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A Report on
BFRs in automobiles and foam

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Introduction

Brominated flame retardants (BFRs) have been used widely in electronics, primarily in the plasticcasings and also in circuit boards. These are added to inhibit ignition and decrease the rate of combustion in the event of an accidental fire. The term brominated flame retardant (BFRs) refers to a wide range of brominated chemicals. Commonly used BFRs include polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA). Flame retardants, including some Bromine based are also used in other products like Automobile, foam, textile etc

Several BFRs, including certain PBDEs and HBCD, have known toxic properties, are highly resistant to degradation in the environment and are able to bio accumulate (build up in animals and humans). Some are now widespread environmental pollutants, with higher levels generally being found in the atmosphere and rivers close to urban and industrialised areas. They are not only found in the air and water bodies close to manufacturing facilities of plastic goods which add BFRs to their products, but are also released from products during use and have been detected in household dust leading to considerable human exposure. When these products reach their end of life, certain disposal and recycling methods release the bromine in hazardous forms like hydrogen bromide and brominated dioxins. This has been found to have an adverse impact on health including thyroid hormone disruption, permanent learning and memory impairment, behavioural changes, hearing deficits, delayed puberty onset, decreased sperm count, foetal malformations and, possibly, cancer.

At an international level, in May 2009 the Parties of the Stockholm Convention for Persistent Organic Pollutants (POPs) decided to list commercial pentaBDE and commercial octaBDE as POP substances. This listing is due to the properties of hexaBDE and heptaBDE, which are components of commercial octaBDE, and to the properties of tetraBDE and pentaBDE, which are the main components of commercial pentaBDE. In june 2017, DecaBDE was added to the Stockholm convention due to similar concerns, however an exemption was made to for the automobile industry to enable a shift to less concerning flame retardants.

Our study on BFR in WEEE plastic few years back indicated the presence of BFR in plastic and how the entire plastic chain was getting contaminated as BFR contaminated plastic was not segregated. This prompted us to explore other plastic products which may be using flame retardants especially the toxic BFRs. Two sectors, namely, automobiles and foam were identified for this. The objective was to assess if there were other sectors using the toxic BFRs.

Methodology

Sampling- The two sectors identified for this study were automobile and foam. Visits were made to waste markets in and around Delhi to collect waste plastic components from different types and brands of vehicles. Waste foams from different sources, including vehicle seats, household furniture, mattresses were also collected. Samples of recycled or rebounded foams were also included.

Total numbers of samples collected were- 30 of foam and 41 samples of automobile plastic.

Testing

Testing for BFRs in these samples was carried out in 3 phases:

Phase I: It is well known that plastic with additives like BFRs have higher density than normal plastic. Hence, float or sink test in salt water solution was carried out.

Phase II: All the foam samples and the automobile plastic samples were then put through the flame test, or Beilstein test. The Beilstein test is a simple qualitative chemical test for halides. It was developed by Friedrich Konrad Beilstein. A copper wire is cleaned and heated in a burner flame to form a coating of copper(II) oxide. It is then dipped in the sample to be tested and once again heated in a flame. A positive test is indicated by a green flame caused by the formation of a copper halide.

Phase III: Based on preliminary tests, some samples were shortlisted and were sent for lab testing to detect presence of BFRs and some heavy metals.

Results and Discussion

Preliminary Testing:

Phase I:Salt water technique: This technique based on density involved using a salt water solution and putting small pieces of plastic in a solution of salt water. The vehicular components were ground into small pieces and each of the samples was separately put in a container containing salt and water in the ratio of 1:5. The plastic pieces were allowed to sink or float. 22 samples floated, indicating low density hence unlikely to have flame retardants. 19 plastic samples sank in the salt water solution, raising a possibility that they may contain the above mentioned chemicals. ***(Table 1)***

The foam, because of its lightweight nature, was not subjected to this test.

Table 1: EOL Automobile Plastic- Phase I & II

Sample No.	EOL Automobile plastic part	Salt water separation	FR	Beilstein test
1.	Nissan Headlight	Float		
1 A	Nissan Headlight	Sink	Yes	No
2.	Maruti Swift Desire Bumper	Float		
3.	Maruti engine	Float		
4.	Maruti dashboard	Float		
5.	Maruti side glass	Float		
6.	Maruti water bottle	Float		
7.	Volkswagen engine cover	Sink	Yes	No
8.	Ford figo headlight	Sink	No	No
8 A	Ford figo headlight	Sink	Yes	No
9.	Chevrolet water bottle	Float		
10.	Maruti dashboard	Float		
11.	Maruti near about dashboard	Float		
12.	Maruti fog light	Float		
13.	Maruti engine cover	Sink	Yes	No
14.	Mahindra light	Float		

