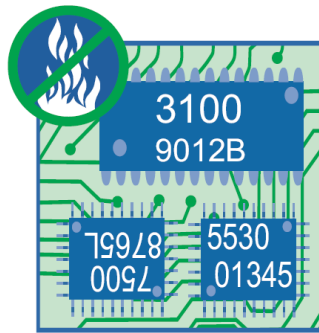


FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

Chapter 5



FINAL REPORT

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5 Potential Exposure to Flame Retardants and Other Life-Cycle Considerations

Many factors must be considered to evaluate the risk to human health and the environment posed by any flame-retardant chemical. Risk is a function of two parameters, hazard and exposure. The hazard associated with a particular substance or chemical is its potential to impair human health, safety, or ecological health. While some degree of hazard can be assigned to most substances, the toxicity and harmful effects of other substances are not fully understood. The exposure potential of a given substance is a function of the exposure route (inhalation, ingestion, and dermal), the concentration of the substance in the contact media, and the frequency and duration of the exposure.

The purpose of this chapter is to identify the highest priority routes of exposure to flame-retardant chemicals used in printed circuit boards (PCBs). Section 5.1 through Section 5.4 provide general background regarding potential exposure pathways that can occur during different life-cycle stages, discuss factors that affect exposure potential in an industrial setting, provide process descriptions for the industrial operations involved in the PCB manufacturing supply chain (identifying the potential primary release points and exposure pathways), and discuss potential consumer and environmental exposures. Following this general discussion, Section 5.5 highlights life-cycle considerations for the ten flame retardants evaluated by this partnership. The chapter is intended to help the reader identify and characterize the exposure potential of flame-retardant chemicals based on factors including physical and chemical properties and reactive versus additive incorporation into the epoxy resin. The information presented in this chapter should be considered with the chemical-specific hazard assessment presented in Chapter 4.

Exposure can occur at many points in the life cycle of a flame-retardant chemical. There is a potential for occupational exposures during industrial operations; exposure to consumers while the flame-retardant product is being used; and exposure to the general population and environment when releases occur from product disposal or end-of-life recycling. Figure 5-1 presents a simplified life cycle for a flame-retardant chemical used in a PCB, and Table 5-1 summarizes the potential exposure routes that can occur during each of these life-cycle stages. The remaining sections of Chapter 5 discuss the information summarized in Figure 5-1 and Table 5-1 in more detail.

Figure 5-1. Life Cycle of Flame-Retardant Chemicals in PCBs (example with Tetrabromobisphenol A (TBBPA) as reactive FR)

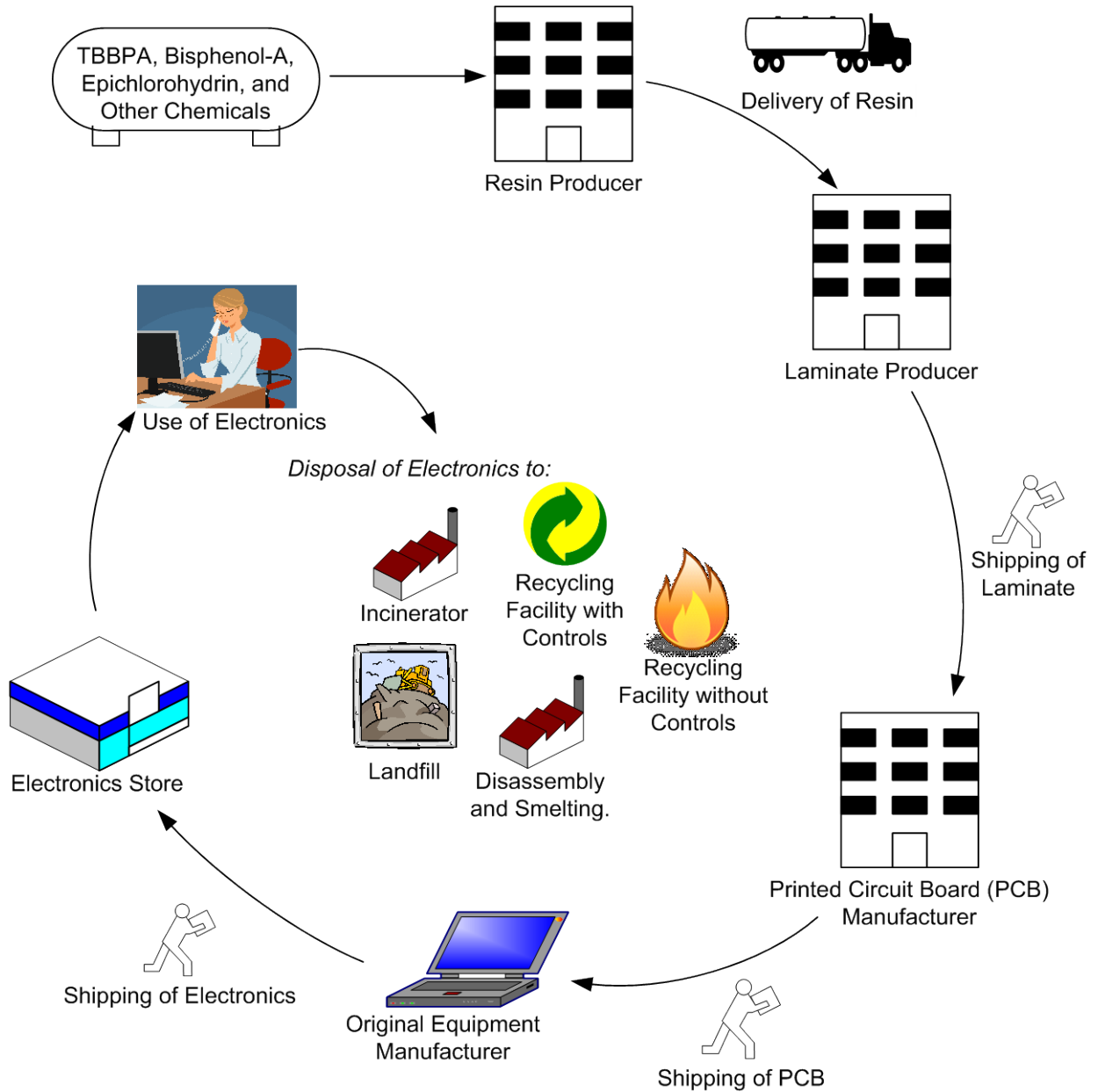


Table 5-1. Potential Exposure to Flame-Retardant Chemicals throughout Their Life Cycle in PCBs

Life Cycle Stage	Potential Exposure
Reactive Flame Retardants	
Manufacture: Chemical manufacture, resin formulation	Manufacture emissions will vary based on manufacturing practices and physical/chemical properties; direct exposure is possible because the neat chemical is handled.
Pre-impregnated material (prepreg) and laminate production	Cutting of material can release minor amounts of dust that contains epoxy resin. Reactive flame retardants are part of the polymer (chemically bound), and only trace amounts of unreacted flame retardant are anticipated to remain in the polymer matrix. Trace quantities are currently unknown* and/or will vary based on manufacturing methods and processes.
PCB manufacturing and assembly	Remaining, unreacted flame retardant may offgas; PCB manufacturing processes, such as drilling, edging, and routing, cut into the base material. In electronic assembly, some soldering processes could induce thermal stress on resins, which could yield degradation products. Testing is needed to determine the potential for formation of these products.
Use	Only residual unreacted flame retardant is available to offgas during use. In order for exposure to occur, offgassing from residual unreacted flame retardant would have to escape product casing. Testing is needed to determine exposure potential.
End of Life	<p><i>Disassembly/Recycling:</i> Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Reactive flame retardants are chemically bound to the polymer; however, levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown.</p> <p><i>Landfill:</i> Testing needs to be conducted to determine exposure potential from leaching from PCBs.</p> <p><i>Incineration:</i> Combustion by-products need to be considered (see combustion experiments).</p> <p><i>Open Burning:</i> Combustion by-products need to be considered (see combustion experiments).</p> <p><i>Smelting:</i> Combustion by-products need to be considered.</p>
Additive Flame Retardants	
Manufacture: Chemical manufacture, resin formulation	Manufacture emissions will vary based on manufacturing practices and physical/chemical properties; direct exposure is possible because the neat chemical is handled.
Prepreg and laminate production	Cutting of material can release minor amounts of dust that contains epoxy resin. Additive flame retardants are not chemically bound to the polymer, and their potential to offgas or leach out of the product is not known. Physical/chemical properties, such as vapor pressure and water solubility, may contribute to the potential for exposure to these chemicals.
PCB manufacturing and assembly	Additive flame retardant may offgas; PCB processes, such as drilling, edging, and routing, cut into the base material. In electronic assembly, reflow or wave soldering processes could induce thermal stress on resins, which could yield offgas products. Physical/chemical properties, such as vapor pressure and water solubility, may contribute to the potential for exposure to these chemicals.
Use	Although flame retardants are embedded in the polymer matrix, testing needs to be conducted to better understand the offgassing potential of additive flame retardants. Dermal exposure is not anticipated since the flame retardants are embedded in the polymer matrix.
End of Life	<p><i>Disassembly/Recycling:</i> Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Additive flame retardants are not chemically bound to the polymer and can be released through the dust. Physical/chemical properties, such as vapor pressure, may contribute to the potential for exposure to these chemicals.</p> <p><i>Landfill:</i> Testing needs to be conducted to determine exposure potential from leaching from PCBs.</p> <p><i>Incineration:</i> Combustion by-products need to be considered (see combustion experiments).</p> <p><i>Open Burning:</i> Combustion by-products need to be considered (see combustion experiments).</p> <p><i>Smelting:</i> Combustion by-products need to be considered.</p>

*For TBBPA, Sellstrom and Jansen (1995) found about 0.7 micrograms of residual (or “free”) TBBPA per gram of PCB.

5.1 Potential Exposure Pathways and Routes (General)

The risk associated with a given chemical or substance is largely dependent on how the exposure potentially occurs. For example, the toxicological effects associated with inhaling the chemical are different from those associated with ingesting the chemical through food or water. As a result, exposure is typically characterized by different pathways and routes.

An exposure pathway is the physical course a chemical takes from the source of release to the organism that is exposed. The exposure route is how the chemical gets inside the organism. The three primary routes of exposure are inhalation, dermal absorption, and ingestion. Depending on the hazard of the chemical, exposure from only one or perhaps all three routes may result in risk.

