

7. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

7.1 PRODUCTION

Polybrominated Biphenyls. The commercial production of polybrominated biphenyls (PBBs) generally involves bromination of biphenyl, a process involving a much more specific reaction and that produces a smaller number of product mixtures than chlorination (Sundstrom et al. 1976a). In one process, biphenyl is brominated with 0–20% stoichiometric excess of bromine chloride (e.g., slightly more than 10 mol of bromine chloride may be reacted with 1 mol of biphenyl to obtain decabromobiphenyl) in the presence of iron or a Friedel-Crafts catalyst (e.g., aluminum chloride). In another process, biphenyl is dissolved in ethylene bromide solvent and reacted with bromine in the presence of a catalyst (either aluminum chloride or bromide) (Neufeld et al. 1977). Research quantities of PBBs can be synthesized by the diazo coupling of brominated aniline with an excess of the corresponding bromobenzene. For example, 2,3,3',4,4',5'-hexabromobiphenyl can be synthesized by the diazo coupling of 3,4,5-tribromoaniline with 1,2,3-tribromobenzene (Kubiczak et al. 1989; Robertson et al. 1983b). Methods for laboratory scale synthesis of 42 congeners of brominated biphenyls are also available (Sundstrom et al. 1976b).

The commercial production of PBBs began in 1970. Approximately 13.3 million pounds of PBBs were produced in the United States from 1970 to 1976. Only three commercial PBB products were manufactured (i.e., hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl) and these three products were based on a limited number of congeners (Hardy 2002b). Hexabromobiphenyl constituted about 11.8 million pounds (ca 88%) and octa- and decabromobiphenyl constituted \approx 1.5 million pounds together of this total (Neufeld et al. 1977). Over 98% of the hexabromobiphenyl was produced as FireMaster BP-6 and the residual as FireMaster FF-1 (Hesse and Powers 1978). Michigan Chemical Corporation, St. Louis, Michigan, the sole producer of hexabromobiphenyl in the United States, stopped producing this PBB in 1975. White Chemical Co., Bayonne, New Jersey, and Hexcel Corporation, Sayreville, New Jersey, manufactured octa- and decabromobiphenyl in the United States until 1979 (IARC 1986; Neufeld et al. 1977). Shortly after the 1973–1974 agriculture contamination episode in Michigan (see Section 5.2), PBB production in the United States was voluntarily discontinued (Hardy 2000); PBBs are no longer produced in the United States (SRI 2001). Re-initiation of manufacture of PBBs requires approval from the EPA. Production of decaPBB in Great Britain was discontinued in 1977 and highly brominated PBBs were produced in Germany until mid-1985. Until the year 2000, the only

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PBB in commercial production was decabromobiphenyl, which was manufactured by one company (Atochem) in France (Hardy 2000).

Polybrominated Diphenyl Ethers. The commercial production of PBDEs generally involves bromination of diphenyl oxide to varying degrees. The degree of bromination is controlled either through stoichiometry or through control of reaction kinetics (Pettigrew 1993). Technical decabromodiphenyl ether is manufactured by bromination of diphenyl oxide in the presence of a Friedel-Crafts catalyst (e.g., aluminum bromide) and excess bromine. Technical decabromodiphenyl ether may also be produced at atmospheric pressure by dissolving diphenyl oxide and bromine in ethylene dibromide in the presence of a Friedel-Crafts catalyst (e.g., aluminum bromide). The use of bromine in an organic solvent requires long reaction times, results in low productivity per volume, and necessitates recycling of the solvent. These limitations have led to the use of bromine as both the reactant and the solvent for this process (Dagani and Sanders 1985).