14 A	Mahindra light	Sink	Yes	No
15.	Hyundai central nosel	Sink	Yes	No
16.	Nisaan dashboard	Float		
17.	Tata indica water bottle	Float		
18.	Maruti net	Float		
19.	Honda city light	Sink	Yes	No
19 A	Honda city light	Sink	Yes	No
20.	Maruti filter	Float		
21.	Toyota oil filter	Sink	Yes	No
22.	Mahindra light	Sink	No	No
22 A	Mahindra light	Sink	Yes	No
23.	Maruti dashboard	Float		
24.	Innova bumper	Float		
25.	Tototo radiator	Sink	No	No
26.	Maruti dashboard	Float		
30.	Honda city door inside	Float		
31.	Honda city backlight	Sink	No	No
32.	Honda city bumper light grill	Float		
33.	Honda city engine hosepipe	Float		
34.	Honda city engine part	Sink	Yes	No
35.	Honda city dashboard	Float		
36.	Honda city engine part	Sink	No	No
37.	Honda city grill for fixing of bumper & dashboard	Sink	No	No
38.	Renault wheel cover	Sink	Yes	No
39.	Renault oil chamber	Sink	Yes	No

Phase II: The Beilstein test was carried out on all the foam and on the automobile plastic samples which tested positive in the salt water separation test (the ones which sank).

Only two foam samples were detected with green flame, indicating presence of halogen (***Table 2***). Out of the automobile samples,though none of the samples tested positive in the Beilstein test, certain samples indicated presence of flame retardants. (***Table 1***)

Table 2: Waste Foam- Phase II

Sample No.	Source of the Waste foam	Beilstein test
1.	Furniture seat	No
2.	Egg	No
3.	Car seat	No
4.	Automobile seat	No
5.	Bike seat	No
6.	Balero car seat	No
7.	Scooter seat	No
8.	Furniture seat	No
9.	Furniture seat	No
10.	Unknown foam	No
11.	Rebounded foam	No
12.	Rebounded foam	No
13.	Packaging foam	No
14.	Automobile seat	No
15.	Car seat	No
16.	Truck seat	No
17.	Dunlop furniture seat	No
18.	Baby pillow foam	No

19.	Mattress foam	No
20.	Rebounded foam	No
21.	Mattress	No
22.	Balero car seat	No
23.	Unknown foam	No
24.	Taxi seat	No
25.	Rebounded foam	Yes
26.	Truck seat	Yes
27.	Bike seat	No
28.	Car seat	No
29.	Car seat	No
30.	Automobile seat	No

Final Testing:

Phase III: Laboratory Testing

Based on the preliminary testing (Salt water separation and Beilstein test), a total of 12 samples were shortlisted for the laboratory testing. These included 2 samples of waste foam and 10 samples of EOL automobile plastic parts (Table 3).

Table 3: Samples sent for Lab testing

Sample No.	Automobile parts and Foam
7	Volkswagen Engine Cover
8	ford figo headlight
13	Maruti engine cover
15	Hundai central nozzle
19	Honda city light
21	Toyota Oil filter

22	Mahindra light
34	Honda city engine part
38	Renault wheel cover
39	Renault Oil chamber
25	Rebounded foam
26	Truck seat

The laboratory did the testing using EDXRF (Energy Dispersing X-Ray Flourescence) spectrometry which is used to detect and quantify the presence of elements in a substance using X-Ray fluorescence. In this method, the atoms in the sample material, which may be any solid, powder or liquid are excited by X-Rays emitted from an X-Ray tube or radioisotope. For increasing sensitivity, the primary excitation radiation can be polarized by using specific targets between the X-Ray tube and the sample (ED-P(polarization)-XRF). All element specific X-Ray fluorescence signals emitted by the atoms after the photoelectric ionization are measured simultaneously in a fixed mounted semi-conductor detector or sealed gas-proportional counter.

The radiation intensity of each element signal, which is proportional to the concentration of the element in the sample, is recalculated internally from a stored set of calibration curves and can be shown directly in concentration units.

Other tests like Ion Chromatography (IC) and ICP-OES (inductively coupled plasma optical emission spectrometry were employed to detect the level of BFR in the plastic samples.

The samples were tested for four bromine based Flame Retardants, namely, Penta BDE, Octa BDE, Deca BDE and TBBPA and none of the samples were detected with the above mentioned chemicals (Table 4).

Table 4: BFRs in select samples

Sample No.	**Sample Description**	**BFRs analysed (in ppm) (BDL: Below Detection Limit)**			
		Penta BDE	Octa BDE	Deca BDE	TBBPA
7	Volkswagen engine cover	BDL	BDL	BDL	BDL
8	Ford figo headlight	BDL	BDL	BDL	BDL
13	Maruti engine cover	BDL	BDL	BDL	BDL

15	Hyundai central nozzle	BDL	BDL	BDL	BDL
19	Honda city light	BDL	BDL	BDL	BDL
21	Toyota oil filter	BDL	BDL	BDL	BDL
22	Mahindra light	BDL	BDL	BDL	BDL
25	Rebounded foam	BDL	BDL	BDL	BDL
26	Truck seat	BDL	BDL	BDL	BDL
34	Honda city engine part	BDL	BDL	BDL	BDL
38	Renault wheel cover	BDL	BDL	BDL	BDL
39	Renault wheel cover	BDL	BDL	BDL	BDL

Further, the selected samples were also tested for presence of bromides and chlorides (using EDXRF and IC).All samples contained high levels of chloride (Table 5), with the highest level of the same recorded in Rebounded foam (8738.9). One of the automobile sample (sample no 15) was also detected with high concentration of chloride. Bromide was detected in 8 of the tested samples, the highest in the waste foam from a truck seat.