Expected environmental releases and potential exposure routes of chemicals are dependent upon their physical and chemical properties. For example, a highly volatile liquid can readily evaporate from mix tanks, potentially resulting in fugitive air releases and potential exposures to workers who breathe the vapors, while chemicals manufactured as solids may expose workers to fugitive dust that may be generated, but are unlikely to generate vapors. Each potential exposure route, along with appropriate endpoints, should be evaluated independently. Endpoints are the specific toxicological effect, such as cancer, reproductive harm, or organ/tissue damage. There are circumstances when a chemical has serious effects for a given endpoint, but due to physical and chemical properties as well as environmental fate, there is minimal potential for the chemical to be transported from the release point to the endpoint. This may essentially eliminate the potential pathway and route of exposure and, therefore, eliminate the associated risk.

Table 5-2 highlights key physical, chemical, and fate properties that affect the likelihood for exposure to occur: the physical state of the chemical, vapor pressure, water solubility, log K_{ow} , bioaccumulation potential, and persistence. The relevance of each physical, chemical, and fate property, as well as its impact on exposure potential, is summarized in Table 5-2. Detailed descriptions of these properties and how they can be used to assess potential environmental release, exposure, and partitioning, as well as insight into a chemical's likelihood to cause adverse toxicological effects, can be found in Chapter 4. More detailed information on physical, chemical, and fate properties of each flame-retardant chemical can be found in the full chemical hazard profiles in Section 4.9.

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals

Physical State of Chemical (ambient conditions)									
<i>Relevance to exposure:</i> Indicates if a chemical substance is a solid, liquid, or gas under ambient conditions. This is determined from the melting and boiling points. Chemicals with a melting point more than 25°C are considered solid. Those with a melting point less than 25°C and a boiling point more than 25°C are considered liquid and those with a boiling point less than 25°C are considered a gas. Physical state influences potential for dermal and inhalation exposure. For chemicals that exist as a gas, there is generally a potential for direct inhalation but not dermal exposure. For solids, there is potential for the inhalation and ingestion of dust particles and dermal contact. For liquids, there is potential for direct dermal contact but not for direct inhalation of the liquid (except in operations that produce aerosols).									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid
Vapor Pressure (mm Hg) at 25°C									
<i>Relevance to exposure:</i> Indicates the potential for a chemical to volatilize into the atmosphere. If a chemical has a vapor pressure leading to volatilization at room temperature or typical environmental conditions, then the chemical may evaporate and present the potential for inhalation of the gas or vapor. For a Design for the Environment (DfE) chemical alternatives assessment, inhalation exposure is assumed to occur if the vapor pressure is greater than 1×10^{-8} mm Hg. A default value of $<10^{-8}$ was assigned for chemicals without data that are anticipated to be nonvolatile this is based on EPA HPV assessment guidance (U.S. EPA 1999).									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.7×10^{-8}	$<10^{-8b,c}$	2.2×10^{-5a}	$<10^{-8b,c}$	$<10^{-8b,c}$	$<10^{-8c}$	$<10^{-8c}$	$<10^{-8d}$	$<10^{-8d}$	$<10^{-8c}$
^a Extrapolated. ^b Estimated based on polymer assessment literature (Boethling and Nabholz, 1997). ^c Estimated based on HPV guidance for nonvolatile compounds. ^d Estimated.									
Water Solubility (mg/L)									
<i>Relevance to exposure:</i> Indicates the potential of a chemical to dissolve in water and form an aqueous solution. Water soluble chemicals present a higher potential for human exposure through the ingestion of contaminated drinking water (including well water). In general, absorption after oral ingestion of a chemical with a water solubility less than 10^{-3} mg/L is not expected. Water soluble chemicals are more likely to be transported into groundwater, absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, and undergo atmospheric removal by rain washout. A water solubility of 10^{-3} mg/L is used for large, high molecular weight (MW) non-ionic polymers according to the literature concerning polymer assessment (Boethling and Nabholz, 1997). A substance with water solubility at or below 10^{-3} mg/L is considered insoluble.									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.16	$<0.001^{a,b,c}$	3,574 ^e	$\leq 0.62^d$ $<0.001^c$	8.4 (n=1) ^b 0.1 (n=2) ^b ≤ 0.001 (n ≥ 3) ^{a,b,c}	≤ 0.09 at 20 °C, pH 6-7	2.5×10^3	2.0×10^4	120	1.78 at 20°C, pH 8.3
^a Estimated based on EPA High Production Volume assessment guidance. ^b Estimated. ^c Estimated based on polymer assessment literature (Boethling and Nabholz, 1997). ^d Estimated based on proprietary components with MW <1,000. ^e Measured value for the hydrolysis product of DOPO.									

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals (Continued)

Log K_{ow}									
<p><i>Relevance to exposure:</i> Indicates a chemical's tendency to partition between water and lipids in biological organisms. A high log K_{ow} value indicates that the chemical is more soluble in octanol (lipophilic) than in water, while a low log K_{ow} value means that the chemical is more soluble in water than in octanol. Log K_{ow} can be used to evaluate absorption and distribution in biological organisms, potential aquatic exposure, and potential general population exposure via ingestion. Generally, chemicals with a log K_{ow} <4 are water soluble and bioavailable, chemicals with a log K_{ow} ≥4 tend to bioaccumulate. Chemicals with a high log K_{ow} also tend to bind strongly to soil and sediment. Log K_{ow} cannot be measured for inorganic substances, polymers, and other materials that are not soluble in either water or octanol. This is indicated in the table with "No data".</p>									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
4.54	7.4 (n=0) ^a 11 (n=1) ^a No data (n≥2)	1.87 ^a	3.7-7 ^b	3.4 (n=1) ^a 4.4 (n=2) ^a 5.3 (n=3) ^a 6.3 (n=4) ^a	No data	-0.44 ^a	<-2 ^a	No data	No data
^a Estimated. ^b Estimated based on proprietary components with MW <1,000.									
Bioaccumulation Potential									
<p><i>Relevance to exposure:</i> Indicates the degree to which a chemical substance may increase in concentration within a trophic level. Bioconcentration describes the increase in tissue concentration relative to the water concentrations (environmental sources); bioaccumulation generally includes dietary and environmental sources. As chemicals bioconcentrate or bioaccumulate, there is a higher potential for them to reach a level where a toxic effect may be expressed. Estimated and/or measured bioconcentration and bioaccumulation values are presented as ranges based on relevant DfE hazard categories for each chemical. The DfE Alternatives Assessment criteria for bioaccumulation potential considers both the bioaccumulation factor (BAF) and bioconcentration factor (BCF) values, as follows: Very High (VH) if BAF (log BAF) or BCF (log BCF) is >5,000 (>3.7); High (H) if BAF or BCF is between 5,000 (3.7-3) and 1,000; Moderate (M) if BAF or BCF is between <1,000 and 100 (<3-2); and Low (L) if BAF or BCF is <100 (<2) (see <i>DfE Program Alternatives Assessment Criteria for Hazard Evaluation</i>).</p>									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
Moderate (100-<1,000)	High (1,000-5,000) ^b	Low (<100) ^b	High (1,000-5,000) ^b	High (1,000-5,000) ^b	Low (<100) ^a	Low (<100) ^a	Low (<100) ^b	Low (<100) ^a	Low (<100) ^a
^a Based on professional judgment. ^b Based on estimated data.									

Table 5-2. Key Physical/Chemical and Fate Properties of Flame-Retardant Chemicals (Continued)

Persistence									
<p><i>Relevance to exposure:</i> Indicates the length of time required for a chemical substance to be completely converted to small building blocks including water, carbon dioxide, and ammonia (“ultimate degradation”). Persistence is typically expressed as a “half-life”, which is the time for the amount of the substance to be reduced by one half. For a DfE chemical alternatives assessment, persistent chemicals include those that have metabolic or degradation products that have long half-lives. The longer a chemical or its degradation/metabolism products exist in the environment, the higher the likelihood for human or environmental exposure. “Compartments” refer to those environmental media to which chemicals may partition and include soil, sediment, water and air as standard compartments for fate assessment. Persistence is considered Very High (VH) if the half-life is >180 days or recalcitrant; High (H) if the half-life is 60-180 days; Moderate (M) if the half-life is <60 days but ≥16 days; Low (L) if half-life is <16 days OR readily passes biodegradability test not including the 10-day window; and Very Low (VL) if passes biodegradability test with 10-day window (see <i>DfE Program Alternatives Assessment Criteria for Hazard Evaluation</i>).</p>									
TBBPA	D.E.R. 500 Series	DOPO	Dow XZ-92547	Fyrol PMP	Aluminum Hydroxide	Aluminum Diethylphosphinate	Melamine Polyphosphate	Silicon Dioxide (amorphous)	Magnesium Hydroxide
High (60-180 days)	Very High (>180 days) ^c	High (60-180 days) ^a	Very High (>180 days) ^c	Very High (>180 days) ^c	High (60-180 days) ^b	High (60-180 days) ^b	High (60-180 days) ^b	High (60-180 days) ^b	High (60-180 days) ^b
<p>^a Based on results from biodegradation estimation model. ^b Based on professional judgment. ^c Estimated based on polymer assessment literature (Boethling and Nabholz, 1997).</p>									

5.2 Potential Occupational Releases and Exposures

The unit operations associated with each part of the PCB manufacturing supply chain result in a unique set of potential release points and occupational exposures to flame-retardant chemicals. This section provides a general overview of occupational pathways and routes of exposure, and then identifies the specific processes and corresponding potential release and exposure points for the unit operations associated with the manufacturing of flame retardants, epoxy resins, laminates, and PCBs. It should be noted that many of the potential occupational exposures identified here have been reduced or eliminated by the use of engineering controls and personal protective equipment. Also, the level of exposure will vary considerably between workers and the general population. Some releases will only result in exposure for workers, while other releases result in exposures for the environment and the general population.

Inhalation Exposures

The physical state of the chemical during chemical manufacturing and downstream processing significantly affects the potential for inhalation exposure of workers. In particular, the physical state can result in three types of inhalation exposures that should be evaluated.

Dust: Chemicals that are manufactured, processed, and used as solids have the potential to result in occupational exposure to fugitive dusts. The potential for fugitive dust formation depends on whether the solid chemical is handled in the crystalline form, as an amorphous solid, or as a fine powder, as well as the particle size distribution and solids handling techniques. If there is exposure to dust, the level of exposure is directly proportional to the concentration of chemical in the particulate form. Therefore, a flame retardant that is used at a lower concentration results in a decreased exposure from this pathway and route (assuming that an equivalent amount of dust is inhaled).

When assessing occupational exposures to flame-retardant chemicals, it is important to note the physical state of the chemical at the potential point of release and contact. The pure chemical may be manufactured as a solid powder, indicating a potential exposure to dust. However, it may be formulated into solution before any workers come in contact with it, thereby eliminating inhalation exposure to dust as a potential route. It is also important to note that the size of the dust particles may have a profound influence on the potential hazards associated with inhalation exposures for those materials that are not anticipated to be absorbed in the lungs. For these materials, the potential hazards are typically associated with smaller, respirable particles (generally those less than 10 microns in diameter).

