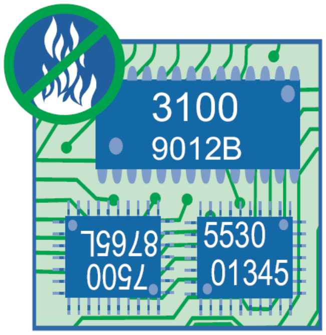
# FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

## Chapter 7



**FINAL REPORT**

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# 7 Considerations for Selecting Flame Retardants

Selecting an alternative chemical flame retardant involves considering a range of factors. Design for the Environment (DfE) chemical alternatives assessments provide extensive information on chemical hazards and provide a more general discussion of other factors relevant to substitution decisions, such as: use information and exposure and life-cycle considerations. Decision-makers will likely supplement the human health and environmental information provided in this report with information on cost and performance that may vary depending on the supplier, the materials involved, and the intended application. Alternative flame retardants must not only have a favorable environmental profile, but also must provide satisfactory (or superior) fire safety, have an acceptable cost, and attain the appropriate balance of properties (e.g., mechanical, thermal, aesthetic) in the final product. Users of information in this report may wish to contact the manufacturers of alternative flame retardants for engineering assistance in designing their products with the alternatives.

This chapter outlines attributes that are appropriate for a decision maker to consider in choosing an alternative to tetrabromobisphenol A (TBBPA). The chapter begins by describing five general attributes evaluated in this assessment that can inform decision-making about chemical hazards: (1) human health, (2) ecotoxicity, (3) persistence, (4) bioaccumulation potential, and (5) exposure potential. The chapter gives special attention to discussion of data gaps in the full characterization of chemicals included in this assessment. The chapter also includes information on the social, performance, and economic considerations that may affect substitution and the chapter concludes by providing additional resources related to state, federal, and international regulations.

The scope of this assessment was focused on the human health and environmental hazards of potential flame retardant substitutes. The report does not include a review or analysis of any additional life-cycle impacts, such as energy and water consumption or global warming potential, associated with any of the baseline or alternative chemicals, or the materials in which they are used. If selection of an alternative flame retardant requires significant material or process changes, relevant life-cycle analyses can be applied to the potentially viable alternatives identified through this hazard-based alternatives assessment, and to the materials in which they are used. Manufacturers may also wish to analyze the life-cycle impacts of materials that do not require the use of a flame retardant, in order to select materials that pose the fewest life-cycle impacts.

## 7.1 Preferable Human Health and Environmental Attributes

This section identifies a set of positive attributes for consideration when formulating or selecting a flame retardant that will meet flammability standards. In general, a safer chemical has lower human health hazard, lower ecotoxicity, better degradability, lower potential for bioaccumulation and lower exposure potential. As described in Chapter 4, the toxicity information available for each of the alternatives varies. Some hazard characterizations are based on measured data, ranging from one study to many detailed studies examining multiple endpoints, doses and routes of exposures. For other chemicals, there is no chemical-specific toxicity information available, and in these cases either structure activity relationship (SAR) or professional judgment must be used. In Table 4-4 and Table 4-5, the hazard designations based on SAR or professional judgment are listed in black italics, while those with hazard designations based on measured test data are listed in color. Readers are encouraged to review the detailed hazard assessments available for each chemical in Chapter 4.

Residual starting materials should be considered and ideally disclosed by the manufacturer in a hazard assessment. If residual monomers were identified as more than 0.1 percent of the product they were considered in the hazard assessment. It is possible DfE was not aware of/did not predict residuals for some products. The user/purchaser of the flame retardants can ask the manufacturer for detailed product certification to answer questions about residuals, oligomer content or synthesis by-products.

### 7.1.1 Low Human Health Hazard

The *DfE Program Alternatives Assessment Criteria for Hazard Evaluation* addresses a consistent and comprehensive list of human health hazard endpoints. Chemical hazards to human health assessed in this report are: acute toxicity, carcinogenicity, genotoxicity, reproductive and developmental toxicity, neurotoxicity, repeated dose toxicity, skin sensitization, respiratory sensitization, eye irritation and dermal irritation. The DfE criteria describe thresholds to define Low, Moderate, and High hazard. As described in Chapter 4, where data for certain endpoints were not available or were inadequate, hazard values were assigned using data for structural analogs, SAR modeling and professional judgment. In some cases (e.g., respiratory sensitization) it was not possible to assign hazard values due to a lack of data, models, or structural analogs.

