

Flame Retardants

Issues of Relevance to Environmental Regulations

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Use of flame retardants

- Because of the risk of fire to the public inherent in powered equipment, and because of various safety regulations, flame retardants of some type will always be required.
 - In fact, flame retardants actually help protect the environment due to the reduction or elimination of fire.
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Flame retardant types

- Hundreds of flame retardants, used in thousands of combinations.
 - Despite all of the press, RoHS actually only bans one flame retardant in current commercial production
 - 3 main types of commercially significant flame retardants:
 - Halogen (mostly bromine, some chlorinated FRs)
 - Phosphorus – Not regulated by RoHS
 - Mineral (ATH, $MgOH_2$) – Not Regulated by RoHS
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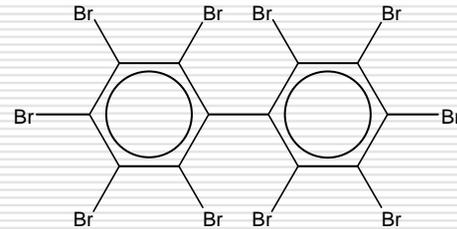
Flame retardants regulated by RoHS



□ Polybrominated biphenyl (PBB)

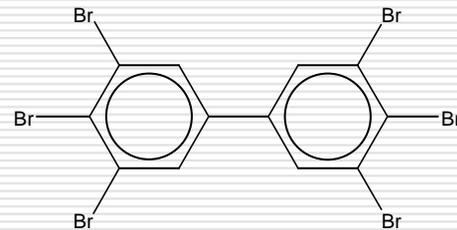
- Decabromobiphenyl manufactured by AtoChem (France) as Adine 102.

Discontinued 2000



- Hexabromobiphenyl manufactured by Michigan Chemical (US) as Firemaster BP6.

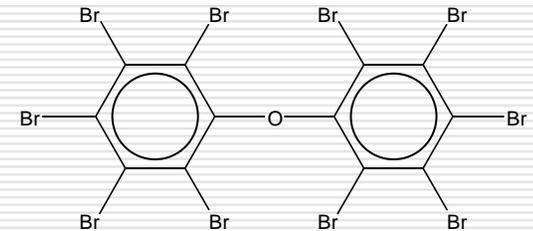
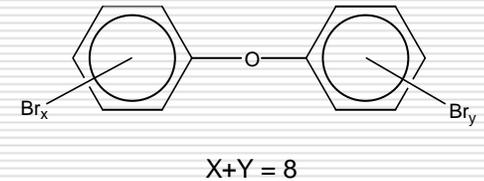
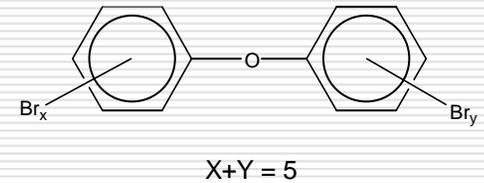
Discontinued 1973



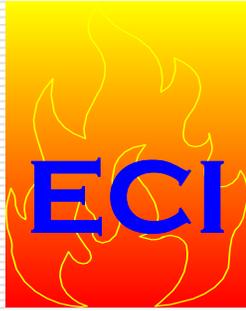
Flame retardants regulated by RoHS



- Polybrominated diphenyl (PBDE)
 - Pentabromodiphenyl Oxide
 - Manufactured as Saytex 115, DE-71, FR-1205. Discontinued 2004
 - Octabromodiphenyl Oxide
 - Manufactured as Saytex 111, DE-79, FR-1208. Discontinued 2004
 - Decabromodiphenyl Oxide
 - Manufactured as Saytex 102, DE-83, FR-1210. Still being produced, ~ 60,000 MT/yr (7-8,000 MT/yr sold in Europe)



Flame retardant content of plastics



- ❑ Flame retardants are added deliberately (at significant cost) to pass required fire tests.
 - ❑ For electronics, only 2 significant tests; UL-94 V-0 or V-2
 - ❑ To pass these tests, relatively large amounts of flame retardants must be added
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Typical flame retardant levels

Polymer	Rating	Bromine	Phosphorus	Mineral
Styrenes	V-0	10	15	25
	V-2	7-8	10	17
Polyolefins	V-0	17	8-15	25
	V-2	7-8	8-15	20
Nylons	V-0	8	7	23
	V-2	0-3	0-3	11

Note: amounts are given in elemental weight %, not ppm!



Flame retardant analysis

- ❑ Because flame retardants are present in such large quantities, trace analysis is not a concern.
 - ❑ The requirements of RoHS ($< 0.1\%$) are such that qualitative analysis may be sufficient.
 - ❑ If the flame retardant is there at all, it will be over the limit.
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Environment of analysis

- Analysis of flame retardant type and amount will either take place in a manufacturing or a recycling environment
 - Manufacturing of either the basic material (plastic) or the device
 - Recycling of WEEE
 - Of the two, recycling will be more difficult
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Plastic manufacturer

- ❑ The plastic manufacturer already knows exactly what flame retardant is being used and the quantity added.
 - ❑ The plastic manufacturer, typically a chemical company, has the equipment and expertise to perform detailed chemical analyses
 - ❑ This information is (or can be) on the C of A and/or MSDS for the raw material or finished plastic
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Device manufacturer

- ❑ For new equipment, only one flame retardant needs to be identified and quantified; decabrom. All others have been discontinued.
 - ❑ The small number of material types makes QC-type analyses feasible
 - ❑ The device manufacturer can insist on a detailed C of A from each material supplier, thereby creating a paper trail
 - ❑ If analysis must be done, only the basic material needs to be analyzed
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Recycler

- The recycler may receive old WEEE, made before the regulated FRs were discontinued:
 - Pentabrom in phenolic PCBs
 - Octabrom in enclosures
 - Decabrom in enclosures and wire
 - PBB in enclosures made in Europe
 - Materials will not be uniform and some FRs may have mutated into other forms or congeners
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Recycler

- In addition to the diversity of materials to be analyzed, the recycler must operate:
 - Quickly – because of the volume of material received. Preferably “on-line”
 - In a “less-than-clean” environment
 - Usually without sufficient technical capabilities
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Location of FR

- In determining what the recycler should analyze, it would be useful to consult with the product TCs to see what parts are required to be FR.
 - For electronics, they are:
 - Outer enclosure – probably contains PBDPE (in older units)
 - Wire & cable – may contain PBDPE
 - Connectors – almost never contain PBDPE
 - Inner fire barriers – may contain PBDPE
 - Other parts (PCBs, etc.) will not contain PBDPEs
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Proposed TC111 methods

- It has been proposed that GC/MS be used to determine FR type and level. Difficulties arise with identification of congeners.
 - Identification of PBDPE or PBB congener may not be necessary as all types are currently “regulated”. The presence of any PBDPE or PBB, in any useful amount, is prohibited.
 - A quick FTIR scan to confirm presence of these materials can be followed by a quantitative elemental analysis, if desired.
 - Or, an XRF scan to detect Br would also work since bromine is only used in significant amounts as a flame retardant in plastics.
 - However, this would not distinguish between the dozens of brominated FRs that are “legal”.
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NIST's contributions

- ❑ Prepare library of spectra for all likely plastic/FR combinations
 - ❑ Work through trade associations (APC, recyclers, etc.) to provide assistance to companies in setting up analytical labs
 - ❑ Continue to provide technical seminars like this one
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