Vapor: Exposure to vapors can occur when liquid chemicals volatilize during manufacturing, processing, and use. Most chemical manufacturing operations occur in closed systems that contain vapors. However, fugitive emissions are expected during open mixing operations, transfer operations, and loading/unloading of raw materials. More volatile chemicals volatilize more quickly and result in greater fugitive releases and higher occupational exposures than less volatile chemicals. Therefore, vapor pressure is a key indicator of potential occupational exposures to vapors.

Mist: Both volatile and nonvolatile liquids can result in inhalation exposure if manufacturing or use operations result in the formation of mist. It is unlikely that flame-retardant chemicals used in PCBs will be applied as a mist.

Dermal Exposures

Occupational dermal exposure is also affected by the physical state of the chemical at the point of release and contact. For example, the likelihood of liquids being splashed or spilled during sampling and drumming operations is different than for similar operations involving polymerized solids, powders, or pellets. Dermal exposure is also generally assumed to be proportional to the concentration of chemical in the formulation. For example, the dermal exposure from contacting a pure chemical is greater than the exposure from contacting a solution that contains only 10 percent of the chemical. Screening-level evaluations of occupational dermal exposure can be based on the worker activities involving the chemical. For example, there may be significant exposure when workers handle bags of solid materials during loading and transfer operations. Maintenance and cleanup activities during shutdown procedures, connecting transfer lines, and sampling activities also result in potential dermal exposures.

Ingestion Exposures

Occupational exposures via ingestion typically occur unintentionally when workers eat food or drink water that has become contaminated with chemicals. Several pathways should be considered. Often the primary pathway is poor worker hygiene (eating, drinking, or smoking with unwashed hands). First, dust particles may spread throughout the facility and settle (or deposit) on tables, lunchroom surfaces, or even on food itself. Vapors may similarly spread throughout the facility and may adsorb into food and drinking water. Another potential pathway for ingestion occurs from dust particles that are too large to be absorbed through the lungs. These “non-respirable particles” are often swallowed, resulting in exposures from this route. While ingestion is considered to be a realistic route of exposure to workers, it is often considered less significant when compared to inhalation and dermal exposures, based on the relative exposure quantities. On the other hand, ingestion during consumer use and to the general population is often as significant as or more important than the inhalation and dermal routes. If persistent and bioaccumulative compounds get into the environment and build up in the food chain, they can become a significant exposure concern.

5.2.1 Flame Retardant and Epoxy Resin Manufacturing

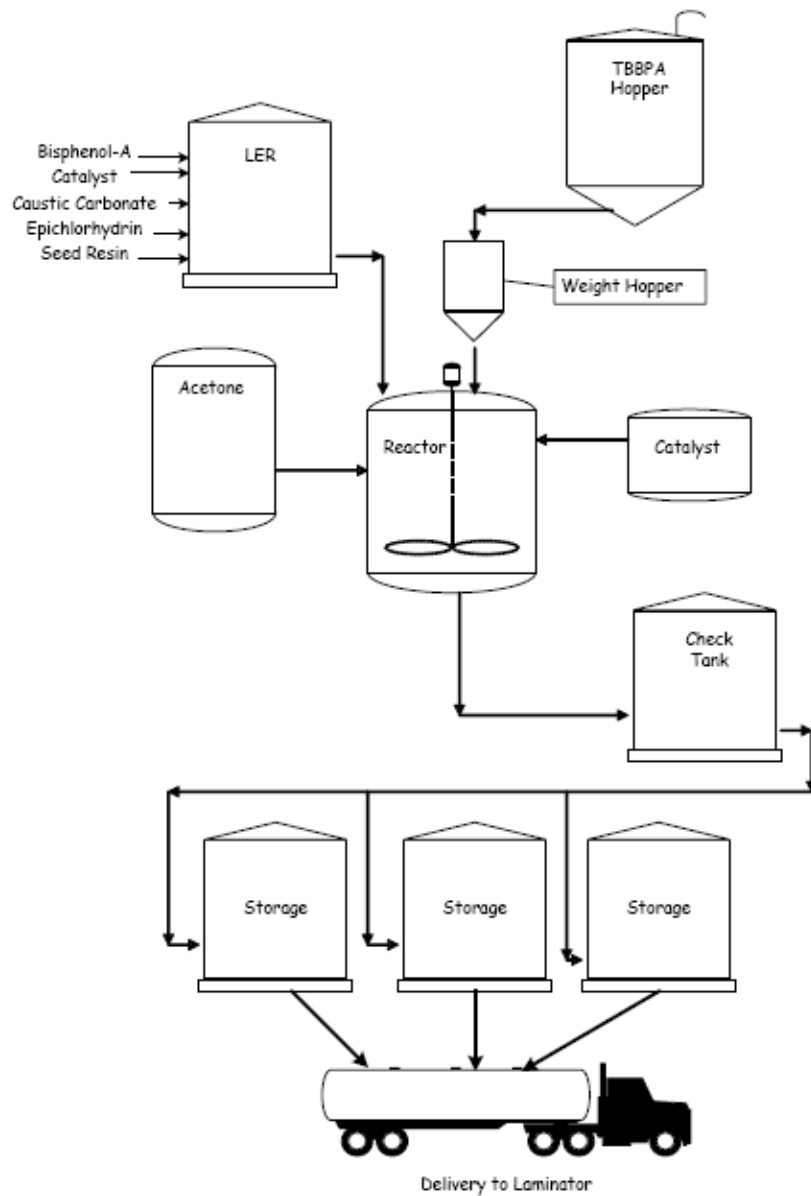
The specific unit operations, operating conditions, transfer procedures, and packaging operations vary with the manufacture of different flame-retardant and resin chemicals. Potential releases and occupational exposures will depend on each of these parameters. While it is outside the scope of this report to identify and quantify the releases and exposures associated with individual chemicals, this section presents a general description of typical chemical manufacturing processes and identifies potential releases.

Figure 5-2 presents a generic process flow diagram for epoxy resin manufacturing. Production volumes and batch sizes associated with flame-retardant and epoxy resin chemicals typically require the raw materials to be stored in large tanks or drums until use. The first step in most

epoxy resin manufacturing processes for standard Flame Resistant 4 materials is to load the raw materials into some type of reactor or mix tanks – as shown in Figure 5-2, the tanks labeled as liquid epoxy resin and reactive flame retardant (e.g. TBBPA) hopper. Next, large-quantity liquids are typically pumped into the reactor, and small-quantity raw materials may be manually introduced or carefully metered via automated systems. Releases may occur from these operations, but occupational exposure potential is typically small due to the number of safety procedures and engineering controls in place.

Throughout the resin manufacturing process, there are several release points that may pose an exposure risk to workers: packaging operations, leaks from pumps and tanks, fugitive emissions from equipment, cleaning of process equipment, and product sampling activities. Additionally, crude or finished products are often stored on-site in drums, day-tanks, or more permanent storage vessels until the flame-retardant epoxy resin is packaged and shipped to the laminator. The transfer and packaging operations, as well as any routine and unplanned maintenance activities, may result in releases of and exposures to hazardous chemicals.

Figure 5-2. Epoxy Resin Manufacturing Process (example with TBBPA as reactive FR)



5.2.2 Laminate and Printed Circuit Board Manufacturing

The laminate and PCB manufacturing processes, summarized in Figure 5-3 and Figure 5-4, can result in occupational exposures to process chemicals if protective measures are not put in place. The potential release of flame-retardant chemicals from laminates is not known, but is probably very low, if there is any at all. As shown in Figure 5-3, the laminator combines the flame-retardant epoxy resin with a curing agent (or hardener) and a catalyst in a mix tank as a first step of the laminate manufacturing process. From there, woven fiberglass mats are embedded with the epoxy resin, resulting in prepreg sheets. A copper clad laminate (CCL) is then assembled by layering the prepreg sheets with copper sheets and stainless steel caul plates, as shown in Figure 5-3. The finished CCL is then shipped to the PCB manufacturing facility.

As summarized in Figure 5-4, PCB manufacturing involves numerous chemical and electrochemical processes to cut, drill, clean, plate, and etch conductive pathways. Almost all of these processes involve immersion of equipment or work pieces into a series of process baths, with each bath followed by a rinsing step. For example, the process of drilling holes in the PCB involves a series of individual steps, including cleaning (or desmearing) the holes with chemicals or gas plasma and plating the holes with copper, and each step requires at least one process bath and rinsing.

Many PCB manufacturers have implemented relatively simple techniques to reduce the amount of chemicals that enter wastewater, such as withdrawing equipment from tanks slowly to allow maximum drainage back into the process tank (CA EPA, 2005). Most manufacturing facilities prevent worker exposure through use of engineering controls, personal protective equipment, and safe work practices.

