United States
Environmental Protection Agency

EPA Document# 740-Q1-4002
August 2015
Office of Chemical Safety and
Pollution Prevention

TSCA Work Plan Chemical
Technical Supplement - Use and Exposure of the Brominated Phthalates Cluster (BPC) Chemicals

Brominated Phthalates Cluster
Flame Retardants

CASRN	NAME
26040-51-7	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1,2-bis(2-ethylhexyl) ester
183658-27-7	Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester
20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1-[2-(2-hydroxyethoxy)ethyl] 2-(2-hydroxypropyl) ester
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol
7415-86-3	1,2-Benzenedicarboxylic acid, 1,2-bis(2,3-dibromopropyl) ester
*	Confidential A
*	Confidential B

*** Confidential Business Information**

August 2015

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1 PRODUCTION VOLUME AND USES

This section discusses the production volume and uses of the five brominated phthalates cluster (BPC) chemicals. The 2006 Inventory Update Reporting (IUR) and 2012 Chemical Data Reporting (CDR) production volumes for these chemicals are listed in Table 1-1. Additional details on production volume for the chemicals can be found in Sections 1.1 and 1.2 for **TBPH** and **TBB**, respectively. A summary of the available production volume data for the other three chemicals in the cluster, **CASRNs 20566-35-2**, **77098-07-8**, and **7415-86-3**, is presented in Section 1.3. Additionally, export volumes of all the chemicals, as reported to CDR, are found in Section 1.1.

Use information can be found in Section 1.5 for **TBPH** and **TBB** and Section 1.6 for the other three chemicals in the cluster. Lastly, potential alternatives to **TBB/TBPH** are discussed in Section 1.7 and Section 1.8.3 presents available price information for the chemicals.

Table 1-1: Production Volumes of the Brominated Phthalates Cluster Chemicals

Cluster Member	Reporting
TBPH: CASRN 26040-51-7	2006 IUR PV ≥ 10 million pounds 2012 CDR PV = 1 to 10 million pounds Not on TRI
TBB: CASRN 183658-27-7	2006 IUR CDR National PV information for the chemical withheld. 2012 CDR National PV information for the chemical withheld. Not on TRI
TBPA-Diol: CASRN 20566-35-2	2006 IUR PV = no record 2012 CDR PV = 1 to 10 million pounds Not on TRI
TBPA-Diol (mixed esters): CASRN 77098-07-8	2006 IUR PV = 1 to 10 million pounds 2012 CDR National PV information for the chemical withheld. Not on TRI
Bromo Alkyl Ester: CASRN 7415-86-3	2006 IUR PV = no record 2012 CDR = no record Not on TRI
Confidential A	Consent Order – testing PV not triggered
Confidential B	2012 CDR National PV information for the chemical withheld.

IUR = Inventory Update Reporting; CDR = Chemical Data Reporting; PV = Production Volume; TRI = Toxic Releases Inventory

1.1 Production of TBPH (CASRN 26040-51-7)

According to the 2012 CDR database, the national production volume of **TBPH** is between one and 10 million pounds (EPA, 2012a): Table **1-2**.

Two companies are identified in the CDR database as manufacturing/importing TBPH: Teknor Apex and Unitex (now part of LanXess) (EPA, 2012a). Unitex developed bromine-chlorine phthalate esters which are part of the company's Uniplex® product line. These plasticizers are most likely combinations of TBPH and dioctyl tetrachlorophthalate oxide and are thought to have an improved flame retardancy over TBPH alone (Weil and Levchik, 2009). No trade literature has indicated the trade name of Teknor Apex's TBPH product. For more detailed information, see Table 1-2.

Chemtura's website indicates that it also produces **TBPH** (Chemtura, 2007a). **TBPH** has been identified as a component of Chemtura's flame retardant products Firemaster® 550, Firemaster® BZ-54, and Firemaster® 552 (Bearr et al., 2010; EPA, 2005; Stapleton et al., 2008a).

1.2 Production of TBB (CASRN 183658-27-7)

EPA's 2012 publicly available CDR database does not provide any data on the production volume of TBB; the national production volume for TBB is withheld and past production volumes are reported as confidential business information (CBI), as shown in

Table 1-3 (EPA, 2012a). However, Chemtura's Firemaster® 550 webpage acknowledges that TBB is the main component of its flame retardant Firemaster® 550 (Chemtura, 2013b). Evidence that **TBB** is manufactured or sold for any other purpose than for Firemaster® products was not found.

1.3 Production of CASRN 20566-35-2, 77098-07-8 and 7415-86-3

According to the 2012 CDR, the production volume of **CASRN 20566-35-2** is between 1 and 10 million pounds per year, as shown in Table 1-4 below (EPA, 2012a). Rubicon and Pelron, Inc. are identified in the CDR database as manufacturers/importers of **CASRN 20566-35-2** (EPA, 2012a).

CDR data identifies Albemarle Corporation as a manufacturer/importer of **CASRN 77098-07-8**. However, national production volumes for **CASRN 77098-07-8** are withheld from the 2012 CDR and past production volume are reported as Confidential Business Information (CBI)(EPA, 2012a), as shown below in Table 1-4.

There are no records for **CASRN 7415-86-3** in the 2012 CDR database (EPA, 2012a).

Table 1-2: 2012 CDR Production Data for TBPH (CASRN 26040-51-7)

Manufacturing Site	Domestic Manufacturing	Imported	Volume Exported (lbs)	Volume Used on the Site (lbs)[1]	Past Production Volume (2010) (import+ manufacture)	**National Production Volume** (2012)
Teknor Apex 751 Dupree Street Brownsville, TN 38012-1708	Withheld	Withheld	64,000	0	1,600,000	1 Million to 10 million lbs/year
CBI	CBI		CBI	311,796	CBI	
Unitex Chemical Corp. 520 Broome Road Greensboro, NC 27406-3799	Withheld	Withheld	781,125	0	3,483,600	

[1] The total volume (domestically manufactured and imported) of the chemical used at the reporting site. This number represents the volume of the chemical that did not leave the manufacturing site.

CBI = Confidential Business Information

Table 1-3: 2012 CDR Production Data for TBB (CASRN 183658-27-7)

Manufacturing Site	Domestic Manufacturing	Imported	Volume Exported	Volume used on the site	Past Production Volume (2010)	National Production Volume for the Chemical
CBI	CBI	No Data Reported	CBI	0	CBI	Withheld

Table 1-4: CDR Production Data for CASRNs 20566-35-2, 77098-07-8 and 7415-86-3

CASRN	Chemical Name	Manufacturing Site	Domestic Manufacturing	Imported	Volume Exported (lbs)	Volume Used on the Site (lbs)[1]	Past Production Volume (2010) (import+ manufacture)	National Production Volume (2012)
20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1-bis[(2-(2-hydroxyethoxy)ethyl] 2-(2-hydroxypropyl) ester	Rubicon, LLC 9156 Hwy 75 Geismar, LA 70734	Withheld	CBI	CBI	CBI	CBI	1 Million to 10 million lbs/year
		CBI	Withheld	Withheld	CBI	CBI	CBI	
		Pelron, Inc. 7847 West 47th St. Lyons, IL 60534	CBI	Withheld	0	CBI	19,793	
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol	Albemarle Corporation 725 Cannon Bridge Road Orangeburg, SC 29115	CBI	Withheld	CBI	CBI	CBI	Withheld
7415-86-3	1,2-Benzenedicarboxylic acid, 1,2-bis(2,3-dibromopropyl) ester	No reports	No reports	No reports	No reports	No reports	No reports	No reports

[1] The total volume (domestically manufactured and imported) of the chemical used at the reporting site. This number represents the volume of the chemical that did not leave the manufacturing site.

CBI = Confidential Business Information

1.4 Import and Export of TBPH and TBB

CDR data do not indicate whether either TBPH or TBB is imported (EPA, 2012a). The only reported product containing TBB is Firemaster® 550; when Chemtura began manufacturing Firemaster® 550, it did so at the company's El Dorado, AR plant (Tullo, 2003). According to the 2012 CDR, Teknor Apex exported 64,000 lbs of TBPH and Unitex exported 781,125 lbs (see Table 1-2).

Pelron, Inc. reported that it did not export **CASRN 20566-35-2** and withheld reports on import volumes; import and export data for Rubicon are reported as CBI (EPA, 2012a).

The CDR database does not provide any data on the import or export of **CASRN 77098-07-8**. There is no CDR record for **CASRN 7415-86-3** (EPA, 2012a).

1.5 Uses of TBPH and TBB

The 2012 CDR provide data on the industrial and consumer uses of TBPH (EPA, 2012a). These data are summarized in Table 1-5 which presents the percent of each site's production volume used in a specific industrial or commercial and consumer use category. As stated in the *Instruction for the 2012 TSCA Chemical Data Reporting* (EPA, 2012a) the percentage of production volume for the industrial sector is the amount that is attributable to the unique combination of type of processing, industrial sector and industrial function[1]. Alternatively, the percentage of production volume for consumer/commercial use is the percent of the production volume is attributed "to each specific consumer and commercial end use carried out". Note that the industrial uses and consumer uses are exclusive of one another.

Sites must report industrial processing and use information for each chemical substance manufactured (including imported) in an amount of 100,000lbs or more in the reporting year 2011. To identify industries using a chemical in the CDR data EPA used 48 Industrial Sectors (IS) Codes adapted from the European Union's (EU's) "Guidance on Information Requirements and Chemical Safety Assessment".

The CDR also collected data on consumer and commercial uses of chemicals. Commercial use is defined as the use of a chemical substance or a mixture (including as part of an article) in a commercial enterprise providing saleable goods or a service. A consumer use, on the other hand, means the use of a chemical substance or a mixture (including as part of an article) when sold to or made available to consumers for their use (EPA, 2012a) (p4-34).

Definitions of the consumer use categories are provided in Appendix B.

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[1] Note, industrial function is not displayed in the tables below.

Table 1-5: Industrial and Consumer Use Data for TBPH (CASRN 26040-51-7) from the 2012 CDR

		Industrial Use Data			Consumer Use Data		
Manufacturing Site	**Type of Processing**	**Sector (NAICS Code)**	**Industrial Use**	**Percent of Production Volume**	**Consumer Use Product Category**	**Commercial or Consumer Use**	**Percent of Production Volume**
Teknor Apex 751 Dupree Street Brownsville, TN 38012-1708	Processing-incorporation into formulation, mixture, or reaction product	Custom Compounding of Purchased Resins (325991)	Plasticizer	100	Electrical and Electronic Products	Both	100
CBI	Processing-incorporation into formulation, mixture, or reaction product	Furniture and Related Product Manufacturing (337)	Flame retardants	90	Furniture and Furnishings not covered elsewhere	Commercial	90
		Construction (23)	Flame retardants	10	Building/ Construction Materials not covered elsewhere	Commercial	10
Unitex Chemical Corp. 520 Broome Road Greensboro, NC 27406-3799	Processing-incorporation into formulation, mixture, or reaction product	Electrical Equipment, Appliance, and Component Manufacturing (335)	Plasticizer	50	Electrical and Electronic Products	Both	100
			Flame retardants	50			

1.5.1 TBPH and TBB Flame Retardants: Firemaster® Products

TBPH (CASRN 26040-51-7) and **TBB** (CASRN 183658-27-7) are two components of Chemtura's flame retardant Firemaster® 550, an additive flame retardant (Chemtura, 2013b; Stapleton et al., 2008a). Additive flame retardants are incorporated into polymers via physical mixing, and are not chemically bound to the polymer. This is contrary to reactive flame retardants which are incorporated into polymers via chemical reactions and must be incorporated at an early stage of manufacturing. Since additive flame retardants can be incorporated into the product up until the final stages of manufacturing, it is usually easier for manufacturers to use additive flame retardants than reactive flame retardants. Additionally, reactive flame retardants have a greater effect on the chemical and physical properties of the polymer into which they are incorporated than do additive flame retardants.

The ratio of **TBB** to **TBPH** in this product is 4:1 (CECBP SGP, 2008). The formulation of Firemaster® 550 comprises **TBPH**, **TBB** and two phosphates: triphenyl phosphate (**TPP**; CASRN 115-86-6) and isopropylated triphenyl phosphate (**ITPP**; CASRN 68937-41-7 (Chemtura, 2010).