The commercial production of PBDEs began in late 1970s (WHO 1994a). As of 2003, in the United States, penta- and octabromodiphenyl ethers (pentaBDE and octaBDE) are produced by the Great Lakes Chemical Corporation in El Dorado, Arkansas (SRI 2002). According to SRI (2002), as of 2003, technical decabromodiphenyl ether (decaBDE) is produced by Albemarle Corporation in Magnolia, Arkansas. Technical PentaBDE is produced commercially in the United States as Great Lakes DE-60F, DE-61, DE-62, and DE-71. Technical octaBDE is produced commercially in the United States as DE-79. Technical decaBDE (BDE 209) is produced commercially in the United States as DE-83R and Saytex 102E. Dead Sea Bromines/Eurobrome and Tosoh are currently producing PBDEs in the Netherlands and Japan, respectively (WHO 1994a). No current estimates of PBDE production quantities were located (SRI 2002).

In 2001, the total market demand for PBDEs in the Americas was 33,100 metric tons (see Table 7-1). Technical decaBDE constituted about 24,500 metric tons (74%), while technical mixtures of octaBDEs and pentaBDEs were 1,500 and 7,100 metric tons (4 and 22 %) of this total, respectively (BSEF 2003). In 2001, the total market demand for PBDEs in the world was 67,390 metric tons. Technical decaBDE constituted about 56,100 metric tons (83%), while technical mixtures of octaBDEs and pentaBDEs were 3,790 and 7,500 metric tons (6 and 11%) of this total, respectively (BSEF 2003). About 98% of the global demand for the technical pentaBDE mixture resides in North America (Hale et al. 2003). The Great Lakes Chemical Corporation recently announced that it is voluntarily phasing out production of

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Table 7-1. Total Market Demand of PBDEs by Regions of the World in 2001^a

	Americas	Europe	Asia	Rest of world	Total
PentaBDE	7,100	150	150	100	7,500
OctaBDE	1,500	610	1,500	180	3,790
DecaBDE	24,500	7,600	23,000	1,050	56,100

Source: BSEF 2003

^aData in metric tons

decaBDE = commercial decabrominated diphenyl ether mixture; octaBDE = commercial octabrominated diphenyl ether mixture; pentaBDE = commercial pentabrominated diphenyl ether mixture

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pentaDBEs and octaDBEs by the end of 2004. Since there are no other pentaDBE manufacturers in the United States, this decision functionally eliminated U.S. production of this compound (Tullo 2003).

Table 7-2 lists the facilities in each state that manufacture or process technical decaBDE, the intended use, and the range of maximum amounts of technical decaBDE that are stored on-site. There are 141 facilities that produce or process technical decaBDE in the United States (TRI01 2003). The data from the Toxics Release Inventory (TRI) listed in Table 7-2 should be used with caution, however, since only certain types of facilities were required to report. The TRI is not an exhaustive list. Facilities are only required to report to the TRI if they manufacture or process more than 25,000 pounds of a TRI listed chemical during the year, or otherwise use more than 10,000 pounds, and have the equivalent of more than 10 full-time employees. According to the EPA, TRI data have certain limitations. TRI data reflect releases and other waste management of chemicals, and not exposures of the public to those chemicals. TRI data alone are not sufficient to determine exposure or calculate potential adverse effects on human health and the environment.

7.2 IMPORT/EXPORT

Polybrominated Biphenyls. PBBs are no longer being imported or exported except possibly in small quantities for laboratory uses. PBBs have not been imported from other countries into the United States, except in finished products (Neufeld et al. 1977). The two companies that manufactured octa- and decabromobiphenyl in the United States between 1976 (0.805 million pounds) and 1978 exported all of their products to Europe (Neufeld et al. 1977).

Polybrominated Diphenyl Ethers. No U.S. import or export data were located in the literature for PBDEs. In 2001, worldwide demands for technical penta-, octa-, and decabromodiphenyl ethers were 7,500, 3,790, and 56,100 metric tons, respectively (see Table 7-1; BSEF 2003).