Figure 5-3. Laminate Manufacturing Process

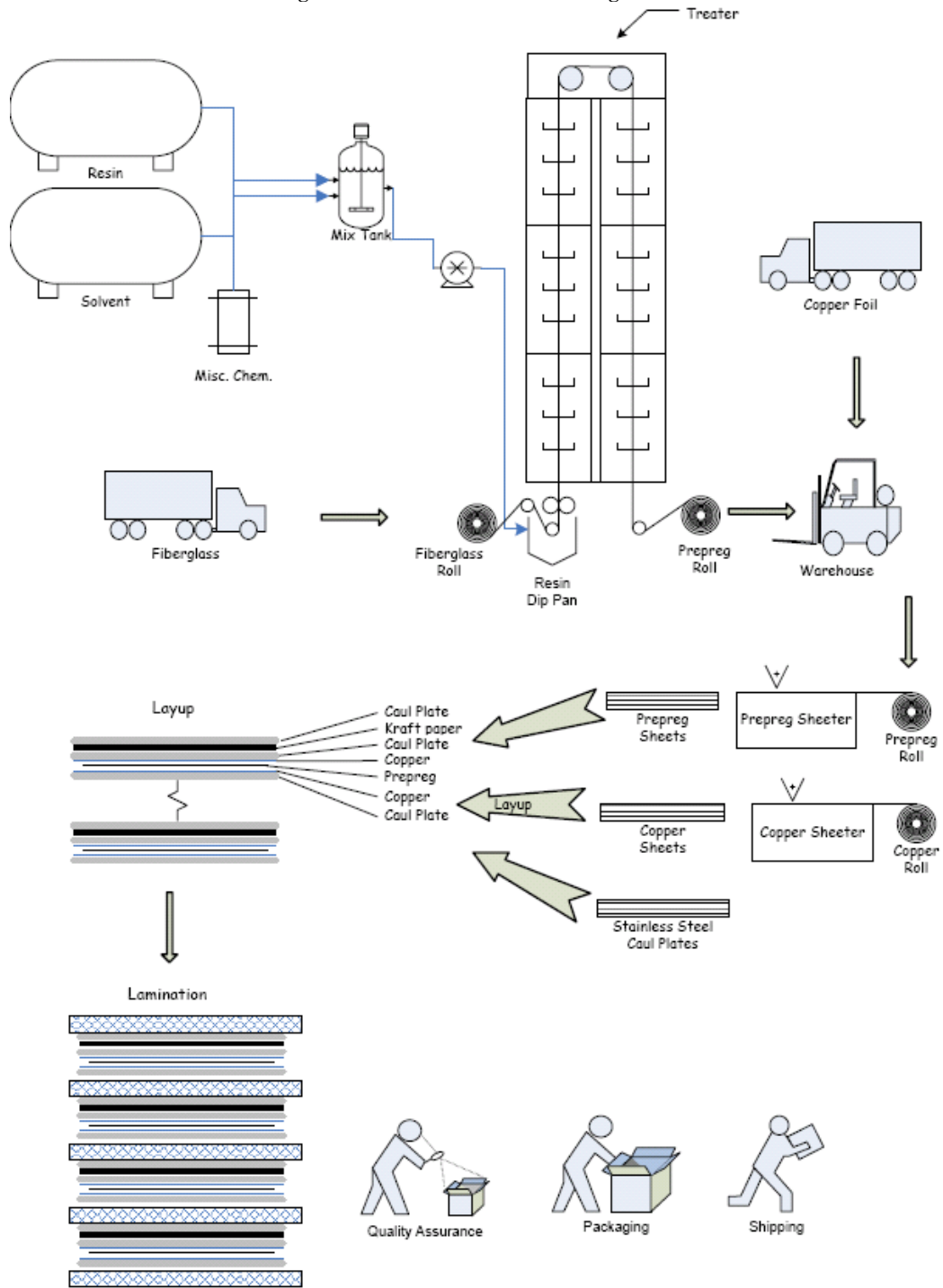
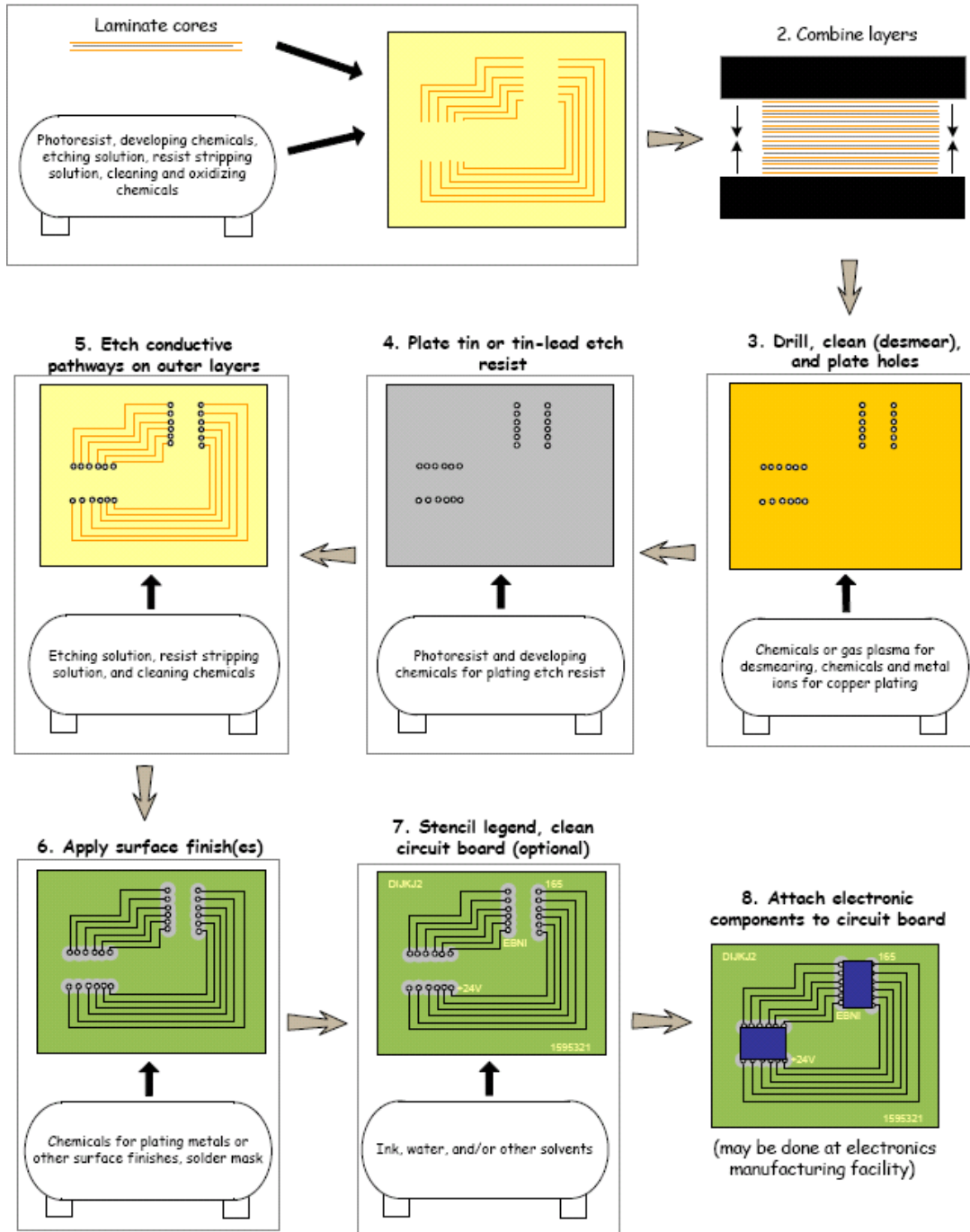


Figure 5-4. Printed Circuit Board Manufacturing Process

1. Etch conductive pathways on inner layers



5.2.3 Best Practices

Incorporating best practices into the manufacturing process can reduce the potential for exposure. The Bromine Science and Environmental Forum (BSEF) set up the Voluntary Emissions Control Action Programme (VECAP) “to manage, monitor and minimize industrial emissions of brominated flame retardants into the environment through partnership with Small and Medium-sized Enterprises.” The program started with decabromodiphenyl ether in Europe. VECAP members follow six central steps to continually improve their processes and reduce emissions: (1) commitment to the VECAP code of good practices; (2) self-audit; (3) mass balance; (4) baseline emissions survey; (5) emissions improvement plan; and (6) implementation and continuous improvement (BSEF, 2007).

ISO, the International Organization for Standardization, has also developed a series of environmental management standards under the 14000 label. ISO 14000 standards establish a “holistic, strategic approach” for continually reducing negative environmental impacts. They are intended to cover a wide range of operations, and thus are not specific to brominated flame retardants (ISO, 2007).

5.3 Potential Consumer and General Population Exposures

Exposures to consumers and the environment are different from exposures to workers and should be evaluated separately for a number of reasons. Occupational exposures typically result from direct contact with chemicals at relatively high concentrations while workers are conducting specific tasks. Conversely, consumers may be exposed over a much longer period, but to a much smaller level because the chemical is incorporated into the product. Also, the general population and the environment will be exposed via different pathways and routes from workers and consumers. For example, a person who does not own a product containing a flame-retardant PCB may still be exposed if the chemical leaches from the disposed product into the drinking water supply. Once in the water supply, groundwater, or surface water, it can be ingested by people or consumed by fish and other animals. Similarly, if the chemical is released to the atmosphere during manufacture, use, or disposal, it may settle out on food crops and be ingested directly by people, or by cattle or other livestock. If the chemical is bioaccumulative, it may concentrate in the animal and reach people through the food chain. For these reasons, exposure to the environment and the general population should be assessed independently from occupational exposure.

A quantitative exposure assessment is outside the scope of this report. However, the primary pathways and routes from environmental, general population, and consumer exposures are discussed in the following sections. Important chemical-specific factors that may help the reader compare potential exposure between various flame-retardant alternatives are also discussed.

5.3.1 Physical and Chemical Properties Affecting Exposures

As previously discussed, the physical and chemical properties of a chemical often determine the pathways and routes of exposure. In addition, the physical and chemical properties will affect how the chemical becomes distributed in the environment once it is released, which will, in turn, influence the potential for the chemical to be transported from the release point to the receptor.

Information about persistence, bioaccumulation, and physical and chemical properties affecting transport in the environment is presented in Section 4.3 of this report as well as Table 5-2.

As discussed in Chapter 3, flame-retardant chemicals can be classified as either additive or reactive and this distinction may affect exposure. Additive flame retardants are added to a manufactured product without bonding or reacting with the product, whereas reactive flame retardants are chemically reacted into the raw materials that are used to make the final product. As of 2008, most PCBs use reactive TBBPA, which loses the identity of the starting monomer material during polymerization. Because they are chemically bound to PCBs, reactive flame retardants are much less likely to pose occupational, consumer, or environmental exposure concerns than additive flame retardants. Moreover, the polymerization processes are typically conducted in totally enclosed systems, thus minimizing the potential for occupational exposure. It should be noted, however, that reactive chemicals or close analogs could be released from the finished product if a portion of the chemicals is not completely reacted during the polymerization process. According to a 1995 study, a trace amount of starting TBBPA material is unreacted after polymerization (4 micrograms per gram) (Sellstrom and Jansson, 1995).

5.3.2 Consumer Use and End-of-Life Analysis

Consumer Use

The nature of exposure to PCBs during use will vary with the composition of the product and the manner in which the product is used. However, little information existed in the literature in 2008 about the emissions potential of alternative flame retardants from the use of electronic products. Similarly, little to no research has addressed whether the type of flame retardants used in PCBs potentially affects these emissions.

Several studies have examined the potential of brominated flame retardants to volatilize or offgas from electronic devices. A study conducted by the German laboratory ERGO, which investigated offgassing potential of TBBPA from computers under both real-world conditions and chamber conditions, found that all emissions of TBBPA were associated with the housing material (additive application of TBBPA), none with the printed circuit boards (reactive application of TBBPA) (HDPUG, 2004). The German Federal Institute of Materials Testing also conducted chamber emission testing of flame retardants from electronic articles and construction products. They found very low emissions, even at the elevated operating temperatures of computers (Kemmlin et al., 2003). Beard and Marzi (2006) investigated the offgassing potential of thermoplastic polymers containing phosphorus-based and brominated flame retardants by simulating extreme indoor car heat conditions as a worst case scenario; the study found very low levels of volatilization (0 to 6 mg/kg).