Bearr, et al. (Bearr et al., 2010) states that Firemaster® BZ-54 is made up of the same **TBB-TBPH** formulation as is in Firemaster®550. The product's technical data sheet describes it as a "tetrabromophthalic anhydride derivative," with a bromine content of 54% (Chemtura, 2007b). According to one source, Firemaster® 552 also has the same components as Firemaster® 550 (EPA, 2005). Chemtura began marketing Firemaster® 552 in 2003 for use in mechanically cooled, flexible polyurethane foam and for improved processing efficiency (Plastics Additives and Compounding, 2003).

Firemaster® 550 is a liquid flame retardant for flexible polyurethane applications. Polyurethane foams are the reaction products of a polyol and an isocyanurate. Polyurethane foams can vary in stiffness and are broken into two categories – flexible and rigid: attributes that may be imparted by the use of other additives and/or mechanical processes during manufacture.

Flexible foam, the type of foam in which Firemaster®550 is typically used, is made using toluene diisocyanate (TDI) as the isocyanurate (Global Insight, 2006; Polyurethane Foam Association, 1991a). Most flexible foams have an open-cell structure, which allows for the movement of air within the foam (North Star Polymers, 2013). Flexible foam is most often used in cushioning applications (Polyurethane Foam Association, 1991b). Flexible foams can be divided into many subsets, including molded, slabstock and viscoelastic and can vary widely by density and pore size, see Appendix B for more details on these foam types.

EPA could not find any indication that **TBB/TBPH** is used in rigid foam. It replaces pentabromodiphenylether (pentaBDE), which was the most widely used flame retardant for furniture foams, that are flexible, in the United States before being phased out at the end of 2004 (Chemtura, 2007b, 2007c; Tullo, 2003; Utech, 2007). Firemaster® 550 is mainly applied to furniture containing polyurethane foam, such as couches, ottomans and chairs. According to the *2008 End-Use Market Survey on the Polyurethane Industry in the US, Canada, and Mexico*, 230 million pounds of flexible slabstock[2] was used in furniture in the United States in 2008, of which 210 million pounds was used in residential furniture and 20 million pounds was used in non-residential furniture (ACC, 2009). However, the percentage of this market that utilizes Firemaster® products is unknown. Firemaster® BZ-54 is also used for flexible polyurethane foam applications and can be blended with alkyphenyl diphenyl phosphate or used alone (Chemtura, 2007b; Weil and Levchik, 2009).

Firemaster® 550 assists furniture manufactures in meeting the State of California Department of Consumer Affairs Bureau of Home Furnishings and Thermal Insulation's Technical Bulletin 117 (California TB117), which requires that polyurethane foam in upholstered furniture sold in the State of California withstand exposure to a small open flame for 12 seconds (California Department of Consumer Affairs, 2000; Stapleton et al., 2011). Baby products that are considered juvenile furniture must also comply with California TB117 (Stapleton et al., 2011).These products include rocking chairs, portable mattresses, changing table pads, and car seats (Stapleton et al., 2011). See Section 1.8 for further discussion of TB117 and the regulatory status of flame retardants in upholstered furniture. Table 1-6 shows the concentrations of Firemaster 550® detected in furniture foam and baby products.

TBPH and **TBB** have also been detected in gymnastics equipment, including foam pit cubes, landing mats, sting mats, and vault runway carpets (Carignan et al., 2013). These chemicals may therefore possibly be found in other facilities containing foam pits or equipment. Further, Firemaster® 550 can also be used in high resiliency (HR) polyurethane foam (Chemtura, 2007b) . HR foams are flexible polyurethane foams, with applications including high-quality mattresses (Dimaflex, 2009). Different additives are used in these types of foam to increase heat transfer, bounce back time, etc. so many HR foam formulae exist and are generally proprietary formulae. Information on the specific HR foam products that Firemaster® 550 is used in could not be located.

Although flexible polyurethane foam applications include mattress foam, trade associations and personal communication with industry have indicated that it is unlikely that **TBPH** and **TBB** are used in mattresses. Mattress manufacturers use barrier technologies rather than flame-retardant-treated foam to meet fire safety standards (Polyurethane Foam Association, 1992a; Trainer, 2013). Additionally, full scale burn tests have shown that the ignitability and rate of burning can be reduced by certain foam fillers, cover materials and inter-liners and therefore flame-retardants are not needed (Randall and Lee, 2010).

PentaBDE was also known to be used in carpet, but current literature does not indicate that Firemaster® 550 is added intentionally to carpet backing. However, carpet cushions are manufactured largely from flexible polyurethane slabstock foam scraps and recycled foam (EPA, 2005) and have lifespans of five to 15 years (Luedeka, 2012). Given that carpet backing is often

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[2] The main type of polyurethane foam used in furniture.

manufactured from recycled foam scrap, carpet backing may have the same amount of **TBB/TBPH** as furniture foam if the scrap foam is from a manufacturer that uses Firemaster® 550 (Polyurethane Foam Association, 2012). The recovery of foam scraps to make carpet cushions is practiced mainly in the United States, Canada, and Mexico, and, to a lesser extent, exported by China to the United States (Luedeka, 2012). According to the Polyurethane Foam Association, in 2010, 212 million pounds of slabstock foam were produced for use in US manufactured upholstered furniture, and 50 million pounds of foam scrap were recovered for use in US manufactured carpet cushions (Luedeka, 2012).

1.5.2 TBPH (CASRN 26040-51-7): Use as a Flame Retardant Plasticizer

Typical polyvinyl chloride (PVC) emits its ester plasticizers when strongly heated, and these plasticizers are flammable. One solution to this problem is to use less flammable or nonflammable plasticizers, such as **TBPH** (CECBP SGP, 2008; Weil and Levchik, 2009). According to the CDR **TBPH** is manufactured for use as a plasticizer by two companies. These two companies state that **TBPH** ends up in consumer and commercial electrical and electronic products that are mainly made of PVC (EPA, 2012a). **TBPH** is usually used in combination with other additives, such as antimony trioxide. It can also be used with phosphate esters, zinc borates, and Ongard® 2, which is a composition from Chemtura containing magnesium oxide and zinc oxide (Weil and Levchik, 2009). Additionally, chemical manufacturers claim that **TBPH** is also used as a flame retardant additive for EPDM (ethylene propylene diene monomer (M-class) rubber), styrene-butadiene rubber (SBR), and neoprene (Chemtura, 2007a; Unitex, 2009). The use of **TBPH** in these polymers constitutes a minor portion of the total PV.

Table 1-6: Loading Levels of Firemaster® 550 for Household Items

Household Item	Firemaster® 550 Loading Amount (i.e., the amount of chemical within the foam)	Chemicals Representing Firemaster ® 550	Source
Couches	19.76 mg/g (5.18-36.85 mg/g)	TPP, TBB, TBPH	(Stapleton et al., 2012) Novel and high use flame retardants in US couches reflective of the 2005 pentaBDE phaseout.
	4.2% by weight	TBB, TBPH	(Stapleton et al., 2009) Detection of organophosphate flame retardants in furniture foam and US house dust.
Resilient foam[a]	3.3 % (3.1-3.5) or 6.0% (5.5-6.2) depending on the foam sample.	TPP, tri(propylphenyl) phosphate, octyl tetrabomobenzoate	(Cobb and Chen, 2005) Analysis of FR Chemicals Added to

Household Item	Firemaster® 550 Loading Amount (i.e., the amount of chemical within the foam)	Chemicals Representing Firemaster ® 550	Source
			Foams, Fabric, Batting, Loose Fill and Barriers.[b]
Children's products[c]	18.51 mg/g (5.85 mg/g - 42.5 mg/g)	TBB,TBPH	(Stapleton et al., 2011) Identification of flame retardants in polyurethane foam collected from baby products.

[a] The types of products that the foam studied in this report was taken from is unclear.

[b] This report is cited as the basis for the amount of Firemaster® 550 used in the CPSC risk assessment of Flame Retardant Chemicals in Upholstered Furniture Foam (Babich, 2006), which used a loading level of 6%.

[c] The products which contained TBB and TBPH included rocking chairs, portable mattress, changing table pad and car seat. Products which were examined that did not contain TBB and TBPH include sleep positioners, nursing pillow, baby carrier, high chair, infant bath mat, baby walkers, stroller, bath toy, car seat pillow, Bumbo chair, nap mat, and toilet seat**.**

1.6 Uses of CASRN 20566-35-2, 77098-07-8 and 7415-86-3

The 2012 CDR data for industrial and consumer uses of **CASRN 20566-35-2** and **CASRN 77098-07-8** are summarized in Table 1-7 below. **CASRN 7415-86-3** was identified as potentially used as a flame retardant in polyester fibers [textiles; (WHO, 1997)]. However, there are no records for **CASRN 7415-86-3** in the CDR database (EPA, 2012a).

1.6.1 CASRNs 20566-35-2, 77098-07-8 and 7415-86-3: Flame Retardants

CASRN 20566-35-2 is listed as an ingredient in Elé Corporation's PEL-RON 9457-LE, a flame retardant in polyurethane (Ele Corporation, 2013). The type of polyurethane this flame retardant can be used in was not specified by Elé Corporation's website.

CASRN 77098-07-8 can be used as a reactive flame retardant in rigid polyurethane foam, as well as in polyurethane reaction injection molding, elastomers, coatings, adhesives, and fibers applications (GLCC, 2010). These foams, elastomers, and coatings are often used in building insulation and specialty coatings (Albemarle - GLCC, 2004). **CASRN 77098-07-8** flame retardants are applied to polyurethane in concentrations of 5-15% (Albemarle - GLCC, 2004). Great Lakes Chemical Corporation lists **CASRN 77098-07-8** as an ingredient in its PHT4-Diol™ flame retardant. In addition, Albemarle manufactures a similar product, Saytex® RB-79, which is also used in rigid polyurethane foams (Weil and Levchik, 2009).

EPA could not located evidence of where **CASRN 7415-86-3** may be used as a flame retardant.

1.7 Chemical Alternatives to Firemaster 550®

EPA's Design for the Environment program recently updated the Alternative Assessment for flame retardants in furniture foam (To be published). In this analysis they identified nineteen flame retardants which may be used any upholstered consumer product containing flexible polyurethane foam. Information on some of the alternative is listed below. For a list of flame retardants which may be used in flexible polyurethane foam in upholstered consumer products see Appendix A.

- **Tris (1,3-dischloroisopropyl) phosphate (TDCPP)**, known to be a major FR in FPUF and produced in a volume between 10 and 50 million pounds per year, was listed by California as a Proposition 65 chemical in late 2011 for concerns about carcinogenicity (EPA, 2012a; OEHHA, 2011). The Proposition 65 listing is expected to have an impact on the marketplace, even though TDCPP need not be labeled outside of California. TDCPP was identified by Stapleton et al (2012) in more than half of samples tested since 2005. In 2012, the major US manufacturer of TDCPP announced a voluntary phase-out of TDCPP production by 2015 (Betts, 2013).

- There has been recent opposition from consumer and environmental groups to the use of **halogenated FRs**, and this opposition may shape the market suitability of these FRs, regardless of hazard data. For example, the New York State Assembly passed a bill prohibiting the use of halogenated FRs in furniture; the bill has not passed the upper house of the Legislature as of this writing, and appears stalled (NY State Assembly 2013). Some shift away from halogenated FRs appears to have already occurred. While the 2005 FFRP report assessed a number of brominated FRs, the two brominated components of Firemaster 550 (2-ethylhexyl-2,3,4,5-tetrabromobenzoate, or TBB, and bis (2-ethylhexyl)-2,3,4,5-tetrabromophthalate, or TBPH) are the only brominated FRs included in the current update report (although several chlorinated FRs were assessed).

- Although **TCEP** was previously not thought to be used in foam, it has been identified in upholstered FPUF products (Stapleton et al., 2011). TCEP is a TSCA work plan chemical for 2013-14, so the DfE AA process is a useful contribution to other EPA activities on this compound (EPA, 2013).

