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INVESTIGATIONS OF THE COMBUSTION PRODUCTS OF FLAME-PROTECTED IMPACT RESISTANT POLYSTYRENE

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ABSTRACT

During the decomposition process of the entitled material in presence of air, the degradation products of the flame retardant (deca-bromdiphenyloxide) are produced as well as polystyrene components. In addition compounds were formed resulting from reactions between the devolatilization products of the polymer and the flame retardant, e.g. especially benzyl bromide, brominated styrene derivates, bromoethylbenzene and 4-bromotoluene.

The apparatus used, has been described in previous papers (1,2), but additionally an instrumental modification of the buring apparatus has been made according to DIN 4102, this work deals with comparison of the results by use of both, the Bayer-ICI-Shell apparatus and our self-designed burning apparatus.

INTRODUCTION

There is a great number of regulation- and testing methods for classifying the combustibility of raw materials. Only a few refer to the identification of compounds in the released gases from burning processes (3). A lot of work in this field of investigations has been carried out by Woolley et al. (4,5). Our experiments described in this paper have been carried out with the same experimental objectives, e.g. to make a simulation of a real combustion of the materials in air atmosphere and to identify the decomposition products qualitatively and in many case quantitatively.

EXPERIMENTAL

Sample Material and adsorption

For our investigation we used impact-resistant polystyrene (BASF, 475 K) containing 13 % decabromodiphenyloxide (Chem.Plant Kalk, Bromkal 82-0 DE) and 5 % antimonytrioxide. The sample plates (size of 0.4x5.0x5.0 cm) have been manufactured by use of the injection molding technique. These products were grinded up to a size of 0.1-1 mm diameter when they were burnt in the mod. Bayer-ICI-Shell combustion apparatus. The DIN 4102 tests were carried out using the whole sample plate.

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For the enrichment of the organic compounds from air occured by means of adsorption on amberlithe XAD-4, XAD-2 (Rohm and Haas) as well as standardized silica and charcoal tubes (SKC Lot 160, SKC Lot 120) according to (1,2). The adsorption reagents have been purified by 6 h soxhlet extraction in n-hexane, and dried at 100°C in vacuum. The desorption rates have been estimated with carbondisulphide as a solvent.

GC-apparatus

The GC-equipment consist of

1. a Perkin-Elmer, sigma 2b gaschromatograph, ECD-detection system and a 50 m fused silica column (SE 54).
   Instrumental settings: Initial temperature 60°C, heating rate 6°C/min, final temperature 290°C, injector temperature 310°C, temperature of the detector 300°C, column-pre-pressure 2 bar, carrier gas argon/methan, split 50 cm^3/min.
2. DANI 3900 gaschromatograph, initial column heater temperature 60°C, heating rate 3°C/min, final temperature 250°C, temperature of the injector system 270°C, temperature of the detection system 270°C, column-pre-pressure 1 bar, detection by FID, carrier gas Helium, fused silica column, 50 m, OV 101, split 10 cm^3/min.

RESULTS AND DISCUSSION

The determination of the degradation products by comparison of the retention times led to the identification of different compounds using the BIS apparatus. The chromatogram is shown in Fig. 1.

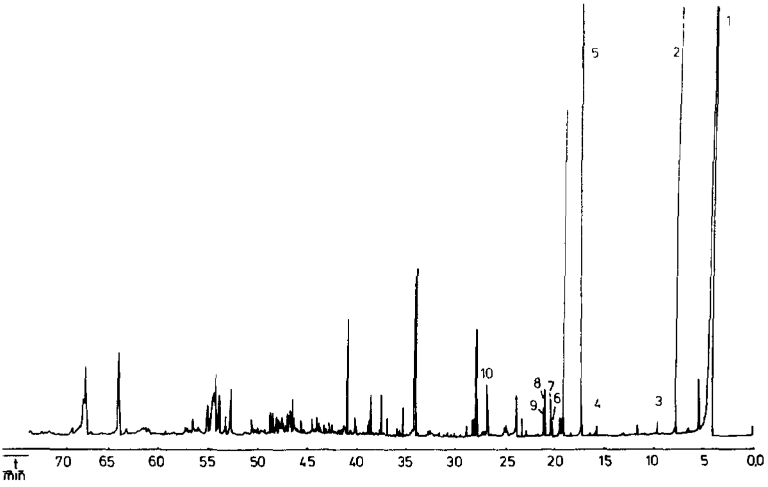

Fig. 1 Chromatogram of the combustion products (BIS apparatus) 600°C, 200 cm³/min air flow rate, XAD 4
1. carbon disulfide, 2. tetrachloroethene, 5. benzyl bromide, 6. 2-bromoethylbenzene, 7. 3- and 4-dibromobenzene, 8. ß-bromostyrene, 9. 1,2-dibromobenzene, 10. 1,3,5-tribromobenzene

The experiments according to DIN 4102 yielded the identification of the same compounds (see Fig. 2).

