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TBBPA: Quantitation of the potential emissions (blooming) from the surface of ABS (Acrylonitrile-Butadiene-Styrene)

Based on ICL internal reports: JR 2685 (2012) and JR 4204 (2017)

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Introduction:

TBBPA is a flame retardant (FR) used in Electric and Electronic Equipment, mainly as a reactive intermediate in the manufacture of printed circuit boards. Less than 20% of the total production are used as raw material for brominated oligomers and polymers (covalently bound) and as an FR additive in plastics, mainly acrylonitrile butadiene styrene (ABS), encapsulated in the polymer matrix.

A quantitative analytical method for assessing the potential blooming of brominated flame retardants (BFRs) from the surface of plastic was developed at ICL-IP. The FR-plastic compositions are mixed, extruded, injection molded and aged at 70 ºC for a period of 5 weeks. Bloomed BFRs are wiped from the surface of the plastics and then analyzed for bromides. Oxygen combustion of the BFRs in a Schöniger apparatus followed by ion chromatography of bromides is used in order to quantify the extent of blooming. Blooming data were obtained for various BFRs added to different matrices. In this study, data obtained for TBBPA in ABS are presented.

Objective:

The goal of this study is to determine the blooming potential of TBBPA from the surface of ABS during accelerated ageing at 70°C for a period of 5 weeks .

Experimental:

1. Preparation of plastic specimens with TBBPA

   The following formulation was used to prepare the plastic samples:

Polymer	TBBPA	Additives	Sum
ABS magnum 3404 ex Dow	17.1% (10% Br)	Antimony Trioxide: 4% Poly Tetra Fluro Ethylene: 0.1% Irganox B-225: 0.2%	100%

1.1 Compounding

- Ingredients were mixed and compounding was performed in a twin-screw co-rotating extruder, with typical processing conditions for ABS (200-240 °C).
- The extruded strands were pelletized and the pellets were dried in a circulating air oven at 80ºC for 3 hours.

1.2 Sample preparation (injection molding)

- Injection molding was performed by specific ABS conditions at the processing temperatures of 210-230 °C.
- Sample dimensions: 127 mm X 12.7 mm X 3.2 mm.

1.3 Number of samples

Two studies were performed. One was performed in 2012 (JR 2685) and one in 2017 (JR 4204). For each study 21 specimens were prepared for the quantitative evaluation.

2. Aging of plastic samples

The specimens were aged at 70 °C for a total of 35 days. At each time point, two specimens were analyzed for blooming. The bloomed material was wiped first from the surfaces of the plastic bars (specimens) immediately after the preparation of the specimen (time 0, first set). The remaining plastic samples were put in a stand with no contact with each other and the entire stand was placed in a circulating air oven heated to 70 ºC. The second and third sets of plastics bars were removed from the oven after 14 and 35 days, respectively, and the same wiping procedure was applied immediately after removal from the oven.

3. Blooming evaluation

The detailed procedure for the blooming evaluation is included in appendix 1.

3.1 Wiping of samples

At each time point (0, 14 and 35 days) two specimens were analyzed for blooming. The bloomed material was wiped from the surface of the plastic bar 4 times using a filter paper suitable for the Schöniger procedure. The wiping procedure was repeated for a second time using a new filter paper. As a result, two filters were obtained for each plastic bar.

3.2 *Schöniger combustion*

The Schöniger method used involves the combustion of a sample in pure oxygen, followed by the absorption of the combustion products in a solution of sodium hydroxide. The filters were put into a platinum gauze, flamed and burned in an oxygen atmosphere. The gases of the combustion were collected in 15 mL of 0.02 wt % NaOH (Merck, pellets pure) prepared using 18.2 MΩ water (Milli-Q) and allowed to settle for one hour to attain full absorption.

3.3 *Determination of bromides using Ion Chromatography*

The solutions obtained from the combustion of the filter papers in the Schöniger process were analyzed by Ion Chromatography. Dionex Ion Chromatograph ICS-2100 was used in order to measure bromide concentrations in the solutions.

4. Results

Two studies were performed. One was performed in 2012 (JR 2685) and one in 2017 (JR 4204). The results of both studies are presented. In these two studies similar results were obtained - blooming levels below LOQ of 0.5µg/cm^2 after 35 days of incubation at 70°C.

