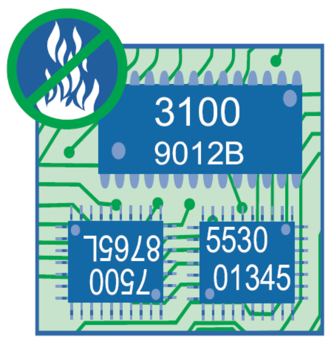
United States Environmental Protection Agency

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

Executive Summary



FINAL REPORT

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Executive Summary

Background

In 2006, U.S. Environmental Protection Agency (EPA)'s Design for the Environment (DfE) Program and the electronics industry convened a multi-stakeholder partnership to identify and evaluate commercially available flame retardants in Flame Resistant 4 (FR-4) printed circuit boards (PCBs). The majority of PCBs are classified as FR-4, indicating that they meet certain performance criteria, as well as the V0 requirements of the UL (Underwriters Laboratories) 94 flammability testing standard. Over 90 percent of FR-4 PCBs used epoxy resins containing the reactive flame retardant tetrabromobisphenol A (TBBPA) to meet flammability standards when the partnership was convened. Because little information existed concerning the potential environmental and human health impacts of the materials being developed as alternatives to the brominated epoxy resins being used in PCBs, the partnership developed information to improve understanding of new and current materials that can be used to meet the flammability requirements. This information was published in a 2008 draft report titled *Partnership to Evaluate Flame Retardants in Printed Circuit Boards*. In addition to this written draft report, experimental testing was conducted as part of this project to learn more about the combustion by-products released during end-of-life disposal processes of PCBs.

In this version of the report, the hazard profiles in Chapter 4 and the accompanying methodology were updated to ensure that most recent information was used for hazard assessment. Each human health and environmental endpoint was evaluated using the 2011 DfE Criteria for Hazard Assessment. The information on the physical-chemical and fate properties of the alternatives in Table 5-2 of Chapter 5 and text in Chapter 7 were also updated. Chapter 6 was revised to describe the results of the combustion testing experiments. Additional edits have been made throughout the report as appropriate in response to public comments received on the 2008 draft report.

Goal of the Partnership and This Report

The partnership, which includes members of the electronics industry, flame retardants industry, environmental groups, academia, and others, developed the information in the report *Partnership to Evaluate Flame Retardants in Printed Circuit Boards* to advance understanding of the human health and environmental impacts of conventional and new flame-retardant materials that can provide fire safety for PCBs. Participation of a diverse group of stakeholders has been critical to developing the information for this partnership. The multi-stakeholder nature of the partnership led to a report that takes into consideration many diverse viewpoints, making the project richer both in approach and outcome.

This partnership report provides objective information that will help members of the electronics industry more efficiently factor human health and environmental considerations into decision-making when selecting flame retardants for PCB applications. This report can also serve as a step toward developing a more comprehensive understanding of the human health and environmental implications of flame-retardant chemicals by noting gaps in the existing human health and environmental literature. For example, future studies could be directed at key human health and environmental toxicological endpoints that are not yet adequately characterized. Additional testing could also be directed at improving understanding of fate and transport of flame-retardant chemicals during the most relevant life-cycle phases.

The objective of the partnership is not to recommend a single best flame retardant for PCB applications or to rank the evaluated flame retardants. In addition to information on environmental and human health impacts, performance, and cost are critical in the final decision. The information in this report could be used in decision-making frameworks that address these critical elements. When using these flame-retardant chemical profiles, it is important to consider other life-cycle impacts, including exposure considerations.

Fire Safety for Printed Circuit Boards (PCBs) and Flame Retardants Evaluated

PCBs are commonly found in consumer and industrial electronic products, including computers and mobile phones. Manufacturers commonly produce PCBs with flame-retardant chemicals to help ensure fire safety. In 2008, the majority of PCBs produced worldwide met the V0 requirements of the UL 94 fire safety standard. This standard was usually achieved through the use of brominated epoxy resins in which the reactive flame retardant TBBPA forms part of the polymeric backbone of the resin. These UL 94 V0 compliant boards are referred to as FR-4 boards, which must meet performance specifications as well as the fire safety standard. While alternative flame-retardant materials are used in only a small percentage of FR-4 boards, in 2008, the use of alternatives was increasing and additional flame-retardant chemicals and laminate materials were under development. In 2008, TBBPA was used to make the epoxy resin base material in more than 90 percent of FR-4 boards while alternative flame-retardant materials were used in only 3 to 5 percent of FR-4 boards.

