

Appendix A: Brominated Flame Retardants

These brief fact sheets are meant to provide the reader with a quick summary of the most common flame retardants' use, environmental behavior, contamination, human exposure, toxicity, and regulation.

PBBs

Polybrominated biphenyls

CAS numbers:

36355-01-8 (hexa-)

27858-07-7 (octa-)

13654-09-6 (deca-)

Use¹

- Commercial production began in 1970.
- Three commercial PBB products were manufactured (hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl).
- Hexabromobiphenyl constituted the majority (11.8 million pounds) of PBB produced in U.S.
- Over 98% of the hexabromobiphenyl produced as FireMaster BP-6.
- Michigan Chemical Corporation (St. Louis, Michigan) was the sole producer of hexabromobiphenyl in the U.S. and stopped production in 1975.
- White Chemical Co. (Bayonne, New Jersey) and Hexcel Corporation, (Sayreville, New Jersey) manufactured octa- and decabromobiphenyl in the U.S. until 1979.
- Used almost exclusively in thermoplastics in electronics such as radio and TV parts. Smaller amounts used as a fire retardant in coating and lacquers, and in polyurethane foam for auto upholstery.
- About 13.3 million pounds of PBBs were produced in the U.S. from 1970 to 1976.

Health Risks

- In 2013, The International Agency for Research on Cancer (IARC) upgraded the classification of PBBs from “possibly” to “probably” carcinogenic to humans based on sufficient evidence of carcinogenicity in experimental animals.²
- EPA has not classified PBBs for carcinogenicity.³
- In early 1973, PBB (sold under the trade name FireMaster) was accidentally sent to Michigan Farm Bureau Services in place of animal feed and entered the food chain through milk and other dairy products, beef products, and

contaminated swine, sheep, chickens and eggs. A long term study of humans exposed to PBB following this accident found:⁴

- Some evidence linking high PBB exposure to an increased risk of cancers of the breast and the digestive system and for lymphoma (not conclusive).
- Increased rates of neurologic, immunologic, dermatologic, and musculoskeletal effects.
- Spontaneous abortion rates elevated among second-generation women born after the Michigan PBB incident.
- PBB was transferred to children in the womb and through breast milk:⁵
 - Breastfed daughters of women with high PBB exposure started menstruating a year earlier than unexposed girls.
 - Daughters of women with high exposure to PBB were more likely to experience a miscarriage.
 - Sons of women with high exposure to PBB were more likely to report a genital or urinary condition.
- The long-term health effects of PBB exposure are being studied at the Rollins School of Public Health at Emory University. Funding is provided by the CDC, NIS, and USEPA.

Exposure

- People living in the lower peninsula of Michigan, especially near PBB contaminated areas, may still be exposed to PBBs.
- PBBs have been found at nine National Priorities List (NPL) sites.⁶

Regulation

- According to the CDC, PBB production was voluntarily discontinued in the U.S.⁷ The EPA states that PBB was banned in the U.S. in 1973.⁸

PBDEs

Polybrominated diphenyl ethers

CAS Number:

PentaBDE: 32534-81-9

OctaBDE: 32536-52-0

DecaBDE: 1163-19-5

Other Names

- PentaBDE: Penta-BDE, PeBDE, penta, PBDPO, DE-71, DE-60F, DE-61, DE-62.
- OctaBDE: Octa-BDE, OBDPE, Octa, OBDE, Octabrom, DE-79
- DecaBDE: Deca-BDE, BDE-209, DE 83R and Saytex 102E

Overview

- Production of PBDEs began in the 1970s.
- PBDEs are classes of structurally similar brominated hydrocarbons.
- Three major commercial mixtures of PBDEs have been produced, each named for the average number of bromines attached to the diphenyl ether structure
 - PentaBDE contains 50-60% of PBDE congeners with five bromines.
 - OctaBDE contains 31-35% with eight bromines.
 - DecaBDE: contains over 97% of PBDE congeners with ten bromines.