### 7.1.2 Low Ecotoxicity

Ecotoxicity includes adverse effects observed in wildlife. An aquatic organism's exposure to a substance in the water column has historically been the focus of environmental toxicity considerations by industry and government during industrial chemical review. Surrogate species of fish, aquatic invertebrates and algae are traditionally assessed to consider multiple levels of the aquatic food chain. Aquatic organisms are a focus also because the majority of industrial chemicals are released to water. Both acute and chronic aquatic toxicity should be considered in choosing a chemical flame retardant. It is common to have limited data on industrial chemicals for terrestrial wildlife. Some human health data (i.e., toxicity studies which use rodents) can be relevant to non-human vertebrates in ecotoxicity evaluations. When evaluating potential concerns for higher trophic level organisms (including humans), bioaccumulation potential (discussed in Section 7.1.4) is an important consideration in conjunction with toxicity for choosing a safer alternative.

### 7.1.3 Readily Degradable: Low Persistence

Persistence describes the tendency of a chemical to resist degradation and removal from environmental media, such as air, water, soil and sediment. Chemical flame retardants must be stable by design in order to maintain their flame retardant properties throughout the lifetime of the product. Therefore, it is not surprising that all ten of the chemicals assessed in this report had a persistence value of High or Very High.

The half-life for a given removal process is used to assign a persistence designation. The half-life measured or estimated to quantify persistence of organic chemicals is not a fixed quantity as is it for a linear decay process such as for the half-life of a radioisotope. Chemicals with half-lives that suggest low or no persistence can still present environmental problems. "Pseudo persistence" can occur when the rate of input (i.e., the emission rate) of a substance exceeds the rate of degradation in, or movement out of, a given area. With the current criteria, DfE did not address pseudo persistence in the assessment which should include analysis of volumes of production and release.

Environmental monitoring could bolster hazard assessments by confirming that environmental fate is as predicted. The lack of such information should not be taken as evidence that environmental releases are not occurring. Environmental detection is not equivalent to environmental persistence; detection in remote areas (e.g., the Arctic) where a chemical is not manufactured is considered to be a sign of persistence and transport from the original point of release. An ideal safer chemical would be stable in the material to which it is added and have low toxicity, but also be degradable at end of life of that material, i.e., persistent in use but not after use. This quality is difficult to achieve for flame retardants.

In addition to the rate of degradation or measured half-life, it is important to be aware of the by-products formed through the degradation process. In some cases, degradation products might be more toxic, bioaccumulative or persistent than the parent compound. Some of these degradation products are discussed in the hazard profiles, but a complete analysis of this issue is beyond the scope of this assessment. The report did not consider toxicity from this potential degradation route.

DfE cannot determine the likelihood of release of degradates. DfE includes this information in the hazard profiles of relevant chemicals. Only degradants that were known or predicted to be likely were included in the hazard assessments in this report. Stakeholders are encouraged to conduct additional analyses of the degradation products of preferable alternatives using the assessment methods described in Chapter 4.

In general, metal-containing chemicals are persistent. This is because the metal moiety remains in the environment. Metal-containing compounds can be transformed in chemical reactions that could change their oxidation state, physical/chemical properties, or toxicity. A metal-containing compound may enter into the environment in a toxic (i.e., bioavailable) form, but degrade over time into its inert form. The converse may also occur. The chemistry of the compounds and the environmental conditions it encounters will determine its biotransformation over time. For metals, information relevant to environmental behavior is provided in each chemical assessment in Chapter 4 and should be considered when choosing an alternative.

### 7.1.4 Low Bioaccumulation Potential

The ability of a chemical to accumulate in living organisms is described by the bioconcentration, bioaccumulation, biomagnification, and/or trophic magnification factors. Some of the alternatives assessed in this report have a high level of potential for bioaccumulation, including Fyrol PMP and the two reactive flame retardant resins. Based on SAR, the potential for a molecule to be absorbed by an organism tends to be lower when the molecule is larger than

1,000 daltons. The inorganic flame retardants assessed in this report have low potential to bioaccumulate. Note that care should be taken not to consider the 1,000 daltons size to be an absolute threshold for absorption – biological systems are dynamic and even relatively large chemicals might be absorbed under certain conditions. Furthermore the initial 1,000 dalton threshold was established based on the consideration of bioconcentration factors (BCFs). Corresponding thresholds for hazard assessments based on bioaccumulation factor have not yet been rigorously established.

