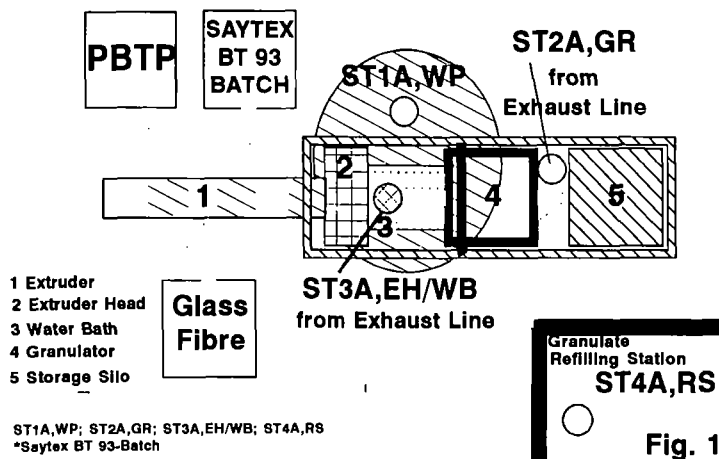
The measured values for granulate samples A (shredded for analysis with cutting grinder) and B (shredded with ultra-centrifugal grinder) are comparable with respect to Tri- and TetraBDFs, the differences for the Di-, Hexa- and HeptaPBDFs are not significant. They indicate a possible artefact formation in the cutting grinder. The Saytex BT 93/PBTP-batch contains Di- to HeptaBDFs, part of which could have formed during batch-production (Fig.6). But this possible formation under the temperature and mechanic stress in the extruder is not validated, yet. The expected dilution effect from batch to granulate can, except for HeptaBDF, be seen. It seems that there might be an overlapping of formation, reaction and dilution effects. There is no sign of significant formation of PBDFs and

PBDDs from the blended granulate during injection molding (Fig.6).

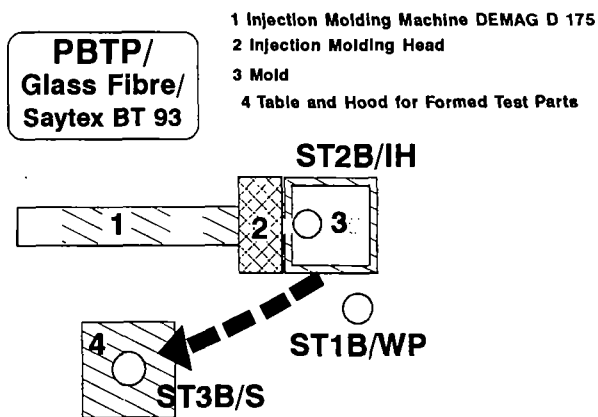
## References

- [1] Brenner K.S., H. Knies, (1993): Workplace Monitoring of Polybrominated Dibenzofurans (PBDFs) and -Dioxins (PBDDs) During Extrusion Production and Injection Molding of a Polybutyleneterephthalate (PBTP)/Glass Fibre Resin Blended with Tetrabromobisphenol A Carbonate Oligomer (BC 52\*)/Sb<sub>2</sub>O<sub>3</sub>; Air Sampling Train and Product Analysis. Toxicol Environ Chem; 38: 81-94

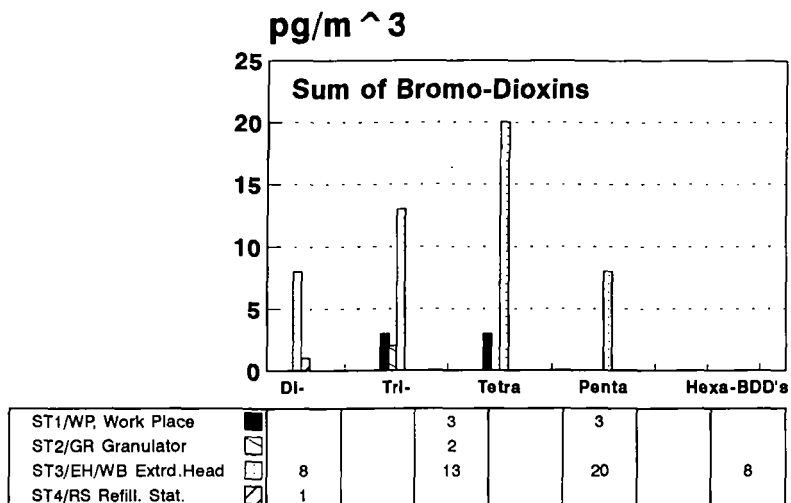
### PBTP/TBPI\* Extruder Experiment Workplace Monitoring, Sampling Points