Table 1-7: Industrial and Consumer Use Data for CASRN 20566-35-2, 77098-07-8 and 7415-86-3

				Industrial Use Data			Consumer Use Data		
CASRN	**Chemical Name**	**Manufacturing Site**	**Type of Processing**	**Sector**	**Industrial Use**	**Percent of Production Volume**	**Consumer Use Product Category**	**Commercial or Consumer Use**	**Percent of Production Volume**
20566-35-2	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1-[2-(2-hydroxyethoxy) ethyl] 2-(2-hydroxypropyl) ester	Rubicon, LLC 9156 Hwy 75 Geismar, LA 70734	N/A	N/A	N/A	N/A	Building/ Construction materials not covered elsewhere	Commercial	100
		Pelron, Inc. 7847 West 47th St. Lyons, IL 60534	N/A	N/A	N/A	N/A	Withheld	Withheld	Withheld
		CBI	N/A	N/A	N/A	N/A	Withheld	Withheld	Withheld
77098-07-8	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, mixed esters with diethylene glycol and propylene glycol	Albemarle Corporation 725 Cannon Bridge Road Orangeburg, SC 29115	Processing-incorporation into formulation, mixture, or reaction product	Construction	Flame retardants	100	Building/ Construction materials not covered elsewhere	Both	100
7415-86-3	1,2-Benzenedicarboxylic acid, 1,2-bis(2,3-dibromopropyl) ester	No Reports	No Reports	No Reports	No Reports	No Reports	No Reports	No Reports	No Reports

N/A = Not Applicable

- **tris(2-Carboxyethyl)phosphine (TCPP) and melamine** are the major FRs used in the United Kingdom to meet the stringent "Crib 5" standard, but use of this mixture is not known to be common in the United States. However, since TCPP was identified in FPUF products by Stapleton et al (2011), it is included in this report.

- The larger molecule "**V6**" (CAS 38051-10-4) has been used in automobile foam, due to its lower volatility, but was also identified by Stapleton et al (2011) in baby products. V6 is a dimer of TCEP, and contains TCEP as an impurity.

There is a lack of reactive or polymeric flame retardants for flexible polyurethane foam. Reactive/polymeric products would be expected to have lower volatility, lower mobility out of the product, and greatly reduced bioavailability; concerns about impurities and breakdown products prevent making a general conclusion about hazard. DfE's alternatives assessment for decaBDE included a number of polymeric flame retardants. In the flexible polyurethane foam market, however, reactive/polymeric flame retardants present technical challenges, in part because of the extremely small nozzle size typically used in mixing the polyols, and more generally because of their limited viscosity and flexibility.

1.8 Regulatory Status and Future Trends

In order to understand the potential future trends of flame retardant chemicals it is important to understand the standards and regulations which require and or ban their use.

1.8.1 Standards Relating to Polyurethane Foam

California Technical Bulletin (TB) 117 has been an influential standard driving the use of flame retardants in furniture manufacturing, as no federal performance standard currently exists to regulate the flammability of upholstered furniture (CPSC, 2013). California remains the only state to have passed a performance standard; however, because manufacturers prefer to produce one product for the entire U market, TB117 subsequently became the *de facto* standard for upholstered furniture manufacturers nationwide. TB117 required residential upholstered furniture foam to withstand an "open flame test," in which an open flame is applied to uncovered foam for 12 seconds. Although the standard did not explicitly require the use of flame retardants, the most cost effective way to meet this standard was often to add a flame retardant to the furniture foam. However, it has been argued that applying an open flame to an uncovered piece of polyurethane foam does not accurately measure the fire resistance of furniture (DiGangi et al., 2010). This is because the open flame standard only tests uncovered foam and does not account for the ability of many fabrics covering the foam to withstand the flame. A flame large enough to ignite the furniture fabric and reach the foam beneath will most likely be larger than the flame used in the open flame test, which in effect renders the open flame standard ineffective (CPSC, 2012).

Given this information, California recently revised the open flame requirement for upholstered furniture manufactured and sold in the state. The new regulation, TB117-2013, only requires residential furniture to pass a “smolder test.” In this test, a small assembly of cover fabric, barrier materials, and filling materials must withstand a smoldering cigarette (Cal/DCA 2013). It is anticipated that most fabrics will be able to meet this standard without the addition of any flame retardants.

However, TB 117-2013 only addresses the flammability of residential furniture. California TB133, which pertains to furniture manufactured and sold for use in public buildings (e.g. dormitories, hospitals), is a more rigorous test that requires assembled furniture to withstand a large open flame, provided by a gas burner, for 80 seconds (Polyurethane Foam Association, 1992b). Other states, including Massachusetts, Illinois, Minnesota, North Carolina, and Ohio, have adopted TB133 as the standard for their own public furniture flammability regulations (see Table 1-8). Given the large open flame standard, it is likely that manufacturers are adding flame retardants to their products to meet the test requirements.

In addition to TB117, the Upholstered Furniture Action Council (UFAC), US National Fire Protection Association (NFPA), and ASTM International have all developed voluntary smolder test standards. Although UFAC states that 90% of industry has adopted its standard, this is likely due to manufacturers complying with TB117, which exceeds the requirements of the voluntary standards. Since 2008, the Consumer Product Safety Commission (CPSC) has also been developing a federal furniture flammability requirement (CPSC, 2008). Although the initial 2008 standard proposes a smolder test applied to cover materials, in March 2013 CPSC posted a notice in the Federal Register requesting comments on introducing an open flame standard (CPSC, 2013). See Table 1-8 for a summary of approved and effective upholstered furniture flammability performance standards.

It is unclear how the introduction of TB 117-2013 will affect the furniture and flame retardant industries. With the growing health and environmental concerns about flame retardants, manufacturers may choose to introduce furniture without flame retardants to this “green” market; however, it is uncertain how wide-spread this market will be. Whether manufacturers will switch to foams that are not treated with flame retardants will also depend on state and local regulations. Many states and local entities reference or model their standards after TB117. For example, in Massachusetts and Illinois, furniture in public buildings equipped with a sprinkler system must meet TB117 standards (State of Illinois, No date; State of Massachusetts, 1994). Thus, the update to TB117 will not have an effect in these locations unless they revise their own regulations. If they do choose to update their standards to match TB117-2013, it may be a number of years before any legislation is passed.

New York and New Jersey are also proposing their own flammability performance standards for residential furniture (New Jersey Assembly, 2012; New York Senate, 2013). Because both bills currently include an open flame test, if either passes it is possible that the open flame will once again become the *de facto* nationwide standard. Manufacturers will also need to consider a possible CPSC national standard. Whether a federal regulation is passed and whether that standard will be based on a smolder or open flame test will largely influence the future use of flame retardants in residential furniture. In addition, the strict standards of TB133 and similar public fire codes will necessitate the continued use of flame retardants in public occupancy furniture. Furthermore, furniture manufacturers may choose to continue using flame retardants to protect themselves against possible liability if a fire were to spread due to furniture ignitability.

In addition to the standards which have been approved several states are currently discussing bills to enact flammability standards and ban specific flame retardants. Both New Jersey and New York have proposed residential flammability performance standard bills (see Table 1-9). A number of other states also have proposed or enacted legislation prohibiting commercial flame retardants such as TCEP, TDCPP and TCPP in children's products and residential upholstered furniture. Because TBB and TBPH are not currently prohibited under any state or national law, the banning of TCEP, TDCPP, and TCPP in children's products and upholstered furniture may result in the substitution of these chemicals for Firemaster® 550.

1.8.2 Electrical and Electronic Equipment Standards

The predominant standard driving flame retardant use in electronic products is Underwriters Laboratories (UL) 94. UL 94 is a voluntary flammability standard which requires plastic materials in devices and appliances to withstand a small scale ignition source (UL, 2013). It determines the material's tendency to either extinguish or spread the flame once it has been ignited. Components are classified based on how long they continue to burn after ignition. V-0 classifications are the most rigorous, requiring electrical components to self-extinguish within 10 seconds of ignition (UL IDES, No Date). V-1 and V-2 classifications each allow the test specimen to burn up to 30 seconds after ignition (UL IDES, No Date). While the standard does not require the use of flame retardants, they are often used in electronic components to meet the high levels of flame resistance specified by the more stringent classifications such as V-0 ratings (Pure Strategies Inc and Lowell Center for Sustainable Production, 2005).

For polymeric materials used in electrical equipment the relevant standard is UL 746C and for printed wiring boards the relevant standard is UL 796. These product standards are based on the requirements of UL 94 (ACC, 2014; UL, 2004, 2013b). See Table 1-10 for further details.

International regulations restricting or requiring reporting of the use of certain flame retardant chemicals include the European Union's Restriction of Hazardous Substance (RoHS) in electrical and electronic equipment and Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH). The RoHS directive requires that polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) chemicals be substituted by safer alternatives. RoHS does not require the substitution of any of the workgroup chemicals (EC, 2014).

There are currently no state bans on any of the workgroup chemicals for use in electrical and electronic equipment.

Table 1-8: Approved and Effective Upholstered Furniture Flammability Performance Standards

Standard	Test Requirement	Notes	Sources
Residential			
CA TB117	Open flame test (12 sec) applied to uncovered foam		Cal/DCA (2000)
CA TB117-2013	Smolder test applied to miniature assembly of cover fabric, barrier materials, and filling materials. Fabric materials failing the smolder test can still be used if a fire barrier layer is added	Approved and will become effective on 1/1/2014 compliance mandatory by 1/1/2015. Uncertain what effect new rule will have on FR use in foam. Whether manufacturers will switch to non-FR foam will also depend on state and local regulations and/or possible CPSC standard.	Cal/DCA (2013)
US National Fire Protection Association (NFPA) 260 and 261	Smolder test applied to furniture mock-up	Similar to ASTM 1353 and UFAC standard. Due to changes to TB117, NFPA held an August 2013 meeting reviewed a request to consider establishing an open flame standard for upholstered furniture. NFPA is currently accepting public comments on the need for a new standard, available resources, and organizations involved in furniture flame retardant standards. Estimated to take 2-3 years to develop. This would be a voluntary standard.	Durso (2013) NFPA (2013)
ASTM E1352	Smolder test applied to furniture assemblies	Similar to NFPA 260 and UFAC standard	ASTM International (2008)
Consumer Product Safety Commission (CPSC)	(1) Smolder test applied to cover materials; or (2) Smolder and open flame test for fire barriers (inter-liners)	First proposed in 2008. In March 2013, CPSC requested comments on a large open flame standard which would be more stringent than the 2008 proposal. Held an April 2013 meeting barrier and other safety technologies.	CPSC (2008) CPSC (2013)
Upholstered Furniture Action Council (UFAC)	Smolder test	Voluntary industry standard. 73 manufacturers have taken UFAC pledge to adhere to smolder testing and has generally been adopted across the country (~90% of industry), despite being a voluntary program. However, this is most likely due to manufacturers adhering to the more rigorous CA TB 117 standard.	Durso (2013) (US Senate, 2012)
British Standard BS5852	Smolder and open flame test	Typically met with combination of additive flame retardants	UK Parliament (1998)

Standard	Test Requirement	Notes	Sources
Public Occupancy			
CA TB133	Large open flame (80 sec) applied to assembled piece of furniture		PFA (1992b)
ASTM E1537	Open flame test	Voluntary standard	ASTM International (2013)
Massachusetts State	Furniture must meet CA TB133 or ASTM 1537. If occupancy equipped with automatic sprinklers, furniture can meet CA TB133 or TB117	Only applies to furniture used in public buildings	Massachusetts Board of Fire Prevention Regulations (1994)
Boston Fire Code	Furniture must meet CA TB133 or ASTM E1537	Only applies to public occupancy furniture sold in the city of Boston	Boston Fire Department (1995)
Illinois State	Furniture must meet CA TB133 (or CA TB117 if protected by an automatic sprinkler system)		Illinois Administrative Code, Title 41 pt. 300.20
Minnesota State	Furniture must meet CA TB133; upholstery fabric and filling must meet CA TB117	Only applies to furniture used in public buildings	Minnesota State Fire Marshal (2006)
North Carolina State	Furniture must meet CA TB133 or ASTM E1537 heat release rate standards. Furniture must resist ignition by cigarettes following NFPA 260 or 261	Only applies to furniture used in public buildings	North Carolina State Fire Marshal’s Association (2012)
Ohio State	Furniture must meet CA TB133 or ASTM E1537 heat release rate standards. Must resist ignition by cigarettes following NFPA 260 or 261	Only applies to furniture used in public buildings	Ohio Administrative Code, 1301:7-7-08

