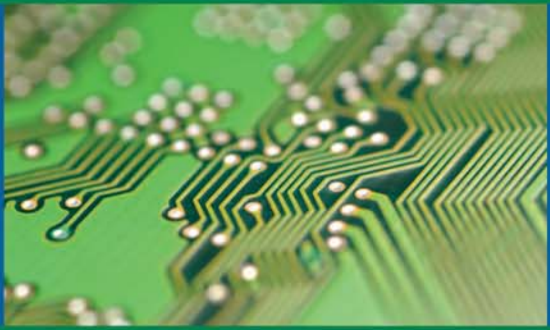
United States
Environmental Protection
Agency

Partnership to Evaluate Flame Retardants in Printed Circuit Boards



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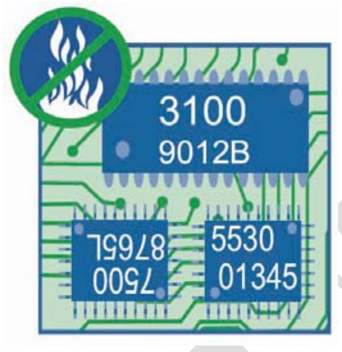
FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS



REVIEW DRAFT

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November 7, 2008

Design for the Environment
U.S. EPA

Disclaimer

This document has not been through a formal external peer review process and does not necessarily reflect all of the most recent policies of the U.S. Environmental Protection Agency (EPA), in particular those now under development. The use of specific trade names or the identification of specific products or processes in this document is not intended to represent an endorsement by EPA or the U.S. government. Discussion of environmental statutes is intended for information purposes only; this is not an official guidance document and should not be relied upon to determine applicable regulatory requirements.

This document contains the first part of a two-part report addressing environmental and human health issues associated with the production, use, and disposal of FR4 PCBs using current and emerging flame retardant technologies. Part one provides an evaluation of the environmental and human health hazards associated with flame retarding chemicals during manufacturing and use of the FR4 boards and a preliminary discussion and identification of end of life issues. Part two of the report will present experimental data from the investigation of the thermal breakdown of boards and the byproducts formed under different combustion and pyrolysis conditions. These data may provide further insight into any issues that may arise, including possible end of life disposal issues. It is anticipated that part two of the report will be completed in 2009. This version of the report contains results from part one only and is considered incomplete until the results from part two are available.

For More Information

To learn more about the Design for the Environment (DfE) Flame Retardant in Printed Circuit Board Partnership or the DfE Program, please visit the DfE Program Web site at: www.epa.gov/dfe.

To obtain copies of DfE Program technical reports, pollution prevention case studies, and project summaries, please contact:

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Acknowledgements

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This document was produced as part of the DfE Flame Retardants in Printed Circuit Boards Partnership under the direction of the partnership's steering committee, including: Ray Dawson, BSEF; Lauren Heine, Clean Production Action; Art Fong, IBM; Steve Tisdale, Intel; Fern Abrams, IPC; Mark Buczek, Supresta; Adrian Beard, Clariant and HFFREC; and Clive Davies, Kathleen Vokes, and Melanie Vrabel, U.S. EPA DfE. The partnership's technical committee also provided technical input, research, and other support. This project could not have been completed without their participation.

The Flame Retardants in Printed Circuit Boards Partnership includes representatives from the following organizations:

ALBEMARLE®

BSEF
Bromine Science and Environmental Forum

Ciba

Clariant

DOW®

ITI
Information Technology Industry Council
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Executive Summary

A broad-based stakeholder group joined with the Design for the Environment (DfE) Program in the U.S. Environmental Protection Agency's (EPA's) Office of Pollution Prevention and Toxics (OPPT) to form the Flame Retardants (FRs) in Printed Circuit Boards (PCBs) Partnership. The partnership, which includes members of the electronics industry, flame retardants industry, environmental groups, academia, and others, came together to generate this report. 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.

Goal of the Partnership and This Report

The partnership developed the information in this report to advance understanding of the human health and environmental impacts of conventional and new flame-retardant materials that can provide fire safety for PCBs. 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)

PCBs are commonly found in consumer and industrial electronic products, including computers and cell phones. Manufacturers commonly produce PCBs with flame-retardant chemicals to help ensure fire safety. Currently, the majority of PCBs produced worldwide meet the V0 requirements of the UL 94 fire safety standard. This standard is usually achieved through the use of brominated epoxy resins in which the reactive flame retardant tetrabromobisphenol A (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, the use of alternatives has been increasing over the past few years, and additional flame-retardant chemicals and laminate materials are under development.

Environmental and Human Health Hazard Information for Flame Retardant Chemicals

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. More established chemicals, including 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 of the New Chemicals Program to estimate the potential impacts of flame retardants when no experimental data were available. The partnership evaluated eight commercially available flame retardants for FR-4 laminate materials for PCBs: TBBPA, DOPO, Fyrol PMP, aluminum hydroxide, Exolit OP 930, Melapur 200, silicon dioxide, and magnesium hydroxide. TBBPA is used to make the epoxy resin base material in more than 90 percent of FR-4 boards. Alternative flame-retardant materials are used in only 3 to 5 percent of the current FR-4 boards. 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 epoxy resin with TBBPA, DOPO, and Fyrol PMP were also evaluated, because both TBBPA and DOPO undergo chemical reactions during manufacturing. As a result, 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. Chapter 4 qualitatively summarizes the toxicological hazard characteristics of the chemicals in each flame-retardant formulation. Chemical components making up less than 1 percent by weight of the flame-retardant formulation were not considered in this assessment. A screening-level summary table (presented below as Table ES-1) is also presented in Chapter 4. Table ES-1 shows relative hazard levels for nine human health effects, two aquatic toxicity effects, and two environmental fate endpoints. Selected flame retardants are presented according to their reactive or additive nature.

Flame-retardant evaluations in this report are hazard assessments with considerations for exposure, not full risk assessments. Whereas hazard measures a material's inherent dangers, risk takes into account both hazard and the amount of material to which workers, the community, or the environment may come into contact (probability of exposure). For example, a highly hazardous material may pose a low level of risk to human health and the environment if there is limited exposure, but a high level of risk if there is a high level of exposure. Similarly, a less hazardous material may pose a high level of risk to human health and the environment if there is a high level of exposure, but a low level of risk if there is limited exposure. For flame-retardant materials with little available information, hazard levels were projected based on chemical structure. This approach relies on structure activity relationships (SAR) analysis involving modeling techniques and professional judgment. An explanation of EPA's chemical assessment methodology and more detailed characteristics of the chemicals in each formulation are presented in Sections 4.1.2 and 4.2.

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 these and other life-cycle considerations. A range of information about life-cycle issues exists for each of the flame retardants, especially when comparing TBBPA to more recently developed and commercialized alternatives. 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 byproducts are only mentioned in the process descriptions.

Combustion and Pyrolysis Testing

As part of this life-cycle thinking, the partnership decided that testing of FR-4 laminates and PCB materials is necessary to better understand the potential byproducts during product use and thermal end-of-life processes. The University of Dayton Research Institute (UDRI) will conduct pyrolysis and combustion testing, which is scheduled to be completed in 2009. The rationale and methods for this testing are described in Chapter 6, with more detailed methods and results to be published in an addendum to this report after test completion.

Selecting Flame Retardants for PCBs

The partnership recognizes that the human health and environmental impacts are important factors in selecting a flame retarding 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 elements are included 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. The performance testing of commercially available halogen-free flame-retardant materials to determine their key electrical and mechanical properties is the focus of a separate but complementary project being conducted by iNEMI. This partnership has worked closely with iNEMI, as well as the High Density Packaging User Group (HDPUG). In contrast to iNEMI, HDPUG is focused on building a database of existing information on halogen-free materials, including halogen-free flame retardants – both commercially available and in research and development.

Table ES-1 Screening Level Toxicology Hazard Summary

This table only contains information regarding the inherent hazards of flame-retardant (FR) chemicals. Evaluation of risk must consider both the hazard and exposure associated with FR chemicals, as well as the hazard and exposure associated with combustion and degradation byproducts. Refer to Table 5-1 for more information on exposure.

The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

L = Low hazard M[1] = Moderate hazard H = High hazard — Endpoints in colored text (L, M, and H) were assigned based on experimental data. Endpoints in black italics (*L, M,* and *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships).

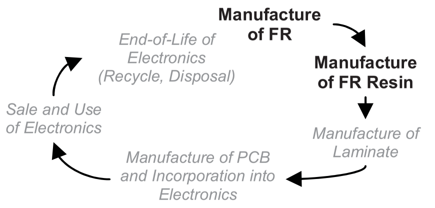
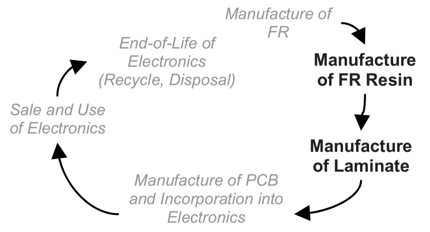
◊ Hazard designations, which are based on the presence of epoxy groups, arise from the analysis of low molecular weight oligomers (molecular weight <1,000) that may be present in varying amounts. The estimated human health hazards for higher molecular weight (>1,000) components, which contain epoxy groups, are low for these endpoints.

‡ Concern based on potential inhalation of small particles less than 10 microns in diameter that may be present in varying amounts.

§ Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter.

∇ Persistent degradation products expected (none found in this report).

R Recalcitrant: substance is or contains inorganics, such as metal ions or elemental oxides, that are expected to be found in the environment >60 days after release.

Chemical	CASRN	Human Health Effects									Aquatic Toxicity		Environmental		Exposure Considerations
		Acute Toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	Availability of FRs throughout the lifecycle for reactive and additive FR chemicals and resins[2]
Reactive Flame-Retardant Chemicals[2]															
Tetrabromobisphenol A (TBBPA) (Albemarle, Chemtura, and others)[3]															
TBBPA	79-94-7	L	L	*L*	L	L	M	L	L	L	H	*H*	M	L	
DOPO (6H-Dibenz[c,e][1,2] oxaphosphorin, 6-oxide) (Sanko Co., Ltd. and others)															
DOPO	35948-25-5	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*M*	*M*	*L*	*L*	
Fyrol PMP (Aryl alkylphosphonate) (Supresta)															
Fyrol PMP	Proprietary	*L*	L	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*H*	*L*	
Reactive Flame-Retardant Resins[2]															
Reaction product of TBBPA - D.E.R. 538 (Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol]) (Dow Chemical)															
D.E.R. 538	26265-08-7	*L*	M	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	M	*L*	*L*	*M*	*L*	
Reaction Product of DOPO – Dow XZ-92547 (reaction product of an epoxy phenyl novolak with DOPO) (Dow Chemical)															
Dow XZ-92547	Proprietary	*L*	M	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	*M*◊	*L*	*L*	*H*	*L*	
Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin (Representative Resin)															
Representative Fyrol PCB Resin	Unknown	*L*	*L*	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	*M*◊	*L*	*L*	*H*	*L*	

[1] The moderate designation captures a broad range of concerns for hazard, further described in Table 4-3.

[2] Reactive FR chemicals and resins may not completely react, and small amounts may be available during other parts of the lifecycle.

[3] The EU has published a comprehensive risk assessment for TBBPA in reactive applications. This risk assessment is a valuable source of information when choosing flame retardants for printed circuit board applications.

Table ES-1 Screening Level Toxicology Hazard Summary

This table only contains information regarding the inherent hazards of flame-retardant (FR) chemicals. Evaluation of risk must consider both the hazard and exposure associated with FR chemicals, as well as the hazard and exposure associated with combustion and degradation byproducts. Refer to Table 5-1 for more information on exposure.

The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

L = Low hazard M[1] = Moderate hazard H = High hazard — Endpoints in colored text (L, M, and H) were assigned based on experimental data.
Endpoints in black italics (*L, M,* or *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships).
◊ Hazard designations, which are based on the presence of epoxy groups, arise from the analysis of low molecular weight oligomers (molecular weight <1,000) that may be present in varying amounts. The estimated human health hazards for higher molecular weight (>1,000) components, which contain epoxy groups, are low for these endpoints.
‡ Concern based on potential inhalation of small particles less than 10 microns in diameter that may be present in varying amounts.
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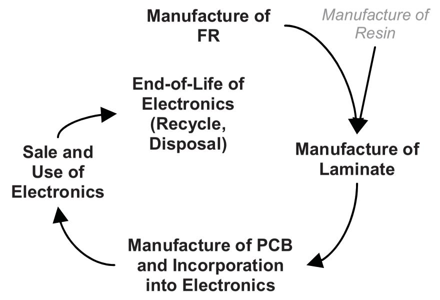
Chemical	CASRN	Human Health Effects									Aquatic Toxicity		Environ-mental		Exposure Considerations
		Acute Toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	Availability of FRs throughout the lifecycle for reactive and additive FR chemicals and resins
Additive Flame Retardants[3]															
Aluminum hydroxide															
Aluminum hydroxide	21645-51-2	*L*	*L*	*L*	*M*	*L*	L	*M*	L	*L*	H	M	*H^{R}*	*L*	
Exolit OP 930 (phosphoric acid, diethyl-, aluminum salt) (Clariant)															
Exolit OP 930	225789-38-8	L	L	*L*	*M*	*L*	*M*	*M*	L	L	M	*M*	*H^{R}*	*L*	
Melapur 200 (Melamine polyphosphate) (Ciba)[4]															
Melapur 200	218768-84-4	L	*L*	*L*	*L*	*L*	*L*	*L*	*M*	*M*	*L*	*L*	*M*	*L*	
Polyphosphoric acid	8017-16-1	L	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*	
Melamine	108-78-1	L	L	L	*L*	*L*	L	*L*	M	M	L	L	M	*L*	
Silicon dioxide amorphous[5]															
Silicon dioxide amorphous	7631-86-9	L	L	L	*L*	L	L	*L*	$H^{\S}$	L	*L*	*L*	*H^{R}*	*L*	
Silicon dioxide crystalline[5]															
Silicon dioxide crystalline	1317-95-9	L	L	$H^{\ddagger}$	$H^{\S}$	L	L	*L*	$H^{\S}$	$H^{\S}$	*L*	*L*	*H^{R}*	*L*	
Magnesium hydroxide															
Magnesium hydroxide	1309-42-8	L	*L*	L	*L*	*L*	*L*	*L*	L	*L*	*L*	*L*	*H^{R}*	*L*	



[1] The moderate designation captures a broad range of concerns for hazard, further described in Table 4-3.
[3] Although additive flame retardants are present throughout the lifecycle of the PCB, they are locked into the polymer matrix of the epoxy laminate material.
[4] Melapur 200 dissociates in water to form polyphosphoric acid and melamine ions. For this reason, Table 4-1 includes both dissociation ions.
[5] Representative CAS numbers are included in this summary table. Section 4.2.9 includes a full list of CAS numbers.

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List of Acronyms and Abbreviations

ABS	Acrylonitrile-butadiene-styrene
ATH	Aluminum trihydroxide (a.k.a. Alumina trihydrate)
BAN	Basel Action Network
BCF	Bioconcentration factor
BFR	Brominated flame retardant
BPA	Bisphenol A
BSEF	Bromine Science and Environmental Forum
BT	Bismaleimide-triazine
CCL	Copper clad laminate
CRT	Cathode ray tube
DfE	Design for the Environment
DGEBA	Diglycidyl ether of bisphenol A
Dicy	Dicyandiamide
EASE	Estimation and Assessment of Substance Exposure
ECOSAR	EPA's Ecological Structure Activity Relationships estimation program
EDSP	Endocrine Disruptor Screening Program
EETD	Economics, Exposure, and Technology Division
EPIWIN	Estimations Program Interface for Windows
EU	European Union
EVA	Ethylene-vinyl acetate
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
GS-MS	Gas chromatography-mass spectrometry
HBCD	Hexabromocyclododecane
HDPUG	High Density Packaging User Group
HPV	High Production Volume
HSDB	Hazardous Substances Data Bank
HSE	Health and Safety Executive
iNEMI	International Electronics Manufacturing Initiative
ISO	International Organization for Standardization
K_{ow}	Octanol/water partition coefficient
LFL	Lower limit of flammability
MITI	Ministry of International Trade and Industry, Japan
NES	No effects at saturation
OECD	Organisation for Economic Cooperation and Development
OPP	Office of Pesticide Programs
OPPT	Office of Pollution Prevention and Toxics
ORD	Office of Research and Development
P2	Pollution prevention
PBDE	Polybrominated diphenyl ether
PEC	Predicted environmental concentration
Prepreg	Pre-impregnated material
PPO	Poly(p-phenylene oxide)
PTFE	Polytetrafluoroethylene
QSAR	Quantitative structure activity relationships

RoHS	Restriction of Hazardous Substances
SAC	Tin-silver-copper alloy
SAR	Structure activity relationships
SMILES	Simplified molecular input line entry specification
SVTC	Silicon Valley Toxics Coalition
TSCA	Toxic Substances Control Act
UDRI	University of Dayton Research Institute
UFL	Upper limit of flammability
UK	United Kingdom
VECAP	Voluntary Emissions Control Action Programme
WEEE	Waste Electrical and Electronic Equipment
XRF	X-ray fluorescence

1 Introduction

The electronics industry is engaging in a multi-stakeholder partnership with EPA's Design for the Environment (DfE) Program to identify and evaluate commercially available flame retardants and their environmental, human health and safety, and environmental fate aspects in FR-4 printed circuit boards (PCBs). The majority of PCBs are classified as FR-4 (Flame Resistant 4), indicating that they meet certain performance criteria, as well as the V0 requirements of the UL (Underwriters Laboratories) 94 flammability testing standard.[1] Currently, for more than 90 percent of FR-4 PCBs, the UL 94 V0 requirement is met by the use of epoxy resins in which the reactive flame retardant tetrabromobisphenol A (TBBPA) forms part of the polymeric backbone of the resin.