### PBTP/TBPI\* Injection Molding Experiment Sampling Points; ST1B/WP; ST2B/IH; ST3B/S



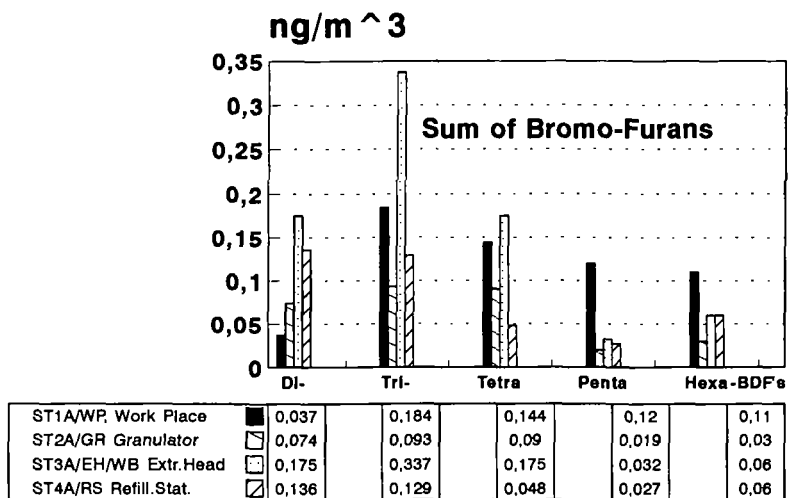
**PBTP/TBPI\* Extruder Experiment  
Workpl. Monitoring.Results,ST1A,2A,3A,4A**



\*Saytex BT 93-Batch

**Fig. 3**

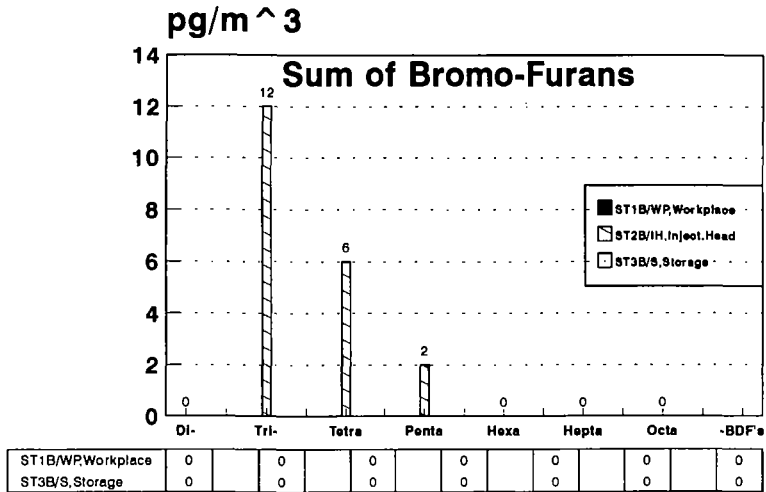
**PBTP/TBPI\* Extruder Experiment  
Workpl. Monitoring;Results,ST1A,2A,3A,4A**



\*Saytex BT 93-Batch

**Fig. 4**

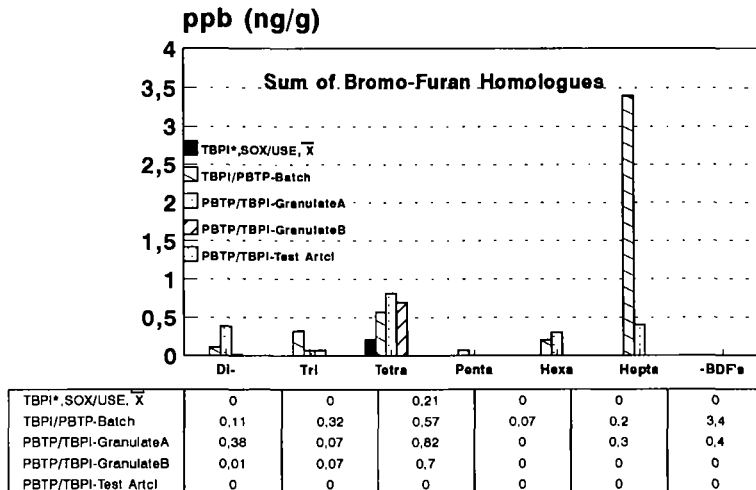
## PBTP/TBPI\* Injection Molding Experiment Workplace Monitoring; Results, ST1B,2B,3B



\*Saytex BT 93-Batch

Fig. 5

## PBTP/TBPI\* Extruder/Inject. Molding Expmt. TBPI\*, TBPI/PBTP-Batch, PBTP-Granulate PBTP-Test Articles



\*Saytex BT 93-Batch

Fig. 6