Table 1: Results – blooming of TBBPA from ABS (µg/cm^2)

Period of ageing (days)	Sample: JR 2685	Sample: JR 4204
0	< LOQ	< LOQ
14	< LOQ	< LOQ
35	< LOQ	< LOQ

5. Conclusions

After ageing at 70°C for 35 days, TBBPA blooming levels from the surface of ABS were found to be below LOQ 0.5µg/cm^2, indicating a low potential of emission.

Appendix 1:

Test Method for Determination of the Blooming of Brominated Flame Retardants from the Surface of Plastic Materials

Test Method for Determination of the Blooming of Brominated Flame Retardants from the Surface of Plastic Materials

1. Scope

1.1. The method covers the quantification of the blooming of brominated FR (BFRs) from the surface of plastic materials.

1.2. After ageing samples of plastics at 70°C for different periods of time, the bloomed FR is swept from the plastic surface by a paper filter. Then, the filter is analyzed using the Schöniger method. The Schöniger method involves the combustion of a sample in pure oxygen, followed by the absorption of the combustion products by a solution of sodium hydroxide.

1.3. The bromide concentration in the solution is measured by ion chromatography and accordingly the BFR's origin concentration is calculated.

2. Equipment

2.1. A Dionex Ion Chromatograph (IC) 2100 series equipped with a conductivity detector and an autosampler AS-DV.

2.2. An IonPac AS-9HC analytical column 250 x 0.46 mm protected by an IonPac AG-9HC guard column 50 x 0.46 mm or equivalent.

2.3. An integrator or data station.

2.4. An apparatus that consists of a heavy-walled conical, deeply lipped, cupped 500 mL flask, fitted with a ground glass stopper to which is fused a test specimen carrier consisting of a heavy-gauge platinum wire and a piece of welded platinum gauze measuring about 1.5 x 2 cm.

2.5. Hot air circulating oven.

2.6. IC plastic vials 5 ml.

2.7. Centrifuge plastic vials 50 ml.

2.8. Standard laboratory glassware.

3. Materials

3.1. Sodium Carbonate Na_2CO_3 for analysis (Merck, 1.06392).

3.2. Potassium Bromide KBr for analysis (Merck, 1.06462).

3.3. Sodium Hydroxide NaOH for analysis (Merck, 1.04905).

3.4. Deionized (DI) water 18.2 MΩ (Mili-Q).

3.5. A roll of Whatman grade No. 1 Chr paper filter (3.0 cm x 100 m) (Whatman, 3001-640).

4. Aging and sweeping procedures

4.1. See safety precautions (Section 12).

4.2. The blooming is measured immediately after the preparation of the specimen (time 0, first set) and after 14 and 35 days of aging at 70ºC. At each time point, two specimens (plastic bars) from each formulation are analyzed for blooming. Prepare 15 specimens, 5 specimens for each aging period. The procedure requires 2 of them; the 3 others are needed in case the analysis has to be repeated.

4.3. Make 15 filter paper flags as shown in Fig. 1a.

4.4. Place the plastic bar (specimen) into the folded flag as shown in Fig. 1b. Sweep 4 times the bloomed flame retardant from the surface of unheated plastic bars, immediately after the preparation of the specimen (time 0, first set).. The number of sweeps was chosen based on the blooming of FR-1210 from the surface of HDPE at 70ºC.

4.5. Fold the paper filter with the bloomed material as shown in Fig. 1c-e.

4.6. Repeat procedures 4.4 and 4.5 using a new filter. This results in two filters for each plastic bar.

4.7. Arrange the rest of the plastic bars on a stand with no contact between them and then place the stand in a circulating air oven, heated to 70ºC. The second set of plastic bars should be in the oven for 14 days and the third one is conditioned for 35 days.

4.8. Repeat 4.4 - 4.6 with the plastic bars of the second and the third sets, immediately after removal from the oven.

5. Combustion procedure

5.1. See safety precautions (Section 12)

5.2. Place the folded filter in the platinum specimen carrier. Place the absorbing liquid (15 ml of 0.02N NaOH) in the flask.