Use

PentaBDE

Pentabromodiphenyl ether

- BDE 47 is a specific PBDE congener found only in the pentaBDE commercial mixture.⁹
- Predominantly used by the furniture industry and mostly used in the U.S.
- Used almost exclusively in polyurethane foam in furniture, mattresses and automobile seats and in scrap foam materials in padding beneath carpets.
- About 7.5% of the more than 2.1 billion pounds of flexible polyurethane foam produced annually in the U.S. contained pentaBDE. The majority of this foam was sold in California.¹⁰
- Prior to U.S. phase-out, about 18 million pounds per year were produced; 95% used in the U.S.¹¹

OctaBDE

Octabromodiphenyl ether

- Primarily used as an additive in acrylonitrile-butadiene-styrene (ABS).

- Used in electronics, automobile trim, telephone handsets, and domestic appliance casings.¹²
- Prior to U.S. phase-out, about 9 million tons per year were produced; 40% used in U.S.¹³

DecaBDE

Decabromodiphenyl oxide

- Only PBDE currently in use.
- Widely used in building materials, electronics, clothes and furniture. Legislative action in some states and a voluntary phase out by industry is reducing demand.
- A mix of several different chemicals, but 97% of the mixture is BDE-209. Older decaBDE formulations, no longer commercially produced in the U.S., contained 1% octaBDE.¹⁴
- National production volume in 2012: 10-50 million pounds.¹⁵

Health Risks

- PBDEs exert a wide range of toxic effects, including thyroid function, neurotoxicity during development, and effects on the immune system. Animal Studies show endocrine disruption, neurodevelopmental and behavioral outcomes, hepatic abnormalities, and possibly cancer.¹⁶
- PBDEs with four to six bromines (PBDE congener 47 in penta-BDE) is bioavailable and has the potential to form metabolites similar to the thyroid hormone.¹⁷
- USEPA concluded BDE-209 has the potential for endocrine and neurodevelopmental effects and ““suggestive evidence of carcinogenic potential” based on animal studies.¹⁸
- Exposure to PBDE-209 during lactation and pregnancy impaired the immune function in rats raising concern about exposure for pregnant women (disruption of endocrine pathways by prenatal exposure to hormonally active environmental chemicals may affect neurodevelopment in children).¹⁹
- Prenatal and childhood PBDE exposures associated with poorer attention, fine motor coordination.²⁰ Children with the highest levels of PBDEs in their umbilical cord blood scored lowest on mental and physical development tests in a study of mothers who delivered in babies in lower Manhattan after the September 11th attack the World Trade Center.²¹
- Statistically significant associations found between PBDE flame retardant levels in the blood of California women and reduced fertility, possibly from alterations in thyroid hormone levels after exposure to the chemicals.²²

Exposure

- PBDEs are “additive” flame retardants and leach out of consumer products.

- PBDEs in indoor air and dust are about one order of magnitude higher in North America than in Europe, a result of different fire safety standards and use patterns.²³
- People living in the U.S. have levels of PBDEs up to 35 times higher than Europeans and the youngest Americans studied (aged 12–19 years) have the highest overall concentrations of PBDEs in their blood. Californians have the highest levels of PBDEs in their blood, nearly twice the national averages. PBDE levels in California homes were four to 10 times higher than other U.S. areas, likely due to California's stringent furniture flammability standards.²⁴
- Children have higher levels of PBDEs than adults and U.S. children have some of the highest levels.^{25 26}
- PBDE serum levels in U.S. toddlers in 2009 and 2012 are similar to levels reported among those over 12 years of age in the 2003–2004, despite the voluntary phase out of PentaBDE in the U.S. in 2004.²⁷
- PBDE levels in infants and children can be 3-fold higher than in adults, likely from exposure to contaminated dust.²⁸ Toddlers may get 100-fold higher exposures to PBDEs from household dust than do adult.²⁹
- Californian Mexican-American children had PBDE blood concentrations seven times higher than children living in Mexico.³⁰
- Workers with close contact with PBDE-containing electronic equipment, foam recyclers, and carpet layers have higher PBDE concentrations in their blood.^{31 32}
- The PentaBDE congener, BDE 47, is the major congener found in environmental samples and human tissue.³³

Regulation

PentaBDE and OctaBDE

- 2004: Banned in Europe, effective August 2004.
- 2004: U.S. production phased out, end of 2004.
- 2006: Use banned in many states.
- 2009: Added to Stockholm POPs treaty – May 2009.
- Products manufactured with pentaBDE or octaBDE still in use.

