Formation of polyhalogenated Dibenzodioxin and Dibenzofurans (PXDD/F) during textile processings

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From the literature[1] it is known, that textiles can contain up to 370 pg I-TE/g polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF). Furthermore investigations show that brominated and brominated/chlorinated dioxins and furans are formed during thermal processes for the production of flame retarded plastics [2] and the operation of incineration engines with commercial fuels [3]. During the textile processes chlorinated as well as brominated compounds are used, sometimes at higher temperature using a open flame. For this reason five textile processes were investigated for polyhalogenated dioxins and furans.

2. Experimental

a) Textile Processes

1. Resin finish on the basis of $MgCl_2$
2. Flame proof finish for fleece material on the basis of Sb_2O_3/HBCD
3. Flame proof finish for upholstery material on the basis of NH_4Br
4. Flame proof finish for fleece material on the basis of NH_4Br
5. Flame proof finish for upholstery material on the basis of PVC

b) Sampling

The emission sampling was carried out using the VDI guideline 3499, page 2[4]. The sampling of the exhaust gas followed by the partical stream sampling according to VDI guideline 2066[5]. The effectivity of sampling was examined by addition of 4 $^{13}C_{12}$- standards.

c) Clean up

The filter and quartz wool of the exhaust sampling was soxhlet extracted by toluene for 24 h. The condensate and impinger were treated by a fluid-fluid extraction. The textiles were soxhlet extracted with toluene and also the chimney depositions (24 h).

Before extraction a internal standard mixtures (10 $^{13}C_{12}$-standard with chlorination grade four to eight and in suspicion of formation of PBDD/F and PBCDD/F marked brominated respectively brominated/chlorinated compounds) was added.
The rest of the clean up was carried out using the method of Hagenmaier et al [6].

d) GC/MS analysis
The GC/MS analysis for PCDD/F and PBDD/F was carried out using a high resolution mass spectrometer VG Autospec. The brominated/chlorinated compounds were analyzed by a Trio 1000 mass spectrometer (Fisons). The brominated and brominated/chlorinated compounds were mainly quantifed with external standards.

3. Results

a) PCDD/F-concentrations in textile processes
In figure 1 the obtained results of the emissions experiments were shown

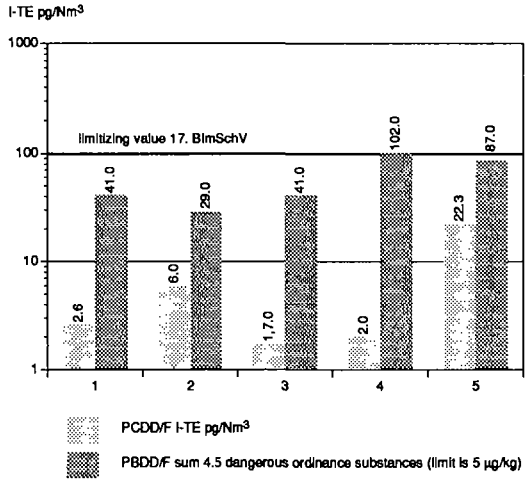

Fig. 1: PDD/F-concentrations in exhaust air

b) PXDD/F-concentrations in textiles
In the next three figures the results were given in relation to the german dangerous ordinance. The limits were:

sum 1:	1 µg/kg
sum 1,2:	5 µg/kg
sum 1,2,3:	100 µg/kg
sum 4:	1 µg/kg
sum 4,5:	5 µg/kg

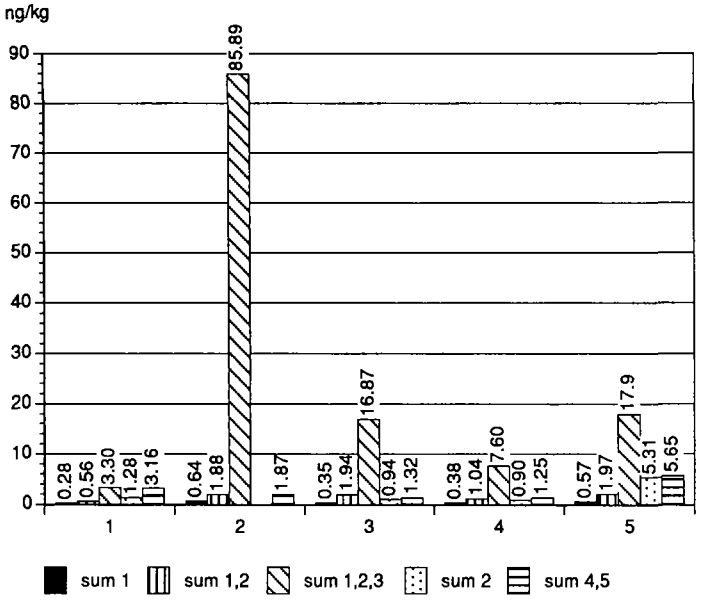

Fig. 2: PXDD/F-concentrations in textile before process in relation to the germans dangerous ordinance