5.3. Flush the air from the flask with a stream of rapidly flowing oxygen for 1 minute.

5.4. Ignite the fuse-strip. Immediately plunge the specimen carrier into the flask, invert the flask so that the absorption solution makes a seal around the stopper and hold the stopper firmly in place as is shown in Fig. 2.

5.5. After combustion is complete, shake the flask vigorously. Add ca. 5 ml DI water to the bell-shaped flaring lip in order to seal the flask. Allow standing for 1 hour.

5.6. Carefully open the flask and rinse it with ca. 10 ml DI water.

5.7. Quantitatively transfer the solution into a 50 ml centrifuge plastic vial and then measure the sample volume.

5.8. Repeat steps 5.2-5.7 with a blank filter.

6. Recovery test

6.1 See safety precautions (Section 12).

6.2 In order to test recovery, place ca.10-20 mg FR on the center of the filter paper and repeat steps 5.2-5.8.

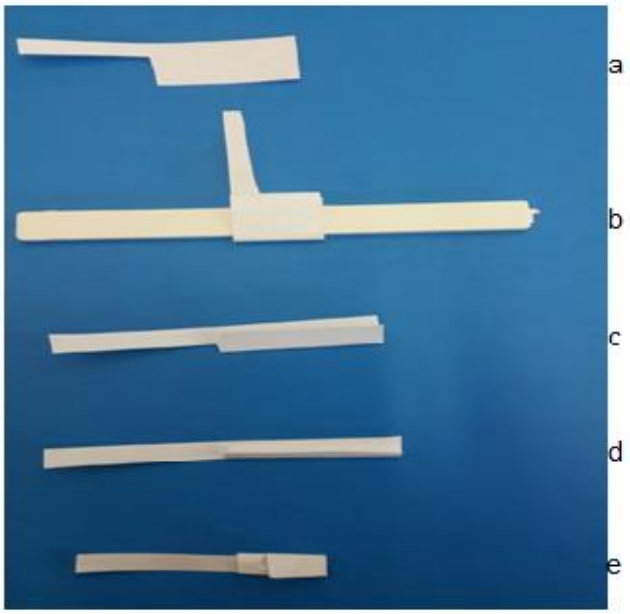

Fig.1 How to fold a filter paper

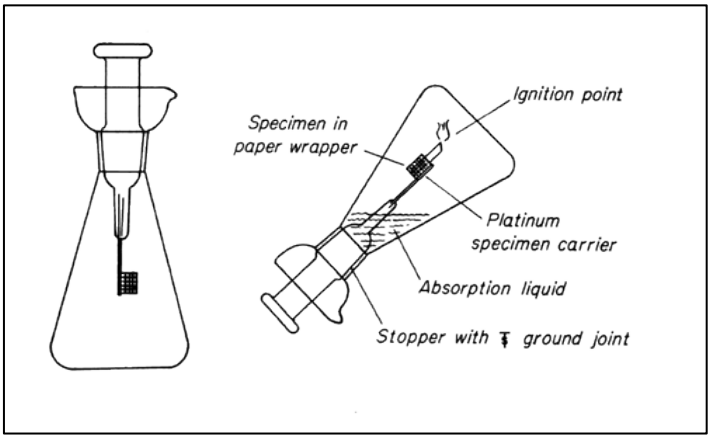

Fig. 2 Schöniger combustion apparatus

7. Preparation of standard solutions for IC calibration

7.1. See safety precautions (Section 12).

7.2. Prepare a 1000 mg/L Br^- stock solution: Weigh accurately ca. 149.7 mg KBr into a 100 ml volumetric flask. Add ca. 50 ml water in order to dissolve the KBr. Add water up to the mark.

7.3. Prepare a 100 mg/L Br^- stock solution: Transfer exactly 10 ml of the solution from step 7.2 into a 100 ml volumetric flask and fill with water up to the line.

7.4. Prepare a 2.5 mg/L Br^- stock solution: Transfer exactly 2.5 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

7.5. Prepare a 2.0 mg/L standard solution: Transfer exactly 2.0 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

7.6. Prepare a 1.5 mg/L standard solution: Transfer exactly 1.5 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

7.7. Prepare a 1.0 mg/L standard solution: Transfer exactly 1.0 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

7.8. Prepare a 0.5 mg/L standard solution: Transfer exactly 0.5 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

7.9. Prepare a 0.1 mg/L standard solution: Transfer exactly 0.1 ml of solution 7.3 into a 100 ml volumetric flask and fill with water up to the line.