DecaBDE

- 2007: Washington first state to ban the manufacture, sale, and use of decaBDE in mattresses, Maine followed with similar ban.
- 2008: DecaBDE use in manufacture of electronics banned in Europe.
- 2009: Vermont and Oregon adopt bans similar to Washington State ban.
- 2009: The two U.S. producers, Albemarle Corporation and Chemtura Corporation, and the largest U.S. importer, ICL Industrial Products, Inc., announced the phase out in the U.S. for most uses by 2012 and all uses by the end of 2013.
- 2010: Maine bans decaBDE in electronics

- No federal restrictions in U.S. States considering restrictions on decaBDE include California, Connecticut, Hawaii, Illinois, Massachusetts, Michigan, Minnesota, Montana, New York, and Oregon.

TDBPP

Tris (2,3,-dibromopropyl) phosphate
“Brominated Tris”
CAS Number: 126-72-7

Registered Trade Names

- 3PBR ; Anfram 3PB; Apex 462-5; Bromkal P 67-6HP; ES 685; FireMaster LV-T 23P; FireMaster T 23; FireMaster T 23P; Flammex AP; Flammex LV-T 23P; Flammex T 23P; Fyrol HB 32; NSC 3240; Phoscon FR 150; Phoscon PE 60; Phoscon UF-S; T 23P; Tris (flame retardant); Zetofex ZN.

Use

- Commercial production of TDBPP in the U.S. began in 1959.
- Used in polyurethane and polystyrene foams, acrylic carpets and sheets, plastic resins, paints and lacquers, styrene-butadiene rubber, and latexes.
- Prior to 1977, children’s sleepwear was treated with TDBPP. Fibers treated included acetate; acetate blends; triacetate and triacetate blends; and 100% polyester.
- By 1975, U.S. production was estimated at between 9 million and 12 million pounds.³⁴
- Since 1986, there has been no evidence of production of TDBPP in the U.S.
- Many other countries have banned or restricted its use. However, numerous global suppliers are listed on the internet.³⁵

Health Risk

- Both WHO and IARC determined that TDBPP has carcinogenic effects in experimental animals. Data from epidemiological studies are not adequate to assess the relationship between human cancer and exposure to TDBPP. IARC (1999) classified TDPBB as probably carcinogenic to humans (Group 2A).
- In the 2011 NTP report on carcinogens it was concluded that it is reasonable to anticipate that TDBPP is a human carcinogen. It is also considered a carcinogen by the State of California.³⁶
- The breakdown products of TDBPP damage DNA and cause mammary tumors in animals, raising questions about whether the same effects could occur in people.³⁷
- The European Food Safety Authority determined that there is “convincing experimental evidence for genotoxicity and carcinogenicity” and therefore could be a health concern.³⁸
- Structurally similar to TDCPP and TCEP.

Exposure

- Widely used in children's sleepwear and mattresses in the past, and leached from clothing during washing.³⁹
- Studies in children demonstrated skin absorption of TDBPP from TDBPP-treated clothing.
- About 65% of the 4,500 tons of TDBPP produced annually in the U.S. in the 1970s was applied to fabrics used for children's clothing (5-10 % by weight).⁴⁰
- Recently detected in 75% of the dust of homes tested in the only study available on TDBPP in house dust.⁴¹

Regulation

- 1977: Banned from use in sleepwear by the CPSC after studies showed it was carcinogenic in animals and could be absorbed by children through the skin or by "mouthing" treated clothing.⁴²
- 1981: Reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals via dermal and oral exposure.⁴³

TBBPA

Tetrabromo-bisphenol-A
CAS Number: 79-94-7

Registered Trade Names

- Saytex CP-2000; FR-1524; BE-59

Use

- TBBPA was first used to replace PBDEs. It was introduced to the market as a substitute for OctaBDE in electrical and electronic equipment.
- It is used as a reactive and additive flame retardant in expanded polystyrene foams and adhesives and used as a reactive flame retardant in epoxy and polycarbonate resins and/or electrical and electronic equipment. Also used in plastics, paper, and textiles; as a plasticizer; in adhesives and coatings; applied to carpeting and office furniture.⁴⁴
- Currently, TBBPA is the most widely used brominated flame retardant worldwide. Primarily (about 90%) used as a reactive flame retardant in circuit boards.⁴⁵
- Global production increased 300% from 1991 to 2000, 35% from 1999 to 2000, and has continued to increase.⁴⁶
- Asia has highest demand for TBBPA (75%), due to high volume of printed wiring boards and electronics components manufactured in that region.⁴⁷
- Produced in U.S., Israel, Jordan, Japan and China and is permitted worldwide.⁴⁸
- National production volume in 2012: Over 100 million pounds.⁴⁹