7.3 USE

Polybrominated Biphenyls. PBBs are no longer used in the United States. In the past, PBBs were used as additive flame retardants to suppress or delay combustion. Additive flame retardants are added to the polymer material, but are not chemically incorporated into the polymer matrix. Because PBBs are not

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Table 7-2. Facilities that Produce, Process, or Use Decabromodiphenyl Ether

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AL	1	10,000	99,999	7, 8
AR	5	1,000	9,999,999	1, 4, 7, 8
CA	5	1,000	999,999	7, 8
CT	3	1,000	99,999	7, 8, 9, 14
FL	2	100	999,999	7
GA	5	100	99,999	2, 3, 5, 7, 8, 11, 12
IL	2	10,000	999,999	7, 8
IN	6	0	99,999	7, 8
KY	2	10,000	99,999	7
LA	1	100,000	999,999	12
MA	12	1,000	99,999	7, 8
MD	1	10,000	99,999	8
MI	5	1,000	9,999,999	7, 8
MN	3	10,000	99,999	7, 8
MO	1	1,000	9,999	7
MS	2	10,000	99,999	7, 8
NC	13	1,000	99,999	7, 8
NE	1	10,000	99,999	8
NH	1	1,000	9,999	7
NJ	4	10,000	999,999	7, 8
NY	3	10,000	99,999	6, 7, 8
OH	10	1,000	999,999	2, 3, 7, 8, 10
PA	7	1,000	9,999,999	7, 8
RI	1	1,000	9,999	7
SC	9	1,000	999,999	7, 8
TN	7	1,000	99,999	7
TX	8	1,000	99,999	1, 2, 3, 7, 8, 12
VA	5	10,000	999,999	7, 8
VT	1	10,000	99,999	2, 5, 7, 12
WA	1	10,000	99,999	8
WI	2	1,000	9,999	7, 8

Source: TRI01 2004

^aPost office state abbreviations used^bAmounts on site reported by facilities in each state^cActivities/Uses:

- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. Produce | 6. Impurity | 11. Chemical Processing Aid |
| 2. Import | 7. Reactant | 12. Manufacturing Aid |
| 3. Onsite use/processing | 8. Formulation Component | 13. Ancillary/Other Uses |
| 4. Sale/Distribution | 9. Article Component | 14. Process Impurity |
| 5. Byproduct | 10. Repackaging | |

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chemically bound to the polymer matrix, they may migrate out of the matrix with time (WHO 1994b). PBB applications were almost exclusively limited to a particular thermoplastic (acrylonitrile-butadiene-styrene, ABS) used in electronic equipment housings (Hardy 2002b). Prior to termination of production, hexabromobiphenyl was used as a fire retardant mainly in thermoplastics for constructing business machine housings and in industrial (e.g., motor housing), and electrical (e.g., radio and TV parts) products. Smaller amounts were used as a fire retardant in coating and lacquers, and in polyurethane foam for auto upholstery (Neufeld et al. 1977). PBDEs and other flame retardants replaced hexabromobiphenyl after its voluntary ban in the late 1970s. Octabromobiphenyl and decabromobiphenyl were never used in the United States, probably because the hexabromobiphenyl was less expensive and equally effective as a fire retardant (Neufeld et al. 1977).

Polybrominated Diphenyl Ethers. PBDEs are used as additive flame retardants in thermoplastics. Additive flame retardants are physically combined with the polymer material being treated rather than chemically combined (as in reactive flame retardants). This means that there is a possibility that the flame retardant may diffuse out of the treated material to some extent. PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 to 30% by weight (EU 2001). As of August 15, 2004, no products containing more than 0.1% penta- or octoBDE by mass can be sold in the European Union (EU 2003b).