The partnership originally evaluated nine commercially available flame retardants or resins for FR-4 laminate materials for PCBs: TBBPA, DOPO, Fyrol PMP, aluminum hydroxide, Exolit OP 930, Melapur 200, silicon dioxide (amorphous and crystalline), and magnesium hydroxide. Three reaction products of epoxy resin with flame retardants (TBBPA, DOPO, and Fyrol PMP) were also evaluated for a total of 12 hazard profiles. These chemicals were identified through market research and consultation with industry and iNEMI (the International Electronics Manufacturing Initiative) as potentially viable options for PCBs. The reaction products of TBBPA, DOPO, Fyrol PMP, and other reactive flame retardants are present during the manufacturing process, and trace quantities may be locked in the PCB polymer matrix. Chemical components making up less than 1 percent by weight of the flame-retardant formulation were not considered in this assessment.

For this updated report, ten flame-retardant chemicals and resins for FR-4 laminate materials for PCBs were evaluated. One of the alternatives from the 2008 draft report – "reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin" – was not reassessed in the updated Chapter 4 because the product is not known to be on the market. In the 2008 draft report, there were two profiles for silicon dioxide – amorphous and crystalline; for this update, the two were combined into one profile that accounts for the differences between the two forms. The ten revised hazard profiles and their accompanying methodology are located in the updated Chapter 4 of the alternatives assessment report. A summary of the hazard assessment results by chemical group are summarized in this updated executive summary.

Hazard Assessment Results

The level of available human health and environmental information varies widely by flame-retardant chemical. Little information exists concerning many of the alternative flame-retardant materials included in this report. TBBPA and silicon dioxide are more fully characterized. To help address this discrepancy, and to increase the usefulness of this report, EPA used the tools and expertise developed for the New Chemicals Program to estimate the potential impacts of flame retardants when no experimental data were available.

Hazard profiles for the **reactive flame retardant alternatives** TBBPA, DOPO, and Fyrol PMP vary; all three have High to Very High persistence. TBBPA is relatively well characterized with empirical data while DOPO and Fyrol PMP have a limited data set and therefore many hazard designations based on analogs, structural alerts, or estimation models. The primary hazard for TBBPA is aquatic toxicity (High to Very High). TBBPA has Moderate potential for bioaccumulation based on measured bioconcentration and estimated bioaccumulation factors. Human health hazard designations for TBBPA are Low to Moderate; Moderate designations were determined for carcinogenicity, developmental toxicity, and eye irritation. Comparatively, DOPO has Low hazard for acute aquatic toxicity and bioaccumulation potential but similar estimated hazards for carcinogenicity, developmental toxicity, neurotoxicity, and eye irritation. DOPO is estimated to have Low bioaccumulation potential due to hydrolysis in aqueous conditions. Fyrol PMP, with the least amount of empirical data, has potential for Low to Moderate human health effects and High aquatic toxicity. Fyrol PMP also has High potential for bioaccumulation based on presence of low molecular weight oligomers.

The **reactive flame retardant resins** D.E.R. 500 Series (TBBPA-based resin) and Dow XZ-92547 (DOPO-based resin) are poorly characterized. The hazard profiles for these alternatives identify Low acute mammalian toxicity. A High skin sensitization designation was assigned based on empirical data and Moderate respiratory sensitization was estimated for Dow XZ-92547. Moderate hazard was estimated for carcinogenicity, genotoxicity, reproductive toxicity, developmental effects, neurotoxicity, and repeated dose toxicity. Acute and chronic aquatic toxicity are estimated to be Low for D.E.R. 500 Series; chronic aquatic toxicity is estimated to be High for Dow XZ-92547. Bioaccumulation potential is estimated High and persistence estimated to be Very High for both reactive flame retardant resins.

The **additive flame retardant alternatives** aluminum diethylphosphinate, aluminum hydroxide, magnesium hydroxide, melamine polyphosphate, and silicon dioxide have varied hazard designations for human health effects. The majority of the endpoints range from Very Low to Moderate hazard with the exception of High repeated dose toxicity for silicon dioxide, which is based upon inhalation of particles less than 10 µm in size. Aluminum diethylphosphinate has Moderate aquatic toxicity hazard while the other four additive flame retardants have Low designations for these endpoints. Persistence is expected to be High for all five of the additive flame retardant alternatives and bioaccumulation potential is expected to be Low. The four additive flame retardant alternatives that contain a metal (aluminum diethylphosphinate, aluminum hydroxide, magnesium hydroxide, and silicon dioxide) were assigned High persistence designations because these inorganic moieties are recalcitrant.