Alternative flame-retardant materials are used in only 3 to 5 percent of the current FR-4 boards, but additional alternative flame-retardant materials are under development. Little information exists concerning the potential environmental and human health impacts of the materials that are being developed as alternatives to the brominated epoxy resins being used today. Environmental and human health impacts can occur throughout the life cycle of a material, from development and manufacture, through product use, and finally at the end of life of the material or product. In addition to understanding the potential environmental and human health hazards associated with the reasonably anticipated use and disposal of flame-retardant chemicals, stakeholders have expressed a particular interest in understanding the combustion products that could be formed during certain end-of-life scenarios.

A risk assessment conducted recently by the European Union did not find significant human health risk associated with reacted TBBPA in printed circuit boards.[2] However, the potential environmental and health impacts of exported electronic waste (e-waste) are not fully understood. A large percentage of e-waste is sent to landfills or recycled through smelting to recover metals. An unknown portion of the waste is recycled under unregulated conditions in certain developing countries, and the health implications of such practices are of concern.

This report aims to increase understanding of the potential environmental and human health impacts of printed circuit boards throughout their life cycle. Information generated from this partnership will contribute to more informed decisions concerning the selection and use of flame-retardant materials and technologies and the disposal and recycling of e-waste.

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[1] FR-4 refers to the base material of the printed circuit board; namely, a composite of an epoxy resin reinforced with a woven fiberglass mat. UL 94 is an Underwriters Laboratories standard for flammability of plastic materials. Within UL 94, V0 classification entails one of the highest requirements.

[2] The EU results, while noteworthy, will not form the basis of this assessment, but rather should be viewed in conjunction with the independent conclusions drawn in this assessment.

1.1 Purpose of the Flame-Retardant Alternatives Analysis

The partnership committee identified the overall purpose of this analysis as follows:

- To identify and evaluate current and alternative flame retardants and their environmental, human health and safety, and environmental fate aspects in FR-4 printed circuit boards.

- To allow industry and other stakeholders to consider environmental and human health impacts along with cost and performance of circuit boards as they evaluate alternative materials and technologies.

1.2 Scope of the Flame-Retardant Alternatives Analysis

The partnership will incorporate life-cycle thinking into the project as it explores the potential hazards associated with flame retardants and potential exposures throughout the life cycle of flame retardants used in FR-4 PCBs. While the report focuses on flame retardants used in FR-4 PCBs, these flame retardants may also be applicable in a wide range of PCBs constructed of woven fiberglass reinforced with thermoset resin.

As appropriate, the scope will include aspects of the life cycle where public and occupational exposures could occur. For example, consideration of exposures from open burning or incineration at the end of life will be included, as will exposures from manufacturing and use.

The following investigations were considered within the scope of the project:

- An environmental, health, and safety (EHS) assessment of commercially available flame-retardant chemicals and fillers for FR-4 laminate materials

- An assessment of environmental and human health endpoints (environmental endpoints include ecotoxicity, fate, and transport)

- A review of potential life-cycle concerns

- Combustion testing to compare the potential byproducts of concern from commercially available FR-4 laminates and PCB materials during offgassing and thermal end-of-life processes, including open burning, incineration, and smelting.

The project's scope will be limited to flame-retardant chemicals used in bare (i.e., unpopulated) FR-4 printed circuit boards. Other elements of PCBs (such as solder and casings) and chemicals in components often attached to PCBs to make an electronic assembly (such as cables, capacitors, connectors, and integrated circuits) will not be assessed.

The report is intended to provide information that will allow industry and other stakeholders to evaluate environmentally safer alternatives for flame retardants in PCBs. The report is organized as follows:

- *Chapter 1 (Introduction):* This chapter provides background to the Flame Retardants in Printed Circuit Boards partnership project including the purpose and scope of the partnership and of this report.
- *Chapter 2 (FR-4 Laminates):* This chapter describes the characteristics, market for, and manufacturing process of FR-4 laminates and investigates possible next generation developments.
- *Chapter 3 (Chemical Flame Retardants for FR-4 Laminates):* This chapter describes chemical flame retardants generally, as well as those specific flame retardants used in FR-4 laminates. The next generation of flame-retardant chemicals is also discussed.
- *Chapter 4 (Evaluation of Flame Retardants):* This chapter explains the chemical assessment methodology used in this report and summarizes the assessment of hazards associated with individual chemicals.
- *Chapter 5 (Potential Exposure to Flame Retardants and Other Life-cycle Considerations):* This chapter discusses reasonably anticipated exposure concerns and identifies potential exposure pathways and routes associated with flame-retardant chemicals during each stage of their life cycle.
- *Chapter 6 (Combustion, Pyrolysis, and Offgassing Testing of FR-4 Laminates):* This chapter describes the rationale and methods for offgassing, combustion, and pyrolysis testing of PCB materials.
- *Chapter 7 (Considerations for Selecting Flame Retardants):* This chapter addresses considerations for selecting alternative flame retardants based on environmental, technical, and economic feasibility.

1.2.1 Life-Cycle Stages Considered

Figure 1-1: Exposure Pathways Considered During the Life Cycle of a PCB

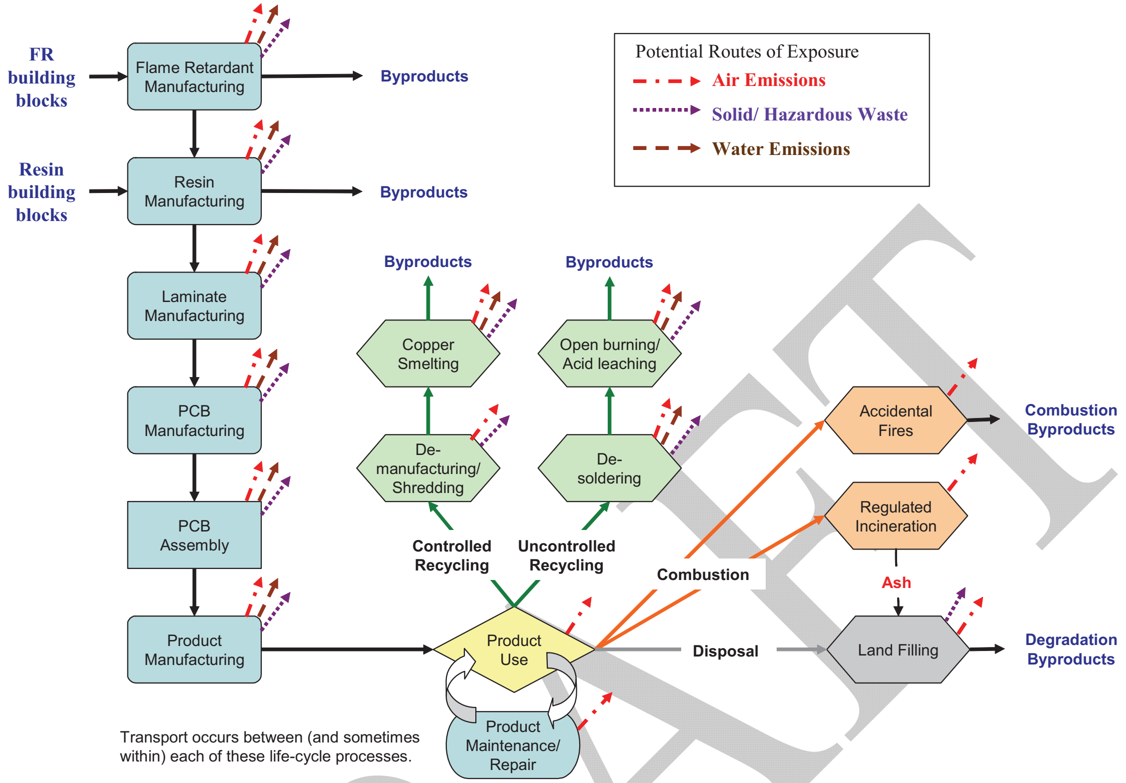

Figure 1-1 above shows the life-cycle stages of a printed circuit board and the associated potential exposure pathways that will be examined in this report. In brief, the flame-retardant chemical is manufactured and then incorporated, either reactively or additively, into the epoxy resin. The epoxy resin is then applied to a woven fiberglass mat and hardened. Layers of copper foil are attached to both sides of the reinforced resin sheet to form a laminate. Next, a printed circuit board is manufactured by combining several laminate layers that have had conductive pathways (i.e., circuits) etched into the copper foil. The layers are then laminated together, and holes are drilled to connect circuits between layers and hold certain electronic components (e.g., connectors or resistors). Once assembled, printed circuit boards are incorporated into various products by original equipment manufacturers (OEMs). When the product is no longer in use, there are several end-of-life pathways that the product may take: landfilling, regulated incineration, unregulated incineration (or open burning), and recycling. All of these life-cycle stages will be discussed in further detail in the subsequent chapters of this report.

1.2.2 Aspects Beyond the Scope of This Assessment

Although the analysis will explore hazard data associated with potential exposure scenarios, the partnership does not intend to conduct a full risk assessment, which would require a full exposure assessment along with the hazard assessment. Likewise, the project will not be a complete life-cycle analysis, which inventories inputs and outputs from processes throughout the life cycle and evaluates the environmental impacts associated with those inputs and outputs.

Process chemicals (i.e., etching or washing solutions used in manufacturing PCBs) are not included in the scope of this assessment. Although PCBs come in many varieties, the scope of this analysis is limited to FR-4 boards which meet the V0 requirements of the UL (Underwriters Laboratories) 94 standard. Boards of this type are used in consumer products such as computers and cell phones and make up a large portion of the PCBs used in consumer products. The assessment may be useful beyond FR-4 boards to the extent that the same flame retardants are used in other laminates constructed of woven fiberglass reinforced with other thermoset resins such as phenolics.

Finally, this assessment is not a technical evaluation of key electrical and mechanical properties of halogenated and halogen-free materials. These properties will be explored in a parallel assessment conducted by iNEMI (International Electronics Manufacturing Initiative). Together, the two reports will provide information on both the performance and environmental properties of the various materials being evaluated.

2 FR-4 Laminates

Flame Resistant 4 (FR-4) laminates are flame-retardant systems of woven glass reinforced with epoxy-like resin, notable for their resistance to heat, mechanical shock, solvents, and chemicals. Unlike lower grade laminates, a finished FR-4 laminate can obtain a V0 rating in the UL 94 test, a vertical burning test for flammability. FR-4 laminates can be categorized as (1) high glass transition temperature (T_g) FR-4 laminates,[3] (2) middle T_g FR-4 laminates,[4] and (3) low T_g FR-4 laminates.[5] Within each of those categories, individual FR-4 laminates are differentiated through reference to their physical properties (e.g., rate of water absorption, flexural strength, dielectric constant, and resistance to heat).

With the introduction of halogen-free FR-4 materials,[6] a similar segmentation is emerging (e.g., high T_g halogen-free, low T_g halogen-free), leading to a multiplication of the number of FR-4 materials available (Beard et al., 2006; Bergum, 2007). As different formulations (different FR systems and different resin chemistries) result in different laminate properties, there can be different materials within one class (e.g., low T_g) having different performance (e.g., dielectrics, mechanics), thus addressing the different market needs. Such differences in performance are not specific to halogen-free materials and may also exist among brominated grades of the same T_g class.

2.1 Overview of FR-4 Laminates Market (Prismark, 2006)

In 2006, global printed circuit board production exceeded $45 billion. PCBs are fabricated using a variety of laminate materials, including laminate, pre-impregnated material (prepreg), and resin-coated copper. In 2006, $7.66 billion of laminate materials were consumed globally. Laminate materials can be sub-segmented according to their composition, and include paper, composite, FR-4, high T_g FR-4, and specialty products (polytetrafluoroethylene (PTFE) and high-performance materials).

- Paper and composite laminates represent 17.1 percent of the global laminate market in value. These materials are used as the basic interconnecting material for consumer applications. The materials are low in cost, and their material characteristics are adequate for use in mainly low-end consumer products.

- The workhorse laminate for the printed circuit board industry is FR-4. In terms of value, approximately 70.4 percent of the material used in the industry is FR-4 glass-based laminate (including high T_g and halogen-free). This material provides a reliable and cost-effective solution for the vast majority of designs.

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[3] High glass transition temperature laminates have a T_g above 170°C.

[4] Middle glass transition temperature laminates are usually considered to have a T_g of approximately 150°C.

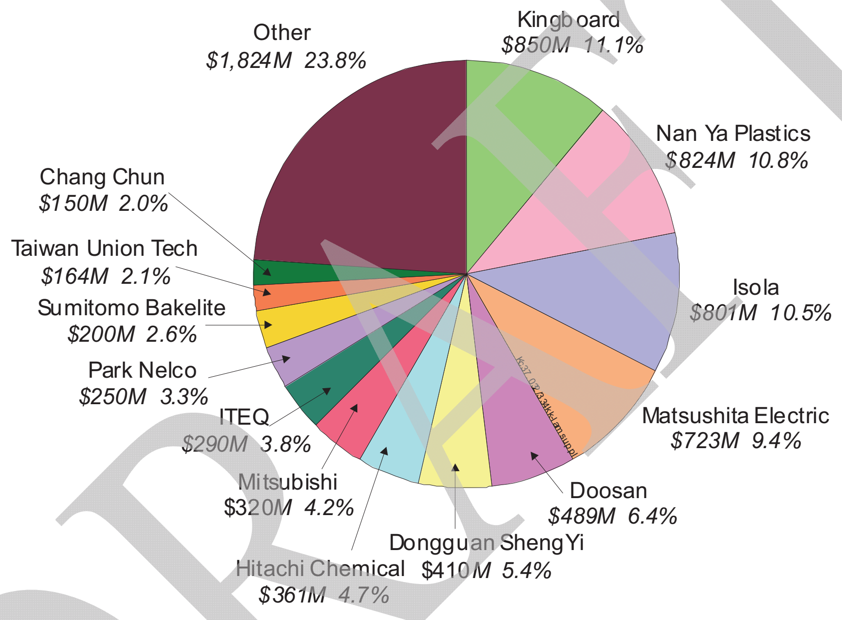
[5] Low glass transition temperature laminates are usually considered to have a T_g of 130°C and below.

[6] In accordance with IEC-61249-2-21, this report defines “halogen-free materials” as materials that are ≤900ppm by weight chlorine; ≤900ppm by weight bromine; and ≤1,500ppm maximum total halogens.

- Many laminators offer halogen-free FR-4 laminate materials. These materials are typically designed to be drop-in replacements for current halogenated materials, but they carry a price premium. Halogen-free materials have been slowly gaining acceptance on a regional basis.

- There are special applications that call for laminate materials with characteristics beyond the capability of FR-4. These materials consist of special integrated circuit packaging substrates and materials for use in wireless or high-speed digital applications, including laminate containing bismaleimide-triazine (BT) resins, poly(p-phenylene oxide) (PPO), high-performance PTFE, and polyimide.

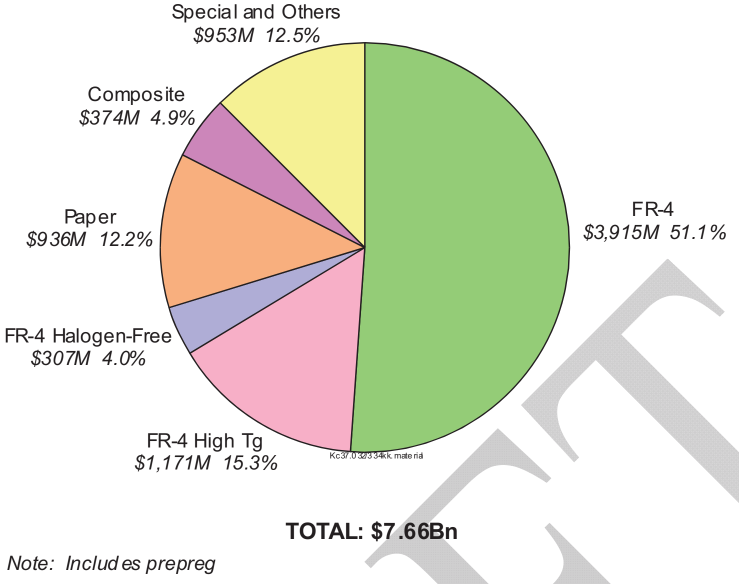
Figure 2-1: 2006 Global PCB Laminate Market by Supplier



TOTAL: $7.66Bn

Note: This market includes prepreg and RCC values.

Figure 2-2: 2006 Global PCB Laminate Market by Material Type



Global sales of laminate materials in 2006 were estimated at $7.66 billion. In terms of area production, it is estimated that more than 420.2 million square meters of laminate was manufactured to support the PCB industry in 2006. The distribution of laminate sales geographically and the leading suppliers to each region are shown in Figures 2-3 and 2-4.