The commercial pentaBDE product is used predominantly (95–98%) for flame retardant purposes as an additive in consumer products manufactured by the furniture industry (ENVIRON 2003a). It is used almost exclusively for flame retard flexible polyurethane foam (FPUF), which is used in bed mattresses and cushioning in upholstered products. The commercial pentaBDE is typically used in FPUF as an additive mixture with aromatic phosphate esters (e.g., mixture of 75% pentaBDE and 25% aromatic phosphate esters). Mattress FPUF contains approximately 2–3% flame retardant mixture and cushion FPUF contains 3–5% flame retardant mixture (ENVIRON 2003a). Scrap materials from both industries have been used as padding beneath carpets, and as a result, carpet padding likely contains 3–5% flame retardant mixture. However, not all of the FPUF found in cushion, mattress, and carpet padding products are treated with commercial pentaBDE. Approximately 7.5% of the more than 2.1 billion pounds of FPUF produced annually in the United States uses the commercial pentaBDE product as a flame retardant additive (ENVIRON 2003a). The majority of FPUF products treated with the commercial pentaBDE product are sold in California, the only state requiring by law that upholstered products achieve a prescribed level of ignition resistance (ENVIRON 2003a). A small percentage of pentaBDE is used in commercial adhesive products. Historical uses of commercial pentaBDE included coatings for specialty

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textiles, printed circuit board components, hydraulic and oilfield completion fluids, and rubber products. However, all of these uses have been discontinued in recent years. In the past, automotive and airplane seating cushions contained FPUF with commercial pentaBDE. However, this use was discontinued in the early 1990s. Prior to approximately 1990, the commercial pentaBDE product may have been used in small quantities as a flame retardant in specialty fire-resistant clothing using polyurethane treatment and in polyurethane coatings in carpets (ENVIRON 2003a). With the exception of small quantities used in rigid polyurethane elastomers for instrument casings, the commercial pentaBDE product is not used in electronic equipment. However, it is possible that electronic equipment containing pentaBDE produced in other countries (principally Asian) could find its way into the United States (EU 2001). The commercial pentaBDE product is not used in acrylonitrile-butadiene-styrene plastics or electronics equipment (ENVIRON 2003a). Other applications of pentaBDE may include use as an additive flame retardant for flexible polyester polyurethane foam, rigid polyurethane, rigid polyurethane foams, epoxies, laminates, adhesives, coatings, unsaturated polyesters, and flexible polyvinyl chloride (PVC) compounds (Great Lakes Chemical Corporation 2004a).

The commercial octaBDE is used by the plastics industry as an additive flame retardant for manufactured products. It is used almost exclusively to flame retard acrylonitrile-butadiene-styrene (ABS) terpolymers used in computer casings and monitors (ENVIRON 2003b). In the European Union, approximately 95% of the total commercial octaBDE product sold to the electronics and plastics industries is used in ABS (EU 2003a). Although data are not available in the United States, similar volumes are expected (ENVIRON 2003b). The commercial octaBDE product is used in ABS products at 12–18% weight loadings of flame retardant. OctaBDE is always used as a flame retardant in conjunction with antimony trioxide. Other minor uses for octaBDE, accounting for the remaining 5% use, include high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers (EU 2003a). Other possible applications of octaBDE include use as additive flame retardant in polycarbonate, phenol-formaldehyde resins, unsaturated polyesters (EU 2003a), nylon, thermoplastic elastomers, polyolefins, adhesives, and coatings (Great Lakes Chemical Corporation 2004b).

The commercial decaBDE product is an additive flame retardant used in a variety of polymer applications. Industry information indicates that decaBDE is used at loadings of 10–15% weight in polymers and is always used in conjunction with antimony trioxide (EU 2002). The major application for decaBDE is in high impact polystyrene (HIPS), which is used in the television industry for cabinet backs. It is also used for a large number of other polymers with end-uses in electrical and electronic equipment (e.g., computers, connectors, electrical boxes, wire and cable, etc.). Examples include polypropylene (for