8. IC analysis of solutions after combustion

8.1. Instrument conditions:

Mobile phase	9 mM Na_2CO_3
Temperature	35°C
Flow rate	1.0 ml/min
Injection volume	25 µL

8.2. IC analysis procedure:

8.2.1. Fill IC vials with 5 ml each of solutions 7.4 - 7.9 to obtain the measurements of 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L Br^- in water

8.2.2. Fill ICs vial with 5 ml each of the sample and the blank solutions.

8.2.3. Inject the standards (8.2.1).

8.2.4. Construct a calibration curve using the 6 concentrations of Br^- standards.

8.2.5. Inject the blank solution in duplicate.

8.2.6. Inject the sample solutions.

9. Retention Time in minutes:

Chloride	6.4
Nitrite	7.7
Bromide	10.1
Nitrate	11.9
Sulfate	19.9

A representative chromatogram of a sample is shown in Fig. 3:

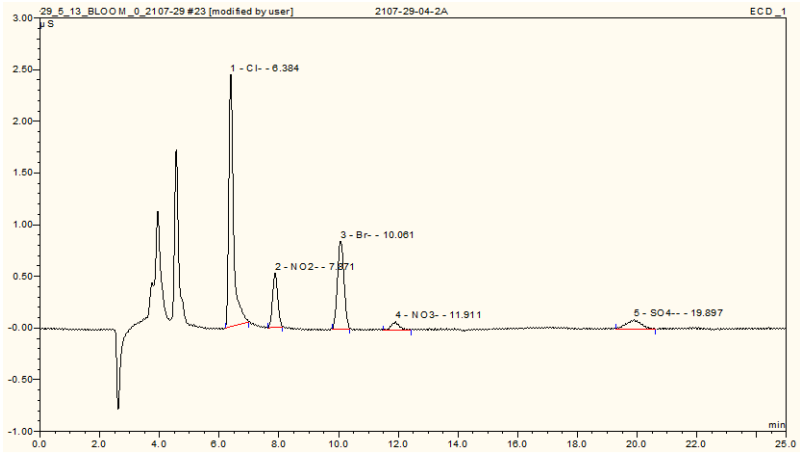

Fig. 3 A chromatogram of the solution obtained after Schöniger combustion of the BFR swept from the surface of the plastic specimen.

10. Calculations:

10.1. Concentrations of bromide in solutions are calculated using the adequate calibration curve

10.2. Blooming of bromine (BL) is calculated according to the following equations:

$$BL_i(\mu g/cm^2)=[((Csa \times Vsa \div Ssa) - B) \times 100/Rec]$$

$$BL = BL_1+BL_2$$

where:

BL_1 and BL_2 are the blooming of FR swept by the first and the second filter, µg/cm^2

Vsa is the volumes of the sample solution, [ml]

Ssa is the area of the sample surface, [cm^2]

B is the blank level, [µg/cm^2]

Rec is the recovery of combustion measured as described in section 6, [%]

11. LOQ and recovery

11.1. Limit of Quantitation (LOQ) of bromide in solution was calculated to be 0.1 µg/mL.

11.2. The obtained values of recovery for the BFRs analyzed were between 86% and 100 %.

12. Safety

12.1. Read the relevant MSDS.

12.2. All laboratory safety precautions should be maintained.

13. References

1. ASTM D573 – 04 (2015): Standard Test Method for Rubber – Deterioration in an Air Oven
2. ASTM D3045-92 (2010): Standard Practice for Heat Ageing of Plastics Without Load
3. ICL-IP Work instruction for sample preparation 07-94-04/PAL-48

4. ICL-IP Work instruction for blooming determination 101-000-7-001
5. ICL-IP Lab safety instructions 19-92-01/29
6. ISO 188:2011: Rubber, vulcanized or thermoplastic – Accelerated ageing and heat resistance tests
7. Schöniger W (1995): Eine Mikroanalytische Schnellbestimmug von Halogenen in organischen Substanzen, Mikrochemica Acta 43 (1), 123-129.

14. More information

More information on the test method can be obtained from ICL by contacting safr@icl-group.com