Table 1-9: Proposed Flammability Performance Standards

State	Bill	Regulation	Status	Notes	Source
New Jersey	A2823	Residential and public upholstered furniture required to meet the combustibility requirements specified in CA TB116, 117, and 133	Introduced 5/10/2012. Referred to Assembly Housing and Local Government Committee		New Jersey Assembly 2823 (2012)
New York	A06557/S04780	Prohibits sale of residential upholstered furniture containing intentionally-added halogenated chemical flame retardants. Beginning 12/1/16, furniture sold in NY must meet open flame standard	Passed in Assembly, proposed in Senate, and reported to finance committee 5/30/2013	Would take effect 7/1/2014	New York Senate Bill 4780 (2013)
Texas	HB2682	Upholstered furniture sold in the state to be made with filling that is burn resistant to an open flame	Business & Industry committee report sent to Calendars Committee 4/15/2011. Never voted on by House or Senate.	The House Calendars Committee holds the authority to place a bill on the House agenda for a vote. HB2682 was reported favorably by the Business & Industry Committee and the bill has not been explicitly rejected. However, because HB2682 was sent to Calendars over 2 years ago, it appears unlikely that it will be scheduled for a vote.	Texas House Bill 2682 (2011)

Table 1-10: Flammability Standards for Electronic Products

Standard	Test Requirement	Notes	Sources
UL 94	V-0 rating: Vertical test. Flame is applied to specimen for 10 seconds. Specimen cannot burn for more than 10 seconds after ignition	Voluntary standard. Small scale ignition resistance test (short circuit or candle) for electronic enclosures.	UL, 2013a; UL IDES, No Date
	V-1 rating: Flame is applied to specimen for 10 seconds. Vertical test. Specimen cannot burn for more than 30 seconds after ignition and must *not* drip flaming particles		
	V-2 rating: Flame is applied to specimen for 10 seconds. Vertical test. Specimen cannot burn for more than 30 seconds after ignition but *can* drip flaming particles		
	HB rating: Horizontal test. Flame is applied to specimen for 30 seconds, and specimen must stop burning before flame reaches 4 inch mark and a burning rate less than 1.5 in./min.		
UL 746C	References UL 94. polymeric material in electronics and electrical parts	Voluntary standard	UL, 2004
UL 796	Standard for printed wiring boards. References UL 94	Voluntary Standard	UL, 2013b

1.8.3 Price

Chemtura has increased the price of Firemaster® 550 several times since the product's introduction (Amdursky, 2008; ICB, 2005). For instance, the company increased the price of Firemaster® 550, 552, 500, and 602 by $0.30/lb, effective August 18th, 2008, citing the rising cost of elemental phosphorous and other raw materials (Amdursky, 2008). It also announced a price increase of all its bromine based products by up to 25% on March 29, 2010, due to the rising cost of bromine (Yacomeni, 2010). Data on the base price of TBB/TBPH could not be located.

Chemtura introduced Firemaster® 800 in 2007, which is a modified version of Firemaster® 550. The company developed the product because Firemaster® 550 was too expensive for the Chinese market. Firemaster® 800 is lower in dosage than Firemaster ® 550, requiring less product (Hilgers, 2007). However, Firemaster 800 is not listed on Chemtura's website and we cannot confirm if it is being produced at this time.

Data on the prices for the other three chemicals in the cluster could not be located.

2 ENVIRONMENTAL EXPOSURE

There has been a rapid increase in the number of monitoring studies that have reported the occurrence of **TBPH** and **TBB** at significant levels in various media (See Table 3-1 and Table 3-2). The additive flame retardant use of **TBPH** and **TBB** as an alternative to polybrominated diphenyl ethers within a variety of products has expanded over time. Detection of **TBPH/TBB** in sludge, sediment and indoor dust indicate a potential for exposures to the environment. Detection of **TBPH** in biota and environmental media indicates exposures have occurred and that global transport is occurring as well. A significant mass of these chemicals are added to many products we use every day such as couches, chairs and other upholstered furniture, etc. Additional data are needed to understand how, at what rate, and in what form **TBPH** and **TBB** migrate out of many types of products. Source characterization, migration rates, and monitoring data are needed to demonstrate how the use of **TBPH**, **TBB** and Confidential A in certain products may result in subsequent exposure through migration of these chemicals into indoor and outdoor environments. More information on these data needs can be found in Section 2.1.

TBPH, TBB and CASRN 7415-86-3 are additive flame retardants while the other cluster members are reactive flame retardants. The nature of Confidential A and Confidential B cannot be disclosed.

Additive flame retardants are incorporated and dispersed throughout a product, but are not chemically bound to it. Additive flame retardants are more likely than reactive flame retardants to migrate from products or articles. Emissions from a single product or article may be small. However, combined emissions from all sources within various indoor microenvironments, residences, schools, public and commercial buildings, cars, trains, airplanes, may be significant. These chemicals may be released into dust and then into household waste water. It is predicted that once in the waste water treatment plant effluent, **TBPH** and **TBB** will partition to sludge. If the sludge is then used as biomass on farm lands and forests then releases would be widespread.

The **TBPA-diols** are reactive chemicals. Because these chemicals are chemically bound to the polymer, it is far less likely they will migrate from products or articles unless there is excess chemical present due to an incomplete polymerization reaction. The reactive members of the BPC, including the primary degradation product tetrabromophthalic acid, have not been reported in literature as being present in environmental or biological media.

2.1 Monitoring Data Summary

Levels of **TBPH** and **TBB** in the environment and biota are comparable to each other. Occurrence of both chemicals follow a similar pattern with higher levels found in sludge, sediment, and indoor dust and a similar amount and distribution of non-detects (ND).

Concentrations of **TBPH** and **TBB** were reported in indoor dust at levels ranging from ND to 75,000 µg/kg. **TBPH** and **TBB** have been detected in indoor dust from homes, schools, commercial office buildings, cars, and airplanes (See Table 3-1 and Table 3-2). There is likely a correlation between reported dust concentrations and the total amount of **TBPH** and **TBB** contained within source products. The total contribution from all these sources, many of which are polyurethane foam articles of various kinds, contributes to the variety of dust concentrations reported from these different microenvironments. The rate and likelihood of migration of these additives from the wide variety of different polyurethane foams is an important data need to understand the relationship of product use and environmental concentrations. There are 11 data sources reporting **TBB** in dust (Table 3-1) and 13 data sources reporting **TBPH** in dust (Table 3-1). **TBPH** was detected in 100% of all dust samples for all studies reviewed to date. Two studies detected **TBPH** and **TBB** in indoor air. Detectable levels of **TBPH** and **TBB** in indoor air are likely to be present as suspended particles which will ultimately deposit to indoor dust over time. Dust can be suspended via many common mechanisms, such as vacuuming, sweeping and the relationship between suspended particles and settled dust is important for understanding exposures over time.

There are five data sources that characterize **TBPH** (Ma et al., 2012; Moller et al., 2012; Schlabach et al., 2011; Shoeib and Jantunen, 2013; Xiao et al., 2012) and **TBB** (Bradman et al., 2012; Ma et al., 2012; Moller et al., 2012; Schlabach et al., 2011; Shoeib and Jantunen, 2013; Xiao et al., 2012) levels in ambient air at reported concentrations up to 3e-1 µg/m^3. Levels are expected to vary spatially. Two of these studies (Moller et al., 2012; Xiao et al., 2012) sampled only extremely remote locations with no known sources of **TBPH** and **TBB** in close proximity, indicating the potential for long-range transport. However, there is not enough data yet available to characterize how levels of **TBPH** and **TBB** may vary spatially or in proximity to centralized or diffuse sources. **TBPH** and **TBB** are generally found in the air associated with particulates, which would be available for human exposure and would be expected, over time, to deposit to terrestrial and aquatic ecosystems.

Biosolids or Sludge treated at industrial and municipal wastewater treatment plants have shown significant concentrations up to 89,900 µg/kg for **TBB** and 33,500 µg/kg for **TBPH** (Davis et al., 2012). The high $\log K_{OW}$ of these chemicals means they are more likely to absorb onto particles and be removed from the water during wastewater treatment. The relative source contribution of these chemicals into wastewater treatment plants is believed to be from non-point sources since point sources should be controlled. The likely very small down the drain loading from several hundred thousand source residential and public and commercial buildings every day may result in the relatively high concentrations reported in the literature.

There are five data sources that characterize **TBPH** and **TBB** (Klosterhaus et al., 2012; La Guardia et al., 2012; La Guardia et al., 2013; Schlabach et al., 2011; Zhu et al., 2013) levels in aquatic environments. These chemicals are not expected to be present in surface water, and instead partition to sediment. These studies report concentrations in sediment ranging from ND to 13,900 for **TBB** (Table 3-2) and ND to 19,200 for **TBPH** (Table 3-1), with more typical concentrations in the tens and hundreds of µg/kg. Higher concentrations were reported near Wastewater Treatment Plants and in urban areas.

There were only 12 studies available that characterized levels of **TBPH** (Table 3-1) and **TBB** (Table 3-2) in one or more of the following biota: terrestrial animals, aquatic animals, fish, birds, vegetation, and humans. For comparison, there were 13 articles summarizing **TBPH** dust levels. Some biota, such as vegetation, human blood, and terrestrial organisms were only represented by one or two studies. For Human blood, a **TBPH** concentration of 260 µg/kg was reported in a 2011 pooled blood sample of 30-39 year old Females in China (He et al., 2013). **TBPH** was not detected in the same study from two pooled 2007 samples (He et al., 2013). **TBPH** and **TBB** have recently been detected in a wide range of biota samples ranging from cat hair, dog hair, arctic fox liver, guillemot bird eggs, cormorant bird eggs, peregrine falcon bird eggs, ring billed gull bird liver, black legged kittiwake bird liver, common eider bird liver, and polar bear blood plasma for terrestrial animals and several species of fish muscle and fish liver, freshwater blue mussels, freshwater clams, freshwater gastropods, ringed seal liver, dolphin blubber, porpoise blubber, and harbor seal blubber for aquatic animals. The highest reported concentration of **TBB** was in a freshwater clam at 2220 µg/kg and the highest reported concentration of **TBPH** was in porpoise blubber at 3589 µg/kg. Table 3-1 provides a summary of available monitoring data for **TBPH** and Table 3-2 provides a summary of available monitoring data for **TBB**. Summary of each individual data sources are provided in Appendix A.

2.2 Data Needs

1) Source Characterization
    a. Type of Foam (with clear definition) and type of end-use product (with clear definition). Explicitly and clearly link these. Review definitions included in Appendix B - Definitions
    b. Percent weight of chemical within the product
    c. Based on the type of foam, what are the properties of those foams: density, rigidity, and structure
2) Migration of Additive chemicals out of Polyurethane Products
    a. Thickness of product
    b. Surface area exposed
    c. Diffusion coefficient
    d. Partition Coefficient
    e. Migration rate of FR over time
3) Monitoring Data
    a. Indoor environments, homes, commercial buildings, cars, trains, where high concentrations of polyurethane products are present
    b. Environmental samples: Soil, sludge, sediment
    c. Biota samples, human blood of highly exposed individuals who spend significant amounts of time in close proximity to products containing TBB and TBPH chemicals, vegetation grown on amended soil with land applied sludge, earthworm, sediment dwelling aquatic organisms

3 HUMAN EXPOSURE

3.1 Occupational Exposures to the Cluster Chemicals

The chemicals in this cluster are not on the Occupational Safety and Health Administration's (OSHA) list of regulated chemicals (OSHA, 2013). There is some non-confidential Chemical Data Reporting (CDR) information on the number of manufacturing workers and concentrations (EPA, 2012a). Based on the physical-chemical properties (e.g., liquid with low vapor pressure ranging from <1E-6 Torr [estimated to <1.0 E-3 Torr at 25 ^{o}C] and available information on manufacturing process, workers in the chemical manufacturing sector are not expected to be exposed to the chemicals via inhalation.

3.2 Occupational Exposures to Polyurethane Foams (PUF) Containing the Cluster Chemicals

Limited information is available on occupational exposure to polyurethane foam during foam manufacturing.