The test guidelines available to predict potential for bioaccumulation have some limitations. For example, they do not require the measurement for the BCFs of different components of a mixture, even if they are known to be present in the test material and sufficiently precise analytical methods are available. This situation often arises for lower molecular weight (MW) oligomers or materials that have varying degree of substitution. Bioconcentration tests tend to be limited for chemicals that have low water solubility (hydrophobic), and many flame retardants have low water solubility. Even if performed properly, a bioconcentration test may not adequately measure bioaccumulation potential if dietary exposure dominates over respiratory exposure (i.e., uptake by fish via food versus via their gills). The Organisation for Economic Cooperation and Development program recently updated the fish bioconcentration test, in which dietary uptake is included for the first time (OECD, 2012). Dietary uptake is of critical importance and may be a more significant route of exposure for hydrophobic chemicals.

### 7.1.5 Low Exposure Potential

For humans, chemical exposure may occur at different points throughout the chemical and product life cycle; by dermal contact, by inhalation, and/or by ingestion; and is affected by multiple physicochemical factors that are discussed in Chapter 5. The DfE alternatives assessment assumes exposure scenarios to chemicals and their alternatives within a ‘functional-use’ class to be roughly equivalent. The assessment also recognizes that in some instances chemical properties, manufacturing processes, chemical behavior in particular applications, or use patterns may affect exposure scenarios. For example, some flame retardant alternatives may require different loadings to achieve the same flammability protection. Stakeholders should evaluate carefully whether and to what extent manufacturing changes, life-cycle considerations, and physicochemical properties will result in markedly different patterns of exposure as a result of informed chemical substitution. For example, one chemical may leach out, or “bloom” out of the polymer it is flame retarding faster than another, thus increasing its relative exposure during use or disposal. The combination of high persistence and high potential for bioaccumulation makes an alternative less desirable. Even if human toxicity and ecotoxicity hazards are measured or estimated to be low, dynamic biological systems don’t always behave as laboratory experiments might predict. High persistence, high bioaccumulation chemicals, or their degradation products, have high potential for exposure and unpredictable hazards following chronic exposures that may not be captured in the hazard screening process.

Even if a chemical has negative human health and environmental attributes, concerns may be mitigated if the chemical is permanently incorporated into a commercial product. In this case, the potential for direct exposure to the chemical is greatly decreased or eliminated. Reactive flame retardants are incorporated into the PCB laminate during the early stages of manufacturing. In the case of TBBPA, it is reacted into the epoxy resin to form a brominated epoxy before the laminate production process begins. This brominated epoxy is the actual flame retardant that provides the fire safety to the PCBs. Studies have shown that levels of free, unreacted TBBPA in the brominated epoxy are extremely low. As referenced earlier in the report, one study by Sellstrom and Jansson extracted and analyzed filings from a PCB containing a brominated epoxy based on TBBPA. The study found that only 4 micrograms of TBBPA were unreacted for each gram of TBBPA used to make the PCB (Sellstrom and Jansson, 1995).

## 7.2 Considerations for Poorly or Incompletely Characterized Chemicals

Experimental data for hazard characterization of industrial chemicals are limited. As described in Chapter 4, for chemicals in this report without full data sets, analogs, SAR modeling, and professional judgment were used to estimate values for those endpoints lacking empirical data. No alternative chemical had empirical data for all of the hazard categories. Three of the 10 chemicals assessed lacked empirical data on at least 10 of the hazard endpoints. Several chemicals included in this assessment appear to have more preferable profiles, with low human health and ecotoxicity endpoints, although they are highly persistent, a frequent property for flame retardants (see Table 4-4, and Table 4-5). There is less confidence in the results of some seemingly preferable chemicals in which the majority of hazard profile designations are based on estimated effect levels compared to chemicals with full experimental data sets. Empirical data would allow for a more robust assessment that would confirm or refute professional judgments and then support a more informed choice among alternatives for a specific use. Estimated values in the report can, therefore, also be used to prioritize testing needs.

In the absence of measured data, DfE encourages users of this alternatives assessment to be cautious in the interpretation of hazard profiles. Chemicals used at high volumes, or likely to be in the future, should be given priority for further testing. Decision-makers are advised to read the full hazard assessments for each chemical, available in Chapter 4, which may inform whether additional assessment or testing is needed. Contact DfE with any questions on the criteria included in hazard assessments or the thresholds, data, and prediction techniques used to arrive at hazard values (www.epa.gov/dfe).

Where hazard characterizations are based on measured data, there are often cases where the amount of test data supporting the hazard rating varies considerably between alternative chemicals. In Table 4-4 and Table 4-5, the hazard characterizations based on SAR or professional judgment are listed in black italics, while those with hazard characterizations based on measured test data are listed in color. The amount of test data behind these hazard characterizations shown in color can vary from only one study of one outcome or exposure, to many studies in many species and different routes of exposure and exposure duration. In some instances, testing may go well beyond basic guideline studies, and it can be difficult to compare data for such chemicals against those with only a single guideline study, even though hazard designations for both chemicals would be considered “based on empirical data” and thus come with a higher level of confidence. Cases where one chemical has only one study but a second chemical has many studies are complex and merit careful consideration. For hazard screening assessments, such as the DfE approach, a single adequate study can be sufficient to make a hazard rating. Therefore, some designations that are based on empirical data reflect assessment based on one study while others reflect assessment based on multiple studies of different design.