Figure 2-3: 2006 Regional Laminate Sales into the Region

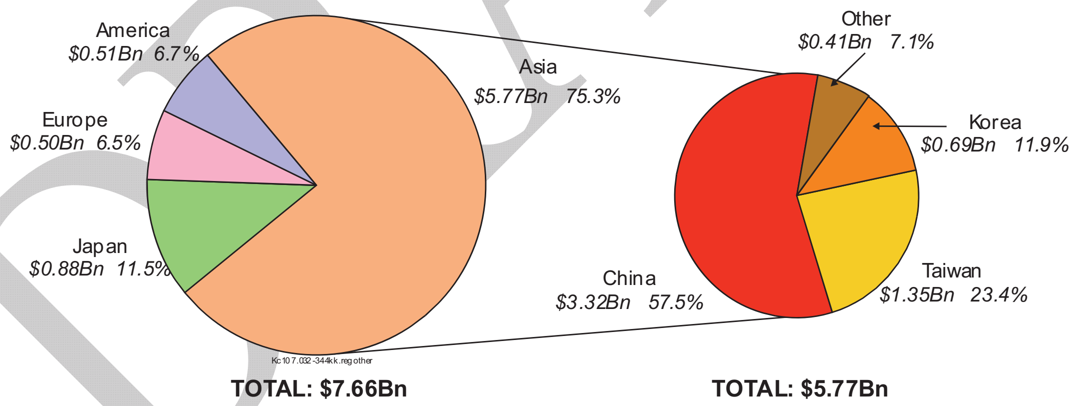
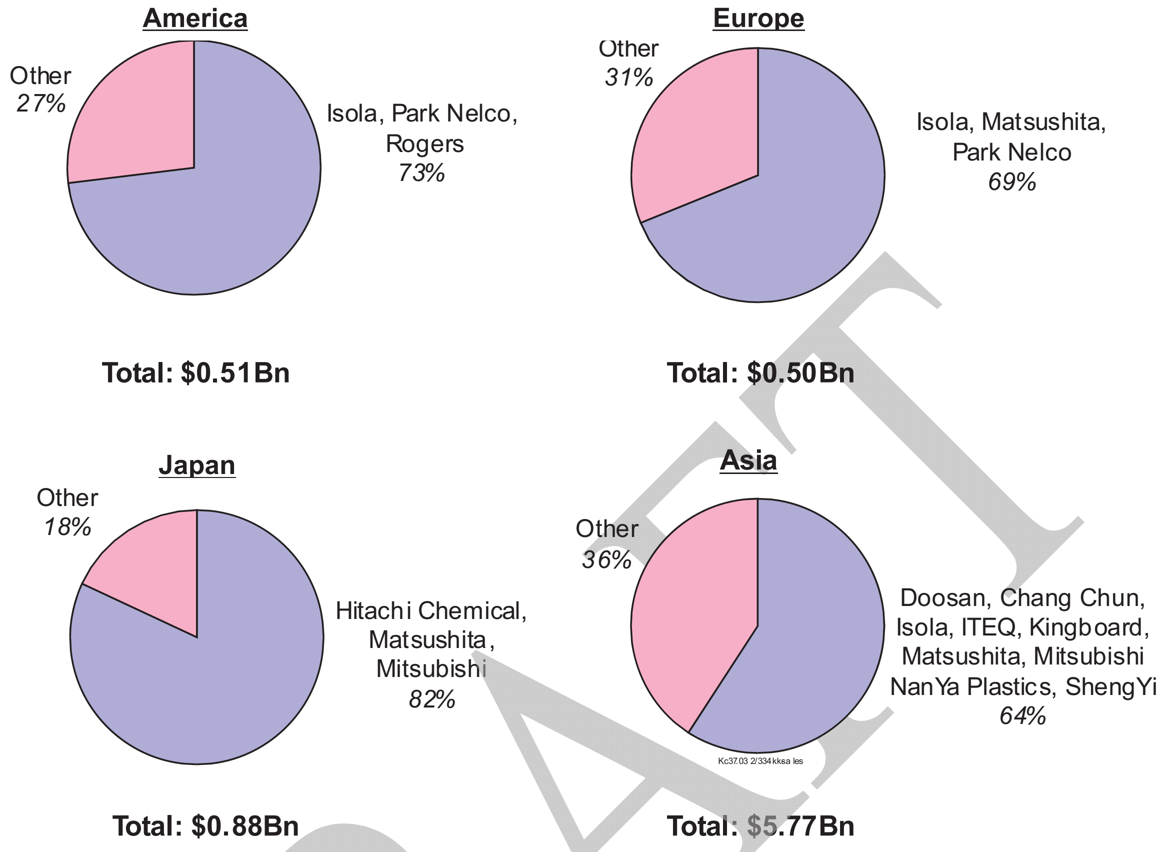


Figure 2-4: 2006 Laminate Sales by Region

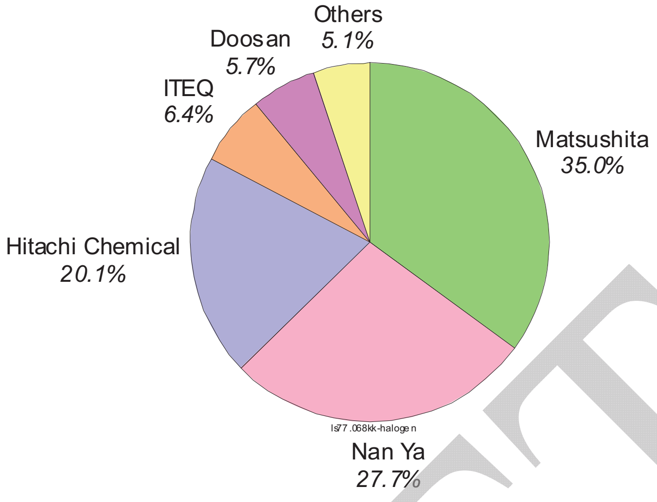


2.2 Halogen-Free Laminate Market

There has been a continuous increase in the demand for halogen-free material over the past few years. In 2003, the global halogen-free laminate market was approximately $60 million. In 2004 this market grew to $161 million, in 2005 it reached $239 million, and it is estimated at $307 million for 2006.

Most laminate suppliers now include halogen-free materials in their portfolio. Pricing for halogen-free laminate is still higher than conventional material by at least 10 percent, and often by much more. Tallying the production volumes of such leading laminate manufacturers as Hitachi Chemical, NanYa, Matsushita, ITEQ, Isola, Park Nelco, and others, Prismark has constructed a market segmentation, shown in Figure 2-5.

Figure 2-5: 2006 Global Halogen-Free Laminate Market



Total Market: 11.5M m^2

2.3 Current Research Efforts

While demand for halogen-free laminates is increasing, there is currently a lack of information regarding their performance and environmental impact. The International Electronics Manufacturing Initiative (iNEMI) and the High Density Packaging User Group (HDPUG) have taken on separate but complementary roles in helping to fill information gaps.

The iNEMI project is focusing on performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties. The current list of laminate materials identified by iNEMI for further study includes nine laminate materials from seven different suppliers:

- NanYa NPG-TL and NPG-170TL
- Hitachi BE-67G(R)
- TUC TU-742
- MEW R1566W
- ITEQ IT140G and IT155G
- Shengyi S1155
- Supresta FR Laminate

While not in the final list for further study, the following laminates were also identified as promising candidates by iNEMI:

- Isola DE156 and IS500
- TUC TU-862
- ITEQ IT170G
- Nelco 4000-7EF

Testing and evaluation of these laminate materials is currently under way.

In contrast to the iNEMI project, HDPUG is collecting existing data on halogen-free flame-retardant materials; no performance testing will be conducted. HDPUG is creating 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 will take a broad look at flame-retardant materials, both ones that are commercially viable and in research and development. The list of materials to be included in the database will be available later this year.

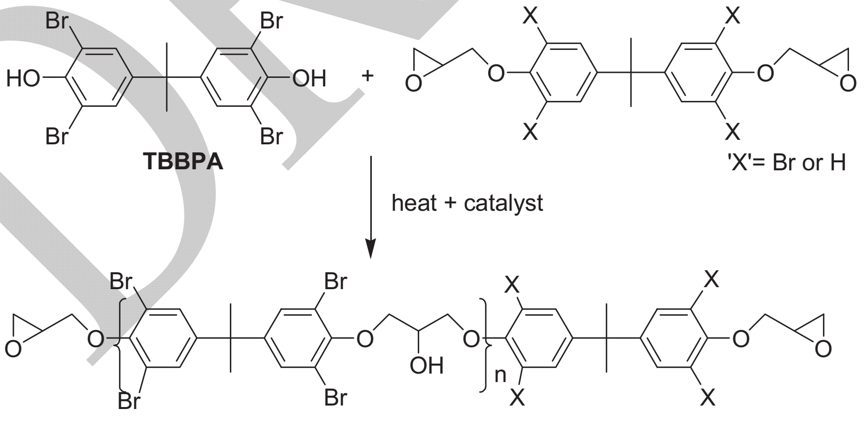
Even though they are taking on different roles, HDPUG and iNEMI have been in contact with each other, as well as this DfE partnership project, to ensure minimal duplication in scope. The results of their efforts will help inform companies that want to select halogen-free laminate materials.

2.4 Process for Manufacturing FR-4 Laminates

This section describes general processes for manufacturing epoxy resins and laminates. Specific chemicals and process steps can differ between manufacturers and intended use of the product.

2.4.1 Epoxy Resin Manufacturing

The process for making brominated epoxy resins that are used to make FR-4 laminates is shown below. Two different classes of oligomers (low molecular weight linear polymers) are in common use. The simplest are prepared by reacting TBBPA with a “liquid epoxy resin” (“X” is hydrogen in this case). The products (for example D.E.R.™ 530) have an M_n (number average molecular weight) of 800-1,000 g/mole and contain about 20 percent bromine by weight After the oligomers are prepared, they are dissolved in a variety of solvents such as acetone or methyl ethyl ketone (2-butanone) to reduce the viscosity. The M_w (average molecular weight) is typically about 2,000 g/mole. An excess of the epoxy resin is used, and therefore essentially all of the TBBPA is converted.

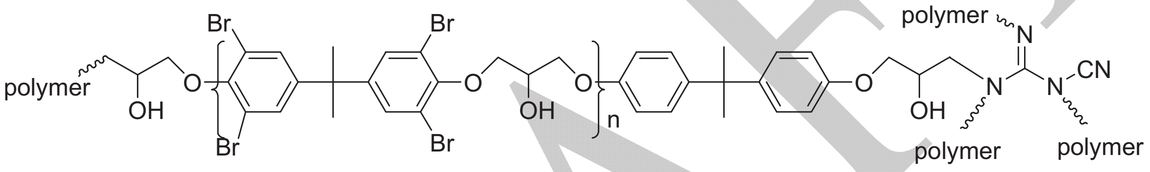


In cases where it is desired to have an oligomer with a higher concentration of bromine, the liquid epoxy resin is replaced with a brominated epoxy resin (“X” = Br in the above structure). The products (D.E.R.™ 560 is a typical example) have similar molecular weights, but the content of bromine is higher (about 50 percent bromine by weight). These “high-brominated” resins are typically used when other non-brominated materials must be added to the formulation (or “varnish”).

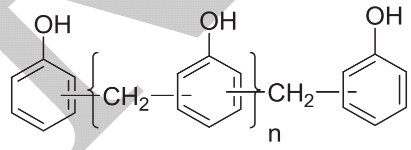
In the past a large majority of laminate varnishes would be prepared by simply combining the 20 weight percent brominated resin with 3 percent weight "dicy" (dicyandiamide) as a curing agent, along with additional solvent. After the solvent was removed and the laminate pressed, the thermoset matrix would contain about 20 percent bromine by weight. This is sufficient bromine to allow the thermoset matrix to pass the V0 performance requirements in the standard UL 94 test. The cure chemistry of dicy is very complex and inadequately understood. However, it is known to be capable of reacting with 4, 5, or even 6 epoxy groups.

"Catalysts" such as 2-methylimidazole are used to increase the cure rate. Imidazoles are not true catalysts: they initiate polymer chains, and become covalently bound to the matrix.

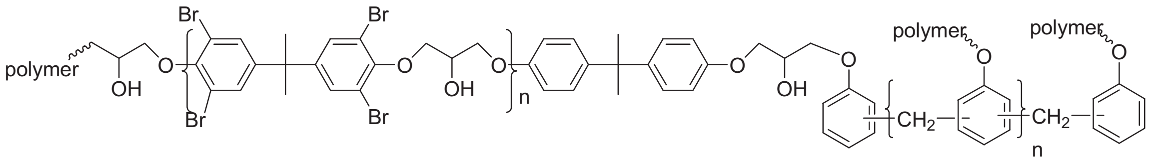
A simplified representation of the final thermoset is shown below. In a properly cured laminate all of the resin has become one molecule, meaning every atom is covalently linked into one three-dimensional structure. This is desirable because it means that there are no leachable (or volatile) materials that can be released during the various procedures used to make a final printed circuit board.



With the advent of lead-free solders that melt at higher temperatures, phenolic hardeners (in place of dicy) are becoming more common. Such formulations typically have higher decomposition temperatures. A common phenolic hardener is an oligomer prepared from phenol and formaldehyde that has the structure shown below. These "novolaks" typically have 2.5 to 5.5 phenolic groups per molecule, which translates to M_n's of 450 to 780 g/mole. Bisphenol A novolak is also becoming increasingly common to boost the glass transition temperature.



The cross-linked matrix formed in this case is represented below. The use of phenolic hardeners in the formulation has the effect of reducing the bromine concentration in the final cured resin. In some cases additional flame retardant is needed to meet the UL 94 V0 classification. This is typically a solid additive such as alumina trihydrate (ATH) or other fillers. Other methods are to mix in a fraction of the fully brominated resin that contains 50 percent bromine by weight. Finally, additional TBBPA and liquid epoxy resin can be mixed into the crosslinked matrix to increase the bromine concentration of the final cured resin, although it is unclear how common this practice is among epoxy resin manufacturers (Mullins, 2008).



This description does not cover all of the formulations used by laminate producers to meet their product specifications. Various epoxy novolaks can be added.

The process of making epoxy resins containing alternative FRs is similar to the process used for making brominated epoxy resins. In the case of phosphorus-based FRs, the epoxy resin is produced by reacting diglycidyl ether of bisphenol A (DGEBA) or an epoxy novolak with a stoichiometric deficiency of phosphorus flame retardant. This gives a new resin containing both an epoxy group and covalently bound phosphorus. Alternatively, a phosphorus-containing hardener can be prepared by condensing a phenolic compound with a phosphorus-containing flame retardant. For example, hydroquinone can condense with phosphorus-containing flame retardants in the presence of an oxidizing agent to give a hydroquinone-phosphorus compound. The laminator uses this hardener in conjunction with an epoxy resin (such as an epoxy novolak) and catalysts. A laminate can also be made halogen-free by using solid inorganic flame retardants (or fillers) to achieve the V0 requirement of the UL 94 fire safety standard. A phosphorus content of about 4 to 5 percent by weight in the laminate is generally sufficient to achieve the V0 requirement of the UL 94 fire safety standard.

2.4.2 Laminate Manufacturing

Most PCBs are composed of 1 to 16 conductive layers separated and supported by layers (substrates) of insulating material. In a typical four-layer board design, internal layers are used to provide power and ground connections with all other circuit and component connections made on the top and bottom layers of the board. The more complex board designs have a large number of layers necessary for different voltage levels, ground connections, and circuit package formats.

The basic layer of the printed circuit board is a woven fiberglass mat embedded with a flame-resistant epoxy resin. A layer of copper is often placed over this fiberglass/epoxy layer, using methods such as silk screen printing, photoengraving, or PCB milling to remove excess copper. Various conductive copper and insulating dielectric layers are then bonded into a single board structure under heat and pressure. The layers are connected together through drilled holes called vias, typically made with laser ablation or with tiny drill bits made of solid tungsten carbide. The drilled holes can then be plated with copper to provide conductive circuits from one side of the board to the other (How Products Are Made, 2006).

Next, the outer surfaces of a PCB may be printed with line art and text using silk screening. The silk screen, or “red print,” can indicate component designators, switch setting requirements, test points, and other features helpful in assembling, testing, and servicing the circuit board. PCBs intended for extreme environments may also be given a conformal coat made up of dilute solutions of silicone rubber, polyurethane, acrylic, or epoxy, which is applied by dipping or spraying after the components have been soldered. This coat will prevent corrosion and leakage currents or shorting due to condensation.

Once printed, components can be added in one of two ways. In through-hole construction, component leads are electrically and mechanically fixed to the board with a molten metal solder, while in surface-mount construction, the components are soldered to pads or lands on the outer surfaces of the PCB. The parts of the circuit board to which components will be mounted are typically “masked” with solder in order to protect the board against environmental damage and solder shorts. The solder itself was traditionally a tin-lead alloy, but new solder compounds are now used to achieve compliance with the Restriction of Hazardous Substances (RoHS) directive in the European Union (EU), which restricts the use of lead. These new solder compounds include organic surface protectant, immersion silver, and electroless nickel with immersion gold coating (Oresjo and Jacobsen, 2005). Tin-silver-copper alloys (SACs) have also been developed, some containing small amounts of an additional fourth element (IPC, 2005; Lasky, 2005).

After construction, the PCB's circuit connections are verified by sending a small amount of current through test points throughout the board. The PCB is then ready to be packaged and shipped for use (Electronic Interconnect, 2007).

2.5 Next Generation Research and Development

Most research and development is oriented around improving the performance of FR-4 laminates. For example, manufacturers are seeking to improve the glass transition temperature (T_g) of FR-4 laminates in order to produce laminates better able to withstand heat. A higher T_g is generally compatible with the use of lead-free solder, which often requires a higher soldering temperature (Thomas et al., 2005). Manufacturers often consider T_g together with the decomposition temperature (T_d) when assembling lead-free assemblies. T_d is the temperature at which material weight changes by 5 percent. Due to marketplace concerns over potential environmental impacts of TBBPA, such as the possible generation of dioxins and furans during combustion, the development of non-halogen flame retardants (discussed in Section 3.2) has also been a priority of manufacturers. However, concerns over the human health and environmental impact, as well as the expense and performance of laminates containing these flame retardants, are still an issue.

There are many types of FR-4 laminates under development that have a resin design different from the epoxy-based construction described above. These typically include more thermally stable inflexible structures (such as biphenyl or naphthalene groups) and/or nitrogen heterocyclic structures (such as reacted-in triazine, oxazoline, or oxazine rings). Another alternative to epoxy resin, polyimide resin, can be produced through condensation reactions between aromatic dianhydrides and aromatic diamines (Morose, 2006). IF Technologies has manufactured an aliphatic liquid epoxy resin system produced from epoxidized plant oils and anhydrides that reduces emissions, decreases toxicity, and replaces bisphenol A and epichlorohydrin. Other technologies in development use substances such as keratin, soybean oil, or lignin in the manufacturing process.

Improvements in the lamination process are also being developed. Technologies may soon enable the formation and multi-layering at room temperature of ceramic film on resin circuit boards, allowing for further multi-functionality, miniaturization, and cost reduction of electronic devices (PhysOrg, 2004). Laser drilling techniques will allow for the production of smaller microvias, which may allow for the creation of smaller circuit boards (Barclay, 2004). Lasers can also be used for direct copper ablation, as they can quickly vaporize copper without damaging the epoxy and glass substrate (Lange, 2005).

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3 Chemical Flame Retardants for FR-4 Laminates

This chapter summarizes the general characteristics of flame retardants and associated mechanisms of flame retardancy. The flame-retardant chemicals currently used in printed circuit boards are also briefly introduced, with more detailed information about their potential exposure pathways, toxicity, and life-cycle considerations presented in later chapters.