Polyurethane foams (PUF) vary widely in their stiffness, but are generally considered as either flexible or rigid types (EPA, 2005). Flexible PU foams can be shaped easily by cutting and molding with a variety of densities. They are typically used behind other materials in products such as the upholstery in furniture, or in flexible plastics. The total amount of flame retardant as percentage of volume of foam is approximately 5 percent (Cobb and Chen, 2005; Stapleton et al., 2009).

Flexible PUF can be divided into two type (EPA, 2005); slabstock and molded foam.

Slabstock foam components are poured onto flat surfaces and expand into a slab shape. Molded foam components are poured into a mold. They are typically used in the automotive industry. Although no exposure information is available, based on the vapor pressure and available information on manufacturing, EPA expects that inhalation exposure is negligible.

No exposure information is available and EPA is unable to address this potential occupational exposure scenario.

Table 3-1: Summary Table of TBPH Monitoring Data

Media	Number of Data Sources	Number of overall Samples	Number of non-detects (ND)*	% Samples not ND	Range	Median (Mean) of quantifiable samples^{+}	References
Environmental Media							
Dust	13	83	0	100%	1 to 47,110 µg/kg	133 (2,200) µg/kg	(Ali et al., 2012; Allen et al., 2013a; Allen et al., 2013b; Bradman et al., 2012; Dodson et al., 2012; Gheorghe et al., 2013; Johnson et al., 2013; Kopp et al., 2012; Sahlstrom et al., 2012; Shoeib et al., 2012; Springer et al., 2012; Stapleton et al., 2008a; Stapleton et al., 2009; Stapleton et al., 2008b; Van den Eede et al., 2012)
Indoor Air	2	6	1	83%	ND to 0.007 µg/m^3	**	(Bradman et al., 2012; Schlabach et al., 2011)
Ambient Air	5	76	15	80%	ND to 0.29 µg/m^3	5.3e-4 (8.1e-3) µg/m3	(Ma et al., 2012; Moller et al., 2012; Schlabach et al., 2011; Shoeib and Jantunen, 2013; Xiao et al., 2012)
Biosolids/Sludge	4	36	5	86%	ND to 33,500 µg/kg	40 (2,040) µg/kg	(Davis et al., 2012; de Wit et al., 2011; La Guardia et al., 2010; Schlabach et al., 2011)
Sediment	5	75	33	56%	ND to 19,200 µg/kg	93 (792) µg/kg	(Klosterhaus et al., 2012; La Guardia et al., 2012; La Guardia et al., 2013; Schlabach et al., 2011; Zhu et al., 2013)
Surface Water	1	1	1	0%	ND	**	(Schlabach et al., 2011)
Biological Media							
Terrestrial animals	2	10	2	80%	ND to 1.6 µg/kg	**	(Ali et al., 2013; Sagerup et al., 2010)

Media	**Number of Data Sources**	**Number of overall Samples**	**Number of non-detects (ND)***	**% Samples not ND**	**Range**	**Median (Mean) of quantifiable samples$^+$**	**References**
Aquatic animals	5	65	37	43%	ND to 3,590 µg/kg	**	(de Wit et al., 2011; La Guardia et al., 2012; Sagerup et al., 2010; Schlabach et al., 2011; Sühring et al., 2013)
Fish	2	17	6	65%	ND to 0.7 µg/kg	**	(Sagerup et al., 2010; Schlabach et al., 2011)
Birds	5	21	7	66%	ND to 465 µg/kg	**	(Gentes et al., 2012; Guerra et al., 2012; Klosterhaus et al., 2012; Sagerup et al., 2010; Schlabach et al., 2011)
Vegetation	1	3	2	33%	0.039 µg/kg	**	(Schlabach et al., 2011)
Human Blood	1	12***	11	9%	260 µg/kg	**	(He et al., 2013)
TOTAL		394	117	70%			

$^+$ "quantifiable samples" do not include samples identified as non-detects

* non-detects conservatively include all samples reported as ND, <Level of Detection, <Level of Quantification, <Minimum Detection Limit, and less than a number which was generally small and was either one of the numbers above or a slightly larger number

** not a sufficient sample size to estimate summary statistics for this media

*** pooled samples several hundred individuals. 10 pooled samples from 2011, and 2 pooled samples from 2007. Quantifiable sample was from 2011.

Table 3-2: Summary Table of TBB Monitoring Data

Media	Number of Data Sources	Number of overall Samples	Number of non-detects (ND)*	% Samples not ND	Range	Median (Mean) of quantifiable samples**	References
Environmental Media							
Dust	11	73	12	84%	ND to 75,000 µg/kg	91 (3,880) µg/kg	(Ali et al., 2012; Allen et al., 2013a; Allen et al., 2013b; Bradman et al., 2012; Dodson et al., 2012; Gheorghe et al., 2013; Johnson et al., 2013; Kopp et al., 2012; Sahlstrom et al., 2012; Shoeib et al., 2012; Springer et al., 2012; Stapleton et al., 2008a; Stapleton et al., 2009; Stapleton et al., 2008b; Van den Eede et al., 2012)
Indoor Air	2	6	2	66%	ND to 0.007 µg/m3	***	(Bradman et al., 2012; Schlabach et al., 2011)
Ambient Air	6	74	25	66%	ND to 5.5e-2 µg/m3	3.8e-4 (2.6e-3) µg/m3	(Ma et al., 2012; Moller et al., 2012; Schlabach et al., 2011; Shoeib and Jantunen, 2013; Xiao et al., 2012)
Biosolids/ Sludge	4	34	12	65%	ND to 89,900 µg/kg	1.8 (5,800) µg/kg	(Davis et al., 2012; de Wit et al., 2011; La Guardia et al., 2010; Schlabach et al., 2011)
Sediment	5	74	20	74%	ND to 13,900 µg/kg	150 (557) µg/kg	(Klosterhaus et al., 2012; La Guardia et al., 2012; La Guardia et al., 2013; Schlabach et al., 2011; Zhu et al., 2013)
Biological Media							
Terrestrial animals	1	4	0	100%	0.9 to 415 µg/kg	***	(Sagerup et al., 2010)

Media	Number of Data Sources	Number of overall Samples	Number of non-detects (ND)*	% Samples not ND	Range	Median (Mean) of quantifiable samples**	References
Aquatic animals	6	44	13	70%	ND to 2,220 µg/kg	***	(Bradman et al., 2012; Klosterhaus et al., 2012; La Guardia et al., 2012; Sagerup et al., 2010; Schlabach et al., 2011; Villaverde-de-Sáa et al., 2013)
Fish	3	18	9	50%	ND to 203 µg/kg	***	(Klosterhaus et al., 2012; Sagerup et al., 2010; Schlabach et al., 2011)
Birds	4	14	4	71%	ND to 39 µg/kg	***	(Gentes et al., 2012; Klosterhaus et al., 2012; Sagerup et al., 2010; Schlabach et al., 2011)
Vegetation	1	2	2	0%	ND	***	(Schlabach et al., 2011)
TOTAL		312	97	69%			

* non-detects conservatively include all samples reported as ND, <Level of Detection, <Level of Quantification, <Minimum Detection Limit, and less than a number which was generally small and was either one of the numbers above or a slightly larger number

"quantifiable samples" do not include samples identified as non-detects* not a sufficient sample size to estimate summary statistics for this media

3.2.1 Slabstock Polyurethane Foam

The slabstock manufacturing process is a continuous process that produces long, rectangular, continuous slabs of foam, called “buns”. Buns are cut into the desired configuration for an application, such as in furniture padding, bedding, automobile padding and seats, packaging materials, and carpet padding.

The typical commercial process for slabstock foam production consists of a single unit operation, operated in batches (Figure 3-1).

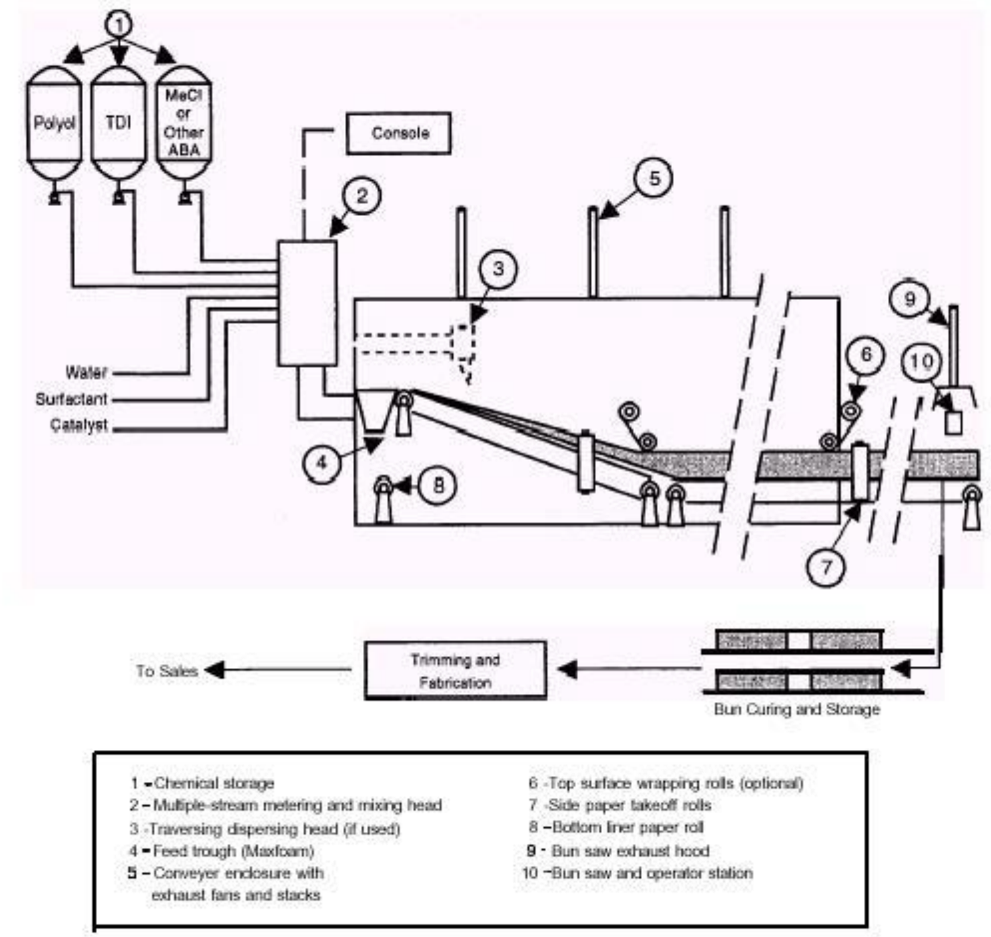


Figure 3-1: Typical Slabstock Production Line for flexible polyurethane foam (EPA, 2005)

3.2.2 Molded Polyurethane Foam

Molded foam is produced when the foam polymerization reaction occurs in a closed mold resembling the final product. Molded foam is used in the transportation industry for seat cushions and interior trim, furniture, bedding, packaging materials, toys, and novelty items.

The typical commercial process for molded foam production consists of a circular production line containing multiple molds and process stations. Figure below (Figure 1-2) presents a diagram of this process.

Raw materials for molded foam are similar to those used in slabstock foam production, including polyol, diisocyanates, water, catalyst, surfactant, and other additives (e.g., flame retardants). The raw materials are pumped to a common mix head above the production line. Many ingredients are premixed to minimize the streams being fed to the head and to ensure precise measurement. The mix head dispenses a measured amount of the mixture into each mold and the molds are then heated to accelerate foam curing. Heating takes place either by passing the mold through a curing oven or passing heated water through tubes in the mold. Then, the mold is opened and emptied. The mold continues through the process line to be conditioned for the next product. After removal from the mold, the foam is further processed into the final desired shape. These activities include curing, trimming, and gluing.