The hazard rating does not convey these differences – the full hazard profile should be consulted to understand the range of the available data.

## 7.3 Social Considerations

Decision-makers should be mindful of social considerations when choosing alternative chemicals. This section highlights occupational, consumer, and environmental justice considerations. Stakeholders may identify additional social considerations for application to their own decision-making processes.

**Occupational considerations**: Workers might be exposed to flame retardant chemicals from direct contact with chemicals at relatively high concentrations while they are conducting specific tasks related to manufacturing, processing, and application of chemicals (see Section 5.2). Many facilities have established risk management practices which are required to be clearly communicated to all employees. The National Institute for Occupational Safety and Health (NIOSH) has established a hierarchy of exposure control practices[16]. From best to worst, the practices are: elimination, substitution, engineering controls, administrative controls and personal protection. Switching from high hazard chemicals to inherently lower hazard chemicals can benefit workers by decreasing workplace risks through the best exposure control practices: elimination and substitution of hazardous chemicals. While occupational exposures are different to consumer exposures, workers are also consumers and as such workers are relevant to both exposure groups.

**Consumer considerations**: Consumers are potentially exposed to flame retardant chemicals through multiple pathways described in Chapter 5. Exposure research documents that people carry body burdens of flame retardants. These findings have created pressure throughout the value-chain for substitution, which impacts product manufacturers. DfE alternatives assessments can assist companies in navigating these substitution pressures.

In recent years there has been a greater emphasis on ‘green’ products. In addition to substituting in alternative chemicals, some organizations advocate for moving away from certain classes of chemicals entirely (e.g., halogenated flame retardants), with product re-design, to avoid future substitutions altogether. Product manufacturers should be mindful of the role of these organizations in creating market pressure for alternative flame retardant chemicals and strategies, and should choose replacement chemicals – or re-designs – that meet the demands of their customers.

**Environmental justice considerations**: At EPA, environmental justice concerns refer to the disproportionate impacts on people based on race, color, national origin, or income that exist prior to or that may be created by the proposed action. These disproportionate impacts arise because these population groups may experience higher exposures, are more susceptible in response to exposure, or experience both conditions. Factors that are likely to influence resilience/ability to withstand harm from a toxic insult can vary with sociodemographics (e.g., co-morbidities, diet, metabolic enzyme polymorphisms) and are therefore important considerations. Adverse outcomes associated with exposure to chemicals may be

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[16] http://www.cdc.gov/niosh/topics/engcontrols/

disproportionately borne by people of a certain race, national origin or income bracket. Insights into EPA's environmental justice policy can be accessed at: www.epa.gov/compliance/ej/resources/policy/considering-ej-in-rulemaking-guide-07-2010.pdf.

Some populations have higher exposures to certain chemicals in comparison to the average member of the general population. Low-income populations are over-represented in the manufacturing sector, increasing their occupational exposure to chemicals. Higher exposures to environmental chemicals may also be attributable to atypical product use patterns and exposure pathways. This may be due to a myriad of factors such as cultural practices, language and communication barriers, and economic conditions. The higher exposures may also be a result of the proximity of these populations to sources that emit the environmental chemical (e.g., manufacturing industries, industries that use the chemical as production input, hazardous waste sites, etc.), access to and use of consumer products that may result in additional exposures to the chemical, or higher employment of these groups in occupations associated with exposure to the chemical.

Considering environmental justice in the assessment of an alternative chemical may include exploring product use patterns, pathways and other sources of exposure to the substitute, recognizing how upstream factors such as socio-economic position, linguistic and communication barriers, may alter typical exposure considerations. One tool available to these populations is the Toxics Release Inventory (TRI), which was established under the Emergency Planning and Community Right-to-Know Act to provide information about the presence, releases, and waste management of toxic chemicals. Communities can use information reported to TRI to learn about facilities in their area that release toxic chemicals and to enter into constructive dialogue with those facilities. This information can empower impacted populations by providing an understanding about chemical releases and the associated environmental impacts in their community. Biomonitoring data for the alternative chemical, if available, can also signal the potential for disproportionate exposure among populations with EJ issues.