Table 5: Bromides and Chlorides

Sample No.	**Automobile part**	**Concentration of Bromide(PPM)**	**Concentration of Chloride (PPM)**
7	Volkswagen Engine Cover	0	588.2
8	Ford figo headlight	0	347
13	Maruti engine cover	27.6	556
15	Hyundai central nozzle	196.3	5349
19	Honda city light	0	621.9
21	Toyota Oil filter	0	174.3
22	Mahindra light	33.5	243.3
25	Rebounded Foam	216.2	8738.9
26	Truck seat	304.1	370.9
34	Honda city engine part	40.2	541.4

38	Renault wheel cover	8.1	185.6
39	Renault Oil chamber	291.3	402.2

The samples were also tested for some heavy metals and other elements. Though no mercury was detected in any of the 12 samples sent for testing, traces of lead were detected in 4 of the samples- all of them automobile plastics and cadmium was detected in 2 samples-again automobile plastics.

Table 6: Heavy metals (in ppm)

Sample no.	Al	Cd	Cr	Cu	Hg	Mg	P	Pb	Sb	Si	Ti	Zn
15	4750.98	5.39	9.72	105.37	ND	1919.26	227.92	19.24	22.73	70803.55	712.95	34.29
34	4550.33	ND	13.81	169.52	ND	2995.85	202.87	5.42	11.08	83772.65	640.60	34.18
39	6254.74	ND	7.97	80.70	ND	2707.64	276.13	ND	ND	87132.69	773.85	30.27
07	26654.57	2.15	42.81	637.37	ND	682.53	234.07	6.32	15.26	76421.49	1462.78	53.69
19	54.44	ND	9.19	1.61	ND	21.04	97.25	ND	8.56	1820.67	5.05	1.38
22	247.10	ND	1.31	56.54	ND	68.89	153.50	ND	7.01	1951.87	15.73	1.92
25	1139.06	ND	13.91	7.72	ND	986.85	1569.16	ND	ND	11402.23	93.44	180.06
26	244.29	ND	2.05	112.80	ND	1230.68	890.26	ND	13.47	11443.71	54.23	14.18
13	2674.69	ND	33.50	34.29	ND	1474.45	314082	2.63	26.39	72953.90	2225.77	131.55
21	6087.13	ND	11.23	139.08	ND	1211.91	15.58	ND	8.93	81744.29	1003.46	49.31
38	348.15	ND	ND	58.59	ND	16099.37	53.52	ND	13.68	72978.59	6303.41	5.65
08	23.37	ND	0.97	ND	ND	28.20	114.02	ND	3.80	3066.35	3.08	0.39

The samples were detected with high concentrations of some of the other elements like Aluminium, Magnesium, Phosphorous and Silicon. Most of the samples also showed high traces of Titanium. These could be because of following reasons (listed some of the applications).

- As a white pigment, Titanium Dioxide (TiO_2) is widely used for its efficiency in scattering visible light, and imparts whiteness, brightness, and high opacity when incorporated into a plastic formulation. Moreover, the ability of titanium dioxide to absorb UV light energy is suppose to provide significant improvement in the weatherability and durability of polymer products.

- MgO (Magnesium Oxide, Calcined Magnesite) is used in the Rubber and Plastic applications as an acid scavenger scorch retarder or curing agent. Magnesium Hydroxide is also used as flame retardant.
- Alumina TriHydrate (ATH) is also a commonly used flame retardant. Aluminium flake pigments are also commonly used in plastic.
- Silicon is also widely used in polymers for long-term elasticity, pliability and flexibility.
- Phosphorous Containing Flame Retardants, including Halogenated organophosphates are used as flame retardants.

Conclusion

The study results indicate that the 'BFRs of concern', Penta, Octa and Deca BDE and TBBPA were not detected in the samples tested and suggest that these may not have been used. Globally some of these flame retardants are being phased though there has been some exemption on use of these for legacy parts and the Indian auto industry also sought such exemption for use of restricted BFRs in vehicle production in India for next ten years. It could be helpful if the auto industry could confirm and substantiate use of such BFRs in specific plastic components of their vehicle and more detailed and exhaustive testing be carried out to confirm presence of such chemicals in plastics.Presence of bromides in some of samples could be due to use to either other bromine based flame retardants, or use of other bromine compounds. Among the halogen free flame retardants, aluminium, magnesium and phosphorus based are quite well known. Though it cannot be said conclusively (limited testing), presence of high levels of aluminium, magnesium and phosphorous in these samples might be because these alternatives are being used.Presence of metals in plastics can also suggest that many of metal compounds are being used as additives to add specific properties to plastics such as softness, colour, hardness etc. More detailed testing of various resin core can establish presence of such chemicals and the reason of their presence.