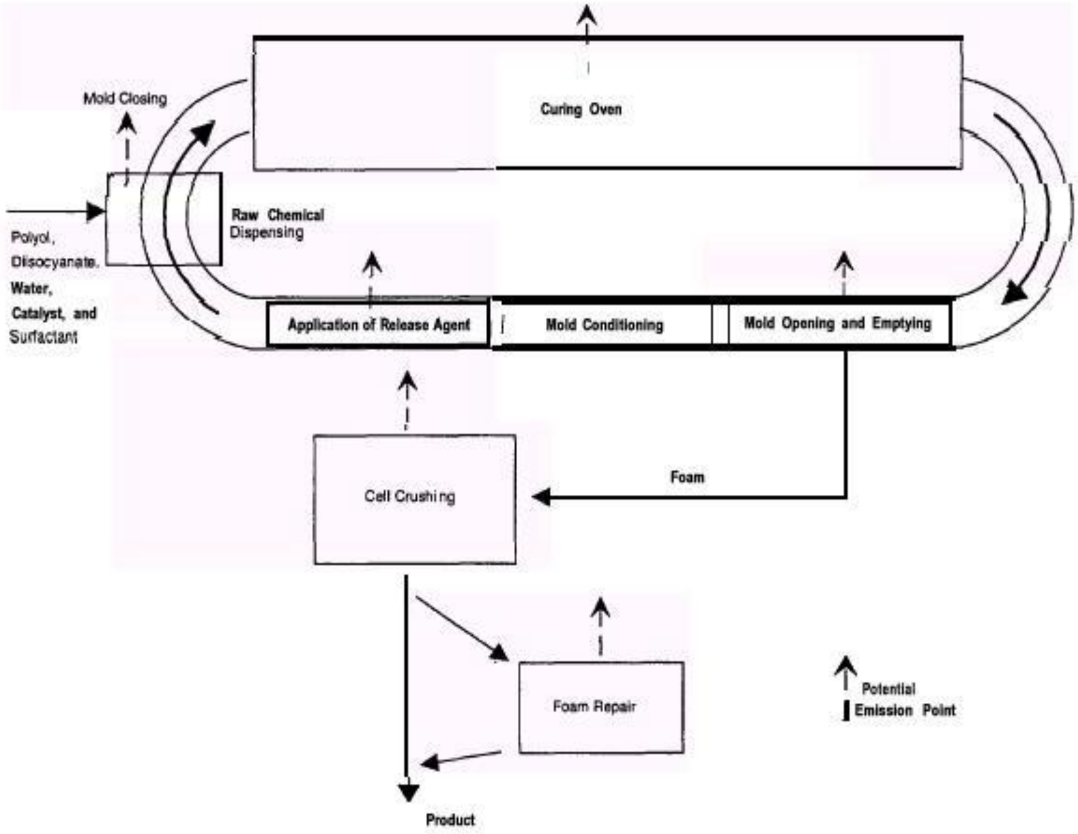


Figure 1-2: Typical Molded Foam Production Line for flexible polyurethane foam (EPA, 2005)

There is no readily available information on the environmental releases of the chemicals in this cluster during the manufacture of PU foams. An existing generic scenario for PU flexible foam manufacturing can be used to estimate releases and occupational exposures.

3.3 Occupational Exposure during the Manufacture of Products containing Polyurethane Foams (PUF)

Foam containing one or more of the chemicals in this cluster is used during manufacture of the products described in Sections 1.5 and 1.6 of this report.

No data are available on occupational exposure during the manufacture of products containing PU foam. Based on OSHA's Particulates Not Otherwise Regulated (inhalable and respirable dust) standards, a "high-end" exposure-based scenario could be used to determine the potential exposure to foam particulates during the manufacture of products containing PU foam.

3.4 Occupational Exposure from the Use of Products containing Polyurethane Foams (PUF)

No exposure information is available and EPA is unable to address this potential occupational exposure scenario.

3.5 Consumer Exposure from the Use of Products containing Polyurethane Foams (PUF)

The exposure potential of **TBPH** and **TBB** is influenced by several parameters of the source material to which these chemicals are added. One of the major sources of exposure is considered to be certain types of polyurethane foam (PUF) products based on the following criteria as compared to other product end uses: major use-based production volume, higher percent of flame retardant chemicals within the product, long service life/product use within indoor environments, diverse set of large articles with large surface areas exposed, and multiple sources present within various indoor environments. Differences in density, rigidity, and structure (closed vs. open cells) dictate which types of foams can be used in various products (see Figure 1.1 Property Matrix of Polyurethanes in Huntsman Polyurethanes Book).

Polyurethanes can be broken into four broad categories:

1) Low Density Flexible Foams- Open Cell
2) Low Density Rigid Foams- Open Cell and Closed Cell –
3) High Density Flexible Foams (microcellular foams) –Open Cell and Closed Cell
4) Solid Polyurethanes (Coatings (paints), Adhesives, Sealants, Elastomers)-

Differences in density, rigidity, and structure (closed vs. open cell) along with the thickness of the product and its exposed surface area influence the likelihood of migration and associated exposure potential of TBB and TBPH over time. Lower density, thinner, open-cell flexible foams, with large amounts of exposed surface area have may have greater potential for additive migration over time. However, it is not clear if there may threshold values for one or a combination of these factors that could influence migration and exposure potential. Definitions of polyurethane foam types and product end uses are provided in Appendix B and comments on these definitions as well as on which products are likely to be major contributors based on available, or collected data is of interest.

3.6 Data Needs

1) Source Characterization
    a. Type of Foam (with clear definition) and type of end-use product (with clear definition). Percent weight of chemical within the product
    b. Percent weight of chemical within product
    c. Based on the type of foam, what are the properties of those foams: density, rigidity, and structure
2) Migration of Additive chemicals out of Polyurethane Products
    a. Thickness of product
    b. Surface area exposed
    c. Diffusion coefficient
    d. Partition coefficient
    e. Migration rate of FR over time
3) Monitoring Data
    a. Indoor environments, homes, commercial buildings, cars, trains, where high concentrations of polyurethane products are present
    b. Environmental samples: Soil, sludge, sediment
    c. Biota samples, human blood of highly exposed individuals who spend significant amounts of time in close proximity to products containing **TBB** and **TBPH** chemicals, vegetation grown on amended soil with land applied sludge, earthworm, sediment dwelling aquatic organisms

4 ENVIRONMENTAL EXPOSURE

4.1 Background and Context of Cluster Chemical Manufacture

The chemicals in this cluster have similarities in structure. One notable similarity is that the various alkyl esters are attached to the main tetrabromophthalate structure. 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (**TBB**) is manufactured by reacting tetrabromophthalic anhydride with appropriate alcohol in the presence of decarboxylation catalyst. This reaction proceeds through rapid esterification of anhydride, followed by decarboxylation to yield the tetrabromobenzoate. Depending on which alkyl group is attached to the alcohol being used, one or more chemicals in this cluster are produced (Albemarle - GLCC, 2004; Hill et al., 1997).

4.2 Releases to the Environment during Cluster Chemical Manufacture

The chemicals in this cluster are not on the Toxic Release Inventory (EPA, 2012a), and no readily available public information on releases from manufacturing was found. Non-CBI (Confidential Business Information) Chemical Data Reporting (CDR) production volumes are available for two of the member chemicals of this cluster: CASRN 26040-51-7 and CASRN 20566-35-2 (EPA, 2012a). The reported production volumes for 2011 were between 1 to 10 million lbs for **TBPH** (CASRN 26040-51-7) and 2-(2-hydroxyethoxy) ethyl 2-hydroxy propyl 3,4,5,6 tetrabromobenzene dicarboxylate (CASRN 20566-35-2). The release of **TBB** to water from manufacturing and processing is regulated by EPA (40 CFR Section 721.2925).

4.3 Releases to the Environment during Polyurethane Foams (PUF) Manufacture

There is no readily available information on the environmental releases of the chemicals in this cluster during the manufacture of PU foams. An existing generic scenario for polyurethane flexible foam manufacturing can be used to estimate releases and occupational exposures. The release of **TBB** to water from manufacturing and processing is regulated by EPA (40 CFR Section 721.2925).

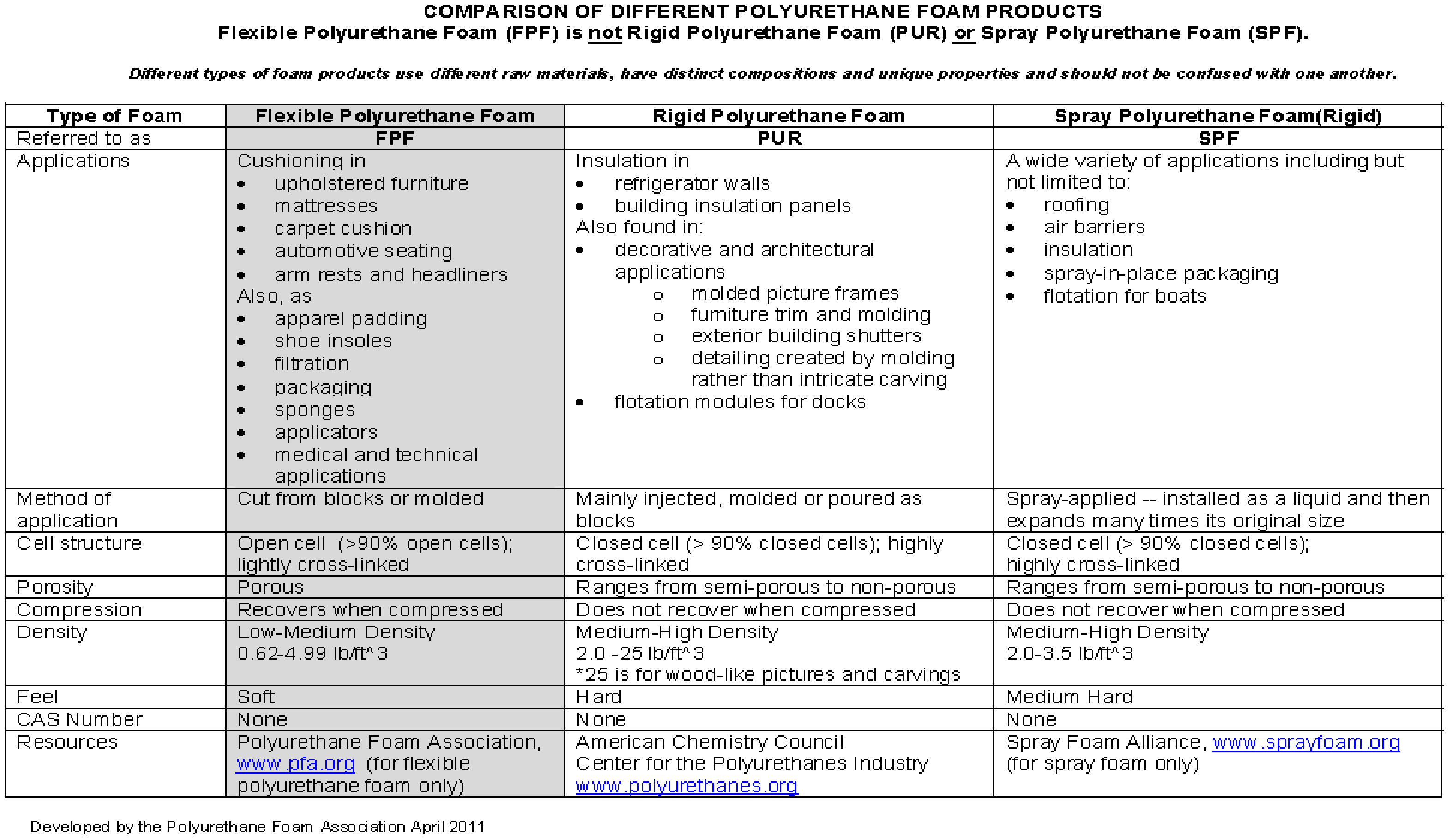
4.4 Releases to the Environment during the Manufacture of Products containing Polyurethane Foams (PUF)

There is no readily available information on the environmental releases of the chemicals during the manufacture of products containing PU foam. EPA can use estimates following the approach taken in the New Chemicals Program to prepare a screening-level assessment based on a selected number of industries/exposure scenarios for the two chemicals for which data are available (**TBPH** and CASRN 20566-35-2).

4.5 Releases to the Environment during the Occupational Use of Products containing Polyurethane Foams (PUF)

No release information is available and EPA is unable to assess release from the uses of products containing PU foam.