## 7.4 Other Considerations

This section identifies performance and economic attributes that companies should consider when formulating or selecting a flame retardant for use in PCBs. These attributes are critical to the overall function and marketability of flame retardants and PCBs and should be considered jointly with the human health and environmental attributes described above.

### 7.4.1 Flame Retardant Effectiveness and Reliability

The DfE approach allows companies to examine hazard profiles of potential replacement chemicals so they can consider the human health and environmental attributes of a chemical in addition to cost and performance considerations. This is intended to allow companies to develop marketable products that meet performance requirements while reducing hazard. This section identifies some of the performance attributes that companies should consider when formulating or selecting a flame retardant, in addition to health and environmental consideration. Performance attributes are critical to the overall function and marketability of flame retardants and should be considered along with other factors.

The ability of a product to meet required flammability standards is an essential performance consideration for all flame retardant chemicals. The primary purpose of all flame retardants is to prevent and control fire. According to the National Fire Protection Association, there were 1,602,000 fires reported in the U.S. in 2005, causing 3,675 civilian deaths, 17,925 civilian injuries, 87 firefighter deaths, and $10.7 billion in property damage (NFPA, 2007). Effective flame retardants are needed to further reduce fire incidents and associated injuries, deaths, and property damage. The fire safety requirements (e.g., a classification like UL (Underwriters Laboratories) 94 V0) determine the necessary level of flame retardant that needs to be added to a resin. Formulations are optimized for cost and performance, so that in some instances it may be equally viable to use a small quantity of an expensive, highly efficient flame retardant or a larger quantity of a less expensive, less efficient chemical.

In addition to flame retardancy properties, the flame-retarded product must meet all required specifications and product standards (e.g., rigidity, compression strength, weight). The polymer/fire retardant combination used in laminates which contain TBBPA may be complex chemical formulations. In some instances, replacements exist which could allow for relatively easy substitution of the flame retardant. However, a true “drop-in” exchange of flame retardants is rare; some adjustment of the overall formulation, product re-design, or use of inherently flame retardant materials is usually required. An alternative with similar physical and chemical properties such that existing storage and transfer equipment as well as flame retardant manufacturing technologies could be used without significant modifications. Unfortunately, chemicals that are closer to being “drop-in” substitutes generally have similar physical and chemical properties, and therefore are likely to have similar hazard and exposure profiles. Those seeking alternatives to TBBPA should work with flame retardant manufacturers and/or chemical engineers to develop the appropriate flame retardant formulation for their products.

Reliability is another aspect to consider in choosing a flame retardant. PCBs are used for many purposes, including telecommunications, business, consumer, and space applications. The environmental stresses associated with each application may be different, and so an ideal flame retardant should be reliable in a variety of situations. Resistance to hydrolysis and photolysis, for example, can influence the long-term reliability of a chemical flame retardant. For some applications, it may be necessary for the flame retardant to be resistant against acidic, alkali, and oxidative substances. These chemically demanding requirements have a direct effect on the persistence of flame retardants (see Section 7.1).

### 7.4.2 Epoxy/Laminate Properties

Small changes in a flame-retardant formulation can significantly affect the manufacturability and performance of PCB epoxies and laminates. In choosing a flame retardant for use in a PCB, it is important to consider how the flame retardant will affect key properties of the PCB epoxy and laminate, including glass transition temperature ($T_g$), mechanics (e.g., warpage, fracture toughness, flexural modulus), electrics, ion migration, water uptake (moisture diffusivity), resin-glass or resin-copper interface, color, and odor.

The glass Tg, for example, is particularly important for manufacturing lead-free PCBs. Due to the higher soldering temperatures required for lead-free PCBs, epoxy and laminate glass $T_g$s must be high enough to prevent delamination of the PCB. Mechanical properties can also alter the manufacturing process by impacting the ability to drill through the laminate.

Changes in a flame-retardant formulation can also affect overall epoxy and laminate performance. Increased moisture diffusivity, for example, can reduce both the laminate and overall PCB reliability. Changes to moisture diffusivity, as well as any other parameter that may affect the electrical properties of the PCB should be considered. If the PCB cannot operate properly, any benefits associated with less hazardous flame retardants are irrelevant. As referenced in Section2.3, iNEMI (International Electronics Manufacturing Initiative) has conducted a series of performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties.

### 7.4.3 Economic Viability

This section identifies economic attributes that companies often consider when formulating or selecting a flame retardant. Economic factors are best addressed by decision-makers within the context of their organization. Accurate cost estimations must be company-specific; the impact of substituting chemicals on complex product formulations can only be analyzed in-house; and a company must determine for itself how changes will impact market share or other business factors. Cost considerations may be relevant at different points in the chemical and/or product life cycle. These attributes are critical to the overall function and marketability of flame retardants and flame-retardant products and should be considered jointly with performance attributes, social considerations, and human health and environmental attributes.