A hazard comparison summary table (presented below as Table ES-1 and Table ES-2) is also presented in Chapter 4. The tables show relative hazard levels for eleven human health endpoints, two aquatic toxicity endpoints, and two environmental fate endpoints. The tables also highlight exposure considerations through the chemical life cycle. Selected flame retardants are presented according to their reactive or additive nature. An explanation of EPA's chemical assessment methodology and more detailed characteristics of the chemicals in each formulation are presented in Chapter 4.

Life-Cycle Thinking and Exposure Considerations

In addition to evaluating chemical hazards, this partnership agreed it was important to apply life-cycle thinking to more fully understand the potential human health and environmental impacts of evaluated flame retardants. Human health and environmental impacts can occur throughout the life cycle: from raw material extraction and chemical manufacturing, to laminate, PCB, and electronic product manufacturing, to product use, and finally to the end of life of the material or product. Factors such as occupational best practices and raw material extraction and subsequent flame-retardant and laminate manufacturing, together with the physical and chemical properties of the flame retardants, can serve as indicators of a chemical's likelihood to pose human health and environmental exposure concerns. During later stages of the life cycle, from PCB manufacturing to end-of-life, human health and environmental exposure potential is highly dependent upon whether the flame retardant was incorporated additively or reactively into the resin system. Chapter 5 explores the exposure considerations of these flame retardants and other life-cycle considerations. The detailed chemical assessments in this report are focused only on the flame-retardant chemicals. Other chemicals, such as feedstocks used to make the flame retardants; chemicals used in manufacturing resins, laminate materials, and PCBs; and degradation products and combustion by-products are only mentioned in the process descriptions.

Combustion Testing Results

As part of this life-cycle thinking, the partnership decided that experimental testing of FR-4 laminates and PCB materials was necessary to better understand the potential by-products during thermal end-of-life processes. The combustion by-products of four epoxy laminates alone and with PCB components added were identified and compared. The four laminates tested were: a brominated flame retardant epoxy laminate (BFR), an additive phosphorus-based flame retardant epoxy laminate (PFR1), a reactive phosphorus-based flame retardant epoxy laminate (PFR2), and a non-flame retardant epoxy laminate (NFR). PCB components designed for conventional boards were provided by Seagate and combined with the laminates as homogeneous powders to simulate a circuit board. A standard halogenated component (SH) blend and a low-halogen component (LH) blend were created and combusted with the various laminates. The two end-of-life processes simulated by a cone calorimeter in this testing were open burning (50 kW/m^2 heat flux) and incineration (100 kW/m^2 heat flux). Halogenated dioxins and furans as well as polyaromatic hydrocarbons (PAHs) emitted during combustion were measured using gas chromatography-mass spectrometry. Cone calorimetry data on CO, CO_2, particulate matter, smoke, and heat release were also recorded. The results of the combustion testing, completed in 2012, are summarized here. A more detailed description of the testing methods, results, and conclusions can be found in Chapter 6 with full study reports in the Appendices.

Analysis of halogenated dioxins and furans was conducted only for the BFRs because initial testing indicated that PFR1 and PFR2 contained low levels of bromine and therefore would not generate detectable levels of polybrominated dibenzo-p-dioxins/furans (PBDD/Fs). Detectable levels of PBDD/Fs were emitted for all BFRs combusted. For the BFRs without components, nearly 40 percent more PBDD/F emissions were generated in open burn conditions compared to incineration conditions. PBDD/Fs were detected in the BFRs containing low-halogen components but could not be quantitated in the samples containing standard halogen components due to significant interference with the standard. Polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) were quantified in the initial testing but could not be quantified in the final studies due to an ineffective quality control standard.

PAH emissions were measured and detected in all laminate types. Of the laminates without components, BFR emitted over three times the amount of PAHs of PFR1 in incineration conditions; BFRs emitted almost three times more PAHs than PFR1 and almost two times more PAHs than PFR2 in open burn conditions. BFR emitted over eight times more PAHs than NFR in open burn conditions, while PFR1 and PFR2 emitted nearly three times and five times the PAHs of the NFR, respectively. In incineration conditions, BFR1 emitted over three times the PAHs of PFR1. Of the samples with standard halogen components in open burn conditions, BFR generated nearly twice the amount of PAHs compared to PFR2 and PFR1; a similar emissions trend was observed for the samples containing low-halogen components.