3.1 General Characteristics of Flame-Retardant Chemicals

Fire occurs in three stages: (a) thermal decomposition, where the solid, or condensed phase, breaks down into gaseous decomposition products as a result of heat, (b) combustion chain reactions in the gas phase, where thermal decomposition products react with an oxidant (usually air) and generate more combustion products, which can then propagate the fire and release heat, and (c) transfer of the heat generated from the combustion process back to the condensed phase to continue the thermal decomposition process (Hirschler, 1992; Beyler and Hirschler, 2002).

In general, flame retardants decrease the likelihood of a fire occurring and/or decrease the undesirable consequences of a fire (Lyons, 1970; Cullis and Hirschler, 1981). The simplest way, in theory, of preventing polymer combustion is to design the polymer so that it is thermally very stable. Thermally stable polymers are less likely to thermally degrade, which prevents combustion from initiating. However, thermally stable polymers are usually difficult and expensive to process, and do not typically perform well. As a result, manufacturers use other methods, such as using flame-retardant chemicals, to impart flame-retardant properties to polymers.

Flame retardants typically function by decreasing the release rate of heat (Hirschler, 1994), thus reducing the burning rate or flame spread of a fire, or by reducing smoke generation (Morose, 2006). In the gas phase, flame retardants can interfere with free radical chain reactions, thereby reducing the tendency of the fire to propagate and spread. Flame retardants can also act in the gas phase by cooling reactants and thereby decrease the rate of combustion. In the condensed, or solid, phase flame retardants can act by forming a solid char (or a glassy layer), which interferes with the transfer of heat back from the gas phase to the condensed phase. This inhibits or prevents further thermal decomposition.

Typically, flame retardants contain one of the following seven elements: chlorine, bromine, aluminum, boron, nitrogen, phosphorus, or antimony (Lyons, 1970; Cullis and Hirschler, 1981; Hirschler, 1982). There are, however, a number of replacements and synergists that are also effective. For example, aluminum (which is most often used as an oxide or hydroxide) can be replaced with magnesium hydroxide or by a magnesium salt. In addition, some elements, such as zinc (often used as zinc borate or zinc stannate) and molybdenum (often used as ammonium molybdates), are effective primarily as smoke suppressants in mixtures of flame retardants.

3.1.1 Flame-Retardant Classification

Flame retardants are generally incorporated throughout the polymeric material, although they can also be coated on the external surface of the polymer to form a suitable protective barrier. Flame retardants can be classified, broadly speaking, into two types according to the method of incorporation:

- *Reactive:* Reactive flame retardants are incorporated into polymers via chemical reactions. The production of existing polymers is modified so that one or more unsubstituted reactant monomers is replaced with a substituted monomer containing flame-retardant heteroelements. The substituted monomers and their heteroelement components become an integral part of the resulting polymer structure. Reactive flame retardants must be incorporated at an early stage of manufacturing, but once introduced they become a permanent part of the polymer structure. Once chemically bound, the reactive flame-retardant chemicals cease to exist as separate chemical entities. Reactive flame retardants have a greater effect than additive flame retardants on the chemical and physical properties of the polymer into which they are incorporated.

- *Additive:* Additive flame retardants are incorporated into the compounds via physical mixing. Compounds containing flame-retardant elements are mixed with existing polymers without undergoing any chemical reactions. As a result, the polymer/additive mixture is less susceptible to combustion than the polymer alone. Since additive flame retardants can be incorporated into the product up until the final stages of manufacturing, it is typically simpler for manufacturers to use additive flame retardants than reactive flame retardants.

Due to the differing physical and chemical properties of flame-retardant chemicals, most are used exclusively as either reactive or additive flame retardants. Both reactive and additive flame retardants can significantly change the properties of the polymers into which they are incorporated. For example, they may change the viscosity, flexibility, density, and electrical properties, and may also increase the susceptibility of the polymers to photochemical and thermal degradation.

Flame retardants can also be classified into four main categories according to chemical composition (IPC, 2003; and Morose, 2006):

- *Inorganic*: This category includes silicon dioxide, metal hydroxides (e.g., aluminum hydroxide and magnesium hydroxide), antimony compounds (e.g., antimony trioxide), boron compounds (e.g., zinc borate), and other metal compounds (molybdenum trioxide). As a group, these flame retardants represent the largest fraction of total flame retardants in use.

- *Halogenated*: These flame retardants are primarily based on chlorine and bromine. Typical halogenated flame retardants are halogenated paraffins, halogenated alicyclic and aromatic compounds, and halogenated polymeric materials. Some halogenated flame retardants also contain other heteroelements, such as phosphorus or nitrogen. When antimony oxide is used, it is almost invariably used as a synergist for halogenated flame retardants. The effectiveness of halogenated additives, as discussed below, is due to their interference with the radical chain mechanism in the combustion process of the gas phase. Brominated compounds represent approximately 25 percent by volume of the global flame-retardant production (Morose, 2006). Chemically, they can be further divided into three classes:

  - Aromatic, including tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls.
  - Aliphatic
  - Cycloaliphatic, including hexabromocyclododecane (HBCD).

- *Phosphorus-based*: This category represents about 20 percent by volume of the global production of flame retardants and includes organic and inorganic phosphates, phosphonates, and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states. There are also halogenated phosphate esters, often used as flame retardants for polyurethane foams or as flame-retardant plasticizers but not commonly used in electronics applications (Hirschler, 1998; Green, 2000; Weil, 2004).

- *Nitrogen-based*: These flame retardants include melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate). It is rare for flame retardants to contain no heteroatom other than nitrogen and to be used on their own. Nitrogen-containing flame retardants are often used in combination with phosphorus-based flame retardants, often with both elements in the same molecule.

3.1.2 Flame Retardant Modes of Action

The burning of polymers is a complex process involving a number of interrelated and interdependent stages. It is possible to decrease the overall rate of polymer combustion by interfering with one or more of these stages. The basic mechanisms of flame retardancy will vary depending on the flame retardant and polymer system.

Flaming Combustion

Chemical Inhibitors **–** Some flame retardants interfere with the first stage of burning, in which the polymer undergoes thermal decomposition and releases combustible gases. Interference during this stage alters polymer breakdown in such a way as to change either the nature of released gases or the rate at which they are released. The resulting gas/oxidant mixture may no longer be flammable.

Fillers – A completely different mode of action is that exerted by inert solids incorporated into polymers. Such materials, known as fillers, absorb heat and conduct heat away by virtue of their heat capacity and thermal conductivity, respectively. As a result, fillers keep polymers cool and prevent them from thermally decomposing. The temperature is kept down even more effectively if the fillers decompose endothermically. Since fillers act predominantly via a physical rather than a chemical process, large levels of fillers are needed.

Protective Barriers **–** Some flame retardants cover the flammable polymer surface with a non-flammable protective coating. This helps insulate the flammable polymer from the source of heat, thus preventing the formation of combustible breakdown products and their escape into the gas phase. The non-flammable coating may also prevent gaseous oxidants (normally air or oxygen) from contacting the polymer surface. Intumescent compounds, which swell as a result of heat exposure, lead to the formation of a protective barrier in which the gaseous products of polymer decomposition are trapped. Alternatively, a non-flammable layer can be directly applied to the surface of the polymer to form a non-intumescent barrier coating. Many phosphorus-containing compounds form such non-intumescent surface chars.

Gaseous Phase Mechanisms **–** Flame-retardant chemicals can also inhibit combustion of the gaseous products of polymer decomposition. These reactions are known as the gaseous flame reactions. As for condensed phase inhibition, there are several rather distinct possible modes of action.

In some cases, flame retardants lead to the release of reactive gaseous compounds into the combustion zone, which can replace highly active free radicals with less reactive free radicals. The less reactive free radicals slow the combustion process and reduce flame speed. In other cases, flame retardants can cause the evolution of a small particle "mist" during combustion. These small particles act as "third bodies" that catalyze free-radical recombination and hence chain termination. This mode of action is typical of halogenated flame retardants, which usually act by decomposing at high temperature to generate hydrogen chloride or hydrogen bromide. These compounds react with oxygenated radicals and inhibit gas phase combustion reactions (Cullis and Hirschler, 1981; Hirschler, 1982; Georlette et al., 2000).

Flame-retardant chemicals can also operate by releasing relatively large quantities of inert gas during decomposition, which can change the composition and temperature of gaseous polymer decomposition products. The resulting mixture of gaseous products and surrounding gaseous oxidants are no longer capable of propagating flame. In some systems, when the polymer burns the flame-retardant chemical is released chemically unchanged as a heavy vapor, which effectively "smothers" the flame by interfering with the normal interchange of combustible gaseous polymer decomposition products and combustion air or oxygen. This mode of action is typical of metal hydroxides, such as aluminum or magnesium hydroxide (Horn, 2000).

Melting and Dripping **–** Some flame-retardant chemicals inhibit combustion by interfering with the transfer of heat from combustion back to the polymer. Certain chemicals may promote depolymerization, which lowers the molecular weight of the polymer and facilitates melting. As the burning melt drips away from the bulk of the polymer it carries with it a proportion of the heat that would otherwise contribute to polymer decomposition and volatilization. By reducing the release of volatile decomposition products into the gas phase, these flame retardants reduce the amount of gaseous decomposition products available to feed the flame. While enhanced melting should decrease flammability in theory, in practice droplets of burning molten polymer may help spread a fire to other combustible materials.

Ablation **–** Combustion can also be retarded by coating or constructing the polymer in such a way that, when it burns, incandescent sections disintegrate from the original polymer and remove with them heat from the combustion zone. This mechanism of action, known as ablation, is in a sense the solid phase parallel of liquid phase melting and dripping. A surface char layer is frequently formed, which isolates the bulk of the polymer material from the high temperature environment. This charry layer remains attached to the substrate for at least a short period while a degradation zone is formed underneath it. In this zone, the organic polymer undergoes melting, vaporization, oxidation, or pyrolysis. The ablative performance of polymeric materials is influenced by polymeric composition and structure, as well as environmental factors, such as atmospheric oxygen content. Higher hydrogen, nitrogen, and oxygen content of the polymer increases the char oxidation rate; higher carbon content decreases the char oxidation rate (Levchik and Wilkie, 2000).

Smoldering (Non-Flaming) Combustion

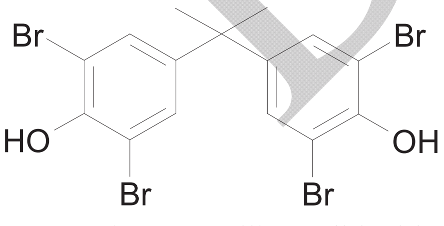
Smoldering (non-flaming) combustion and the closely related phenomenon of glowing combustion occur primarily with high-surface area polymeric materials that break down during combustion to form a residual carbonaceous char (typically cellulosic materials). In general, it is possible to inhibit non-flaming combustion either by retarding or preventing the initial breakdown of the polymer to form a char, or by interfering with the further combustion of this char. Boric acid and phosphates are the primary flame retardants used for preventing non-flaming combustion of organic polymers.

3.2 Flame-Retardant Chemicals Currently Used in FR-4 Laminates

Over the last several years, the electronics industry has been increasingly focused on researching and developing halogen-free alternatives to TBBPA, due in large part to environmental concerns and the anticipation of possible regulatory actions in the European Union. Several flame-retardant chemicals are commercially available to meet fire safety standards for FR-4 laminates. Currently, the halogenated flame retardant TBBPA is used in approximately 90 percent of FR-4 PCBs. The majority of halogen-free alternatives to TBBPA are based on phosphorus compounds that are directly reacted into the epoxy resin or combined with aluminum trioxide or other fillers (De Boysère and Dietz, 2005). This section briefly discusses TBBPA, dihydrooxaphospha-phenanthrene (DOPO), Fyrol PMP, and four commonly used halogen-free fillers: aluminum hydroxide, melamine polyphosphate, metal phosphinate, and silica. In this report, these four fillers are also referred to as additive flame retardants.

Reactive Flame-Retardant Chemicals

TBBPA

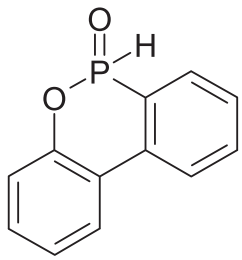


TBBPA is a crystalline solid with the chemical formula $C_{15}H_{12}Br_4O_2$. TBBPA increases the glass transition temperature (T_g) of the epoxy resins, and enables the resin to achieve a UL 94 V0 flammability rating. TBBPA is most commonly reacted into the epoxy resin through "chain extension," meaning TBBPA is reacted with a molar excess of diglycidyl ether of bisphenol A

(DGEBA), or other similar epoxy. Once the TBBPA is chemically bound, the finished epoxy resin typically contains about 18 to 21 percent bromine (Weil and Levchik, 2004).

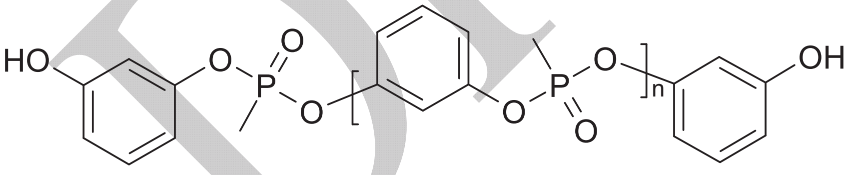
TBBPA is produced by several flame-retardant manufacturers. According to HDPUG (2004) and Morose (2006), TBBPA's market dominance is due primarily to its moisture resistance, thermal stability, cost-effectiveness, compatibility with the other components of PCBs, and ability to preserve the board's physical properties. Aside from PCBs, another primary application of TBBPA is its use as an additive flame retardant in the acrylonitrile-butadiene-styrene (ABS) resins found in electronic enclosures of televisions and other products.

DOPO



DOPO is a hydrogenphosphinate made from *o*-phenyphenol and phosphorus trichloride. Similar to TBBPA, it can be chemically reacted to become part of the epoxy resin backbone. DOPO was originally developed as a flame retardant for polyester textile fibers and also has applications as an antioxidant-type stabilizer (Weil and Levchik, 2004). Due to DOPO's higher cost (it costs nearly four times as much as TBBPA), its use has been limited by laminate manufacturers. To decrease the cost of their formulations, some laminate manufacturers are using DOPO in combination with less expensive materials such as ATH and/or silica (Thomas et al., 2005) or along with more cost-effective compounds like metal phosphinates (De Boysère and Dietz, 2005).

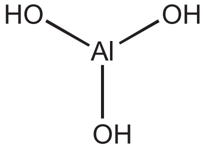
Fyrol PMP



Fyrol PMP is an aromatic phosphonate oligomer with high phosphorus content (17 to 18 percent). Similar to TBBPA and DOPO, Fyrol PMP can be chemically reacted to become part of the epoxy resin backbone. When reacted into a phenol-formaldehyde novolak epoxy, Fyrol PMP provides good flame retardancy at loadings as low as 20 percent (Weil, 2004).

Flame-Retardant Fillers

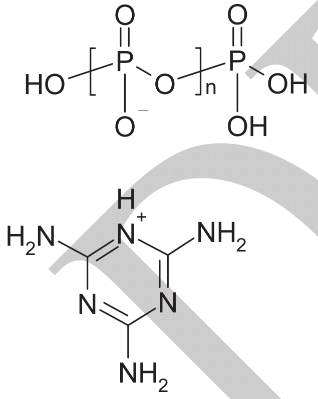
Aluminum Hydroxide



While the current use of aluminum hydroxide ($Al(OH)_3$) in FR-4 PCBs is relatively low, it remains the largest volume flame retardant used worldwide, with an estimated 42 percent volume market share in 2006 (BCC, 2006). Aluminum hydroxide is commonly referred to as alumina trihydrate (ATH) and is currently used to impart flame retardancy and smoke suppression in carpet backing, rubber products, fiberglass-reinforced polyesters, cables, and other products. It is also used in the manufacture of a variety of items – antiperspirants, toothpaste, detergents, paper, and printing inks – and is used as an antacid.

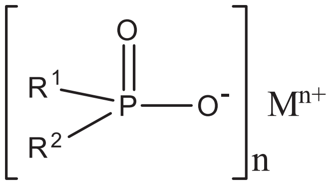
ATH is difficult to use alone to achieve the FR-4 rating of laminates, and as a result, high loadings relative to the epoxy resin, typically up to 60 to 70 percent by weight, are needed (Morose, 2006). ATH is most commonly used in FR-4 PCBs as a flame-retardant filler, in combination with DOPO or other phosphorus-based compounds. When heated to 200-220°C, ATH begins to undergo an endothermic decomposition to 66 percent alumina and 34 percent water (Morose, 2006). It retards the combustion of polymers by acting as a "heat sink" – i.e., by absorbing a large portion of the heat of combustion (HDPUG, 2004).

Melamine Polyphosphate



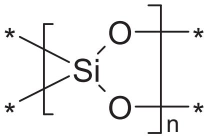
Melamine polyphosphate, an additive-type flame retardant based on a combination of phosphorous and nitrogen chemistries, is typically used as crystalline powder and in combination with phosphorus-based compounds. Its volume market share in 2006 was slightly more than 1 percent (BCC, 2006) but is expected to increase as the demand for halogen-free alternatives increases. Similar to ATH, melamine polyphosphate undergoes endothermic decomposition but at a higher temperature (350°C). It retards combustion when the released phosphoric acid coats and therefore forms a char around the polymer, thus reducing the amount of oxygen present at the combustion source (Special Chem, 2007). Melamine polyphosphate does not negatively impact the performance characteristics of standard epoxy laminates, and functions best when blended with other non-halogen flame retardants (Kaprinidis, 2008). Melamine polyphosphate dissociates in water to form melamine cations and phosphate anions, both of which are shown in Table 4-1.