Substituting chemicals can involve significant costs, as industries must adapt their production processes, and have products re-tested for all required performance and product standards. Decision-makers are advised to see informed chemical substitution decisions as long-term investments, and to replace chemicals with those they anticipate using for many years to come. This includes attention to potential future regulatory actions motivated by adverse human health and environmental impacts, as well as market trends. One goal is to choose from among the least hazardous options to avoid being faced with the requirement to substitute again.

To ensure economic viability, flame retardants must be easy to process and cost-effective in high-volume manufacturing conditions. Ideally the alternative should be compatible with existing process equipment at PCB manufacturing facilities. If it is not, the plants will be forced to modify their processes and potentially to purchase new equipment. The ideal alternative would be a drop-in replacement that has similar physical and chemical properties such that existing storage and transfer equipment as well as PCB production equipment can be used without significant modifications.

The four steps in the Flame Resistant 4 (FR-4) manufacturing process that typically differ between halogenated and halogen-free materials are pressing, drilling, desmearing, and solder masking (Bergendahl, 2004). As a result, manufacturing and processing facilities may need to invest in new equipment in order to shift to alternatives flame retardants. In addition, daily operation costs may be different for the new process steps required to manufacture PCBs with alternative flame retardants.

Flame-retardants that are either more expensive per pound or require more flame retardant per unit area to meet the fire safety standards will increase the PCB's raw material costs. In this situation, a PCB manufacturer will attempt to pass the cost on to its customers (e.g., computer manufacturers), who will subsequently pass the cost on to consumers. However, the price premium significantly diminishes over the different stages of the value chain. For an alternative laminate, the price may be up to 20 to 50 percent higher per square meter, but for the final product (e.g., a personal computer), the price premium can be less than 1 percent.

Handling, disposal, and treatment costs, as well as options for mechanical recycling, may be important considerations when evaluating alternatives. Inherently high hazard chemicals may require special engineering controls and worker protections that are not required of less hazardous alternatives. Disposal costs for high hazard chemicals may also be much higher than for low hazard alternatives. High hazard chemicals may be more likely to result in unanticipated and costly clean-up requirements or enforcement actions should risk management protections fail or unanticipated exposures or spills occur. Also, some chemicals may require specific treatment technologies prior to discharge through wastewater treatment systems. These costs can be balanced against potentially higher costs for the purchase of the alternative chemical. Finally, initial chemical substitution expenses may reduce future costs of mitigating consumer concerns and perceptions related to hazardous chemicals.

It should be noted that, while some assessed alternative chemicals included in this report are currently manufactured in high volume, not all are currently available in quantities that would allow their widespread use immediately. However, prices and availability may change if demand increases.

### 7.4.4 Smelting Practices

Changes in flame-retardant formulation may also have implications for smelting processes. Smelters have had to adapt their practices over time to respond to changing compositions and types of electronic scrap as well as regulatory requirements (e.g., Waste Electrical and Electronic Equipment directive). As discussed in Section 5.3.2, smelters process PCB materials through complex, high-temperature reactions to recover precious and base metals (e.g., gold, silver, platinum, palladium and selenium, copper, nickel, zinc, lead). Primary smelters in the world (e.g., 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.

The consequences associated with the increased use of alternative flame retardants in FR-4 PCBs from a smelting perspective are largely unknown. For example, the flame-retardant fillers silicon dioxide and aluminum hydroxide are not expected to pose problems given that smelters routinely process silicon dioxide and aluminum hydroxide because they are found in other feedstock. Silicon dioxide is also beneficial in that it is used to flux the slag formed through the smelting process. Aluminum oxide, derived from either metallic aluminum or from aluminum oxide or hydroxide, can be tolerated in limited amounts. However, aluminum oxides are less effective than brominated flame retardants, so a greater load of aluminum oxide is needed to achieve similar flame retardancy. Whereas brominated flame retardants are typically found at 3 percent of feedstock weight, aluminum hydroxide flame retardants can account for 15 percent of feedstock weight (Lehner, 2008). Since the slag used in base metals metallurgy have a limited solubility for $Al_2O_3$, completely replacing brominated flame retardants with aluminum oxide flame retardants would challenge the smelters' recovery or energy balance. A substantial increase in aluminum load would force smelters to use higher temperatures to overcome higher liquid temperatures, or experience higher slag losses as a result of adding slag for dilution. The added slag contains small, but measurable, contents of precious and base metals.