Table 4-1: Comparison of Different Polyurethane Foam Products



COMPARISON OF DIFFERENT POLYURETHANE FOAM PRODUCTS
Flexible Polyurethane Foam (FPF) is not Rigid Polyurethane Foam (PUR) or Spray Polyurethane Foam (SPF).

Different types of foam products use different raw materials, have distinct compositions and unique properties and should not be confused with one another.

Type of Foam	Flexible Polyurethane Foam	Rigid Polyurethane Foam	Spray Polyurethane Foam(Rigid)
Referred to as	FPF	PUR	SPF
Applications	Cushioning in • upholstered furniture • mattresses • carpet cushion • automotive seating • arm rests and headliners Also, as • apparel padding • shoe insoles • filtration • packaging • sponges • applicators • medical and technical applications	Insulation in • refrigerator walls • building insulation panels Also found in: • decorative and architectural applications o molded picture frames o furniture trim and molding o exterior building shutters o detailing created by molding rather than intricate carving • flotation modules for docks	A wide variety of applications including but not limited to: • roofing • air barriers • insulation • spray-in-place packaging • flotation for boats
Method of application	Cut from blocks or molded	Mainly injected, molded or poured as blocks	Spray-applied -- installed as a liquid and then expands many times its original size
Cell structure	Open cell (>90% open cells); lightly cross-linked	Closed cell (> 90% closed cells); highly cross-linked	Closed cell (> 90% closed cells); highly cross-linked
Porosity	Porous	Ranges from semi-porous to non-porous	Ranges from semi-porous to non-porous
Compression	Recovers when compressed	Does not recover when compressed	Does not recover when compressed
Density	Low-Medium Density 0.62-4.99 lb/ft^3	Medium-High Density 2.0 -25 lb/ft^3 *25 is for wood-like pictures and carvings	Medium-High Density 2.0-3.5 lb/ft^3
Feel	Soft	Hard	Medium Hard
CAS Number	None	None	None
Resources	Polyurethane Foam Association, www.pfa.org (for flexible polyurethane foam only)	American Chemistry Council Center for the Polyurethanes Industry www.polyurethanes.org	Spray Foam Alliance, www.sprayfoam.org (for spray foam only)

Developed by the Polyurethane Foam Association April 2011

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APPENDICES

Appendix A Summary of Monitoring Data Sources

A-1 Indoor Environments

Dust samples from the living rooms, bedrooms, and vacuum bags were collected from homes in Boston. Detection rates were 100% for **TBPH** and ranged from 86% to 100% for **TBB**. Concentrations ranged from 1.5 to 10,360 µg/kg for **TBPH** and ranged from ND to 15,030 ug/kg for **TBB**. Concentrations of dust were generally higher in the main living room areas of the homes (Stapleton et al., 2008a).

A pooled sample of 50 **TBB** and **TBPH** dust samples taken over five years from Boston Homes was reported in 2009. The concentration of TBB in dust ranged from ND to 75,000 µg/kg and the concentration of **TBPH** ranged from ND to 47,110. It is noteworthy, that the 75,000 µg/kg value is the highest reported concentration (Stapleton et al., 2009).

Thirty-four living room dust and sixteen mattress vacuum dust samples were taken from New Zealand homes. **TBB** was detected at concentration ranging from <2 to 2,285 µg/kg and **TBPH** in the range of <2 to 640 µg/kg. There was a correlation ($p < 0.05$) between floor and mattress dust concentrations in each house for **TBPH** (Ali et al., 2012).

Dust samples from 19 airplanes were collected in two locations: vacuumed carpet and vacuumed air return vents from the airplane wall. **TBB** and **TBPH** were detected in 100% of the 40 samples. Dust Concentrations of **TBB** ranged from 200 to 3,000 µg/kg on the floor and 300 to 5,000 µg/kg in vents. Dust Concentrations of **TBPH** ranged from 400 to 1,600 µg/kg on the floor and 350 to 3,600 µg/kg in vents (Allen et al., 2013b).

Sixteen paired samples of dust were taken from California homes in 2006 and then again in 2011. Decreases in dust concentrations of PBDEs and increased dust concentrations of **TBB** and **TBPH** were reported. It was reported that these trends were likely due to changes in product composition within homes over this time period; that is the substitution of **TBB** and **TBPH** for PBDEs. In 2006, concentrations of **TBB** ranged from 4 to 740 µg/kg g and in 2011 concentrations increased and ranged from 45 to 5900 µg/kg. In 2006, concentrations of **TBPH** ranged from 36 to 1900 µg/kg and in 2011 concentrations increased and ranged from ND to 3800 µg/kg. Median concentrations also increased by a factor of 2. The authors reported that there was a significant statistical association ($p<0.05$) between reduced PBDE concentrations and participant-reported new product installation in three homes, suggesting that replacement of articles can reduce exposure (Dodson et al., 2012).

Samples were collected from apartments in Romania. **TBB** and **TBPH** concentrations were similar, with a median value reported for TBPH of 31 µg/kg. The authors note that carpet, as opposed to hard surface floors, may be an important reservoir for dust (Gheorghe et al., 2013).

Thirty-eight samples from vacuum bags in the United States detected **TBB** and **TBPH** at 47% and 63% respectively. The concentrations of **TBB** ranged from ND to 72,460 ug/kg and the concentrations of **TBPH** ranged from ND to 47,110 µg/kg (Johnson et al., 2013).
Samples were collected from vacuum cleaner bags from German homes. Concentrations of **TBB** in dust ranged from 3 to 8 µg/kg and concentrations of **TBPH** in dust ranged from 24 to 535 µg/kg (Kopp et al., 2012).

TBB and **TBPH** were measured in six apartments in Sweden. The concentrations of **TBB** ranged from 25 to 330 µg/kg and the concentrations of **TBPH** ranged from 260 to 950 µg/kg (Sahlstrom et al., 2012).

Vacuum bag dust samples were collected from homes in Vancouver Canada. 96% of 116 samples detected **TBB** and 100% of 116 samples detected **TBPH**. Concentrations of **TBB** ranged from ND to 18,000 µg/kg and concentrations of **TBPH** ranged from 0.1 to 6400 µg/kg (Shoeib et al., 2012).

Reported **TBPH** dust concentrations were significantly different in residences, offices, and cars. Dust samples were collected in Boston, MA after 10 minutes of vacuuming in each different microenvironment. **TBPH** was detected in: 74% of house dust with a median concentration of 150 µg/kg (range LOD to 12,400 µg/kg, 100% of office dust with a median concentration of 410 µg/kg (range 95 to 15,500 µg/kg), and 90% of car dust with a median concentration of 400 µg/kg (range LOD to 830 µg/kg) (Springer et al., 2012).

Twelve vacuum cleaner dust samples were taken from indoor residences in Europe (Belgium). All the samples for **TBB** were below the level of quantification for the analytical method used in this study (9 µg/kg). The concentrations of **TBPH** ranged from 2.4 to 12.7 µg/kg (Van den Eede N et al., 2011).

Three indoor air samples of **TBB** and three indoor air samples of **TBPH** were collected in Oslo, Norway. Indoor air sampling volumes were approximately 5 m^3 and the sampling time was one week. It was reported that levels of brominated ethers and esters were higher in the indoor air samples compared to outdoor air from this study (Schlabach et al., 2011).

A 2012 study of childcare environments in California prepared for California Air Resources Board measured **TBB** and **TBPH** in the dust and indoor air of childcare environments. **TBB** and **TBPH** were both detected in 100% of dust samples. **TBB** concentrations ranged from 85.2 to 14,812 µg/kg and **TBPH** concentrations ranged from 28.8 µg/kg to 7489 µg/kg. **TBB** was detected in 15% of 40 of indoor air samples with concentrations ranging from ND to 0.016 $\mu g/m^3$, and **TBPH** was detected in 17% of samples with concentrations ranging from ND to 0.005 $\mu g/m^3$ (Bradman et al., 2012).

A-2 Ambient Air

An extensive monitoring study was conducted at six sites around the Great Lakes Region with 502 air samples collected between 2008 and 2010. **TBB** and **TBPH** were detected in the particle phase only in over half of the samples. Urban areas tended to show higher concentrations, and air concentrations tended to increase over the sampling timeframe. The maximum concentration of **TBB** was 5.5e-2 and the maximum concentration for **TBPH** was 2.9e-1µg/m^3 (Ma et al., 2012).

Vapor and Particulate ambient air samples were taken above the ocean on a cruise from Southeast Asia toward the Antarctic. Despite the remote location, **TBB** and **TBPH** were detected in the particulate phase, with maximum concentrations of TBB up to 2.1e-4 µg/m^3 and concentrations of **TBPH** up to 2.8e-3 µg/m^3 (Moller et al., 2012).

TBB was one of the substances most frequently detected in ambient air in a 2011 study of Nordic countries. The maximum reported ambient air concentrations for **TBB** and **TBPH** were similar and were both collected in Oslo Norway. The maximum concentration for TBB was 1.4e-3 µg/m^3 and the maximum concentration for **TBPH** was 1.7e-3 µg/m^3 (Schlabach et al., 2011).

About 500 m^3 of high volume air samples were collected over 24 hours in the ambient air over the Great Lakes. **TBB** and **TBPH** were detected less frequently and at lower levels than other flame retardants at concentrations up to 1.8-3 µg/m^3(Shoeib and Jantunen, 2013).

Over the course of approximately one year, ambient air samples were taken in the Tibetan Plateau and the Canadian High Arctic. Both of these sites are extremely remote. The authors note that **TBB** and **TBPH** were detected at concentrations similar to Brominated Diphenyl Ethers. The maximum ambient air concentration for **TBB** was 2.2e-3 µg/m^3, and the maximum ambient air concentration of **TBPH** was 1.5e-3 µg/m^3 (Xiao et al., 2012).

A 2012 study of childcare environments in California prepared for California Air Resources Board measured **TBB** and **TBPH** in ambient air near childcare centers. **TBB** and **TBPH** were both detected in 12.5% of 40 samples. **TBB** concentrations ranged from ND to 0.001 ug/m3 and **TBPH** concentrations ranged from ND to 0.004 µg/m^3 (Bradman et al., 2012).

A-3 Sludge/Biosolids

Sewage sludge from the drying lagoons was collected from a Mid-Atlantic treatment plant between 2002 and 2008. The reported concentration of **TBB** ranged from 3430 to 89,900 µg/kg of total organic compounds (TOC), and the reported concentration of **TBPH** ranged from 64 to 33,500 µg/kg TOC. The authors suggest that domestic sources may be responsible for a large percentage of **TBB** and **TBPH** detected in sewage sludge (La Guardia et al., 2010).

Sewage sludge was collected from eight wastewater treatment plants. **TBB** was detected in two of the eight plant's sewage sludge at concentrations of 128 and 2491 ng/g dw. TBPH was detected in all but one of the plant's sewage sludge at concentrations that ranged from 206 to 1631 ng/g dw. The authors suggest that migration out of consumer products and during the wastewater treatment process is related to observed concentrations of TBB and TBPH in sewage sludge.

Concentrations of **TBB** in sewage sludge from a wastewater treatment plant in San Francisco ranged from 40 to 1,412 ug/kg and concentrations of TBPH ranged from 57 to 515 µg/kg (Klosterhaus et al., 2012).

TBPH had a high frequency of detection and also had the highest concentration in sludge when compared to all other flame retardants measured during this study with a concentration of 1,420 µg/kg in sludge. **TBB** was also detected with high frequency and concentrations in sludge ranged from ND up to 2.6 µg/kg (Schlabach et al., 2011).

A-4 Aquatic Environments

Several sediment samples were taken near and downstream from a waste water treatment plant (WWTP) that processed both industrial and municipal wastewater in North Carolina. Concentrations for both **TBB** and **TBPH** were highest at the outfall of the WWTP and decreased with distance. Concentrations of **TBB** at outfall were 38,500 µg/kg and decreased to 80 µg/kg 40 km downstream. Concentrations of **TBPH** at outfall were 19,200 µg/kg and decreased to 2,000 µg/kg 40 km downstream (La Guardia et al., 2012).

Forty-five sediment samples were detected in urban waterways in South Africa. **TBB** was detected in 91% of samples and concentrations ranged from ND to 13,900 ug/kg with a mean of 545 µg/kg. **TBPH** was detected in 60% of samples and concentrations ranged from ND to 899 µg/kg with a mean of 96 µg/kg (La Guardia et al., 2013).