Without further information on the exposure potential associated with printed circuit board use, the differences between flame-retardant alternatives cannot be estimated. Additive flame retardants, which are not commonly used in PCBs, are more likely to generate emissions than reactive flame retardants. However, for additive flame retardants the potential for offgassing is directly related to the volatility of the chemical (vapor pressure), which again is related to molecule size and weight.

End-of-Life Pathways

The amount of electronic waste (e-waste) generated annually in the U.S. is growing rapidly. According to an EPA study, the amount of electronic products either recycled or disposed of annually increased from an estimated 1.1 million tons in 1999 to 2.2 million tons in 2005 (OSW 1, 2007). While electronics represent less than 2 percent of the total municipal solid waste stream, electronics contain many toxic substances that can adversely affect the environment and human health (OSW 1, 2007).

In the U.S., used electronic goods are typically purchased by equipment handlers, such as brokers and liquidation or auction services, or by equipment processors, such as refurbishers and recyclers. Most used electronic goods then undergo a series of tests to determine their condition. If a device is in good condition, it is reused either in part or in whole. Devices not in satisfactory condition become e-waste, and are sent to demanufacturing and destruction facilities where raw materials are either disposed of or recycled.

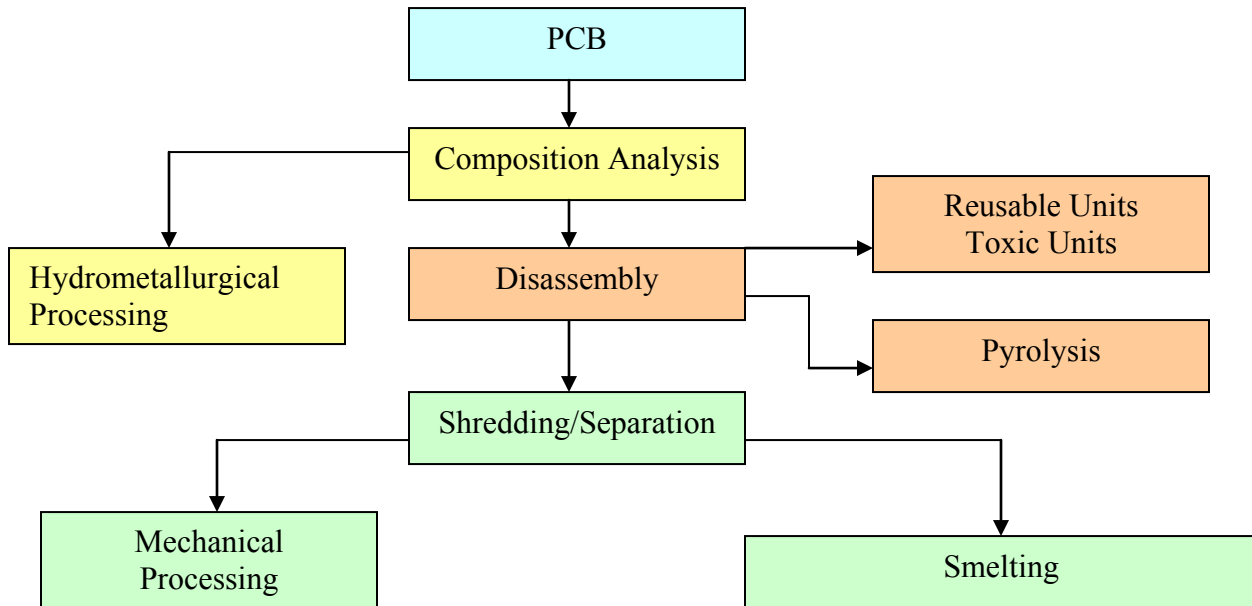
The manner in which electronic waste is disposed of or recycled determines the potential environmental and human health impacts.¹¹ An EPA study indicates that 15 to 20 percent of e-waste is recycled, and 80 to 85 percent is disposed of (includes landfill and incineration) (OSW 1, 2007). Of the e-waste that is recycled, a portion is shipped overseas. For example, 61 percent, or 107,500 tons of cathode ray tubes were shipped overseas in 2005 for remanufacture or refurbishment (OSW 2, 2007). Of the e-waste shipped overseas, an unknown portion is disassembled and recycled under largely unregulated conditions. The following sections describe disassembly and recycling practices typical of unregulated overseas conditions and summarize the nature of their potential impact.

Recycling

As Figure 5-5 shows, the PCB recycling process can involve both thermal processing, such as smelting to recover precious metals, and nonthermal processing, such as disassembly, shredding, separation, and chemical treatment. The potential level of exposure to workers and the general population that results from these processes will vary depending on the type of operation employed. Many recycling operations employ these methods in safe conditions that minimize the potential for exposure, and recover valuable metals that are part of finished boards.

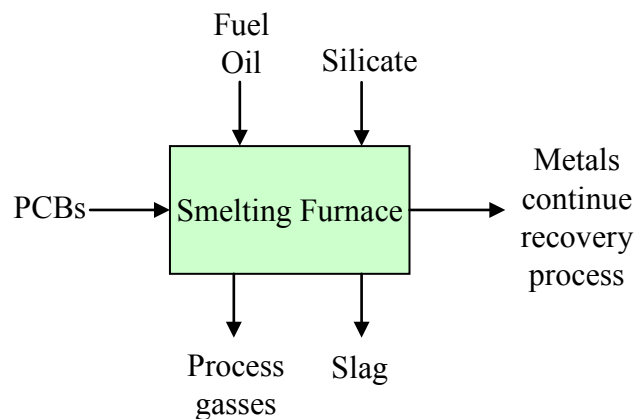
¹¹ According to a 2005 UN report, up to 50 million metric tons of e-waste is generated annually. In the U.S., the amount of e-waste is increasing at three times the rate of general waste. <http://www.rrcap.unep.org/policy2/13-Annex%204a-e-wastes%20SEPD2.pdf>

Figure 5-5. Sketch of the PCB Recycling Process (Li et al., 2004)



The thermal process of smelting separates valuable metals, such as gold, silver, platinum, palladium, selenium, and copper, from impurities in PCBs (Figure 5-6). The process operates by heating PCBs in a furnace to about 1,200 to 1,250°C in the presence of a reducing agent, which is usually carbon from fuel oil or the organic portion of PCBs. Silicate, such as silicon dioxide, is also added to help control reaction temperatures, and excess process gases are burned and purified to remove contaminants (Kindesjo, 2002). Therefore, silicon dioxide-based flame retardants are beneficial to the smelting process (Lehner, 2008).

Figure 5-6. Smelting Process (Kindesjo, 2002)



The smelting process generates two layers inside the furnace, a top layer of slag and a bottom layer of “black copper.” The bottom black copper layer can be directly sent to a copper recovery unit, such as a copper converter or leaching and electrowinning facility (Umicore, 2007). The top layer of slag is further processed to separate metals from impurities. After slag processing is complete, leftover slag is deposited in impoundment areas (Kindesjo, 2002).

In the absence of proper control equipment, the smelting process may pose risks to workers and the public through exposure to toxic chemicals. Halogenated flame retardants, for example, can lead to the formation of dioxins during the smelting process if proper safety measures are not installed (Tohka, 2002). However, the three primary smelters in the world as of 2008 – Boliden, Umicore, and Noranda – have learned how to operate with high loads of halogenated electronic scrap and effectively control emissions of dioxins and furans, mercury, antimony, and other toxic substances. In addition to the potential emission of toxic chemicals, high operating temperatures may create occupational hazards. High loads of bromine or chlorine may induce corrosion of gas-cleaning equipment. In sensitive areas, a process step for halogenide recovery may need to be added (Lehner, 2008).

In contrast to the recycling practices described above, a large portion of the e-waste shipped overseas to China, India, Pakistan, and other developing countries is subjected to unregulated recycling practices that may pose significant exposure concerns. Much of the PCB waste in unregulated operations is subject to open burning and acid leaching to recover precious metals. The Basel Action Network (BAN), which has visited open burning sites in Asia, reports that the general approach to recycling a circuit board first involves a de-soldering process. The PCBs are placed on shallow wok-like grills that are heated underneath by a can filled with ignited coal. In the wok-grill is a pool of molten lead-tin solder. The PCBs are placed in the pooled solder and heated until the chips are removable, and then the chips are plucked out with pliers and placed in buckets. The loosened chips are then sorted between those valuable for re-sale and those to be sent to the acid chemical strippers for gold recovery. After the de-soldering process, the stripped circuit boards go to another laborer who removes small capacitors and other less valuable components for separation with wire clippers. After most of the board is picked over, it then goes to large scale burning or acid recovery operations. It is this final burning process that potentially emits substantial quantities of harmful heavy metals, dioxins, beryllium, and polycyclic aromatic hydrocarbons (PAHs) (BAN and SVTC, 2002). The chemicals released through these processes can be inhaled by workers or could leach into the soil and water surrounding the area. In 2005, Greenpeace collected industrial wastes, indoor dusts, soils, river sediments, and groundwater samples from more than 70 industrial units and dump sites in Guiyu, China, and New Delhi, India, and found elevated levels of lead, tin, copper, cadmium, antimony, polybrominated diphenyl ethers, and polychlorinated biphenyls (Greenpeace, 2005).

In terms of the size of the population potentially at risk from open burning practices, the local government website of Guiyu reported that the city processes 1.5 million tons of e-waste every year, resulting in \$75 million in revenue (Johnson, 2006). The *People's Daily*, the state-run newspaper, reported in 2007 that Guiyu's more than 5,500 e-waste businesses employed more than 30,000 people, and state media estimated that almost 9 out of 10 people in Guiyu suffered from problems with their skin, nervous, respiratory, or digestive systems, which may be linked to these practices (Chisholm and Bu, 2007).

In order to better understand the effects of combustion processes, the relationship between specific combustion scenarios and the release of specific quantities of harmful substances has been further analyzed as part of this project. The results of these tests are presented in Chapter 6.

Landfills

E-waste sent to a landfill can lead to the creation of leachate (i.e., the mixture of rainwater and liquids within the waste). This leachate has the potential to seep into the ground or drain into nearby surface water, where it could affect the environment and have a negative impact on food and water supplies.

Most leachability studies as of 2008 in the literature have focused on the potential for discarded electronic devices to leach lead and other heavy metals. A relatively small number of these studies have investigated leachability potential of brominated flame retardants, and in general, have found either no or very small concentrations of brominated compounds in the leachate. When brominated flame retardants are added versus reacted into the resin system, the potential for the brominated flame retardants to leach from PCBs is much greater (KemI, 1995).