Phosphorus-based flame retardants are not expected to significantly change the composition of the slag product or cause significant problems. However, formation of phosphine ($PH_3$) from phosphorus-based flame retardants, and acrolein, hydrogen cyanide, and PAH from nitrogen-based flame retardants, is possible since most smelters operate under highly reducing conditions. Furthermore, little to no information is available in the literature on the combustion byproducts of phosphorus-based flame retardants under normal combustion conditions or elevated temperatures approaching those found in incinerators or smelters. As is standard practice, smelters will need to continuously evaluate if and how changes in flame-retardant formulation, as well as the overall composition of PCBs, will affect their operating procedures and health and safety practices.

## 7.5 Moving Towards a Substitution Decision

As stakeholders proceed with their substitution decisions for flame retardants in PCBs, the functionality and technical performance of each product must be maintained, which may include product performance in extreme environments over a life cycle of many years. Critical requirements, such as product safety during operation cannot be compromised. When alternative formulations are developed, the stakeholders should also consider the hazard profiles of the chemicals used to meet product performance, with a goal to drive towards safer chemistry on a path of continuous improvement.

When chemical substitution is the necessary approach, the information in this report can help with selection of safer, functional alternatives. The hazard characterization, performance, economic, and social considerations are all factors that will impact the substitution decision. When choosing safer chemicals, alternatives should ideally have a lower human health hazard, lower ecotoxicity, better degradability, lower potential for bioaccumulation, and lower exposure potential. Where limited data are available characterizing the hazards of potential alternatives, further testing may be necessary before a substitution decision can be made.

Switching to an alternative chemical is a complex decision that requires balancing all of the above factors as they apply to a particular company's cost and performance requirements. This report provides hazard information about alternatives to TBBPA to support the decision-making process. Companies seeking a safer alternative should identify the alternatives that may be used in their product, and then apply the information provided in this report to aid in their decision-making process.

Alternative chemicals are often associated with trade-offs. For any chemical identified as a potential alternative, some endpoints may appear preferable while other endpoints indicate increased concern relative to the original chemical. A chemical may be designated as a lower concern for human health but a higher concern for aquatic toxicity or persistence. For example, in the case of high MW polymers, where health hazards and potential bioaccumulation are predicted to be low, one trade-off is high persistence. Additionally, there may be limited information about the polymer's combustion by-products, or how the polymer behaves in the environment and eventually degrades.

Trade-offs can be difficult to evaluate, and such decisions must be made by stakeholders taking into account relevant information about the chemical's hazard, expected product use, and life-cycle considerations. For example, chemicals expected to have high levels of developmental or reproductive toxicity should be avoided for products intended for use by children or women of child-bearing age. Chemicals with high aquatic toxicity concerns should be avoided if releases to water cannot be mitigated. Nonetheless, even when certain endpoints are more relevant to some uses than others, the full hazard profile must not be ignored.

## 7.6 Relevant Resources

In addition to the information in this report, a variety of resources provide information on regulations and activities that include review or action on flame retardants at the state, national and global levels, some of which are cited in this section.

### 7.6.1 Resources for State and Local Government Activities

University of Massachusetts at Lowell created a database which "houses more than 700 state and local legislative and executive branch policies from all 50 states from 1990 to the present. The online database makes it simple to search for policies that your state has enacted or introduced, such as those that regulate or ban specific chemicals, provide comprehensive state policy reform, establish biomonitoring programs, or foster "green" chemistry…" (National Caucus of Environmental Legislators, 2008).
http://www.chemicalspolicy.org/chemicalspolicy.us.state.database.php

The Interstate Chemicals Clearinghouse (IC2) is an association of state, local, and tribal governments that promotes a clean environment, healthy communities, and a vital economy through the development and use of safer chemicals and products. The IC2 also created a wiki page to allow stakeholders and members of state organizations to share resources for conducting safer alternatives assessments.
http://www.newmoa.org/prevention/ic2/
http://www.ic2saferalternatives.org/

### 7.6.2 Resources for EPA Regulations and Activities

EPA's website has a number of resources regarding regulation development and existing regulations, along with information to assist companies in staying compliant. Some of these sites are listed below.