Metal Phosphinates



Flame retardants based on phosphinate chemistry are a relatively new class of halogen-free flame retardants on the market. One such phosphinate-based flame retardant – Exolit OP930, produced by Clariant – is a fine-grained powder with high phosphorus content (23 to 24 percent) used as a filler in FR-4 laminates (De Boysère and Dietz, 2005). It is designed primarily for use in FR-4 laminate materials with T_g greater than 150°C (mid-range and high T_g applications). Like most phosphorus-based compounds, metal phosphinates achieve flame retardancy by forming a char barrier upon heating, thereby cutting off access to the oxygen needed for the combustion process. Due to its low density and high surface area, Exolit OP 930 cannot be used alone. It is typically used as a powerful synergist in combination with modified resins and sometimes other filler-type FRs.

Silica



Also known as silicon dioxide (SiO_2), silica is characterized by its abrasion resistance, electrical insulation, and high thermal stability. Silica is not a flame retardant in the traditional sense. It dilutes the mass of combustible components, thus reducing the amount of FR necessary to pass the flammability test. Silica is most commonly used in combination with novolak-type epoxy resins. For example, silica clusters can be reacted with phenolic novolak resins (the resin bonds to hydroxyl groups on the silica cluster) to form a silica-novolak hybrid resin (Patent Storm, 2002). It can be used as an inert, low expansion material in both the epoxy resin and electronic circuit. One drawback is its abrasiveness, which affects drilling operation during the PCB manufacturing process.

Magnesium Hydroxide

$\mathrm{HO{-}Mg{-}OH}$

Magnesium hydroxide is functionally similar to ATH, in that it endothermically decomposes at high temperatures to produce an oxide (MgO) and water. The absorption of heat retards the combustion of polymers, and the release of water may create a barrier that prevents oxygen from supporting the flame (Huber, 2007). However, whereas ATH undergoes thermal decomposition at 200-220°C, magnesium hydroxide decomposes at approximately 330°C. This allows manufacturers to use magnesium hydroxide when processing temperatures are too high for ATH (Morose). Just like for ATH, high loadings of magnesium hydroxide are required to achieve the

FR-4 rating. In many polymer systems, in order to reduce loadings, magnesium hydroxide is sometimes combined with more effective flame retardants, such as phosphorus (Morose, 2006).

Other Chemicals

Following is a brief description of other chemicals that can be used as flame retardants in FR-4 PCBs but are not evaluated in this paper.

Ammonium Polyphosphate

Ammonium polyphosphate is an intumescent flame retardant, meaning that it swells when exposed to heat, and can be used in epoxies. However, it is not commonly used in electronic applications. At high temperatures (>250°C) ammonium polyphosphate decomposes into ammonia and polyphosphoric acid. When exposed to water, polyphosphate reacts to form monoammonium phosphate, a fertilizer (Chemische Fabrik Budenheim, 2007).

Red Phosphorus

Red phosphorus is produced from white phosphorus by heating white phosphorus in its own vapor to 250°C in an inert atmosphere. It is fairly stable and is used in the manufacture of several products, such as matches, pesticides, and flame retardants (Lide, 1993; Diskowski and Hofmann, 2005). Its main use as a flame retardant is in fiberglass-reinforced polyamides. Although it does function in epoxy resins, it is not recommended for electronic applications, because red phosphorus can form phosphine (PH_3) and acidic oxides under hot and humid conditions (Clariant, 2002). The oxides can lead to metal corrosion, and hence electric defects can occur (Clariant, personal communication 2007).

Antimony Oxide

Antimony oxide, typically antimony trioxide (Sb_2O_3), can be used as a flame retardant in a wide range of plastics, rubbers, paper, and textiles. Antimony trioxide does not usually act directly as a flame retardant, but as a synergist for halogenated flame retardants. Antimony trioxide enhances the activity of halogenated flame retardants by releasing the halogenated radicals in a stepwise manner. This retards gas phase chain reactions associated with combustion, which slows fire spread (Hastie and McBee, 1975; Hirschler, 1982; Chemical Land 21, 2007).

Melamine Cyanurate

Melamine cyanurate is relatively cheap and highly available. However, it is a poor flame retardant and requires high dosage (>40 percent weight) (Albemarle, 2007).

3.3 Next Generation Research and Development of Flame-Retardant Chemicals

Some companies are already offering halogen-free alternatives to TBBPA. JJI Technologies, for example, is developing new activated, non-halogen flame-retardant formulations for PCBs – both additive and reactive. An activated flame retardant is one that provides enhanced flame retardancy through the incorporation of an activator, which may consist of either a char-forming catalyst or phase-transfer catalyst or both. Activated flame retardants may improve flame-retarding features, including faster generation of char, higher char yield, denser char, selfextinguishing performance, thermal insulation, and lower smoke emissions (JJI Technologies, 2007).

In addition to halogen-free alternatives to TBBPA, flame-retardant manufacturers are currently exploring ways to achieve a V0 rating in the UL 94 fire test result through the redesign of flame-retardant chemicals and epoxy resin systems. One of the largest areas of research and development involves the use of nanotechnology to impart flame retardancy and increased functionality to PCBs and other electronics products. However, their technical and commercial viability is still limited, and their future use in commercial settings remains unknown. So far, only combinations of nano flame retardants with traditional flame retardants have met performance requirements. In addition, these new nano-traditional flame-retardant combinations are only usable in certain polymer systems.

One type of halogen-free nano flame retardant is being developed through the synthesis of ethylene-vinyl acetate (EVA) copolymers with nanofillers (or nanocomposites) made of modified layered silicates (Beyer, 2005). Nanofillers are incorporated into the olefin polymer during the polymerization process by treating the surface of the nanofiller to induce hydrophobic tendencies. The hydrophobic nanofiller disperses in the olefin monomors, which then undergo polymerization and trap the nanofillers (Nanocor, 2007). Nanocomposites can also incorporate aluminum into their structures, and can be combined with additive flame retardants, such as aluminum hydroxide (ATH), leading to a reduction of the total ATH content and a corresponding improvement in mechanical properties (Beyer, 2005).

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4 Evaluation of Flame Retardants

This section summarizes the toxicological and environmental fate aspects of TBBPA and each alternative flame-retardant chemical that is considered a viable substitute for TBBPA for FR-4 PCBs. Chemical components less than 1 percent by weight were not considered in this assessment. The characteristics of the chemicals in each formulation are summarized qualitatively in Section 4.1 using a relative ranking scheme, and more detailed characteristics of the chemicals in each formulation are presented in Section 4.2. This report does not include information on performance testing or cost.

4.1 Summary of Flame Retardant Assessments

These flame retardant evaluations are hazard assessments, not full risk assessments. Whereas hazard measures a material's inherent dangers, risk takes into account both hazard and the amount of material to which workers, the community, or the environment comes into contact (probability of exposure). In other words, risk = hazard x exposure. This means that chemicals with high hazards do not necessarily pose a large risk. However, evaluating exposure is an arduous and sometimes unnecessary task; if the hazard for a chemical is low, then risk is also probably low. For chemicals with moderate or high hazards, risk may be low, moderate, or high depending on exposure. This report provides screening-level information for hazard, which could be combined with exposure information at a later date to calculate risk.

Although this report does not evaluate exposure, Chapter 5 provides information for evaluating potential routes of exposure. A full exposure assessment considers the quantity, frequency, duration, and route of exposure. In contrast, potential exposure only indicates the possibility of exposure, not the probability of exposure. Physical, chemical, and environmental fate properties, as well as whether the chemical is incorporated reactively or additively into a polymer, serve as indicators of exposure potential. Potential exposure indicates whether a certain route of exposure *can* occur; a full exposure assessment evaluates whether certain routes of exposure *do* occur and to *what extent*. Understanding the potential for exposure routes and pathways to occur is critical for conducting an exposure assessment. The concentration of a chemical in the mixture factors into the overall exposure assessment and, therefore, the potential risk associated with the commercial formulations of the flame-retardant alternatives.

Table 4-1 summarizes the toxicological and potential exposure characteristics of the chemicals in each formulation considered in the alternatives analysis. The table qualitatively summarizes toxicological endpoints for each chemical, including seven human health effects, two ecotoxicity effects, and two environmental endpoints. Each of these endpoints is explained in Table 4-2.

Each toxicological endpoint in Table 4-1 is assigned a rating of L, M, or H to indicate whether the chemical presents a low (L), moderate (M), or high (H) hazard. If the L, M, or H indicator is colored, then the assignment was made using experimental data on the chemical. If the L, M, or H indicator is italicized, then experimental data were not available for that chemical, and the assignment was estimated using structure activity relationships (SAR) analysis involving modeling techniques and professional judgment.

Table 4-1 Screening Level Toxicology Hazard Summary

This table only contains information regarding the inherent hazards of flame retardant (FR) chemicals. Evaluation of risk must consider both the hazard and exposure associated with FR chemicals, as well as the hazard and exposure associated with combustion and degradation byproducts. Refer to Table 5-1 for more information on exposure.

The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

L = Low hazard   M[1] = Moderate hazard   H = High hazard — Endpoints in colored text (L, M, and H) were assigned based on experimental data.
Endpoints in black italics (*L, M,* and *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships).

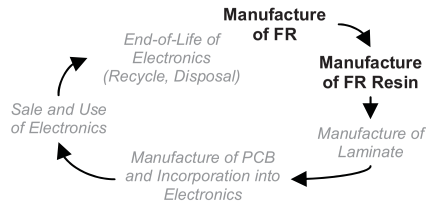
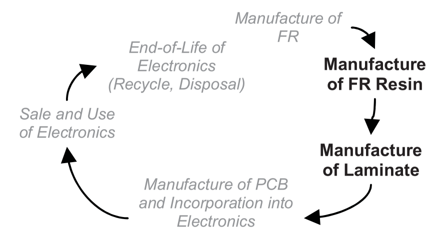
◊ Hazard designations, which are based on the presence of epoxy groups, arise from the analysis of low molecular weight oligomers (molecular weight <1,000) that may be present in varying amounts. The estimated human health hazards for higher molecular weight (>1,000) components, which contain epoxy groups, are low for these endpoints.

‡ Concern based on inhalation of small particles (generally less than 10 microns) that may be present in varying amounts.

§ Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter.

∇ Persistent degradation products expected (none found in this report).

R Recalcitrant: substance is or contains inorganics, such as metal ions or elemental oxides, that are expected to be found in the environment >60 days after release.

Chemical	CASRN	Human Health Effects									Aquatic Toxicity		Environ-mental		Exposure Considerations
		Acute Toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	**Availability of FRs throughout the lifecycle for reactive and additive FR chemicals and resins[2]**
Reactive Flame Retardant Chemicals[2]															
Tetrabromobisphenol A (TBBPA) (Albemarle, Chemtura, and others)[3]															
TBBPA	79-94-7	L	L	*L*	L	L	M	L	L	L	H	*H*	M	L	
DOPO (6H-Dibenz[c,e][1,2] oxaphosphorin, 6-oxide) (Sanko Co., Ltd. and others)															
DOPO	35948-25-5	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*M*	*M*	*L*	*L*	
Fyrol PMP (Aryl alkylphosphonate) (Supresta)															
Fyrol PMP	Proprietary	*L*	L	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*H*	*L*	
Reactive Flame Retardant Resins[2]															
Reaction product of TBBPA - D.E.R. 538 (Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol]) (Dow Chemical)															
D.E.R. 538	26265-08-7	*L*	M	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	M	*L*	*L*	*M*	*L*	
Reaction Product of DOPO – Dow XZ-92547 (reaction product of an epoxy phenyl novolak with DOPO) (Dow Chemical)															
Dow XZ-92547	Proprietary	*L*	M	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	*M*◊	*L*	*L*	*H*	*L*	
Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin (Representative Resin)															
Representative Fyrol PCB Resin	Unknown	*L*	*L*	*M*◊	*L*	*M*◊	*M*◊	*L*	*L*	*M*◊	*L*	*L*	*H*	*L*	

[1] The moderate designation captures a broad range of concerns for hazard, further described in Table 4-3.

[2] Reactive FR chemicals and resins may not completely react, and small amounts may be available during other parts of the lifecycle.

[3] The EU has published a comprehensive risk assessment for TBBPA in reactive applications. This risk assessment is a valuable source of information for choosing flame retardants for printed circuit board applications.

Table 4-1 Screening Level Toxicology Hazard Summary

This table only contains information regarding the inherent hazards of flame retardant (FR) chemicals. Evaluation of risk must consider both the hazard and exposure associated with FR chemicals, as well as the hazard and exposure associated with combustion and degradation byproducts. Refer to Table 5-1 for more information on exposure.

The caveats listed in the legend and footnote sections must be taken into account when interpreting the hazard information in the table below.

L = Low hazard   M[1] = Moderate hazard   H = High hazard — Endpoints in colored text (L, M, and H) were assigned based on experimental data. Endpoints in black italics (*L, M,* or *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships).

◊ Hazard designations, which are based on the presence of epoxy groups, arise from the analysis of low molecular weight oligomers (molecular weight <1,000) that may be present in varying amounts. The estimated human health hazards for higher molecular weight (>1,000) components, which contain epoxy groups, are low for these endpoints.

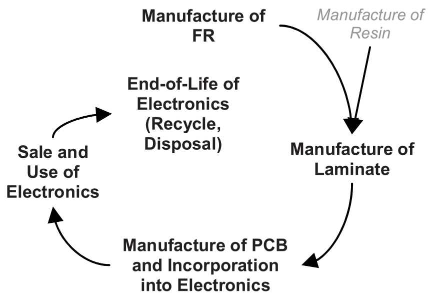
‡ Concern based on potential inhalation of small particles less than 10 microns in diameter that may be present in varying amounts.

§ Concern linked to direct lung effects associated with the inhalation of poorly soluble particles less than 10 microns in diameter.

∇ Persistent degradation products expected (none found in this report).

R Recalcitrant: substance is or contains inorganics, such as metal ions or elemental oxides, that are expected to be found in the environment >60 days after release.

Chemical	CASRN	Human Health Effects									Aquatic Toxicity		Environ-mental		Exposure Considerations
		Acute Toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	Availability of FRs throughout the lifecycle for reactive and additive FR chemicals and resins
Additive Flame Retardants[3]															
Aluminum hydroxide															
Aluminum hydroxide	21645-51-2	*L*	*L*	*L*	*M*	*L*	L	*M*	L	*L*	H	M	*H^R*	*L*	
Exolit OP 930 (phosphoric acid, diethyl-, aluminum salt) (Clariant)															
Exolit OP 930	225789-38-8	L	L	*L*	*M*	*L*	*M*	*M*	L	L	M	*M*	*H^R*	*L*	
Melapur 200 (Melamine polyphosphate) (Ciba)[4]															
Melapur 200	218768-84-4	L	*L*	*L*	*L*	*L*	*L*	*L*	*M*	*M*	*L*	*L*	*M*	*L*	
Polyphosphoric acid	8017-16-1	L	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*	
Melamine	108-78-1	L	L	L	*L*	*L*	L	*L*	M	M	L	L	M	*L*	
Silicon dioxide amorphous[5]															
Silicon dioxide amorphous	7631-86-9	L	L	L	*L*	L	L	*L*	H§	L	*L*	*L*	*H^R*	*L*	
Silicon dioxide crystalline[5]															
Silicon dioxide crystalline	1317-95-9	L	L	H‡	H§	L	L	*L*	H§	H§	*L*	*L*	*H^R*	*L*	
Magnesium hydroxide															
Magnesium hydroxide	1309-42-8	L	*L*	L	*L*	*L*	*L*	*L*	L	*L*	*L*	*L*	*H^R*	*L*	



[1] The moderate designation captures a broad range of concerns for hazard, further described in Table 4-3.

[3] Although additive flame retardants are present throughout the lifecycle of the PCB, they are locked into the polymer matrix of the epoxy laminate material.

[4] Melapur 200 dissociates in water to form polyphosphoric acid and melamine ions. For this reason, Table 4-1 includes both dissociation ions.

[5] Representative CAS numbers are included in this summary table. Section 4.2.9 includes a full list of CAS numbers.

Table 4-2: Definitions of Toxicological and Environmental Endpoints

Toxicological Category	Toxicological Endpoint	Definition
Human Health Effects	Cancer Hazard	Any growth or tumor caused by abnormal and uncontrolled cell division.
	Skin Sensitizer	Chemical that causes an allergic skin reaction characterized by the presence of inflammation; may result in cell death.
	Reproductive	Adverse effects on the reproductive systems of females or males, including structural/functional alterations to the reproductive organs/system, the related endocrine system, mating, or fertility/reproductive success.
	Developmental	Adverse effects on the developing organism (including structural abnormality, altered growth, or functional deficiency or death) resulting from exposure prior to conception (in either parent), during prenatal development, or postnatally up to the time of sexual maturation.
	Neurological	Adverse effects on the central or peripheral nervous system.
	Systemic	Adverse effect (other than those listed separately) that is of either a generalized nature or that occurs at a site distant from the point of entry of a substance: a systemic effect requires absorption and distribution of the substance in the body.
	Genotoxicity	Induction of genetic changes in a cell as a consequence of gene sequence changes (mutagenicity), or chromosome number/structure alterations.
Ecotoxicity	Adverse effects observed in living organisms that typically inhabit the wild. The assessment focused on effects in aquatic organisms (fish, invertebrates, algae).	
	Acute	Short-term, in relation to exposure or effect. Exposures are typically less than 96 hours.
	Chronic	Effects observed after repeated exposures.
Environmental	Persistence	Attribute of a substance that indicates how long it remains in the environment before degrading or becoming assimilated by biological organisms. Screening assessments examine two types of degradation: biodegradation, which is degradation of material through microbial processes; and abiotic degradation, which is degradation of material through chemical reactions. For the purposes of the screening, persistence is determined in air, water, soil, and sediment.
	Bioaccumulation	Ability of living organisms to concentrate a substance obtained either directly from the environment or indirectly through its food. Bioaccumulation is the sum of bioconcentration (the increase in the concentration of a chemical over that in an organism's surroundings, such as water) and biomagnification (the increase in the concentration of a chemical over that in an organism's diet). For a screening assessment, the bioconcentration factor (BCF) is used to determine the potential for bioaccumulation.