A study conducted by Beard and Marzi (2006) investigated the leachability potential of phosphorus-based and brominated flame retardants from thermoplastic polymers and found that small amounts of phosphorus and bromine respectively leached from the polymer. Another study (Yoneda et al., 2002) reported that a small amount of phosphate ions leached from a Fujitsu-developed dielectric material consisting of a bisphenol A epoxy with an additive type organic phosphate in hot water and aqueous alkaline solutions. When Fujitsu developed and tested a dielectric material consisting of a naphthalene-based epoxy with reactive-type organic phosphate, no phosphate ions leached from the material.

Aside from the studies referenced above, little information exists in the literature about the leachability potential of alternative flame retardants in landfill environments. Similarly, little to no research has addressed whether the type of flame retardants used in PCBs potentially affects the leachability of heavy metals.

5.4 Methods for Assessing Exposure

The European Union (EU)'s risk assessment of TBBPA offers insight into how personal and environmental exposure can be evaluated for flame-retardant chemicals. The EU risk assessment consists of two parts: the human health assessment, which was finalized in 2006, and the environmental assessment, which remains in draft form. As part of the human health and environmental risk assessments, exposure assessments have been conducted to estimate the levels of TBBPA released in occupational settings and in the general environment. In both, the EU differentiated between reactive and additive TBBPA and considered different stages of the life cycle when estimating releases. While the results of the EU risk assessment are not being used as part of this partnership project, Table 5-3 and Table 5-4 highlight some of the key methods and assumptions used to estimate emissions of TBBPA used as a reactive flame retardant in epoxy and other resins.

In the human health exposure assessment, the term exposure is used to denote personal exposure without the use of any personal protective equipment. The EU used both measured and predicted exposure data. Given the lack of TBBPA exposure data, the United Kingdom (UK) Health and Safety Executive (HSE) commissioned sampling studies within the UK at four sites: two sites involved in the production of polymers where TBBPA is incorporated into the finished product

(one of which manufactures resin laminates), and two sites where polymer products are recycled. The EU supplemented the measured exposure data with predicted data from the EASE (Estimation and Assessment of Substance Exposure) model, which is widely used across the EU for occupational exposure assessment of new and existing chemicals.

Table 5-3. Human Health Exposure Assessment (EU Risk Assessment, 2006)

Life-Cycle Stage	Key Methods/Assumptions	Source of Data
Production of laminates	<p><u>Inhalation exposure:</u> HSE visited a manufacturing facility of copper/resin laminates used for PCBs in 2002 to measure personal inhalation exposure. Used one personal sampler during the bromination step and multiple personal and static samplers during other steps of the laminate process. Due to uncertainty surrounding the measured estimates, EU used EASE model to estimate “typical” and “worst-case” inhalation values for bromination and other laminate production steps.</p> <p><u>Dermal exposure:</u> EASE model used to estimate “typical” and “worst-case” dermal values for bromination and other laminate production steps.</p>	Sampling results from 2002 study at UK laminate manufacturing facility; EASE model
Computer recycling	<p><u>Inhalation exposure:</u> HSE visited recycling facility where PCBs are shredded and exported for recovery of precious metals in 2002. Used personal and static samplers during shift. EU used EASE model to estimate “typical” and “worst-case” inhalation exposures.</p> <p><u>Dermal exposure:</u> EASE model used to estimate dermal exposure values. Predicted to be very low; consequently, dermal exposure values not used by EU in exposure assessment.</p>	Sampling results from 2002 study at UK recycling facility; EASE model
PCB Assembly	<p><u>Inhalation exposure:</u> Results of Sjodin et al., 2001 study, which measured levels of TBBPA in a factory that assembles PCBs, used to establish “typical” and “worst-case” inhalation values.</p> <p><u>Dermal exposure:</u> Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.</p>	Sjodin et al., 2001; professional judgment of risk assessors
Office environment	<p><u>Inhalation exposure:</u> Results of Sjodin et al., 2001 study, which measured levels of TBBPA in a factory that assembles PCBs, used to establish “typical” and “worst-case” inhalation values.</p> <p><u>Dermal exposure:</u> Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.</p>	Sjodin et al., 2001; professional judgment of risk assessors
Plastic recycling	<p><u>Inhalation exposure:</u> EASE model used to predict “typical” and “worst-case” inhalation values.</p> <p><u>Dermal exposure:</u> EASE model predicted dermal exposure to be very low; consequently, dermal exposure values not used by EU in exposure assessment.</p>	EASE model
Consumer exposure	EU concluded that consumer exposure to TBBPA is likely to be insignificant, and that any attempt to quantify it would result in significant errors due to the small exposure levels anticipated.	Professional judgment of risk assessors
Indirect exposure via environment	EUSES 2.0 model used to estimate the concentrations of TBBPA in food, air, and drinking water.	EUSES 2.0 model

In the environmental exposure assessment, the EU estimated environmental releases using industry-specific information, supplemented by defaults for life-cycle stages where sufficient industry-specific information was unavailable. These are used together with fate and behavior data to derive predicted environmental concentrations (PECs) in different media. The specific

methods used in the PEC calculations are described in the EU's Technical Guidance Document on Risk Assessment, last revised in 2003 (EU Technical Guidance Document, 2003).

Table 5-4. Environment Exposure Assessment (EU Risk Assessment, 2007 draft)

Life-Cycle Stage	Key Methods/Assumptions	EU Data Source
Production	Emissions associated with production not considered in the risk assessment since no TBBPA is currently produced in the EU.	--
Use/ Processing	Total amount of TBBPA used in the EU estimated at 6,500 tonnes per year, of which 90% (or 5,850 tonnes per year) assumed to be reactive flame retardant in epoxy and other resins.	2003 consumption data from EFRA and EBFRIIP
	Default emissions factor of 0.001% to air and 0.001% to water used due to a lack of specific release information for EU sites.	Technical Guidance Document 2003
	Levels of residual TBBPA present in finished epoxy resins assumed to be <0.02% by weight of the resin, or <0.06% of the amount of TBBPA used to make the resin.	Information reported by Industry as part of survey; no references provided
Lifetime of Products	Releases associated with finished products based on estimated volume of TBBPA used as a reactive flame retardant in finished products, as well as estimate that 0.06% of the amount of TBBPA used to make epoxy resin is present, or free, for release.	Information reported by Industry as part of survey; no references provided
	Amount leached from products over their lifetime is assumed to be very low for purposes of this risk assessment.	Professional judgment of EU risk assessors
	A yearly emission factor of 8.0×10^{-5} % (of the residual amount of TBBPA in polymers) due to volatilization used. Assumed that reactive flame retardants volatilize at same release factor as additive flame retardants.	Emissions data from ERGO 2002
	No loss of residual TBBPA through wear and weathering is assumed over the lifespan of products where TBBPA is used as a reactive flame retardant	Professional judgment of EU risk assessors
Recycling and Disposal	Emissions of TBBPA from the collection, separation, and regrinding of PCBs (or other plastics where TBBPA is used as a reactive flame retardant) assumed to be limited.	Professional judgment of EU risk assessors

5.5 Chemical Life-Cycle Considerations

This section discusses the environmental and human health impacts for each of the ten flame retardants that can occur throughout the life cycle: from raw material extraction and manufacture, through product use, and finally at end of life of the material or product. For each stage of the chemical's life cycle, this section addresses potential exposure concerns for workers, the general population, and the environment. It should be noted that a greater level of information exists for TBBPA as compared to the more recently developed flame-retardant alternatives.

5.5.1 TBBPA

TBBPA is used as both an additive and reactive flame retardant in a wide variety of electronic equipment. As discussed in Section 3.2, TBBPA is most commonly used as a reactive flame retardant in PCBs and is incorporated through chemical reactions with the epoxy resin.

Raw Material Extraction

Bromine is produced from salt brines in the United States and China, from the Dead Sea in Israel and Jordan, and from ocean water in Wales and Japan (BSEF, 2007). Bromine is typically isolated via a series of redox reactions involving chlorine, sulfur dioxide and acid (MIT, 2003; York, 2007). During these reactions the seawater is acidified and then chlorinated to oxidize bromide to elemental bromine. At this stage, the bromine is not concentrated enough to practically collect and liquefy, so sulfur dioxide is added to reduce the bromine to hydrobromic acid. Chlorine is then added to re-oxidize hydrobromic acid to elemental bromine. At this point, bromine gas is collected and condensed (Grebe et al., 1942). While caustic substances are involved in these processes, they are typically contained in an enclosed tower, which mitigates worker exposure and environmental release.

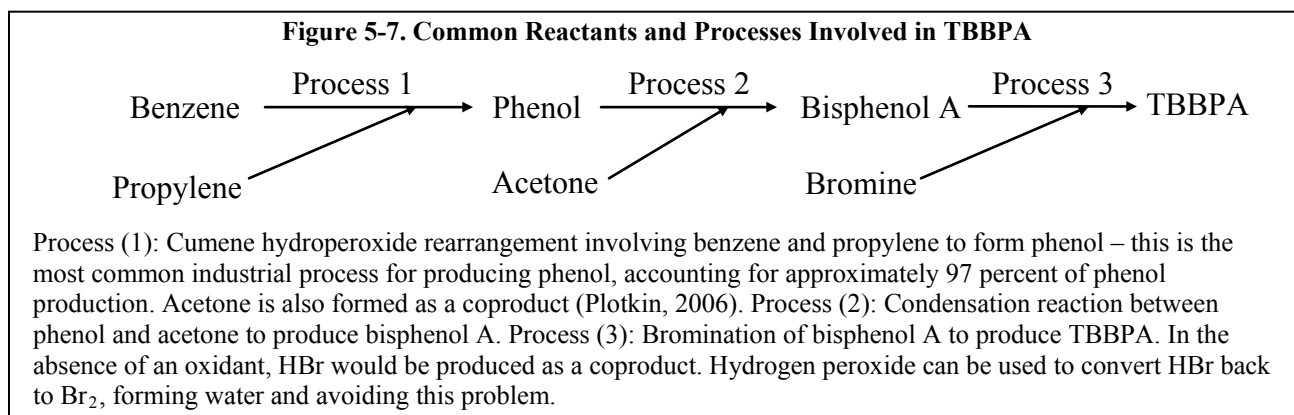
Manufacture of Flame Retardant, Laminate, and PCB

TBBPA is produced by brominating bisphenol A (BPA) in the presence of solvent. This reaction is highly exothermic, and no catalyst is required. Co-products will depend on the solvent used and the process conditions. The use of some solvents results in co-products, while the use of other solvents does not result in co-products. Co-products are typically either sold as products or disposed of as wastes.