Data on smoke, particulate matter, CO and CO_2 releases, and heat release were collected for all laminate types. Smoke release was nearly twice as high for BFRs compared to PFR1 and PFR2 for laminates without components in both combustion scenarios. A similar trend was observed for smoke release from laminates with standard halogen components. Particulate matter emissions for PFR1 without components were nearly twice that of NFR in open burn conditions. Of the samples containing standard halogen components, BFRs emitted over 25 percent more particulate matter than PFR2; BFRs emitted over 50 percent more particulate matter than PFR2 in samples containing low-halogen components. However, particulate matter trends did not always align with smoke release emissions. While differences in CO release between samples were negligible, CO_2 emissions varied depending on laminate type. Heat release results showed flame retardant laminates to have lower peak heat releases compared to the non-flame retardant laminates in open burn scenarios. In incineration conditions, the BFRs lowered heat release compared to the NFRs. PFR1 emitted heat at levels about equal or slightly higher than the NFRs; heat release was not measured for PFR2 in incineration conditions.

Selecting Flame Retardants for PCBs

The partnership recognizes that the human health and environmental impacts are important factors in selecting a flame-retardant chemical or formulation to provide fire safety in a PCB. However, the partnership also believes other factors are important, such as flame retardant effectiveness, electrical and mechanical performance, reliability, cost, and impacts on end-of-life emissions. These factors are discussed as considerations for selecting flame retardants in Chapter 7. While the report focuses on human health and environmental attributes of each flame-retardant chemical, it is important to note that many of these flame-retardant chemicals must be used together in different combinations to meet the performance specifications. It is also important to note that performance requirements will vary depending on the use of the PCB.

In parallel with this draft assessment, industry trade groups tested alternative non-halogenated flame retardants and found that they function equally as well as TBBPA-based circuit boards for certain products. Performance testing for commercially available halogen-free flame-retardant materials to determine their key electrical and mechanical properties has been the focus of several separate but complementary projects conducted by iNEMI. This partnership worked closely with iNEMI to develop this alternatives assessment, as well as the High Density Packaging User Group (HDPUG). iNEMI recently conducted performance testing of halogen-free alternatives to traditional flame-retardant PCB used in the high-reliability market segment (e.g., servers, telecommunications, military) as well as those used by desktop and laptop computer manufacturers. The HFR-Free High-Reliability PCB Project found that the eight halogen-free flame-retardant laminates tested generally outperformed the traditional FR-4 laminate control. The HFR-Free Leadership Program, which assessed the feasibility of a broad conversion to HFR-free PCB materials used by desktop and laptop computer manufacturers, found the halogen-free flame-retardant laminates tested have electrical and thermo-mechanical properties that meet or exceed those of brominated laminates and that laminate suppliers can meet the demand for halogen-free flame-retardant PCB materials. HDPUG completed a project in 2011 to build a database of existing information on halogen-free materials, including halogen-free flame retardants – both commercially available and in research and development.[1]

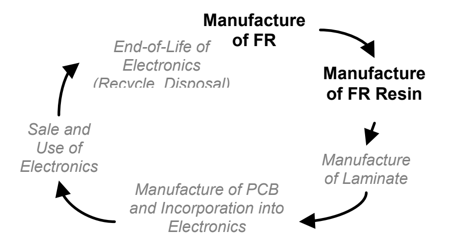
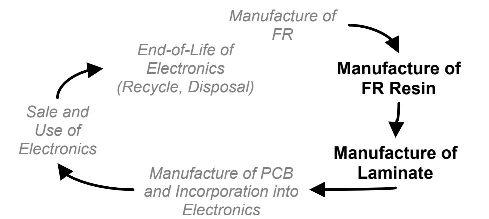
[1] http://hdpug.org/content/completed-projects#HalogenFree

ES-1. Screening Level Hazard Summary for Reactive Flame-Retardant Chemicals & Resins

This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion by-products are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics (*VL, L, M, H,* and *VH*) were assigned using values from predictive models and/or professional judgment.

♦ TBBPA has been shown to degrade under anaerobic conditions to form bisphenol A (BPA; CASRN 80-05-7). BPA has hazard designations different than TBBPA, as follows: MODERATE (experimental) for reproductive, skin sensitization and dermal irritation. [§] Based on analogy to experimental data for a structurally similar compound. [‡]The highest hazard designation of any of the oligomers with MW <1,000. [¥] Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