4.1.1 Explanation of Chemical Assessment Methodology

Chemical assessments reviewed toxicological characteristics for chemical components of the flame-retardant formulations that constituted more than 1 percent by mass of the flame retardant formulation. This level of review involved a comprehensive analysis of both primary and secondary data, as described in detail in Sections 4.1.2 and 4.1.3. A less comprehensive review was conducted for chemical components that constituted less than 1 percent by mass of the flame retardant, as well as other materials of potential concern associated with the life cycle of the flame retardants (see Section 4.3). Information regarding characteristics that affect potential exposure was also compiled to complement the hazard assessments.

The methodology used to identify and evaluate experimental values in this screening assessment followed a tiered approach. For each chemical assessed, data were collected in a manner consistent with the High Production Volume (HPV) Chemical Challenge Program guidance on searching for existing chemical information and data. This process resulted in a comprehensive search of the literature for available experimental data. This, in turn, led to the collection and review of articles from the scientific literature, industrial submissions, encyclopedic sources, and government reports. In addition, data present in EPA databases (both public and confidential) were obtained for this project. Generally, foreign language (non-English) reports were not used unless they provided information that was not available from other sources.

The experimental studies and collected data were then reviewed and evaluated for adequacy using a tiered approach with the following hierarchy:

- One or more studies were conducted in a manner consistent with established testing guidelines
- Experimentally valid but non-guideline studies
- Reported data without supporting experimental details
- SAR methods for data gaps.

Studies were then evaluated to establish if the hazard data were of sufficient quality to meet the requirements of the assessment process, as described in Section 4.1.

Data were considered adequate to fully characterize an endpoint if they were obtained using the techniques identified in the HPV data adequacy guidelines. Studies performed according to Harmonized EPA or Organisation for Economic Cooperation and Development (OECD) guidelines were reviewed to confirm that the study followed all required steps. Experimental studies published in the open literature were reviewed for their scientific rigor and were also compared and contrasted to guideline studies to identify potential problems arising from differences in the experimental methodology. Data from adequate, well-performed, experimental studies were used to assign hazard levels in preference to those reported in inadequate studies. When multiple adequate studies were available for a given endpoint, any conflicts that were identified were addressed using a weight-of-evidence approach to characterize the endpoint whenever possible. It should be noted, however, that the screening-level assessment followed the criteria used by the EPA New Chemicals Program for new chemicals submitted under the Toxic Substances Control Act (TSCA), which may have resulted in a moderate hazard level for toxicity being assigned if there was a single, adequate study that was suggestive of potential adverse effects.

Although experimental data from a guideline or well-performed experimental study was used preferentially, for some endpoints, information from secondary sources, Material Safety Data Sheets, or online databases (such as the National Library of Medicine's Hazardous Substances Data Bank [HSDB]) could be applied successfully to the assessment process. These evaluations considered the magnitude of the reported value relative to the criteria and cutoffs used in the assessment as well as the complexity of the endpoint. For example, a melting point value may have been considered adequate if all values reported in the literature for this endpoint were in agreement with one another (but not necessarily identical), even though no experimental details were provided. Similarly, a boiling point value reported in only one source (without supporting experimental details) may have been considered adequate if its value was of a magnitude such that any conclusions were consistent with the requirements of the assessment (e.g., a high boiling, non-volatile material). The complexity of the experimental method was a critical component of this determination. Melting point determinations are relatively trivial techniques and may not require the same degree of review that is necessary for more complex experimental methods, such as aquatic toxicity or water solubility studies. The level of analysis given to a particular endpoint is provided in the "Data Quality" column of the chemical summary assessment in Section 4.2, as appropriate.

For three chemicals assessed in this project, silicon dioxide, aluminum hydroxide, and magnesium hydroxide, the literature review was limited primarily to available secondary sources because these chemicals were anticipated to have been reviewed previously. Using high-quality secondary sources therefore maximized available resources and eliminated potential duplication of effort. However, more than one secondary source was typically used to verify reported values, which also reduced the potential for presenting a value that was transcribed incorrectly in the open literature. For these three chemical substances, only a single source for the experimental value was usually referenced in the chemical summary assessment. Typically, this was the data source consulted first. Although other sources might have also contained the same experimental value for an endpoint, effort was not focused on building a comprehensive list of these references, as it would not enhance the ability to reach a conclusion in the screening assessment. If data for an endpoint could not be located in a secondary source for silicon dioxide or aluminum hydroxide, then the primary literature was searched, experimental studies were retrieved, and the assessment proceeded using the methodology discussed above.

For additional information on data adequacy and HPV guidelines, please see:

- HPV data adequacy guidelines: (http://www.epa.gov/chemrtk/pubs/general/datadfin.htm)
- HPV guidance on searching for existing chemical information and data: (http://www.epa.gov/chemrtk/pubs/general/srchguid.htm

4.1.2 Explanation of Toxicological and Environmental Endpoints Rating

The chemical assessments combine primary and secondary data on flame-retardant alternatives from six sources: (1) publicly available, measured (experimental) data obtained from a comprehensive literature review; (2) measured data from EPA OPPT confidential databases; (3) SAR-based estimations from the EPA New Chemical Program's Pollution Prevention (P2) Framework and Sustainable Futures predictive methods; (4) estimations from the EPA Chemical Categories document, which groups chemicals with shared chemical functionality and toxicological properties into categories based on the EPA's experience at evaluating chemicals under the New Chemicals Program; (5) professional judgment of EPA staff who identified experimental data on closely related analogs; and (6) confidential studies submitted by chemical manufacturers. When experimental data were lacking, the expert judgment of scientists from EPA's New Chemical Program was used to assess physical/chemical properties, environmental fate, aquatic toxicity, and human health endpoints.

Criteria Used to Assign Hazard Levels

Table 4-3 lists the criteria that were used to interpret the data collected in this document. These criteria are used by the EPA New Chemicals Program to assign hazard levels to new chemicals submitted under TSCA. EPA has published these criteria in several sources including USEPA (1992) and USEPA (1994). EPA New Chemicals Program persistence criteria have been published in the Federal Register (USEPA, 1999).

Table 4-3: Criteria Used to Assign Hazard Levels

Hazard Level	Persistence Criteria
High	Half-life in water, soil, or sediment > 180 days
Moderate	Half-life in water, soil, or sediment between 60 and 180 days
Low	Half-life in water, soil, or sediment < 60 days
Hazard Level	**Bioaccumulation Criteria**
High	Bioconcentration factor (BCF) > 5,000
Moderate	BCF between 1,000 and 5,000
Low	BCF < 1,000
Hazard Level*	**Aquatic Toxicity Criteria**
High	Value is ≤ 1 mg/L (chronic value <0.1 mg/L)
Moderate	Value is between 1 and 100 mg/L (chronic value 0.1 and 10 mg/L)
Low	Value is >100 mg/L (chronic value >10 mg/L) or log K_{ow} is greater than 8
Hazard Level	**Human Health Criteria**
High	Evidence of adverse effects in human populations *or* conclusive evidence of severe effects in animal studies
Moderate	Suggestive animal studies, analog data, *or* chemical class known to produce toxicity; covers a broad range of concerns from in vitro studies with limited effects to many animal studies with substantial effects.
Low	No basis for hazard identified

*If the water solubility is estimated, the chemical will not be considered to have "no effects at saturation" if the estimated value is within a factor of 10 percent of the cutoff value. The hazard level will be considered low if "no effects at saturation" (below the solubility limit).

More information on the EPA New Chemicals Program criteria used to assign hazard levels can be found on the Sustainable Futures Initiative Web site: http://www.epa.gov/oppt/sf/.

There are many other hazard classification systems that can be applied to the experimental data listed in Section 4.2. Examples of these systems include:

- Globally Harmonized System of Classification and Labeling of Chemicals (GHS): http://www.unece.org/trans/danger/publi/ghs/ghs_rev00/00files_e.html
- EPA's Office of Pesticide Programs (OPP) A comparison of the OPP criteria and GHS criteria: http://www.epa.gov/oppfead1/international/global/ghscriteria-summary.pdf?OpenDocument
- EU Dangerous Substance Directive: Links to the directive, annexes and all amendments can be found here: http://europa.eu.int/comm/environment/dansub/main67_548/index_en.htm
- Annex 6 of the Directive lists the general labeling and classification requirements for dangerous substances and preparations: http://europa.eu.int/comm/environment/dansub/pdfs/annex6_en.pdf
- Canadian Hazardous Products Act (Canada), The Consumer Chemical Container Regulations: http://laws.justice.gc.ca/en/H-3/SOR-2001-269/text.html
- The Controlled Products Regulations: http://laws.justice.gc.ca/en/H-3/SOR-88-66/text.html

Physical/Chemical Property Endpoints

Physical/chemical properties provide basic information on the nature and characteristics of a chemical substance that are used throughout the screening assessment process. These endpoints provide information required to assess potential environmental release, exposure, and partitioning as well as insight into the potential for adverse toxicological effects to be expressed. The physical/chemical property endpoints that appear in the chemical screening assessment are described below. For information on the key physical/chemical properties of flame retardants, please refer to Table 5-2.

Molecular Weight (MW)

The molecular weight is an intrinsic property of a chemical substance. For discrete, monomeric chemical substances, the molecular weight is the sum of the atomic weights of all atoms making up a molecule and can be obtained directly from the molecular formula. A molecular weight greater than 1,000 atomic mass units (amu) is typically used as a cutoff for assessing the properties described below.

Polymeric substances do not have a unique molecular weight because these materials contain a distribution of components that depend on the monomers used, their molar ratios, the total number of monomeric units in the polymer chain, and the manufacturing conditions. The average molecular weight (also called the n-average molecular weight) is used in the assessment of polymers to account for this. The average molecular weight of polymers is determined experimentally. Those polymers with a molecular weight <1,000 are assessed using an appropriate representative structure that has a molecular weight that is less than or equal to the average molecular weight. For polymers with an average molecular weight of >1,000 and significant amounts of low molecular weight material (>25 percent below 1,000 and >10 percent below 500), the low molecular components are assessed for their potential toxicity in order to identify any possible hazards for the most bioavailable fraction. The properties for polymers with an average molecular weight >1,000 and minimal amounts of low molecular weight components (<25 percent below 1,000 and <10 percent below 500) are generally evaluated as a single high molecular weight material for each of the properties described below. The presence of substantial amounts of unreacted monomers requires that the assessment consider these components for polymers of any molecular weight range.

Melting Point (MP) and Boiling Point (BP)

These two properties provide an indication of the physical state of the material. Chemicals with a melting point >25 ºC are assessed as a solid. Those with a melting point <25 ºC and a boiling point >25 ºC are assessed as a liquid and those with a boiling point <25 ºC are assessed as a gas. The physical state is used throughout the assessment, such as in the determination of potential routes of human and environmental exposure, as described in Section 5.2. The melting and boiling points are also useful in determining the potential environmental fate, ecotoxicity, and human health hazards of the chemical. For example, neutral organic compounds with high melting points generally have low water solubility and low rates of dissolution. These properties influence a material's bioavailability and are therefore taken into account in both the assessment process and the evaluation of experimental studies. Similarly, chemicals with a low melting point also have a higher potential to be absorbed through the skin, gastrointestinal tract, and lungs.

Vapor Pressure (VP)

The vapor pressure is useful in determining the potential for a chemical substance to volatilize to the atmosphere from dry surfaces; from storage containers; or during mixing, transfer, or loading/unloading operations (see Section 5.2). In the assessment process, chemicals with a vapor pressure of $<10^{-6}$ mm Hg have a low potential for inhalation exposure resulting from gases or vapors. The vapor pressure is also useful for determining the potential environmental fate of the substance. Those with a vapor pressure $>10^{-4}$ mm Hg generally exist in the gas phase in the atmosphere; those with a vapor pressure between 10^{-4} and 10^{-8} mm Hg exist as a gas/particulate mixture; and those with a vapor pressure $<10^{-8}$ mm Hg exist as a particulate. The potential atmospheric degradation processes described below generally occur when a chemical exists in the gas phase. Gases in the atmosphere also have the potential to travel long distances from their original point of release. Materials in the liquid (aerosol) or solid (particulate) phases in the atmosphere generally undergo deposition to the Earth's surface.

Water Solubility (WS)

The water solubility of a chemical provides an indication of its distribution between environmental compartments, potential for environmental exposure through release to aquatic compartments, and potential for human exposure through ingestion of drinking water. It is also used extensively to determine potential human health and ecotoxicity hazards. In general, chemicals with a water solubility of $<10^{-3}$ mg/L have low concern for the expression of adverse effects, and potential aquatic and general population exposure due to their low bioavailability. However, chemicals with a low bioavailability also tend to be more environmentally persistent.

Chemicals with a water solubility >10,000 mg/L can be described within the context of the screening assessment as very soluble, those at 1,000–10,000 mg/L as soluble, 100–1,000 mg/L as moderately soluble, 0.1–100 mg/L as slightly soluble, and <0.1 mg/L as insoluble (noting that these guidelines are not followed consistently within the scientific literature). Chemicals with higher water solubility are more likely to be transported into groundwater with runoff during storm events, be absorbed through the gastrointestinal tract or lungs, partition to aquatic compartments, and undergo atmospheric removal by rain washout, and they have a higher potential for human exposure through the ingestion of contaminated drinking water. Chemicals with lower water solubility are generally more persistent and have a higher potential to bioconcentrate. Chemicals that are essentially insoluble in water are typically of low human health, ecotoxicity, and bioaccumulation hazard because they tend not to be bioavailable (although the lack of bioavailability also tends to increase their environmental persistence).

The water solubility of a substance is also used to evaluate the quality of experimental ecotoxicity and oral exposure human health studies as well as the reliability of ecotoxicity estimates. If the water solubility of a substance is lower than the reported exposure dose in these experiments, then the study is likely to be regarded as inadequate due to potentially confounding factors arising from the presence of undissolved material. For ecotoxicity estimates obtained using SAR, if the estimated toxicity is higher than a chemical's water solubility (i.e., the estimated concentration in water at which adverse effects appear cannot be reached because it is above the material's water solubility), then the chemical is described as having no effects at saturation (NES). When NES occurs, the material is considered to have a low ecotoxicity hazard.

While assessing the water solubility of a chemical substance, its potential to form a dispersion in an aqueous solution is also considered. Ideally, this information can be obtained from scientific literature. In the absence of experimental data, dispersibility can be determined from chemical structure and/or comparison to closely related analogs. There are two general structural characteristics that lead to the formation of dispersions in water: (1) chemicals that have both a hydrophilic (polar) head and a hydrophobic (non-polar) tail, and (2) relatively large molecules that have a large number of repeating polar functional groups (e.g., poly ethylene oxide).

The potential for a chemical to form a dispersion influences potential exposure, environmental fate, and toxicity. Dispersible chemicals have grater potential for human and environmental exposure, leachability, and aquatic toxicity than what might be anticipated based on the material's water solubility alone. None of the FRs assessed in this project are expected to form dispersions.

Octanol/Water Partition Coefficient (K_{ow})

The octanol/water partition coefficient, commonly expressed as its log value (i.e., log K_{ow}) is one of the most useful properties for performing a screening assessment. The log K_{ow} provides the partitioning between octanol and water, where octanol is used to mimic fat and other hydrophobic components of biological systems. Chemicals with a log K_{ow} <1 are highly soluble in water (hydrophilic), while those with a log K_{ow} >4 are not very soluble in water (hydrophobic). A log K_{ow} >8 indicates that the chemical is not readily bioavailable and is essentially insoluble in water.

The log K_{ow} can be used as a surrogate for the water solubility in a screening assessment and is frequently used to estimate the water solubility if an experimental value is not available. It can also be used to estimate other properties important to the screening assessment, including bioconcentration and soil adsorption, and is a required input for SAR models used to estimate ecotoxicity values.

Flammability (Flash Point)

The flash point of a substance is defined as the minimum temperature at which it emits sufficient vapor to form an ignitable mixture with air. Flash point can be used to identify hazards associated with the handling of volatile chemicals. Substances with a flash point greater than 37.8°C (100°F) are commonly referred to as non-flammable, as this is the flammability cutoff used in the shipping industry. It should be noted that, when using this definition, chemicals have been described as non-flammable when, in fact, they may form explosive mixtures in air.

Explosivity

Limits of flammability may be used to quantify the potential for a chemical to form explosive mixtures in air. The lower limit of flammability (LFL) is defined as the minimum concentration of a combustible substance that is capable of propagating a flame through a homogenous mixture in the presence of an ignition source. The upper limit of flammability (UFL) is similarly defined as the highest concentration that can propagate a flame. LFLs and UFLs are commonly reported as the volume percent or volume fraction of the flammable component in air at 25°C. Knowledge that a material does not or is not expected to form explosive mixtures in air is also useful in identifying potential hazards associated with the manufacture and use of a chemical substance.

pH

This property refers to the pH of the solution resulting from the addition of a chemical substance to water. It is used primarily to identify potential hazards associated with dermal contact with a chemical or its aqueous solutions. The corrosive nature of chemicals that form either strongly basic (high pH) or strongly acid (low pH) solutions is likely to be harmful to skin and other biological membranes. Some experimental studies, such as biodegradation tests, require additional analysis for corrosive chemicals to determine if the tests were performed at concentrations that were sufficiently high to harm the microbial population (and, therefore, may be incorrectly identified as persistent in the environment). For chemicals that form moderately basic or acidic solutions in water, the pH of the resulting solution can be used in lieu of measured dissociation constant to help determine if a chemical will ionize under environmental conditions.

Henry's Law Constant (HLC)

The Henry's Law constant is the ratio of a chemical's concentration in the gas phase to that in the liquid phase (at equilibrium). In environmental assessments, the Henry's Law constant is typically measured in water at 25°C. The Henry's Law constant provides an indication of a chemical's volatility from water, which can be used to derive partitioning within environmental compartments and the amount of material removed by stripping in a sewage treatment plant. Henry's Law constants of $<10^{-7}$ atm-m^3/mole indicate slow volatilization from water to air (the Henry's Law constant for the volatilization of water from water is 10^{-7} atm-m^3/mole) and values $>10^{-3}$ atm-m^3/mole indicate rapid volatilization from water to air. To aid in determining the importance of volatilization, the screening assessment uses two models based on the Henry's Law constant. These models determine the half-life for volatilization of a model river and a model lake.