Methanol and n-propanol are two examples of solvents that lead to the formation of co-products. Use of methanol produces methyl bromide, and use of n-propanol produces n-propyl bromide (Noonan, 2000). These co-products are typically removed through purification processes that can include the use of caustic neutralizers.

In 2008, TBBPA was commercially produced by Albemarle Corporation (Magnolia, AR) and Chemtura (El Dorado, AR). At that time, both corporations used proprietary processes that did not yield methyl bromide (Haneke, 2002).

While commercially employed bromination processes are proprietary, most involve bromination of BPA. Figure 5-7 gives a general overview of the main chemicals and reactions involved in TBBPA production. Please note that Figure 5-7 is a general outline of processes involved, and is not a complete list of chemicals or process steps.



While Figure 5-7 presents an overview of common reactants and processes involved in TBBPA production, there are also other processes that can be involved in producing TBBPA. To analyze the hazards associated with the production of any given TBBPA product, one would have to trace the line of production and identify which methods were used and what chemicals were involved, including catalysts, solvents, and other reagents.

Potential exposure to or release of TBBPA particulates may occur during manufacture or subsequent loading/unloading, transfer, or mixing operations (those that occur before its incorporation into the epoxy resin). When TBBPA is used as a reactive flame retardant, there may be unreacted (or free) TBBPA left over in the resin, leading to the presence of free TBBPA in the laminate and subsequently produced PCBs. The amount of free TBBPA is anticipated to be relatively low when it is used as a reactive flame retardant, although quantitative data on the amount of free TBBPA present in PCBs was limited at the time of report publication. Sellstrom and Jansson (1995) found approximately 0.7 micrograms per gram in a basic extraction of PCB filings from an off-the-shelf product purchased in Sweden (approximately 4 micrograms per gram TBBPA used). Studies have been conducted by Nelco to investigate the amount of residual TBBPA, but the results have not yet been published (PSB Corporation, 2006). One complication is that it is possible to add TBBPA to the varnish rather than pre-reacting it with an epoxy (as is done to make D.E.R. 500 Series). Even though all of the TBBPA should react, there is more potential to have unreacted TBBPA present when it is added to the varnish. It is not known how common this practice is.

D.E.R. 500 Series, the reaction product of TBBPA with an epoxy resin, may be released to the environment from its use in PCBs through dust-forming operations during its manufacture or subsequent loading/unloading, transfer, or mixing operations (those that occur before its incorporation into the laminate or PCB). Increased health hazards for this reaction product arise from the epoxy functional groups present on the polymer molecules. There may be unreacted D.E.R. 500 Series present in the laminate and, subsequently, the PCBs produced. The amount of free D.E.R. 500 Series is generally anticipated to be low given that it is incorporated as a reactive flame retardant, although quantitative data on the amount of free material that may be present are currently not available.

BPA, the unbrominated precursor to TBBPA, may also pose potential hazards to human health and the environment. The EU's risk assessment of BPA in 2003 concluded that for occupational exposures, "there is a need for limiting the risk" to workers based on eye and respiratory tract irritation, effects on the liver, and reproductive toxicity (effects on fertility and on development) during the manufacture of BPA and epoxy resins, as well as concerns for skin sensitization in all occupational exposure scenarios where there is a potential for skin contact (EU, 2003). For workers, consumers, and the general public, the EU concluded that further information and/or testing is needed in relation to developmental toxicity at low doses. The EU also assessed environmental hazards, concluding that further information is needed on the risk of BPA production to aquatic and terrestrial organisms, as well as the risk of epoxy resin production on aquatic organisms (EU, 2003). Steps have also been taken in the U.S. in recent years to identify the hazards associated with BPA. For uses under the Toxic Substances Control Act, U.S. EPA issued the BPA Action Plan¹² in March 2010, which summarized hazard, exposure, and use

¹² http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/bpa_action_plan.pdf

information, and identified actions to address BPA in the environment based on concerns for potential effects on aquatic species.¹³ The Action Plan states that dermal exposure to BPA may occur in workers producing flame retardants during the loading/unloading of BPA from containers, and that occupational exposure via inhalation is not expected (U.S. EPA, 2010). As part of the Action Plan, U.S. EPA tasked its Design for the Environmental Program with conducting an alternatives assessment for BPA in thermal paper. BPA and 19 potential chemical alternatives in thermal paper were evaluated on their human health effects, ecotoxicity, and environmental fate. A final version of this alternatives assessment was released in January 2014.¹⁴ The report also contains information on general exposure and lifecycle information on BPA, and can be used to inform decision-making and to guide the development of new alternatives. More information about the Agency's current efforts to address BPA can be found at: <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/bpa.html>.

Use and End of Life

Since TBBPA is reacted with an epoxy resin to form D.E.R. 500 Series, which is then reacted with a hardener to form a crosslinked polymer, low levels of unreacted TBBPA and D.E.R. 500 Series may remain in trace concentrations in PCBs; release of these low levels could theoretically occur during the use and disposal of PCBs. Because TBBPA is difunctional¹⁵, there is less potential for release compared to DOPO, which is monofunctional, and more potential for release compared to Fyrol PMP, which is tetrafunctional. TBBPA has been detected in the air of electronic recycling plants (Sjodin et al., 2001, 2003), although these facilities also recycled products where TBBPA is used as an additive flame retardant. Although its water solubility is low under neutral conditions, free TBBPA could also be released from PCBs in landfills that come in contact with basic leachate. However, unlike other brominated flame retardants, TBBPA is not very stable in air under basic conditions. In addition, there is potential for emissions of brominated dioxins and furans or other by-products when products containing TBBPA are combusted during end-of-life processes. Levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown.

5.5.2 DOPO

Raw Material Extraction

Phosphorus is usually obtained from phosphate rock, which contains the mineral apatite, an impure tri-calcium phosphate. Large deposits of phosphate rock are found in Russia, Morocco, Florida, Tennessee, Utah, Idaho, and elsewhere (Lide, 1993). By one process, tri-calcium phosphate, the essential ingredient of phosphate rock, is heated in the presence of carbon and silica in an electric furnace or fuel-fired furnace. Elementary phosphorus is liberated as vapor

¹³ The U.S. Food and Drug Administration (FDA) is expected to take the lead on assessing potential human health impacts associated with exposure to BPA. See <http://www.fda.gov/NewsEvents/PublicHealthFocus/ucm064437.htm>.

¹⁴ <http://www.epa.gov/dfe/pubs/projects/bpa/about.htm>

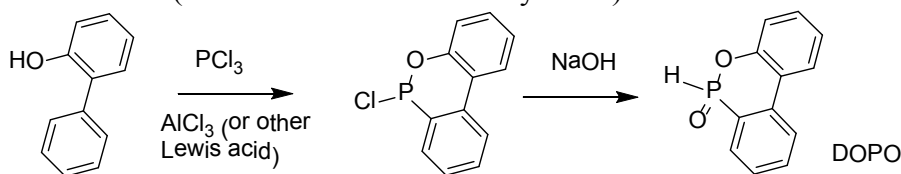
¹⁵ A molecule with two reactive sites.

and may be collected under water (Lide, 1993). While elementary phosphorus can form a diatomic molecule with a triple bond, it more readily forms a tetrahedral P₄ molecule. P₄, also called white or yellow phosphorus, exists in the gas phase and also as a waxy solid and viscous liquid. The degree of purity determines the “whiteness” of the phosphorus. At room temperature, phosphorus can exist in an amorphous or semi-crystalline state, called red phosphorus, which is produced from white phosphorus by extended heating in an inert atmosphere (Calvert, 2004).

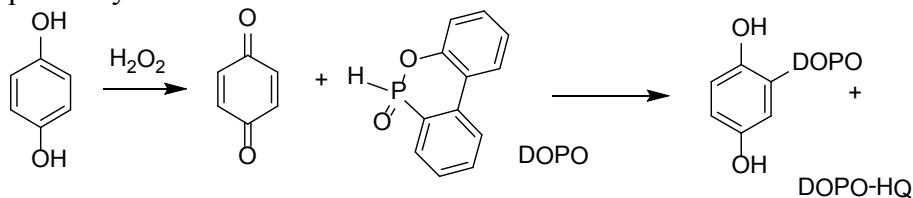
Some phosphorus-based flame retardants are based on phosphate esters derived from yellow phosphorus. Approximately 80 percent of the global phosphorus is mined in China in the form of phosphate ore (Shigeru, 2007). Yellow phosphorus produced from phosphorus ore co-produces arsenic, mercury, lead and other heavy metals as impurities that should be well controlled and treated before disposal of wastewater. If Chinese producers of yellow phosphorus appropriately treat their wastewater, then there is little concern for environmental and human health effects. However, improperly treated wastewater can lead to major adverse environmental impacts (Shigeru, 2007).

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Chemistry that can be used to make DOPO is shown below. The by-products of this chemistry are salts of the Lewis acid (such as aluminum chlorohydrates) and NaCl from the second step.



Further chemistry must be performed to react DOPO into the thermoset backbone. The largest manufacturer of organophosphorus flame retardants for electrical laminates at the time this partnership was convened was Tohto-Kasei. The details of their product are not known, but it is widely thought that their product is “DOPO-HQ”, or the adduct of DOPO with hydroquinone as shown below. This phenolic is then combined with an epoxy novolak and a catalyst in a solvent to make a varnish suitable for electrical laminates. Fillers are typically added to these formulations primarily to reduce costs.



Potential human and environmental exposure to DOPO may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations.

Dow XZ-92547, the reaction product of DOPO with an epoxy phenyl novolak, may be released from PCBs as a fugitive emission during manufacture of resins and laminates, or during subsequent loading/unloading, transfer, or mixing operations. The amount of Dow XZ-92547 that may be released from laminates or PCBs during their production and operational stages has

not been determined quantitatively; however, the low vapor pressure of Dow XZ-92547 indicates that it is not likely to undergo direct volatilization. Increased health hazards for this reaction product arise from the epoxy functional groups present on the polymer molecules.

Use and End of Life

As a reactive flame retardant, DOPO is not expected to be released from laminates. Its vapor pressure suggests that it has at least some potential to volatilize at elevated temperatures. Potential releases of DOPO particulates from PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. DOPO's water solubility suggests that it may migrate from PCBs deposited in landfills if contact with water ensues. Release of DOPO during the open burning of PCBs may also lead to environmental exposures. Because it is monofunctional, there is more potential for release compared to TBBPA, which is difunctional. DOPO may be released from PCBs during disposal or recycling, and potentially through dust-forming operations, such as PCB shredding. Leaching of Dow XZ-92547 from PCBs deposited in landfills is not likely given its low water solubility, high MW and functionality. Leaching of DOPO is more likely given its relatively low MW and because it is bound to the polymer by only one covalent bond. DOPO also oxidizes to a species containing a P-OH group in place of the P-H group. The toxicological properties of this species are unknown. Levels of exposure and any subsequent effects of exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, are unknown.