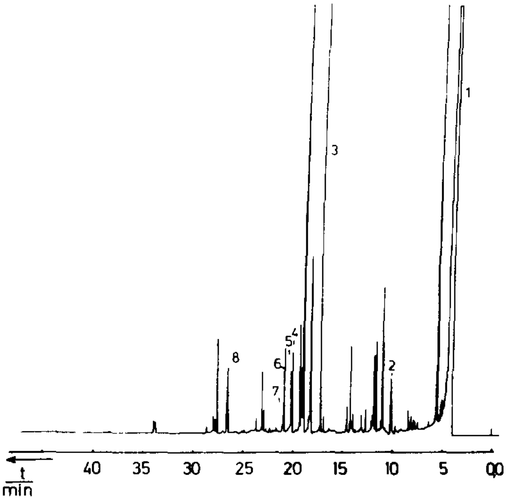

Fig. 2 Chromatogram of the decomposition products according to DIN 4102
1. CS_2, 2. tribromomethane, 3. benzyl bromide, 4. 2-bromoethylbenzene, 5. 3- and 4-dibromobenzene, 6. ß-bromostyrene, 7. 2-dibromobenzene, 8. 1,3,5-tribromobenzene

A comparison of both chromatograms shows that in applying of open flame combustion nearly the same brominated degradation products were formed as in the combustion experiments performing controlled conditions in a quartz-tube. Significant differences only appear in the range of high-boiling components. In addition to the impact resistant polystyrene the pure flame retardant decabromodiphenyloxide has been decomposed. The compounds bromobenzene, 1,2-dibromobenzene and 1,2,5-tribromobenzene could be detected.

It can be assumed that all other compounds result from reactions between degradation products of flame retardant and polystyrene, by mainly side chain bromination. The aromatic substitution of bromine is less important. Among the possible brominated derivates of styrene only bromostyrene and 2-bromoethylbenzene has been determined. No cyclic aromatic substituted derivates of styrene have been detected, as in the case of toluene, while yielded 4-bromotoluene and no 2- and 3-bromotoluene.

The quantitative determination of the decomposition products requires the estimation of the desorption- and recovery-rates. The recovery-rates have been determined for XAD 4 as the most effective adsorption reagent regarding brominated compounds.

compound	desorption rate %				recovery rate (%)
	XAD 4	XAD 2	silica	charcoal	XAD 4, N_2 400°C
Tribromomethane	92,8	90,3	82,1	81,8	88,9
Benzyl bromide	98,1	99,9	98,5	96,5	93,3
2-Bromoethylbenzene	96,6	95,5	90,3	93,5	92,9
Bromostyrene	93,8	82,6	85,7	98,1	93,6
1,3,5-Tribromobenzene	96,5	97,5	-	94,0	91,3
Brombenzene	90,0	96,9	87,1	88,9	90,6
4-Bromotoluene	90,0	97,0	87,1	73,9	87,8
3- and 4-Dibromobenzene	97,6	99,2	68,1	96,9	93,8
2-Dibromobenzene	93,8	88,9	89,0	95,7	91,1

- not measured

Table 1 Desorption and recovery rates of some brominated compounds. The relationship between the recovery-rate and the degradation products applying different temperatures and an air flowrate of 200 cm/min led to the results listed in Table 2.

compound	400°C	600°C	800°C	1000°C
	mg/g weight of the sample			
Tribromomethane	$2,45\cdot10^{-2}$	$1,04\cdot10^{-2}$	$1,71\cdot10^{-2}$	$2,12\cdot10^{-2}$
Benzylbromide	$2,93\cdot10^{-1}$	$3,27\cdot10^{-1}$	$5,60\cdot10^{-1}$	$1,23\cdot10^{-2}$
2-Bromoethylbenzene	$4,14\cdot10^{-1}$	$5,06\cdot10^{-1}$	$1,16\cdot10^{-1}$	$5,43\cdot10^{-2}$
ß-Bromostyrene	$3,75\cdot10^{-2}$	$3,22\cdot10^{-2}$	$1,68\cdot10^{-1}$	$8,52\cdot10^{-2}$
1,3,5-Tribromobenzene	$7,54\cdot10^{-2}$	$9,45\cdot10^{-2}$	$7,75\cdot10^{-2}$	$5,12\cdot10^{-2}$
Bromobenzene	$9,21\cdot10^{-2}$	$5,97\cdot10^{-1}$	2,37	1,64
4-Bromotoluene	$5,77\cdot10^{-2}$	$4,59.10^{-2}$	$1,05.10^{-1}$	$3,46\cdot10^{-2}$
3- und 4-Dibromobenzene	$4,24\cdot10^{-2}$	$5,46\cdot10^{-2}$	$1,03\cdot10^{-1}$	$5,48\cdot10^{-2}$
2-Dibromobenzene	$6,35\cdot10^{-4}$	$3,31\cdot10^{-2}$	$5,64\cdot10^{-2}$	$3,28\cdot10^{-2}$

sampleweight 40 mg

relative standard derivation 10-20 %

Table 2 Quantitativ determination of some brominated compounds.

Tests at 100-, 300-, and 400 cm^3/min air flow rate have been carried out additionally, showing no significant influence on the results in contrast to the variation of the temperature.

The side chain brominated compounds Benzyl bromide and Bromoethylbenzene are formed by radical substitution- e.g. additional reactions with a similar course of their concentration and a maximum at 600°C independant on the air flow rate.

In the case of the bromobenzene and dibromobenzene the maximum concentration has been found at 800°C, whereas tribromobenzene shows a decrease of concentration with increasing temperature.

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