Sediment/Soil Adsorption/Desorption Coefficient (K_{oc})

The soil adsorption coefficient provides a measure of a chemical's ability to sorb to the organic portion of soil and sediment. This provides an indication of the potential for the chemical to leach through soil and be introduced into groundwater, which may lead to human exposure through the ingestion of drinking water drawn from underground sources. The soil adsorption coefficient also describes the potential for a chemical to partition from environmental waters to suspended solids and sediment. Strong adsorption may impact other fate processes, such as the rate of biodegradation, by making the chemical less bioavailable.

The soil adsorption coefficient, K_{oc}, is normalized with respect to the organic carbon content of the soil. The cutoffs for the degree that a chemical is adsorbed to soil within the context of the screening assessment can be described qualitatively as very strong (>30,000), strong (>3,000), moderate (>300), low (>30), and negligible (<3). When determining the potential for a chemical to adsorb to soil and suspended organic matter, the potential for a chemical to form irreversible chemicals bonds with humic acids also needs to be considered.

Dissociation Constant in Water

The dissociation constant in water provides the amount of the dissociated and undissociated forms of an acid, base, or organic salt in water. Knowledge of the dissociation constant is required to assess the importance of the other physical/chemical properties used in the screening assessment. As the percentage of ionization increases, the water solubility increases while the vapor pressure, Henry's Law constant, and octanol/water partition coefficient decrease. For acids and bases, the dissociation constant is expressed as the pK_A and pK_B, respectively.

Reactivity

The potential for a substance to undergo irreversible chemical reactions in the environment can be used to assess persistence. The most important reaction considered in the screening assessment is hydrolysis, or the reaction of a chemical substance with water. Because the rate of hydrolysis reactions can change substantially as a function of pH, studies performed in the pH range typically found in the environment (pH 5-9) are considered. The second reaction considered in the screening assessment is photolysis, the reaction of a chemical with sunlight. Both hydrolysis and photolysis are operative in air, water, and soil, while only hydrolysis is considered in sediment. For the atmospheric compartment, persistence also includes the evaluation of oxidative gas-phase processes. These processes include the reaction with ozone, hydroxyl radicals, and nitrate radicals.

Biodegradation

In the absence of rapid hydrolysis, biodegradation is typically the primary environmental degradation process. Determining the importance of biodegradation is, therefore, an important component of the screening assessment. Biodegradation processes are divided into two types. The first is primary biodegradation, in which a chemical substance is converted to another substance. The second is ultimate biodegradation, in which a chemical is completely mineralized to small building-block components (e.g., CO_2 and water). Chemical substances that undergo rapid primary degradation but only slow ultimate biodegradation are considered to have stable metabolites in the screening assessment.

Biodegradation processes can also be classified as either aerobic or anaerobic. Aerobic biodegradation is an oxidative process that occurs in the presence of oxygen. Anaerobic biodegradation is a reductive process that occurs only in the absence of oxygen. Aerobic biodegradation is typically assessed for soil and water, while anaerobic biodegradation is assessed in sediment. For determining the persistence hazard, the importance of both aerobic and anaerobic biodegradation as well as partitioning and transport in the environment are considered.

One aspect of the screening assessment is to determine the potential for biodegradation of a chemical substance within a sewage treatment plant. In this assessment, the term "ready biodegradability" refers to a chemical's potential to be removed in sewage treatment plants, which is typically determined in guideline laboratory studies. Chemicals that are considered readily biodegradable in these studies undergo 60 percent removal in 28 days.

Structure Activity Relationships Analysis

If measured data pertaining to persistence, bioaccumulation, aquatic toxicity, or human health criteria are not available, they can be estimated with a SAR analysis. SAR uses the molecular structure of a chemical to infer a physicochemical property, environmental fate attribute, and/or specific effect on human health or an environmental species. These correlations may be qualitative (simple SAR) or quantitative (quantitative SAR, or QSAR). Information on EPA's use of SAR analysis has been published in USEPA (1994).

SAR estimations for several physical and chemical properties were obtained using the models of EPA's P2 Framework. The P2 Framework is an approach to risk screening that incorporates pollution prevention principles in the design and development of chemicals. These models are screening-level methods and are intended to be used when data are unavailable or need supplementation. They are not intended to replace data from well-designed studies. For physical/chemical properties and environmental fate parameters, estimates were obtained from the Estimations Program Interface (EPI) for Windows (EPIWIN) suite methodology. These methods were used to obtain melting point, boiling point, vapor pressure, octanol/water partition coefficient, water solubility, Henry's Law constant, atmospheric oxidation rate, biodegradation potential, soil adsorption coefficient, bioconcentration factor, hydrolysis rate, volatilization rates, and removal in a sewage treatment plant as applicable. For aquatic toxicity potential, EPA's Ecological Structure Activity Relationships (ECOSAR) estimation program was used. This methodology uses chemical structure to estimate toxicity of an industrial chemical to fish, invertebrates, and algae in the surface water to which the chemical has been discharged. The program determines both acute (short-term) toxicity and, when available, chronic (long-term or delayed) toxicity. The potential for a chemical to cause cancer in humans was estimated using OncoLogic. This program uses a decision tree based on the known carcinogenicity of chemicals with similar chemical structures, information on mechanisms of action, short-term predictive tests, epidemiological studies, and expert judgment. All estimates obtained in this project were reviewed by EPA scientists with appropriate expertise. The SAR methods with the EPI models were run for flame retardants that are discrete organic chemicals (or a suitable representative structure) with a molecular weight less than 1,000. Estimates for inorganic chemicals and metal containing compounds were obtained using professional judgment, often employing an analog approach.

The persistence of a chemical substance in a screening assessment is based on determining the importance of removal processes that may occur once a chemical enters the environment. As noted above, chemicals with a half-life of less than 60 days are expected to be of low hazard in regards to persistence. The persistence screening assessment does not directly address the pathways in which a flame retardant might enter the environment (e.g., volatilization or disposal in a landfill) and focuses instead on the removal processes that are expected to occur once it is released into air, water, soil, or sediment. Determining how a chemical enters the environment is typically a component of a complete exposure assessment or life-cycle analysis and is discussed in Section 3. Similarly, the persistence screening assessment does not address what might happen to a chemical substance throughout its life cycle, such as disposal during incineration of consumer or commercial products.

Environmental removal processes are generally divided into two categories: chemical and biological. One of the most important chemical degradation processes is hydrolysis. The importance of hydrolysis can be determined from experimental data (on both the compound of interest and closely related analogs) and by using the half-life obtained from the models within EPIWIN. Photolysis may also be an important environmental removal process and was considered in this assessment when experimental data were available. Estimation methods for photolysis are not available within EPA's Sustainable Futures pilot project.

Biodegradation is also considered in determining the persistence of a chemical substance in the environment. If experimental data on the biodegradation of a chemical substance are not available, then the potential of the chemical to undergo this process can be assessed from the results of the EPIWIN models. These models fall into three classes:

1. Probability of rapid biodegradation models based on linear and non-linear regressions that estimate the probability that a chemical substance will degrade fast

2. Expert survey models – semi-quantitative models that determine the rate of ultimate and primary biodegradation

3. Probability of ready biodegradability.

The first set of models are useful for determining if a chemical substance has the potential to biodegrade quickly in the environment, but do not provide a quantitative indication of its half-life. If a chemical is likely to biodegrade quickly, its half-life is expected to be less than 60 days, and it is therefore expected to have a low hazard for persistence. The results of the estimates from the first set of models are used in concert with the semi-quantitative output from the second set of models, which include an ultimate and primary survey model for evaluating persistence. These models provide a numeric result, ranging from 1 to 5, as an indication of the amount of time required for complete mineralization (ultimate degradation) and removal of the parent substance (primary degradation) of the test compound. The numeric result is converted to a more meaningful time frame for removal for the user based on the scheme presented in the following table. The results from the ultimate degradation model can also be used to estimate the half-life for a chemical, which is also provided in Table 4-4.

Table 4-4: Information for Estimating Half-Life

Model Results for Primary and Ultimate	Time for Removal	Approximate Half-Life (Days, Based on Ultimate)
>4.75	Hours	0.17
4.75 to >4.25	Hours to Days	1.25
4.25 to >3.75	Days	2.33
3.75 to >3.25	Days to Weeks	8.67
3.25 to >2.75	Weeks	15
2.75 to >2.25	Weeks to Months	37.5
2.25 to >1.75	Months	60
≤1.75	Recalcitrant	180

The third set of models (also known as MITI models), and the ready biodegradability test that they correspond to, are more applicable to determining a chemical's potential for removal in a sewage treatment plant than its persistence in the environment.

When determining environmental persistence, screening assessments also consider the potential persistence of breakdown products resulting from biodegradation and chemical removal processes. This assessment is performed because of the potential for human and environmental exposure to persistent breakdown products. Breakdown products resulting from hydrolysis can be determined experimentally or by using professional judgment based on analogs with similar functional groups. Breakdown products may also be reported in experimental biodegradation tests or can be determined using professional judgment. When the rate for ultimate degradation is much slower than that for primary degradation, there is potential for persistent breakdown products.

Use of Endocrine Disruption Data

Endocrine disruption studies were available for some but not all of the flame-retardant chemicals being assessed. Available studies are listed in the detailed chemical assessments in Section 4.2, as appropriate. However, endocrine disruption studies were not evaluated as part of the chemical assessments.

The document *Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis* (http://cfpub.epa.gov/ncea/raf/recordisplay.cfm?deid=12462) describes EPA's activities regarding endocrine disruption. This report was prepared under the auspices of EPA's Risk Assessment Forum, which brings together scientists from around the Agency to promote scientific consensus on risk assessment issues. The report provides an overview of the current state of the science for endocrine disruption, and can serve as a resource to EPA and others seeking to understand the issue. This report was requested by EPA's Science Policy Council to serve as an interim assessment to inform Agency risk assessors of major findings and uncertainties and to serve as a basis for a Science Policy Council position statement. Within the special report, the Science Policy Council's Interim Position states that "Based on the current state of the science, the Agency does not consider endocrine disruption to be an adverse endpoint per se, but as a step that could lead to toxic outcomes, such as cancer or adverse reproductive effects, routinely considered in reaching regulatory decisions" and that "Evidence of endocrine disruption alone can influence priority setting for further testing and the assessment of results of this testing could lead to regulatory action if adverse effects are shown to occur."

The 1996 Food Quality Protection Act, which amended the Federal Food, Drug, and Cosmetic Act, directed EPA to develop a screening program, using appropriate validated test systems and other scientifically relevant information, to determine whether certain substances may have hormonal effects in humans. In response, EPA established the Endocrine Disruptor Screening Program (EDSP; http://www.epa.gov/scipoly/oscpendo/index.htm). The EDSP is developing requirements for the screening and testing of thousands of chemicals for their potential to disrupt the endocrine system. When complete, EPA will use these screening and testing approaches to set priorities and conduct further testing when warranted.

The science related to measuring and demonstrating endocrine disruption is relatively new, and validated testing methods are still being developed. The EDSP is using a two-tiered approach that includes initial screening followed by more in-depth testing when warranted (http://www.epa.gov/oscpmont/oscpendo/pubs/assayvalidation/index.htm). The Tier 1 screening battery is intended to identify chemicals with the potential to interact with the estrogen, androgen, or thyroid hormone systems through any of several recognized modes of action. Positive findings for Tier 1 tests screen for potential for an interaction with endocrine systems, but do not fully characterize the nature of possible effects in whole animals. Tier 2 testing is intended to confirm, characterize, and quantify the effects for chemicals that interact with estrogen, androgen, and thyroid hormone systems. These test methods must undergo a 4-stage validation process (protocol development, optimization/prevalidation, validation, and peer-review) prior to regulatory acceptance and implementation. Each of the Tier 1 and Tier 2 test methods is in a different stage of development and validation. Information on the status of assay development and validation efforts for each assay in EPA's Endocrine Disruptor Screening Program can be found at:

http://www.epa.gov/oscpmont/oscpendo/pubs/assayvalidation/status.htm. Once validated test methods have been established for screening and testing of potential endocrine disruptors, guidance must be developed for interpretation of these test results using an overall weight-of-evidence characterization.

4.1.3 References

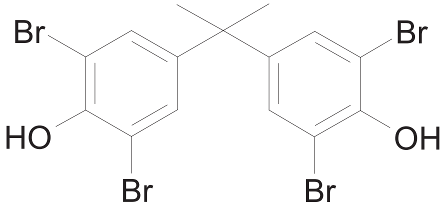
U.S. EPA. 1992. *Classification Criteria for Environmental Toxicity and Fate of Industrial Chemicals*. Office of Prevention, Pesticides and Toxics, Chemical Control Division. Washington, DC.

U.S. EPA. 1994. *US EPA/EC Joint Project on the Evaluation of (Quantitative) Structure Activity Relationships*. Office of Prevention, Pesticides and Toxic Substances. EPA 743R-94-001. Washington, DC. http://www.epa.gov/oppt/newchems/21ecosar.htm

U.S. EPA. 1999. "Category for Persistent, Bioaccumulative, and Toxic New Chemical Substances." *Federal Register*. 64(213): 60194-60204. November 4. http://www.epa.gov/fedrgstr/EPA-TOX/1999/November/Day-04/t28888.htm

4.2 Chemical Summary Assessments

4.2.1 Tetrabromobisphenol A

<table>
<tr><td>Record ID: Tetrabromobisphenol A</td><td>CAS No. 79-94-7</td></tr>
<tr><td rowspan="4">
</td><td>MW: 543.88</td></tr>
<tr><td>MF: $C_{15}H_{12}Br_4O_2$</td></tr>
<tr><td>Physical Forms:
Neat: Solid</td></tr>
<tr><td>Use: Flame retardant, Additive or Reactive (Only reactive in PCBs)</td></tr>
<tr><td colspan="2">SMILES: Oc1c(Br)cc(cc1Br)C(C)(C)c2cc(Br)c(O)c(Br)c2</td></tr>
<tr><td colspan="2">Name: Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-</td></tr>
<tr><td colspan="2">Synonyms: Tetrabromobisphenol A; TBBPA; 4,4’-Isopropylidenebis(2,6-dibromophenol)</td></tr>
<tr><td colspan="2">Life-Cycle Considerations: TBBPA is used as both an additive and reactive flame retardant in a wide variety of electronic equipment. However, in PCBs, TBBPA is only used as a reactive FR chemical. As indicated in Section 3.2, TBBPA is most commonly used as a reactive flame retardant in PCBs and is incorporated into this product through chemical reactions with the epoxy resin. Potential workplace exposures to dust may occur during bagging (manufacturing) and mixing (use) prior to TBBPA’s reaction with the epoxy resin. The amount of free TBBPA is generally anticipated to be relatively low when it is used as a reactive flame retardant for PCBs although quantitative data on the amount of free TBBPA present in PCBs is currently limited. The following studies are representative (also see Section 6.2). 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). In a more recent study (PSB Corporation, 2006), free TBBPA was not detected in the extraction of a prepreg sample, but full experimental details are unknown at this time.

TBBPA has been detected in the air of electronic recycling plants (Sjodin et al., 2001, 2003), although its presence in the air of this facility likely arises from products where it was used as an additive flame retardant. Studies on the release of TBBPA from PCBs after disposal in landfills were not available but would likely be low due to the low levels of unreacted TBBPA. The potential for TBBPA and other compounds to be released from the incineration or open burning of PCBs is discussed in Section 6.1.</td></tr>
<tr><td colspan="2">Risk Assessments: Risk assessment completed for TBBPA by European Union in 2006 (European Union, 2006)</td></tr>
</table>

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	206 (Estimated)	EPI	
	181 (Measured)	WHO, 1995; Albemarle Corporation, 1999	Inadequate, the submitter comment indicated that the measurement was performed on the commercial product which was not 100% pure.
Boiling Point (°C)	Decomposes at 316 (Measured)	Stenger, 1978; WHO, 1995	Adequate, TBBPA will decompose before boiling based on measurements on the commercial product, which may not have been 100% pure.
Vapor Pressure (mm Hg)	$<8.9 \times 10^{-8}$ (Measured)	Lezotte and Nixon, 2001	Adequate
	<1 (Measured)	WHO, 1995; Hardy and Smith, 1999	Inadequate
Water Solubility (g/L)	1.2×10^{-6} (Estimated)	EPI	
	8.2×10^{-5} (pH = 7.6-8.1) (Measured)	NOTOX, 2000; Submitted confidential study	Inadequate, the measured water solubilities were dependent on the flow rates through the column. The cause of the flow rate dependency is unknown. The flow rate dependency is not caused by a failure to reach equilibrium, since higher flow rates gave higher solubilities. The samples were centrifuged to remove dispersed TBBPA. The study was properly performed, and the actual water solubility is probably near this range.
	1.48×10^{-4} at pH 5 1.26×10^{-3} at pH 7 2.34×10^{-3} at pH 9 (Measured)	MacGregor and Nixon, 2002; Submitted confidential study	Inadequate, the samples were not assessed for the presence of colloidal material before analysis.

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	$7.2x10^{-4}$ at 15°C $4.16x10^{-3}$ at 25°C $1.77x10^{-3}$ at 35°C (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
	TBD	Commenter indicated that a water-solubility study will be finished by the end of 2007.	Commenter indicated that a water-solubility study is being conducted to address issues with previous studies.
Log K_{ow}	7.2 (Estimated)	EPI	
	4.5-5.3 (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
	5.903 (Measured)	MacGregor and Nixon, 2001; Submitted confidential study	Adequate
Flammability (Flash Point)			No data
Explosivity	Dust Explosivity: Maximum Explosion Pressure (P_{max}) = 7.7 bar; Maximum Rate of Pressure Rise $(dP/dt)_{max}$ = 379 bar/s; K_{st} Value = 103 bar.m/s (weak explosion) (Measured)	Churchwell and Ellis, 2007; Submitted confidential study	Adequate
pH			No data
pK_a	$pK_a = 9.40$ (Measured)	Lezotte and Nixon, 2002; Submitted confidential study	Adequate
	$pK_{a1} = 7.5$ and $pK_{a2} = 8.5$ (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The estimated water solubility of 1.2×10^{-6} g/L, vapor pressure of $<10^{-6}$ torr, and measured K_{oc} values ranging from 1.1×10^{5} to 2.3×10^{6} indicate that TBBPA will partition predominantly to soil and sediment. The estimated Henry's Law constant of 2.31×10^{-13} atm-m^3/mole indicates that TBBPA will not volatilize from water to the atmosphere. The measured K_{oc} values ranging from 1.1×10^{5} to 2.3×10^{6} indicates that TBBPA is not anticipated to migrate through soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm-m^3/mole)	2.31×10^{-13} (Estimated)	EPI	
	Sediment/Soil Adsorption/Desorption Coefficient – K_{oc}	5.6×10^{5} (Estimated)	EPI	
		TBBPA is shown to adsorb to soil based on laboratory soil mobility tests. TBBPA was not eluted from the soil column after 11 pore volumes were displaced. No quantitative values for the rate of soil migration were measured. (Measured)	Larsen et al., 2001	Adequate
		1.1×10^{5} at 6.8% organic carbon (Measured) 2.0×10^{5} at 2.7% organic carbon (Measured) 2.3×10^{6} at 0.25% organic carbon (Measured)	Breteler, 1989	Adequate, the K_{oc} values were calculated from the reported K_d values and the percent organic carbon for each sediment sample.