5.5.3 Fyrol PMP

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

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No information regarding the manufacture of Fyrol PMP was available at the time of publication due to the chemical's proprietary nature.

Use and End of Life

As a reactive flame retardant, Fyrol PMP is not expected to be released from laminates, and its low vapor pressure indicates that it is not likely to undergo direct volatilization. When PCBs are openly burned, it is possible that high temperatures could break the phosphorous-carbon bonds that hold Fyrol PMP to the crosslinked resin, which may result in the release of Fyrol PMP to the environment. Because it is tetrafunctional, Fyrol PMP is less likely to be released than TBBPA or DOPO, which are, respectively, difunctional and monofunctional. Even so, Fyrol PMP may be released from PCBs during its disposal or recycling, potentially through dust-forming operations, such as the shredding of PCBs. However, it is possible that methyl phosphonate may leach out of PCBs due to hydrolysis of phenol-phosphonate bonds. Exposure to the reacted flame retardant products during the disposal phase of the life cycle, in which flame retardants may become mobilized through direct intervention processes, such as shredding, is unknown.

5.5.4 Aluminum Diethylphosphinate

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

Manufacture of Flame Retardant, Laminate, and PCB

Potential human and environmental exposure to aluminum diethylphosphinate may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations. No additional information regarding the manufacture of aluminum diethylphosphinate was available at the time of publication in 2008 due to the chemical's proprietary nature.

Use and End of Life

As an additive flame retardant, aluminum diethylphosphinate may also be released from laminates and PCBs. After incorporation into the resin and/or the laminate, potential releases of aluminum diethylphosphinate during the useful life cycle of PCBs is not anticipated, except by an extractive processes upon contact with water. Potential releases of aluminum diethylphosphinate particulates during the disposal of PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. Its water solubility suggests that it may also migrate from PCBs deposited in landfills upon contact with water.

5.5.5 Aluminum Hydroxide

Raw Material Extraction

Aluminum is one of the most plentiful elements in Earth's crust, and is usually present as bauxite ore. Bauxite can contain three different aluminum minerals, including gibbsite ($\text{Al}(\text{OH})_3$), and böhmite and diaspore (different crystalline structures of $\text{AlO}(\text{OH})$). Bauxite ore also typically contains clay, silt, iron oxides, and iron hydroxides. The majority of bauxite is mined from surface deposits, but some is excavated from underground deposits (International Aluminium, 2000). Nearly all of the bauxite consumed in the U.S. is imported (EPA, 2007).

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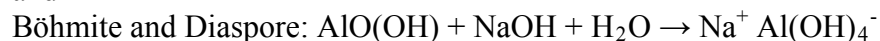
Once bauxite is recovered from deposits and broken into manageable pieces, it is shipped to a processing facility where it goes through the Bayer process. During this process, the bauxite ore is washed, ground, and dissolved with caustic sodium hydroxide. While the end product of the Bayer process is alumina (Al_2O_3), aluminum hydroxide ($\text{Al}(\text{OH})_3$) can be isolated following the precipitation step (see process steps below) (International Aluminium, 2000). In the past, more than 90 percent of domestic bauxite conversion to alumina occurred at refineries in Louisiana and Texas (EPA, 2007).

Bayer process steps:

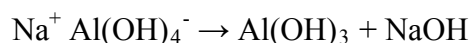
- 1) Digestion—bauxite ore treated with heated sodium hydroxide solution to form sodium aluminate:



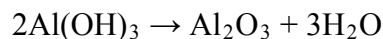
and



- 2) Clarification—insoluble impurities (red mud) are separated from the suspension.
- 3) Precipitation—aluminum hydroxide crystals are added to the solution to seed the precipitation of aluminum hydroxide crystals:



- 4) Calcification—the agglomerates of aluminum hydroxide are calcinated to produce pure alumina. (Note that while this step is included in the Bayer process, it is not relevant to the production of aluminum hydroxide; however, this is the reaction that occurs when aluminum hydroxide acts as a flame retardant.)



During clarification, clay, silt, iron oxides, iron hydroxides, and other non-aluminum components are removed from the bauxite ore. These components are disposed of as “red mud,” which is highly alkaline (pH \approx 13), and can be hazardous to human health and the environment. Red mud is viewed as a corrosive and hazardous substance requiring careful handling (Liu et al., 2007). While there are methods to reduce the hazard of red mud, its disposal can still be problematic.

Use and End of Life

Once aluminum hydroxide is produced, it can be released into the environment as a fugitive emission during loading/unloading, transfer, or mixing operations. After incorporation into a PCB resin and/or the laminate, potential exposure to finely divided aluminum hydroxide particulates is not expected during the remainder of the operational stages of the PCB life cycle. Aluminum hydroxide particulates may also be released during the disposal phase of the life cycle where they can become mobilized through direct intervention processes (such as shredding operations). The impact of aluminum hydroxide in smelting operations needs to be investigated further due to concerns about impacts on slags. Aluminum hydroxide thermally degrades to alumina in the smelting process. Alumina has a limited solubility in smelter slags. If large concentrations are added, this may lead to either increased slag volumes or higher operational temperatures, which lead to increased energy consumption (Lehner, 2008).

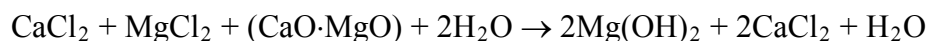
5.5.6 Magnesium Hydroxide

Raw Material Extraction

There are several million tons of mineral magnesium hydroxide, called brucite, in Earth's crust around the world (USGS, 2008; Amethyst, 2008). However, magnesium hydroxide is typically recovered from seawater and magnesia-bearing brines, which constitutes an even greater and more readily available resource than brucite. In 2007, magnesium oxide and other magnesia compounds (including magnesium hydroxide) were recovered from seawater by three companies in California, Delaware, and Florida; from well brines by two companies in Michigan; and from lake brines by two companies in Utah (USGS, 2008).

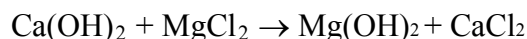
Manufacture of Flame Retardant, Laminate, and PCB

Recovering magnesium hydroxide from brine and seawater typically involves the addition of lime calcined dolime (CaO·MgO), which is obtained from a mineral source such as dolomitic limestone (CaMg(CO₃)₂). Magnesium-bearing brine and seawater contain varying concentrations of calcium chloride (CaCl₂) and magnesium chloride (MgCl₂), which are mixed with appropriate concentrations of calcined dolime and water (if necessary) to facilitate the following reaction (Martin, 2008):



The resulting magnesium hydroxide exists as solid particles suspended in an aqueous phase containing dissolved calcium chloride. The magnesium hydroxide particles settle to the bottom of the aqueous suspension, where they are separated, filtered, and washed to remove chlorides (Martin, 2008).

Hydrated lime (Ca(OH)₂) can also be used to precipitate magnesium hydroxide via the following reaction (NIEHS, 2001):



Potential human and environmental exposure to magnesium hydroxide may occur through dust-forming operations from its manufacture, or during loading/unloading, transfer, or mixing operations. As an additive flame retardant, it may also be released from laminates and PCBs.

Use and End of Life

After incorporation into the resin and/or the laminate, potential exposure to finely divided magnesium hydroxide particulates is not expected during the remainder of the operational stages of the PCB life cycle. Magnesium hydroxide particulates may also be released during the disposal phase of the life cycle where they can become mobilized through direct intervention processes, such as shredding operations. The impact of magnesium hydroxide in smelting operations needs to be investigated further due to concerns about impacts on slags. Magnesium hydroxide thermally degrades to magnesium oxide in the smelting process. However, magnesium oxide has a limited solubility in smelter slags. If large concentrations are added, this may lead to either increased slag volumes or higher operational temperatures, which lead to increased energy consumption (Lehner, 2008).

5.5.7 Melamine Polyphosphate

Raw Material Extraction

For a description of phosphorus extraction, please refer to the above entry for DOPO.

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A two-step process is typically used to prepare melamine polyphosphate (Patent Storm, 2002). In the first step, melamine, urea, and an aqueous orthophosphoric acid solution (containing at least 40 wt percent orthophosphoric acid) are combined, mixed, and dehydrated to produce a powdery product. In the second step, this powdery product is heated to between 240 and 340°C for 0.1 to 30 hours to obtain melamine polyphosphate (Patent Storm, 2002)

Potential human and environmental exposure to melamine polyphosphate may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations. As an additive flame retardant, it may also be released from laminates and PCBs.

Use and End of Life

After incorporation into the resin and/or the laminate, potential releases of melamine polyphosphate during the useful life cycle of PCBs is not anticipated, except by an extractive process upon contact with water. Potential releases of melamine polyphosphate particulates during the disposal of PCBs may arise during the disposal phase of the life cycle via shredding or other operations where it may become mobilized. Its water solubility suggests that it may also migrate from PCBs deposited in landfills upon contact with water.

5.5.8 Silicon Dioxide

Raw Material Extraction and Manufacture

Silicon dioxide, or silica (sand), is a naturally occurring compound. It is usually mined with open pit or dredging mining methods, which have limited environmental impact (USGS, 2007). Silicon dioxide can also be made synthetically in autoclaves under pressures ranging from 1,500 to 20,000 pounds per square inch and at temperatures of 250°C to 450°C (Lujan, n.d.). In some cases, silicon dioxide is synthesized by adding an acid to a wet alkali silicate solution to precipitate amorphous silicate, which is then filtered, washed, and dried (Degussa, 2007). The conditions in which silicon dioxide is formed, such as temperature and pressure, determine its structural properties, such as whether it is amorphous or crystalline. The structure of silicon dioxide, in turn, affects its potential to cause harm to the environmental and human health.

Potential health concerns arise from the inhalation of finely divided particulates that are generally less than 10 microns in diameter. The potential health concerns for silicon dioxide, a poorly soluble respirable particulate, arise from effects on the lungs as well as other effects that may be linked to an adverse effect on the lungs. Assessment of the life cycle for the use of this compound in PCBs suggests that inhalation exposure to finely divided silicon dioxide

particulates may potentially occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations.

Use and End of Life

After incorporation into the resin and/or the laminate, potential inhalation exposure to finely divided silicon dioxide particulates is not anticipated during the remainder of the operational stages of the PCB life cycle. Finely divided silicon dioxide particulates that are less than 10 microns may also be released to the air during the disposal phase of the life cycle, where they can become mobilized through direct intervention processes (such as shredding operations). In the smelting process, silicon dioxide-based flame retardants are preferred since silicon dioxide is used as a flux in the process (Lehner, 2008).

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