Health Risks

- TBBPA is a synthesized derivative of BPA.
- Nominated by the National Institute of Environmental Health Sciences (NIEHS) for toxicological characterization based on neurodevelopmental toxicity studies and carcinogenicity based on its high production volume, widespread human exposures, and suspicion to cause thyroid toxicity and thyroid tumors.⁵⁰
- Estrogenic activity in animals; exhibits thyroid hormone activity in vivo and in vitro.⁵¹
- A recent study at the National Institute of Health found that TBBPA binds to and inhibits an enzyme that is supposed to metabolize estrogen, which can lead to a buildup of estrogen in the body.⁵²
- BPA is a metabolite of TBBPA.

Exposure

- Detected in soils, sediments, fish, marine mammals and predatory bird eggs.⁵³
- Detected in people and can cross the placenta.⁵⁴
- Detected in breast milk samples throughout the world.⁵⁵
- Levels in plasma found laboratory personnel; circuit board producers; computer technicians; smelter workers; and electronics dismantlers, with highest concentrations found in the later group.⁵⁶
- Found in air samples in rooms containing computers and electrical equipment.⁵⁷
- A 2013 Chinese study found that exposure to indoor dust inhalation and ingestion contributes more to personal exposure than diet.⁵⁸

Regulation

- No federal restrictions on use as flame retardant.
- Listed as a Persistent, Bioaccumulative and Toxic (PBT) chemical under Washington State's PBT rule (WAC 173-333-320).⁵⁹

HBCD

Hexabromocyclododecane

Also, HBCDD

CAS Number:

25637-99-4: hexabromocyclododecane

3194-55-6: 1,2,5,6,9,10-hexabromocyclododecane

Registered Trade Names

- Saytex HP-900, FR-1206, CD-75P

Use

- Used in polystyrene foams in the late 1980s, but introduced in the world market in the 1960s. Global market demand increased between 2001 and 2008.⁶⁰
- Third most widely used BFR worldwide. Primarily used in polystyrene foam insulation boards. Also used in numerous products, including upholstery furniture, seating in transportation vehicles, draperies, wall coverings, packaging material, and electronic equipment.
- Produced in the U.S., Europe, and Asia. Main share of the market volume is in Europe.
- Use has increased with the growth in polystyrene foam insulation in the 1980s.⁶¹
- Polystyrene insulation's energy-efficiency has led to wide use in building and construction, earning credits under LEED Green Building for optimizing energy performance.⁶²
- National production volume not reported. EPA began requiring companies to report all new uses of HBCD in 2012.
- About 62 million pounds of HBCD are produced annually worldwide, and 90 percent of it is added to polystyrene insulation. The demand for HBCD is increasing as a result of the phase out of Penta BDE and OctaBDE, as are the levels in the environment.⁶³

Health Effects

- Very toxic to aquatic organisms. Animal test results indicate potential reproductive, developmental and neurological effects.⁶⁴
- Oral exposure of rats resulted in changes in thyroid weight and levels of thyroid stimulating hormone. The liver is a target for HBCD toxicity.⁶⁵