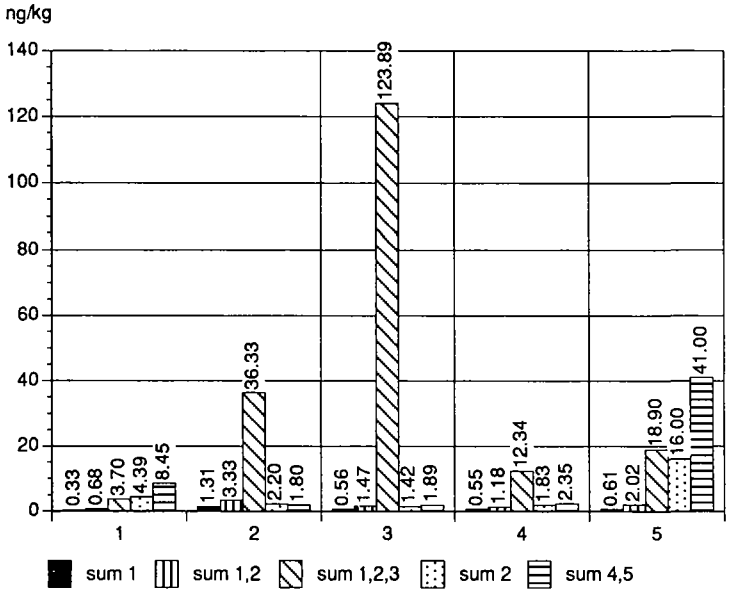

Fig. 3: PXDD/F-concentrations in textile after process in relation to the germans dangerous ordinance

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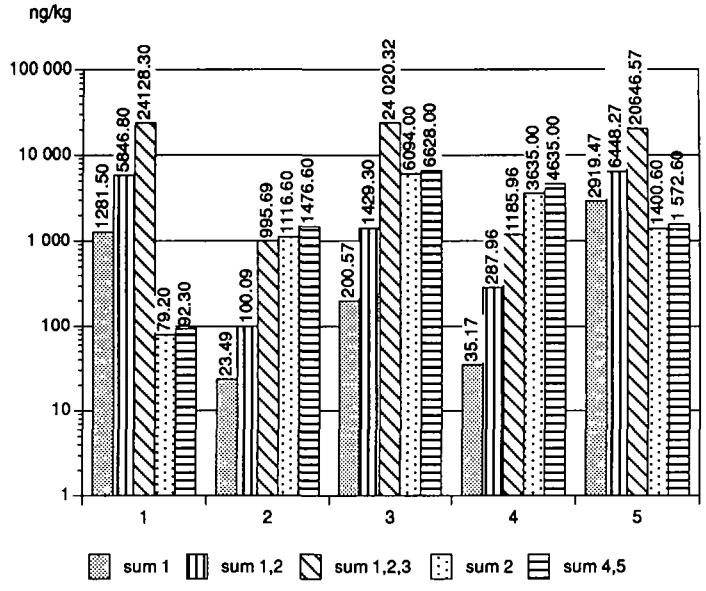

Fig. 4: PXDD/F-concentrations in chimney deposition in relation to the germans dangerous ordinance

4. Discussion

The following results were obtained:

- In all investigated cases no relevant amounts of PCDD/F could be detected in the exhaust air (< 0,01 ng/Nm ^{3} I-TE).
- The PBDD/F-concentrations sum 4,5 were in the range of 29.0 to 102.0 pg/Nm ^{3}. Mixed compound were only detected in process 4.
- The analysis of textiles before and after the refinement show only small differences in relation to the PCDD/F-concentrations. The detected concentrations are in the same magnitude published by other authors [7].
- Also the brominated concentrations were in the same magnitude.
- There are two kinds of chimney depositions The greasy deposition show relatively high amounts on PCDD/F (up to 241 243 ng/kg PCDD/F relating to the german decree of hazardous compounds, 6 618 ng/kg PBDD/F relating to the german decree of hazardous compounds). The limit of these decree was overstepped. The powdery depositions contained smaller amounts (up to 42.4 ng/kg I-TE, 1 185 ng/kg PCDD/F relating to the german decree for hazardous compounds, 4 635 ng/kg PBDD/F relating to the german decree of hazardous compounds). The high concentrations in the accumulation or high loaded depositions

during a short time.

- In the textiles only traces of PBCDD/F could be detected. The concentrations of PBCDD/F in chimney depositions were in the high ng/kg level upto 17 µg/kg.

The results show that in textile processing there are no problems with PCDD/F in the exhaust air and also in the textile. The only problem are the chimney depositions with concentrations up to 241 283 ng/kg sum 1,2,3.

5. Literature

1) **Horstmann, M., Mc Lachlan, M.,** Organohalogen Compounds 22,309 (1995)
2) **Brenner, K. S., Knies, H.,** Organohalogen compounds 2, 319 (1990)
3) Untersuchungen zur Emission halogenierter Dibenzodioxine und Dibenzofurane aus Verbrennungsmotoren beim Betrieb handelsüblicher Betriebsstoffe, **GSF-Forschungszentrum für Umwelt und Gesundheit mbH, München 1992**
4) **VDI 3499 Blatt 2** Messen von Emissionen; Messen von polychlorierten Dibenzo-p-dioxinen (PCDD) und Dibenzofuranen (CDF); Filter/Kühlermethode, VDI-Handbuch Reinhaltung der Luft, Band 5 (1993)
5) **VDI 2066 Blatt 1** Messen von Partikeln; Staubmessungen in strömenden Gasen; Gravimetrische Bestimmung der Staubbeladung, Oktober 1975, Düsseldorf
6) **Hagenmaier, H., Brunner, H., Haag, R., Kunzendorf, H.-J., Tichaczek, K., Weberruß, U.,** VDI-Berichte 634, 61 (1987)
7) **Hartmann, M., Mc Lachlan, M., Mellinand**, Textilberichte 1-2(1995)