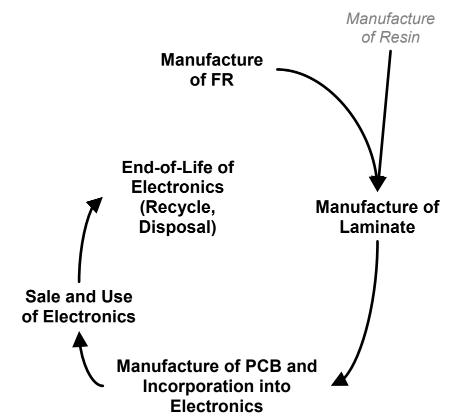
Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.9)	CASRN	Human Health Effects											Aquatic Toxicity		Environ-mental Fate		Exposure Considerations
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins
Reactive Flame-Retardant Chemicals																	
Tetrabromobisphenol A	79-94-7	L	M	L	L♦	M	L	L	L♦		M	L♦	VH	H	H	M	
DOPO	35948-25-5	L	*M*	L	*L*[§]	*M*	*M*	L	M		M	VL	L	*M*	*H*	*L*	
Fyrol PMP	63747-58-0	L	*L*[§]	*L*[§]	*M*[§]	*M*[§]	*M*[§]	*M*[§]	L		L	L	*H*[‡]	*H*[‡]	*VH*	*H*[‡]	
Reactive Flame-Retardant Resins																	
D.E.R. 500 Series[¥]	26265-08-7	*L*	*M*	*M*	*M*	*M*	*M*	*M*	H		*M*[‡]	*M*[‡]	*L*	*L*	*VH*	*H*[‡]	
Dow XZ-92547[¥]	Confidential	L	*M*[‡]	*M*[§]	*M*[‡]	*M*[‡]	*M*[‡]	*M*[‡]	H	*M*[‡]	VL	L	*L*	*H*	*VH*	*H*[‡]	

ES-2. Screening Level Hazard Summary for Additive Flame-Retardant Chemicals

This table contains hazard information for each chemical; evaluation of risk considers both hazard and exposure. Variations in end-of-life processes or degradation and combustion by-products are discussed in the report but not addressed directly in the hazard profiles. The caveats listed below must be taken into account when interpreting the information in the table.

VL = Very Low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very High hazard — Endpoints in colored text (VL, L, M, H, and VH) were assigned based on empirical data. Endpoints in black italics *(VL, L, M, H, and VH)* were assigned using values from predictive models and/or professional judgment.
[R] Recalcitrant: Substance is comprised of metallic species (or metalloids) that will not degrade, but may change oxidation state or undergo complexation processes under environmental conditions. [§] Based on analogy to experimental data for a structurally similar compound. [¤]Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter. [^] Depending on the grade or purity of amorphous silicon dioxide commercial products, the crystalline form of silicon dioxide may be present. The hazard designations for crystalline silicon dioxide differ from those of amorphous silicon dioxide, as follows: VERY HIGH (experimental) for carcinogenicity; HIGH (experimental) genotoxicity; MODERATE (experimental) for acute toxicity and eye irritation. [¥] Aquatic toxicity: EPA/DfE criteria are based in large part upon water column exposures which may not be adequate for poorly soluble substances such as many flame retardants that may partition to sediment and particulates.

Chemical (for full chemical name and relevant trade names see the individual profiles in Section 4.9)	CASRN	Human Health Effects											Aquatic Toxicity		Environmental Fate		Exposure Considerations
		Acute Toxicity	Carcinogenicity	Genotoxicity	Reproductive	Developmental	Neurological	Repeated Dose	Skin Sensitization	Respiratory Sensitization	Eye Irritation	Dermal Irritation	Acute	Chronic	Persistence	Bioaccumulation	Availability of flame retardants throughout the life cycle for reactive and additive flame-retardant chemicals and resins
Additive Flame-Retardant Chemicals																	
Aluminum Diethylphosphinate[¥]	225789-38-8	L	*L*[§]	L	L	*M*[§]	*M*[§]	*M*[§]	L		L	VL	M	M	*H*[R]	*L*	
Aluminum Hydroxide[¥]	21645-51-2	L	*L*[§]	L	*L*[§]	L	M	*M*[§]	L		VL	VL	L	L	*H*[R]	*L*	
Magnesium Hydroxide[¥]	1309-42-8	L	L	L	L	L	*L*	L	L		M	L	*L*	*L*	*H*[R]	*L*	
Melamine Polyphosphate[1¥]	15541-60-3	L	*M*	*M*	*H*	*M*	*M*	*M*	*L*		L	VL	L	L	*H*	*L*	
Silicon Dioxide (amorphous)	7631-86-9	L[^]	L[^]	L[^]	L	L	*L*[§]	H[¤]	L		L[^]	VL	L	*L*	*H*[R]	*L*	



[1] Hazard designations are based upon the component of the salt with the highest hazard designation, including the corresponding free acid or base.