Exposure

- Strong potential to bioaccumulate and biomagnify, is persistent in air, and is found in remote regions such as in the Arctic, where concentrations in the atmosphere are elevated.⁶⁶
- Concentrations in the environment have increased as a result of the phase out of Penta BDE and OctaBDE.⁶⁷
- Detected in breast milk, adipose tissue and blood, and scalp hair.⁶⁸
- Measured in air and sediment in Scandinavian countries, North America and Asia; detected in marine and arctic birds and mammals, freshwater and marine fish, aquatic invertebrates, birds and bird eggs, and one plant species.
- Biomagnifies in the food chain and is detected in lipid rich foods, including several types of fish and deli meat and at relatively high levels in peanut butter in some samples, but not in others.⁶⁹ The source of food contamination is unknown but HBCD in soil can transfer into vegetables.⁷⁰
- Body burdens of HBCD in infant mice are higher than adult levels, raising concerns about exposures in children.⁷¹
- Dietary exposure of vegetarians to HBCDs is lower than that for people consuming a mixed diet.⁷²
- Fish and meat are considered the major sources of exposure in Europe, the U.S. and China, but dust is also an important source of exposure in both adults and toddlers.⁷³
- Concentrations of HBCDs in mussels from Japan and Korea, in tilapia from Ghana, and in fresh water fish from Czech rivers indicate global environmental pollution by HBCDs.⁷⁴
- Release of HBCD during the service life of products was found to be the dominating source of HBCDs in a Swiss study. In EU releases from industrial point sources were dominate source of exposure.⁷⁵
- Exposure to HBCD is expected to increase, as insulation boards from construction activities are land-filled or incinerated.⁷⁶
- Detected in child car seats.⁷⁷

Products containing HBCD⁷⁸:

- Packaging (not food packaging)
- Furniture: upholstered
- Fabrics: interior textiles
- Mattresses (ticking)
- Car interior textiles
- Electronics
- Paints

Regulation

- 2009: Determination by the European Chemicals Agency under REACH:⁷⁹
 - HBCD is a substance of very high concern
 - Should not be used without specific authorization
 - Persistent, bioaccumulative and toxic
 - Used widely in very high volumes

- 2011: EPA initiated rulemaking to add HBCD to the Toxics Release Inventory (TRI) and assess alternatives to encourage industry to move away from using HBCD.
- 2012: EPA began requiring companies to report all new uses of HBCD, noting it “has concerns regarding the potential exposure to and human health and environmental effects of HBCD”.⁸⁰
- 2012: UN chemical experts of the Persistent Organic Pollutants (POPs) Review Committee adopted a recommendation that HBCD be eliminated from the global marketplace “to protect human health and the environment.”⁸¹

FIREMASTER 550

Proprietary mixture containing TPP, TBPH, and TBB,
CAS Number: Proprietary

Registered Trade Name

- CN-2635

Use

- Developed by Great Lakes Chemical Corporation (now Chemtura) to replace PentaBDE in polyurethane foam used in furniture, automobiles, beds, packaging foam, insulation and acoustics.⁸²
- Introduced by Chemtura in 2001 as a proprietary mixture of brominated and non-halogen flame retardants.
- Marketed as a safe substitute for PentaBDE that would not escape from treated products.⁸³ Chemtura includes Firemaster 550 in its *Greener Innovation* program.
- May be in a wide variety of polyurethane foam products and has been detected in crib mattress.⁸⁴
- Production statistics not available.

Health Risks

- An animal study associated weight gain, early puberty, and cardiovascular health effects at levels relevant to human exposure and lower than the no observable adverse effects level reported by the manufacturer.⁸⁵
- TBB detected in fat of exposed dams and offspring, indicating it is capable of crossing the placenta during pregnancy, reaching infants via breast milk, or both.⁸⁶
- TBPH is a brominated analogue of DEHP, which is associated with health impacts and is listed in California as a known carcinogen and developmental toxin.
- TPP is toxic to aquatic organisms.⁸⁷
- Carcinogenicity, reproductive and development studies have not been conducted on the brominated components of Firemaster 550.
- The material safety data sheet has little health information but notes it is toxic to aquatic organisms and should not be released to water and ingestion and inhalation may cause nervous system effects.⁸⁸

Exposure

- Detected in household dust, in the air around the Great Lakes, and in wildlife around the world.

- TBPH detected in sewage sludge from wastewater treatment plants in San Francisco Bay.⁸⁹
- Flame retardant most widely used in California.⁹⁰
- Concentrations of Firemaster 550 components were higher in dust from California homes in 2011 than 2006, consistent with its use as a PentaBDE replacement.⁹¹
- Detected in infant recliner made with dense foam in tests conducted by Washington Toxics Coalition and Safer States.⁹²

Regulation

- 2004: EPA requested health information on Firemaster 550 based on its predicted reproductive, neurological, and developmental toxicity and persistent degradation products.⁹³
- 2013: EPA announced plans to conduct risk assessments for two of the ingredients in Firemaster 550, TBB and TBPH.⁹⁴

References