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PIM #4: Brominated Fire Retardants: Pentabromoethylbenzene

Brominated compounds can be used to prevent the spread of fires. Tetrabromo bisphenol A, hexabromocyclododecane, decabromodiphenyl ether, octabromodiphenyl ether, and pentabromodiphenyl ether are five commonly used brominated fire retardants, BFR, (*1*). These compounds prevent the spread of fires by chemical and physical means. Chemically, BFR decompose in fires to produce bromine radicals. These radicals react with hydrocarbon vapors to produce HBr radicals. The H^+ ions and OH radicals needed to oxidize hydrocarbon vapors in a fire are destroyed by the HBr radicals to produce water vapor and more bromine radicals (*2*). Physically, BFR's prevent fires from spreading by cutting off the oxygen supply and absorbing the heat needed to produce more hydrocarbon fuel vapors. BFR tend to be denser than air, so they displace the oxygen from the reaction site (*3*). In addition to bromine radicals, diatomic bromine molecules are formed in fires (*3*). These molecules absorb heat before cleaving to form two bromine radicals (*3*). This absorption of heat prevents more hydrocarbon fuel vapors from forming (*3*). Other halogens could be used to make fire retardants, but bromine is preferred. Bromine compounds tend to decompose at temperatures consistent with fires (*3*).

Pentabromoethylbenzene, PBEB, is shown in Figure 1. It was used in the 1970's and 1980's to make the thermoset polyresins found in circuit boards, textiles, adhesives, wires, cables, and polyurethanes (*1*).

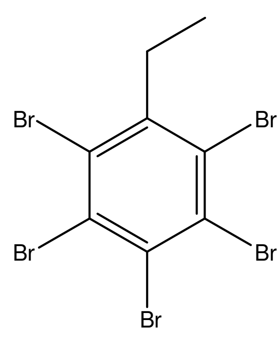

Figure 1: Pentabromoethylbenzene (CAS: 85-22-3)

In 1985, the EPA proposed a rule to test for PBEB's environmental impacts (*1*). The manufacture of PBEB drastically dropped from 45-450 tons in 1977 to 5-255 tons in 1986 (*1*). The EPA reported that no PBEB was produced in 2002 (*4*). Due to a lack of production, the EPA withdrew the rule (*1*). In 1989, the EPA put into effect a significant new use rule in regards to PBEB (*5*). Starting June 12, the EPA needed to be notified ninety days before PBEB was to be manufactured, imported, or processed (*5*). PBEB is not a major flame retardant. Rather, it is used as a synergistic co-additive in expandable graphite and inorganic flame retardants (*1*). More recently, the San Francisco Estuary Institute reported that PBEB was being considered as a replacement BFR for decabiphenylether, DBE, (*4*).

The advantages of a chemical's use can sometimes be overshadowed by its disadvantages. A chemical's adverse effects can be grouped into three categories, as follows: persistence, bioaccumulation, and toxicity (PBT). Persistence refers to a chemical's ability to resist degradation by OH radicals, UV/visible light, and other environmental factors. Relatively small OH radical rate constants, vapor pressures, and Henry's law constants (K_{AW}) are all indicative of a persistent chemical. Bioaccumulation refers to a chemical's ability to increase in concentration in an organism. A log K_{OW} greater than 5 and a relatively small water solubility are indicative of a bioaccumulative chemical. Toxicity refers to a chemical's ability to cause acute, chronic, carcinogenic, or mutagenic effects. A relatively small LD_{50} is indicative of a toxic chemical. The international scientific community has identified a list of twelve persistent organic pollutants (POP) known as the dirty dozen. Table 1 shows the PBT data for nine of the twelve POP as well the average for the group. In addition, the PBT data has been included for PBEB. The data shows that PBEB is more persistent than the dirty dozen averages in all areas. The log K_{OW} and water solubility show that PBEB is more bioaccumulative than the dirty dozen averages. The lack of LD_{50} data for PBEB does not allow for comparison.

		Persistence				Bioaccumulation		Toxicity	
Toxin	CAS #	OH rate	Kaw HLC	vapPress (mmHg)	vapPress (kPa)	Log Kow	Water Solubility (mg/L)	Oral LD50 rats (mg/kg)	
DDT (*6*)	50-29-3	3.44E-12	8.32E-06	1.6E-07	2.1E-05	6.91	0.0055	116	(*16*)
Aldrin (*7*)	309-00-2	6.46E-11	4.4E-05	1.2E-04	1.6E-02	6.50	0.017	39.0	(*17*)
Dieldrin (*8*)	60-57-1	9.2E-12	1E-05	5.89E-06	7.9E-04	5.4	0.195	38	(*18*)
Endrin (*9*)	72-20-8	9.2E-12	6.36E-06	3E-06	4.0E-04	5.20	0.25	3	(*19*)
Chlordane (*10*)	57-74-9	5.04E-12	4.86E-05	9.75E-06	1.3E-03	6.16	0.056	200	(*20*)
heptachlor (*11*)	76-44-8	6.11E-11	2.94E-04	4E-04	5.3E-02	6.10	0.18	40	(*21*)
hexachlorobenzene (*12*)	118-74-1	2.7E-14	1.7E-03	1.8E-05	2.4E-03	5.73	0.0062		
mirex (*13*)	2385-85-5	0	8.11E-04	8E-07	1.1E-04	6.89	0.085	235	(22)
toxaphene (*14*)	8001-35-2	2.25E-12	6E-06	6.69E-06	8.9E-04	5.90	0.55	50	(23)
AVERAGE Dirty Dozen		**2E-11**	**3E-04**	**6E-05**	**8E-03**	**6.09**	**0.15**	**90**	
PBEB (*15*)	85-22-3	1.15E-12	5.73E-05	4.69E-06	6.25E-04	7.48	0.0467	?????	

Table 1: PBT data for nine of the twelve dirty dozen POP and PBEB. LD_{50} data was not included for hexchlorobenzene because literature values ranged from 3.5 to 10,000 mg/kg. The LD_{50} for DDT is the average of the range for in the literature.

Chicago air samples confirmed that PBEB was persistent in the environment. A maximum concentration of 550pg/m^3 and an average concentration of 520pg/m^3 were recorded (*1*). These concentrations were relatively low in comparison to the concentrations of other polybrominateddiphenyl ethers measured, though (*1*). Herring gull eggs at the Great Lakes and Glaucous gull eggs in the Norwegian Arctic have shown that PBEB is bioaccumulative (*4*). Mutagenic tests on hamster and rat livers showed no positive results to PBEB (*24*). It seems that more research needs to be conducted to confirm the toxicity of PBEB. The EPA has taken the necessary action to limit this BFR because it believes that PBEB could be “hazardous to human health and the environment” (*5*).

Brominated fire retardants have been included in many everyday materials to limit the spread of fires. The persistence, bioaccumulation, and toxicity of these chemicals, including pentabromoethylbenze, need to be monitored, though, to prevent these chemicals from adversely affecting the environment and its organisms. The data shows that PBEB is comparable to at least nine of the twelve chemicals included on the dirty dozen list of POP. Future revisions to the list of POP should consider adding PBEB.

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