Ten sediment samples were taken in San Francisco Bay in 2012. **TBB** and **TBPH** were not detected in these samples. However the authors report that detection may have been compromised by matrix interferences in all samples (Klosterhaus et al., 2012).

A Nordic study found a low frequency of detection for **TBPH** (3 out of 12) and **TBB** (2 out of 12) in sediment. The concentration of **TBB** ranged from 0.04–0.2 µg/kg. **TBPH** concentrations were higher and ranged from 0.2 to 3 µg/kg. The highest concentration was found in sediment close to a WWTP outlet in Sweden (Schlabach et al., 2011).

TBPH was detected in six samples of riverine sediment in the Yangtze River of China, with a mean concentration of 1 µg/kg and a range of 0.5 to 3 µg/kg. **TBB** was detected in two samples with a mean concentration of 0.4 µg/kg and a range of ND to 1 µg/kg. Both TBPH and TBB were not detected in 24 marine sediment samples (Zhu et al., 2013).

A-5 Aquatic Animals and Fish

Several samples of bivalves and gastropods were taken near and downstream from a WWTP that processed both industrial and municipal wastewater in North Carolina. Concentrations of **TBB** in bivalves at outfall were 2220 µg/kg and were not detected at any distance downstream, and concentrations in gastropods at outfall were 1740 µg/kg at outfall and were not detected at any distance downstream. Concentrations of **TBPH** in bivalves at outfall were 1370 µg/kg and decreased to 37 µg/kg 40 km downstream, and concentrations in gastropods were 380 µg/kg at outfall and decreased to 36 µg/kg 40 km downstream (La Guardia et al., 2012).

Seventeen dolphins and thirty-three porpoises were sampled in South China. All the dolphin samples had **TBB** concentrations below the level of quantification (LOQ) which was 0.04 µg/kg lipid weight. The average concentration of **TBB** in porpoises was 5.6 µg/kg with a range of <LOQ to 70 µg/kg. **TBPH** was detected in dolphins with an average concentration of 0.51 µg/kg and a range of <LOQ to 5.3 µg/kg. The average concentration of **TBPH** in porpoises was 342 µg/kg with a range of <LOQ to 3859 µg/kg, which also is the highest reported concentration of **TBPH** in biota. The authors report a lack of knowledge of the sources, distribution, and fate of **TBB** and **TBPH** and recommend additional research to determine exposure pathways (Lam et al., 2009).

TBB was detected in 21 samples of porpoise blubber from the UK in 2008. Samples ranged from ND to 3.44 µg/kg wet weight (Law et al., 2013).

TBB was not detected in a small number of samples of white croaker, perch, and adult and pup harbor seal blubber collected in San Francisco Bay in 2012. **TBPH** was not detected in a small number of samples of cormorant eggs. However the authors report that detection may have been compromised by matrix interferences in all samples (Klosterhaus et al., 2012).

Seven different species in Scandinavia were sampled for a variety of flame retardants including **TBB** and **TBPH**. Two of these species were aquatic. The Capelin is a smelt fish that is an important food source for other fish. Ten samples were collected for each species. TBB was detected in 100% of samples with a mean whole fish wet weight concentration of 0.37 µg/kg. TBPH was detected in 90% of samples with a mean whole fish wet weight concentration of 0.72 µg/kg. Ten ringed seal liver samples were collected. **TBB** was detected in 100% of samples with a concentration of 0.43 µg/kg. **TBPH** was detected in 60% of samples with concentration of 0.57 µg/kg (Sagerup et al., 2010).

Five samples of fish liver, nine samples of fish muscle, and three samples of mussel were sampled for **TBB** and **TBPH** as well as several other flame retardants in Norway. The concentration of TBPH in fish liver ranged from ND to 0.049 µg/kg. The concentration of **TBPH** in fish liver ranged from ND to 0.46 µg/kg, and the concentration of TBPH in mussels ranged from 0.009 to 0.057 µg/kg. The concentration of **TBB** in fish liver ranged from ND to 0.12 µg/kg.

The concentration of **TBB** in fish muscle ranged from ND to 0.022 µg/kg, and the concentration in mussels ranged from 0.0041 to 0.0049 µg/kg (Schlabach et al., 2011). **TBB** was not detected in raft cultured mussel, clam, or cockle samples, but was detected in wild mussel samples with a concentration of 0.06 µg/kg (Villaverde-de-Sáa et al., 2013).

A-6 Terrestrial Animals, Vegetation and Birds

Samples were taken from the serum and hair of twenty cats and sixteen dogs in Pakistan. **TBB** was detected in approximately one-half of hair samples at levels up to 1 µg/kg in cats and 1.25 µg/kg in dogs. **TBPH** was also detected in approximately one-half of hair samples at levels up to 1.65 µg/kg in cats and 0.8 µg/kg in dogs. **TBB** and **TBPH** were not detected in serum samples (Ali et al., 2012).

TBB was detected in 11% of 28 ring bill gull liver samples collected from the St. Lawrence River, Canada with concentrations ranging from ND to 1.55 µg/kg wet weight and ND to 38.6 µg/kg lipid weight. **TBPH** was detected in 89% of 28 ring bill gull liver samples with concentrations ranging from ND to 17.6 µg/kg wet weight and ND to 465 µg/kg lipid weight. The average concentration of **TBPH** was 2.16 µg/kg wet weight and 58.3 µg/kg lipid weight. **TBB** and **TBPH** were not detected in 30 plasma samples of ring bill gulls (Gentes et al., 2012).

TBPH was detected in 4 of 12 peregrine falcon eggs in Canada ranging from <LOD to 4.5 µg/kg lipid weight. **TBPH** was detected in 1 of 13 peregrine falcon eggs from Spain at a concentration of 1.2 µg/kg lipid weight (Guerra et al., 2012).

TBB was not detected in a small number of samples of cormorant eggs collected near the San Francisco Bay area in 2012. However the authors report that detection may have been compromised by matrix interferences in all samples (Klosterhaus et al., 2012).

Seven different species in Scandinavia were sampled for a variety of flame retardants including **TBB** and **TBPH**. Five of these species were aquatic. Ten samples were collected for each species. Three bird species were sampled: common eider liver, Guillemot eggs, and Kittiwake liver. **TBB** was detected in: 100% of common eider liver samples with a mean concentration of 0.86 µg/kg, 90% of guillemot eggs with a mean concentration of 1.21 µg/kg, and 90% of kittiwake liver samples with a concentration of 0.73 µg/kg. TBB was also detected in two mammals: the arctic fox and polar bear. **TBB** was detected in: 90% of arctic fox liver samples with a concentration of 0.97 µg/kg, and 90% of polar bear plasma samples with a concentration of 3.46 µg/kg. **TBPH** was not detected in the arctic fox or polar bear samples. **TBPH** was detected in: 60% of common eider liver samples with a mean concentration 1.65 µg/kg; 70% of guillemot eggs with a mean concentration of 1.79 µg/kg; and 50% of kittiwake liver samples with a concentration of 0.8 µg/kg (Sagerup et al., 2010).

TBB and **TBPH** were detected in bird eggs and one moss sample in Scandinavia. The frequency of detection in bird eggs and other biota was high when compared to moss. Concentrations of

TBB in bird eggs ranged from ND to 0.18 µg/kg and concentrations of **TBPH** ranged from ND to 0.021 µg/kg. Only one sample detected TBB in moss at a concentration of 0.039 µg/kg (Schlabach et al., 2011).

A-7 Human Blood

For human blood, a **TBPH** concentration of 260 µg/kg was reported in a 2011 pooled blood sample of 30-39 year old Females in China. **TBPH** was not detected in the same study from two pooled 2007 samples. The authors note that the pooled sample may have included individuals who could have been occupationally exposed, but does recommend further biomonitoring to understand possible trends of **TBPH** occurrence in human serum for the study area (He et al., 2013).

Appendix B Definitions

B-1 Overall types of Polyurethane (2)

- *Open cell:* structure of foam which allows for the movement of air throughout (North Star Polymers, 2013).
- *Closed cell*: unbroken and tightly packed foam cells and is thus largely impermeable to air and liquid (North Star Polymers, 2013).
- *Flexible foam:* An open cell polyurethane foam type made using toluene diisocyanate (TDI) as the isocyanurate, most often used in cushioning applications (Global Insight, 2006; Polyurethane Foam Association, 1991a).
- *Semi-rigid (or semi-flexible) foam:* a type of flexible foam. The difference between standard flexible foam and semi-rigid foam is the molecular weight per cross-link, the equivalent weight and functionality of the polyol and the type and functionality of the isocyanate (Ashida and Iwasaki, 1995). Semi-rigid foams possesses higher load-bearing, impact resistance, and compression recovery properties than flexible foam (Ashida and Iwasaki, 1995). Additionally, semi-rigid foam has a higher hydroxyl number[3].
- *Subsets of standard flexible polyurethane foam*:
    - *Molded foam*: formed by pouring foam reaction products into a mold and allowing the contents to react and expand. Molded foam is often used for automotive cushions (Uhlig, 1999).
    - *Slabstock foam*: formed by pouring flexible foam reaction products onto a flat surface and allowing it to react and expand into a slab shape. Once the foam cures, it is subsequently cut into desired shapes (Uhlig, 1999).
    - *Viscoelastic foam* (also known as memory foam): a closed-cell flexible polyurethane foam that traps in air and/or gas. Viscoelastic foam is characterized by its slow recovery

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[3] A measure of the concentration of the hydroxyl groups on the polyol

to its original configuration after compression, as well as its low resiliency (i.e., high energy absorption)(Polyurethane Foam Association, 2003).

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-*Rigid foam* is a hard, closed-cell foam. Rigid foam exhibits low flexibility and permanent deformation after compression (Ashida and Iwasaki, 1995; North Star Polymers, 2013). It is mainly used in insulation applications (Ashida and Iwasaki, 1995) and is always made using methylene diphenyl diisocyanate (MDI) (Markets and Markets, 2011).

B-2 CDR Use Categories for Brominated Phthalate Cluster

Industrial Use
-*Plasticizer:* Chemical substances used in plastics, cement, concrete, wallboard, clay bodies, or other materials to increase their plasticity or fluidity. Examples include phthalates, trimellitates, adipates, maleates, and lignosulphonates (EPA, 2012e).
-*Flame Retardants:* Chemical substances used on the surface of or incorporated into combustible materials to reduce or eliminate their tendency to ignite when exposed to heat or a flame for a short period of time. Examples include inorganic salts, chlorinated or brominated organic compounds, and organic phosphates/phosphonates (EPA, 2012e).

Consumer Use
-*Electrical and electronic products:* Chemical substances contained in electrical and electronic products that are intended for consumer or commercial use are reported under this code. Examples of electrical and electronic products include computers, office equipment, appliances, electric lighting, electrical wire and cables, radios, televisions and monitors, telephones, multi-media devices, digital cameras, adapters, alarms (burglar, fire, smoke), and communication equipment (EPA, 2012e).
-*Furniture and furnishings not covered elsewhere:* Chemical substances contained in furniture and furnishings made from metal, wood, leather, plastic or other materials that are intended for consumer or commercial use are reported under this code. Examples of products include movable and installed furniture such as tables, chairs, benches, desks, cabinets, shelving, stools, television stands, display cases, book cases, and storage units. This code does not include foam seating and bedding products (EPA, 2012e).
-*Building/construction materials not covered elsewhere:* Chemical substances contained in building and construction materials not covered elsewhere that are intended for consumer or commercial use are reported under this code. Examples of products include insulation materials such as foams and fibers, roofing and gutters, ceiling products, exterior siding, drywall, concrete, masonry and cement, building hardware, fencing, decking, hardware and fasteners (nuts, bolts, screws, nails, and tacks), plumbing, duct work, abrasive and sanding products, sheet metal, plaster, weather stripping, wire or wiring systems, and bricks (EPA, 2012e).

B-3 Applications/End-uses of Polyurethanes

- Furniture
- Construction
- Footwear
- Transportation
- Flooring Underlay
- Bedding
- Furniture
- Packaging
- Textiles
- Other