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electronics), acetate copolymers (ethylene-vinyl acetate [EVA] and other copolymers for wire and cable), ethylene-propylene-diene terpolymer (EPDM) and thermoplastic elastomers (for wire and cable), and polyester resins (for electronics). Other minor uses include styrenic rubbers, polycarbonates, polyamides, and terphthalates, and small amounts are reported to be used in hot-melt adhesives (EU 2002). Other possible applications of decaBDE are as an additive flame retardant for low-density polyethylene (LDPE), unsaturated polyester, epoxy, coatings, adhesive systems, and backcoatings for fabrics (Great Lakes Chemical Corporation 2004c). Upholstered furniture in commercial settings in the United States is required to meet federal flammability standards and may utilize upholstery textiles that are flame retarded with a backcoating containing decaBDE at 5 mg/m² (BFRIP 2002).

Currently, technical decaBDE is the most widely used PBDE flame retardant worldwide, followed by technical pentaDBE. About 95% of technical pentaBDE is used in the manufacture of flexible polyurethane foam used as cushioning in upholstery. Flexible polyurethane foam is also used in foam-based laminated automotive applications, for domestic furniture, and in foam-based packaging (EU 2001). Technical octaBDE is mainly used in the preparation of acrylonitrile-butadiene-styrene terpolymer (ABS), which is used in the manufacture of computer and business equipment housings. Technical octaBDE is also used in adhesives and coatings applications (WHO 1994a). Technical decaBDE is primarily used in combination with antimony trioxide in high impact polystyrene (HIPS) applications, such as electronic enclosures (e.g., television cabinets). Other minor uses of technical decaBDE are in textile applications to flame retard upholstery fabric (e.g., polyester fiber additives and coatings for automobile fabric, tarpaulins, and tents) (WHO 1994a).

7.4 DISPOSAL

Polybrominated Biphenyls. PBBs are no longer commercially produced in the United States. In the past, an estimated 0.0046 pounds have been lost to sewers for every 1,000,000 pounds of PBBs produced at manufacturing sites (Neufeld et al. 1977). The Michigan Chemical Corporation discharged an estimated 0.25 pounds of PBBs/day to the Pine River as effluent (Di Carlo et al. 1978). The Michigan Chemical Corporation estimated that the solid waste generated during the manufacture of FireMaster BP-6 was 5% of the FireMaster BP-6 and FireMaster FF-1 produced (Di Carlo et al. 1978). Since Michigan Chemical Corporation produced ≈11.8 million pounds of FireMaster BP-6 and FireMaster FF-1 from 1970 to 1974 (Di Carlo et al. 1978), solid wastes containing a total of 590,000 pounds of PBBs would have been sent to disposal. About one-half of this waste was deposited in the Gratiot County landfill in St. Louis, Michigan (Di Carlo et al. 1978), and the rest was possibly landfilled at other locations. Contaminated animal

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carcasses, poultry and eggs, animal feed, butter, cheese, and other milk products following the Michigan agriculture contamination episode were disposed of in a sanitary landfill in Cadillac, Michigan (Dunckel 1975).

Approximately 11.8 million pounds of hexabromobiphenyl were used in commercial and consumer products in the United States, most in the production of plastic products with an estimated use life of 5–10 years (Neufeld et al. 1977). Since the cessation of production, all of these products, such as TV cabinet and business machine housings, must have been disposed of by land filling or incineration (Neufeld et al. 1977). The formation of polybrominated dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) during the incineration of plastics containing PBBs remains a distinct possibility (Luijk and Govers 1992; O'Keefe 1978).

Polybrominated Diphenyl Ethers. PBDEs are currently used as flame retardants in a wide range of consumer products (see Section 7.3). In the United States, waste disposal of PBDE-containing consumer products is described as transfers to disposal (landfill), recycling, energy recovery (incineration), or publicly owned treatment works (POTWs) (Darnerud et al. 2001). No other information was located on the past or present volumes of PBDE-containing consumer products disposed of by each method of waste transfer.