Laws and Regulations
http://www.epa.gov/lawsregs/

Office of Pollution Prevention and Toxics (OPPT): Information on Polybrominated Diphenyl Ethers
http://www.epa.gov/oppt/pbde/

EPA – OPPT's Existing Chemicals Program
http://www.epa.gov/oppt/existingchemicals/index.html

America's Children and the Environment
http://www.epa.gov/ace/

Integrated Risk Information System (IRIS)
http://www.epa.gov/IRIS/

Design for the Environment Program (DfE)
http://www.epa.gov/dfe

### 7.6.3 Resources for Global Regulations

The European Union (EU)'s REACH (**R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances) legislation was enacted in 2007 and has an "aim to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances" (European Commission, 2011a). Their website contains information on legislation, publications and enforcement.
http://ec.europa.eu/environment/chemicals/reach/enforcement_en.htm

Under REACH, applicants for authorization are required to control the use of Substances of Very High Concern (SVHC). If a SVHC does not have available alternatives, applicants must carry out their own alternatives assessments. The European Chemicals Agency has published a guidance document for this application that provides direction for conducting an alternatives assessment, as well as creating a substitution plan.
http://echa.europa.eu/documents/10162/17229/authorisation_application_en.pdf

The EU also has issued the Restriction of Hazardous Substances directive which ensures that new electrical and electronic equipment put on the market does not contain any of the six banned substances: lead, mercury, cadmium, hexavalent chromium, poly-brominated biphenyls or PBDEs above specified levels (European Commission, 2011b).
http://www.bis.gov.uk/nmo/enforcement/rohs-home

### 7.6.4 Resources from Industry Consortia

iNEMI is a consortium of electronics manufacturers, suppliers, associations, government agencies, and academics. iNEMI has carried out a series of projects to determine the key performance properties and the reliability of halogen-free flame-retardant PCB materials. Each project has observed different outcomes, with the latest findings indicating that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of traditional brominated laminates. Technology improvements, especially those that optimize the polymer/fire retardant combinations used in PCBs, have helped shift the baseline in regards to the performance of halogen-free flame-retardant laminates.

At the time the 2008 draft report was released, iNEMI was conducting performance testing for commercially available halogen-free flame-retardant materials to determine their key electrical and mechanical properties under its HFR-free Program Report. The results of the testing and evaluation of these laminate materials were made public in 2009.
The overall conclusions from the investigation were (1) that the electrical, mechanical, and reliability attributes of the eleven halogen-free laminate materials tested were not equivalent to FR-4 laminates and (2) that the attributes of the halogen-free laminates tested were not equivalent among each other (Fu et al., 2009). Due to the differences in performance and material properties among laminates, iNEMI suggested that decision-makers conduct testing of materials in their intended applications prior to mass product production (Fu et al., 2009).
http://thor.inemi.org/webdownload/newsroom/Presentations/SMTA_South_China_Aug09/HFR-Free_Report_Aug09.pdf

iNEMI also conducted two follow-on projects to its HFR-free Program Report: (1) the HFR-Free High-Reliability PCB Project and (2) the HFR-Free Leadership Program.

The focus of the HFR-Free High-Reliability PCB Project was to identify technology readiness, supply capability, and reliability characteristics for halogen-free alternatives to traditional flame-retardant PCB materials based on the requirements of the high-reliability market segment (e.g., servers, telecommunications, military) (iNEMI, 2014). In general, the eight halogen-free flame-retardant laminates tested outperformed the traditional FR-4 laminate control (Tisdale, 2013).
http://www.inemi.org/project-page/hfr-free-high-reliability-pcb

The HFR-Free Leadership Program assessed the feasibility of a broad conversion to HFR-free PCB materials by desktop and laptop computer manufacturers (Davignon, 2012). Key electrical and thermo-mechanical properties were tested for six halogen-free flamed-retardant laminates and three traditional FR-4 laminates. The results of the testing demonstrated that the computer industry is ready for a transition to halogen-free flame-retardant laminates. It was concluded that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of brominated laminates and that laminate suppliers can meet the demand for halogen-free flame-retardant PCB materials (Davignon, 2012). A “Test Suite Methodology” was also developed under this project that can inform flame retardant substitution by enabling manufacturers to compare the electrical and thermo-mechanical properties of different laminates based on testing (Davignon, 2012).
http://www.inemi.org/project-page/hfr-free-leadership-program
http://thor.inemi.org/webdownload/Pres/APEX2012/Halogen-Free_Forum/HFR-Free_PCB_Materials_Paper_022912.pdf

HDPUG is a trade organization for companies involved in the supply chain of producing products that utilize high-density electronic packages. HDPUG created a database of information on the physical and mechanical properties of halogen-free flame-retardant materials, as well as the environmental properties of those materials. The HDPUG project, completed in 2011, broadly examined flame-retardant materials, both ones that are commercially viable and in research and development. For more information about the database and other HDPUG halogen-free projects, visit: http://hdpug.org/content/completed-projects#HalogenFree.

## 7.7 References

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