Landfill disposal of plastic consumables containing pentaBDE (e.g., polyurethane foams), octaBDE (e.g., computer monitors) and decaBDE (e.g., televisions) to landfills is likely to increase in the United States due to their limited useful lifespan. Given that all PBDEs have low water solubilities (see Table 6-6), the potential for leaching of PBDE from landfills appears to be small (EU 2002). Well-designed landfills will include measures to minimize leaching and those measures would also be effective in minimizing the leaching of any PBDE particulates present (EU 2002).

PBDEs in sewage are disposed of in publicly owned treatment works (POTWs), as indicated by analysis of sewage sludge from various countries. Tetra- and penta-BDEs have been detected in sewage sludge from POTWs in the United States with the composition of PBDEs in these biosolids closely resembling the DE-71 (i.e., pentaBDE) commercial formulation (La Guardia et al. 2000). Hale et al. (2001b) reported that the practice of land application of sewage sludges may introduce significant amounts of the pentaBDE commercial mixture into the environment, although levels have not yet been quantified.

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Incineration of waste materials containing PBDEs is thought to be a potential source of PBDFs and/or PBDDs. The formation of PBDFs/PBDDs as a result of uncontrolled landfill fires is also a possibility, although no data are available on the scale of this source. The results of pyrolysis experiments showed that PBDEs can form PBDFs and PBDDs (in much smaller quantities) under a wide range of heating conditions. If chlorine is present, mixed halogenated furans/dioxins can be formed (Oberg et al. 1987; Zier et al. 1991). Unless sufficiently high temperatures and long residence times are maintained, PBDFs/PBDDs can be generated during the incineration of products containing PBDEs. When heavy metals are present, the concentration of PBDDs and PBDFs are higher than when no metals are present. Sakai et al. (2001a) measured residues of PBDFs/PBDDs in effluents from a municipal incineration plant burning domestic waste materials. Flue gases, fly ash, and bottom ash reportedly contained PBDFs/PBDDs at concentration ranges of 0.28–3.3 ng/N m³, 0.082–13 ng/g, and 0.0058–27 ng/g, respectively. However, modern, properly operated municipal waste incineration should not emit significant quantities of PBDFs/PBDDs, regardless of the composition of municipal waste (WHO 1994a).

In the United States, waste disposal of industrial by-products containing PBDEs may also be described as transfers to disposal (landfill), recycling, energy recovery (incineration), industrial treatment works, or POTWs. The types of waste transfer may be different for manufacturing versus processing sectors, and also from within different types of processing. Waste disposal from manufacturing processes is predominantly to secure chemical landfills (e.g., those built with liners and leachate collection). For example, solid wastes (e.g., filter cakes) from the commercial production of technical octaBDE are disposed of in hazardous waste landfills as these wastes may contain toluene from the production process (EPA 1995). Plastic processors typically transfer most waste to disposal (landfill), recycling, energy recovery (incineration), and industrial treatment works, while minimal releases are to POTWs. In contrast, textile processors typically transfer most waste to POTWs. This difference in waste transfers between the plastic and textile sectors is because textile processors use water in their processing operation and other processors (e.g., processors of plastic) do not.

Recycling of plastic materials containing PBDEs is a common practice in industry. It has been demonstrated that decaBDE-containing resins can be successively recycled without generation of PBDDs/PBDFs (Brenner and Knies 1990; Donnelly et al. 1987); McAllister et al. 1990). For example, virgin high impact polystyrene (HIPS) resins (containing antimony trioxide [Sb₂O₃] and decaBDE) and repeatedly ground and injected molded (e.g., “recycled”) HIPS/decaBDE/Sb₂O₃ resins both met the requirements of the German Chemicals Banning Ordinance with respect to 2,3,7,8-substituted PBDD/PCDF congeners. These resins were at least 1 order of magnitude below the regulated limit values

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for PBDDs/PCDFs (1 ppb for the sum of four congeners, 5 ppb for the sum of all eight regulated congeners).