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Bioaccumulation		**LOW: The measured fish BCFs are less than 1000.**		
	Fish BCF	13,550 (Estimated)	EPI	
		30-485 (*Cyprinus carpio*) (Measured)	CITI, 1992; CERIJ, 2007	Adequate
		A BCF (*Pimephalus promelas*) of 1200 was measured based on total ^{14}C radioactivity; however, extraction and thin layer chromatograph of the residue in the body of the fish determined that only 24.9% of the ^{14}C radioactivity was due to TBBPA, with the remainder due to metabolites, giving a BCF of 300 for TBBPA. Elimination half-life < 24 hours for total ^{14}C radioactivity. (Measured)	Fackler, 1989a; Submitted confidential study	Adequate
	Daphnids BCF			No data
	Green Algae BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**MODERATE: Experimental aerobic biodegradation studies in soil and sediment indicate that the aerobic primary biodegradation half-life is less than 180 days, but not less than 60 days. Experimental anaerobic biodegradation studies in soil and sediment indicate that the anaerobic primary biodegradation half-life is less than 60 days. Mineralization under both aerobic and anaerobic conditions in soil and sediment is low, indicating that persistent degradation products are formed. An experimental photolysis half-life of 24 minutes at pH 7.4 in water indicates that TBBPA may photolyze rapidly; however, it is not anticipated to partition significantly to water. Although adequate experimental data are not available, degradation of TBBPA by hydrolysis is not expected to be significant as the functional groups present on this molecule do not tend to undergo hydrolyze. The atmospheric half-life for the gas phase reactions of TBBPA is estimated at 3.6 days, though it is expected to exist primarily as a particulate in air.**		
Water	**Aerobic Biodegradation**	Primary: weeks-months (Estimated)	EPI	

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Ultimate: recalcitrant (Estimated)	EPI	
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI	
	Ready Biodegradability	No biodegradation was observed according to a Japanese MITI test using TBBPA (100 mg/L) in activated sludge (30 mg/L) for 2 weeks. (Measured)	CITI, 1992; CERIJ, 2007	Adequate
Soil	**Aerobic Biodegradation**	Aerobic biodegradation of TBBPA was measured in three soil types. After 64 days, the amount of ^{14}C-TBBPA in the soil ranged from 36 to 82%. Less than 6% applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler, 1989b; Submitted confidential study	Adequate
		A transformation study in soil calculated an aerobic DT_{50} of 5.3-7.7 days for the soil extracts. The disappearance appears to be predominantly due to binding to soil and not due to biodegradation. Insufficient material was extracted to identify the transformation products. After 6 months, 17.5-21.6% of the dose was mineralized in the aerobic soils and 2.5-8.4% in the anaerobic soils. (Measured)	Schaefer and Stenzel, 2006a	Inadequate, the DT_{50} was calculated for the soil extracts; however, the majority of the material remained bound to soil and was not extracted. The non-extractable (bound) radioactivity or residues in the soil were not characterized as called for in the OECD guidelines. The abiotic degradation rate under sterile conditions was not estimated as called for in the OECD guidelines. Anaerobic conditions were not maintained in the anaerobic transformation samples.

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		TBBPA showed 1.9% respiration inhibition of activated sludge microorganisms. (Measured)	Schaefer and Siddiqui, 2002; Submitted confidential study	Adequate
		In a test of the adverse effects of TBBPA on the nitrogen transformation activity of soil microorganisms, a dose dependant response pattern was not observed. EC_{10} >1000 mg/kg soil. (Measured)	Schaefer and Siddiqui, 2005; Submitted confidential study	Adequate
	Anaerobic Biodegradation	Anaerobic biodegradation of TBBPA was measured in three soil types. After 64 days, the amount of TBBPA remaining in the soils ranged from 43.7 to 90.6%. Less than 0.5% applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler, 1989c; Submitted confidential study	Adequate
		TBBPA debromination products were isolated during an enrichment process in an anaerobic semi continuous batch reactor. (Measured)	Arbeli and Ronen, 2003	Adequate
	Soil Biodegradation w/ Product Identification	Under anaerobic conditions, TBBPA was mostly dehalogenated within 10 days, and complete dehalogenation to bisphenol A was achieved after 45 days. The resulting bisphenol A was not degraded anaerobically after 3 months. Di- and tribromobisphenol A were observed as intermediates. Under aerobic conditions, bisphenol A was degraded to 4-hydroxybenzoic acid and 4-hydroxyacetophenone. (Measured)	Ronen and Abeliovich, 2000	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	Sediment/Water Biodegradation	Half-lives of 48 to 84 days were determined in an aerobic natural river sediment/water test system. Less than 8% applied radioactivity was recovered as CO_2, suggesting only partial biodegradation. (Measured)	Fackler, 1989d, Submitted confidential study	Adequate
		An anaerobic mineralization and transformation study in freshwater aquatic sediment systems calculated an anaerobic DT_{50} of 24-28 days for the whole system. Very little mineralization was observed. The transformation products included bisphenol A and 3 unidentified materials. (Measured)	Schaefer and Stenzel, 2006b; Submitted confidential study	Adequate
		An anaerobic mineralization and transformation study in digester sludge calculated an anaerobic DT_{50} of 19 days. Very little mineralization was observed. The transformation products included bisphenol A and 3 unidentified materials. (Measured)	Schaefer and Stenzel, 2006c; Submitted confidential study	Adequate
Air	**Atmospheric Half-life**	3.6 days (Estimated)	EPI	
Reactivity	**Photolysis**	Photolysis half-lives in water of 16, 24, and 350 minutes at pH values 10, 7.4, and 5.5 were measured under fluorescent UV radiation representing environmental wavelengths. (Measured)	Eriksson et al., 2004	Adequate
		Reported half-lives in water of 6.6, 10.2, 25.9, and 80.7 days during summer, spring, fall and winter, respectively. (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		A study of TBBPA on silica gel was reported. The wavelength studied was too short to derive any environmental conclusions. (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
	Hydrolysis	<1 year (Estimated)	Professional judgment	
	Pyrolysis	Purified TBBPA was pyrolized in open quartz tubes at 700, 800, and 900 ˚C for 10 minutes resulting mainly in mono-, di-, tri- and tetra-PBDD and PBDF The formation of PBDD and PBDF occurred at 0.02, 0.16, and 0.1% for 700, 800, and 900 ˚C. (Measured)	Thoma et al., 1986	Adequate
Biomonitoring		**Several studies were found related to biomonitoring; however, they were not reviewed as part of this assessment. Since TBBPA is also used additively for ABS plastics, the source of TBBPA in the biomonitoring studies cannot solely be attributed to the use of TBBPA in PCBs. In fact, the additive use would be more likely to contribute to levels in the environment than the reacted chemical. Citations for these studies are included at the end of the reference list found at the end of this table. These studies are provided for stakeholders to review and consider as appropriate.**		
		ECOTOXICITY		
ECOSAR Class		Phenols		
Acute Toxicity		**HIGH: The measured LC_{50} for fish, the estimated LC_{50} for daphnids and the estimated EC_{50} for green algae are all less than 1 mg/L.**		
Fish LC_{50}		14-da LC_{50} = 0.291 mg/L (Estimated)	EPI	
		Rainbow trout 96-hour LC_{50} = 0.40 mg/L (Measured)	Calmbacher, 1978	Adequate
		Bluegill sunfish 96-hour LC_{50} = 0.51 mg/L (Measured)	Calmbacher, 1978	Adequate
		Fathead minnow 96-hour LC_{50} = 0.54 mg/L (Measured)	Surprenant, 1988	Adequate

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Killifish 48-hour LC_{50} = 8.2 mg/L (Measured)	CITI, 1992	Inadequate, study details and test conditions were not available.
	Lepomis macrochirus 96-hour NOEC = 0.1 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Salmo gairdneri 96-hour NOEC = 0.18 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Pimephales promelas 96-hour NOEC = 0.26 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Oncorhynchus mykiss 96-hour LC_{50} = 1.1 mg/L (Measured)	Blankinship et al., 2003a; Submitted confidential study	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
Daphnid LC_{50}	48-hr LC_{50} = 0.742 (Estimated)	EPI	
	Daphnia magna 48-hour LC_{50} = 0.96 mg/L (Measured)	Morrissey, 1978	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
	D. magna 48-hour LC_{50} = 0.96 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	D. magna 48-hour LC_{50} = 960 µg/L (Measured)	Anonymous, 2003	Inadequate, study details and test conditions were not available.
	D. magna 48-hour EC_{50} = 1.8 mg/L (Measured)	Blankinship et al., 2003b; Submitted confidential study	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
Other Freshwater Invertebrate LC_{50}	Eastern oyster 96-hour LC_{50} = 0.098 mg/L (Measured)	Surprenant, 1989a	Adequate
Saltwater Invertebrate LC_{50}	Mysid shrimp 96-hour LC_{50} = 0.86-1.2 mg/L (Measured)	Goodman et al., 1988	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Mysid shrimp 96-hour LC_{50} = 860 µg/L (Measured)	Goodman et al., 1989	Inadequate, study details and test conditions were not available.
	Crassostrea virginica 96-hour EC_{10} = 2.6 µg/L (Measured)	Anonymous, 2003	Inadequate, study details and test conditions were not available.
Green Algae EC_{50}	96-hr EC_{50} = 0.095 (Estimated)	EPI	
	Selenastrum capricornutum EC_{50} > 5.6 mg/L (Measured)	Giddings, 1988	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
	Skeletonema costatum 72-hour EC_{50} = 0.09-1.14 mg/L (Measured)	Walsh et al., 1987	Inadequate, study details and test conditions were not available.
	Thalassiosira pseudonana 72-hour EC_{50} = 0.13-1.0 mg/L (Measured)	Walsh et al., 1987	Inadequate, study details and test conditions were not available.
	72-hour EC_{50} = 0.09 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	S. capricornutum NOEC = 5,600 µg/L (Measured)	Anonymous, 2003	Inadequate, study details and test conditions were not available.
Chronic Toxicity	**HIGH: The estimated green algae chronic value is less than 0.1 mg/L.**		
Fish ChV	0.044 mg/L (Estimated)	EPI	
	Fathead minnow NOEC = 0.16 mg/L (Measured)	Surprenant, 1989b	Adequate
	Fathead minnow MATC = 0.22 mg/L (Measured)	Surprenant, 1989b	Adequate
Daphnid ChV	0.035 mg/L (Estimated)	EPI	
	NOEC(reproduction) = 0.30 mg/L (Measured)	Surprenant, 1989c	Adequate

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	NOEC(survival) = 0.98 mg/L (Measured)	Surprenant, 1989c	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
	MATC >0.98 mg/L (Measured)	Surprenant, 1989c	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
Saltwater Invertebrate ChV	*Mytilus edulis* LOEC (shell length) = 32 µg/L, NOEC (shell length) = 17 µg/L (Measured)	Brown et al., 2005	Adequate
	M. edulis LOEC (wet weight) = 126 µg/L, NOEC (wet weight) = 62 µg/L (Measured)	Brown et al., 2005	Adequate
Green Algae ChV	0.091 mg/L (Estimated)	EPI	
	5.6 mg/L (Measured)	Giddings, 1988	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.
Sediment Dwelling Organisms ChV	*Chironomus tentans* 14-day NOEC = 228-341 mg/kg (sediment); NOEC = 0.039-0.046 mg/L (interstitial water) (Measured)	Breteler, 1989	Adequate
	Lumbriculus variegates with 2% TOC 28-day EC_{50} = 294 mg/kg sediment dry weight (dw) (Measured)	Krueger et al., 2002a	Adequate
	L. variegates with 2% TOC 28-day LOEC = 151 mg/kg sediment dw; NOEC = 90 mg/kg sediment dw (Measured)	Krueger et al., 2002a	Adequate

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	L. variegates with 5% TOC 28-day EC_{50} = 405 mg/kg sediment dw (Measured)	Krueger et al., 2002b	Adequate
	L. variegates with 5% TOC 28-day LOEC = 426 mg/kg sediment dw; NOEC = 254 mg/kg sediment dw (Measured)	Krueger et al., 2002b	Adequate
	Hyalella azteca 28-day EC_{50} > 1000 mg/kg sediment dw; LOEC = 500 mg/kg sediment dw; NOEC = 250 mg/kg sediment dw (Nominal) (Measured)	Krueger et al., 2006; Submitted confidential study	Adequate
Earthworm Subchronic Toxicity	*Eisenia fetida*, 28-day NOEC (survival) = 4840 mg/kg dry soil; EC_{50} >4840 mg/kg dry soil; 56-day NOEC (reproduction) = 2.11 mg/kg dry soil; Did not bioaccumulate in tissue (Measured)	Aufterhiede et al., 2003	Adequate
Reproductive Toxicity to Birds	Negative for reproductive effects, Japanese quail, oral, intravenous and ovo exposure (Measured)	Halldin et al., 2001	Adequate
	Negative for estrogen-like effects in Japanese quail (Measured)	Berg et al., 2001	Adequate
	Negative for effects on sexual behavior or reproductive organ morphology, Japanese quail (Measured)	Halldin et al., 2005	Inadequate, study details and test conditions were not available.
	Negative for endocrine effects, Japanese quail and domestic chicken (Measured)	Anonymous, 2003	Inadequate, study details and test conditions were not available.
Teratogenicity in Frog Embryos	Negative for development effects, *Xenopus laevis* embryo (Measured)	Garber et al., 2001	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Toxicokinetics		**A laboratory study using human skin indicates TBBPA is not well absorbed though the skin. The results indicated 0.73% of the applied dose penetrated through the skin. Oral administration to rats showed that TBBPA is rapidly metabolized and eliminated in the feces (>80%). TBBPA and metabolites were observed in plasma and traces of TBBPA and metabolites were detected in urine. The estimated bioavailability following oral dosing is 1.6%. Human volunteers had no detectable TBBPA in plasma following ingestion of low doses; however, TBBPA metabolites were detected. TBBPA metabolites (< 0.1% of the administered dose) were also detected in the urine.**		
Dermal Absorption in vitro		Human split-thickness skin: Absorbed dose = 0.73% applied dose (14.06 μg/cm^2); Dermal delivery = 1.60% applied dose (32.05 μg/cm^2) (Measured)	Roper, 2005, Submitted confidential study	Adequate
Absorption, Distribution, Metabolism & Excretion	**Oral**	Oral Dosing to Rat: Fecal excretion = 91.7% of dose Urine excretion = 0.3% of dose Residue in tissue = 2% of dose (Primarily large and small intestines) Oral Dosing to Bile-duct Cannulated Rat: Fecal excretion = 26.7% of dose Biliary excretion = 71.3% of dose Residue in tissue < 1% of dose Primary metabolites: Glucuronic acid and sulfate ester conjugates. Over 95% of extractable fecal ^{14}C was parent TBBPA (Measured)	Hakk et al., 2000	Adequate
		Human: Primary metabolites: TBBPA-glucuronide TBBPA-sulfate Route of elimination: Urine: < 0.1% (Measured)	Schauer et al., 2006	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Rats: Primary metabolites: TBBPA-sulfate TBBPA-glucuronide Route of elimination: Feces: >80% (Measured)	Schauer et al., 2006	Adequate
		Recovery of TBBPA (measured as radioactivity) following single oral administration to rats: Feces: 90-95% Urine: < 1% Tissues: 0.4% (Measured) Recovery of TBBPA (measured as radioactivity) following repeated oral administration to rats (1, 5 or 10 days): Feces: 82-98% Urine: < 0.5% Tissues: < 1% Unexcreted intestinal contents: 1-10%. The rats were sacrificed 24 hours after the last dose. (Measured) Following oral administration of ^{14}C-TBBPA to rats, 47% and 51% of the dose was excreted in the bile within 2 hours, primarily as 2 metabolites: TBBPA-glucuronide and TBBPA-diglucuronide Estimated systemic bioavailability after oral dosing: 1.6%	Kuester et al., 2007	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Acute Toxicity		**Low: Experimental study indicates TBBPA, administered orally to rats and mice and dermally to rabbits, does not produce substantial mortality at levels up to 50,000 and 10,000 mg/kg, respectively.**		
Acute Lethality	**Oral**	Rat oral LD_{50} >50,000 mg/kg (Measured)	Int. Bio-Res., 1967a	Adequate
		Rat oral LD_{50} >10,000 mg/kg (Measured)	Hill Top, 1966	Adequate
		Rat oral LD_{50} >5000 mg/kg (Measured)	Pharmakon et al., 1981a	Adequate
		Mouse oral LD_{50} >10,000 mg/kg (Measured)	IRDC, 1978a	Adequate
	Dermal	Rabbit dermal LD_{50} >2000 mg/kg (Measured)	Pharmakon et al., 1981b	Adequate
		Rabbit dermal LD_{50} >10,000 mg/kg (Measured)	Hill Top, 1966	Adequate
	Inhalation	Rat 1-hour inhalation LC_{50} >1,267 ppm (Measured)	Hill Top, 1966	Inadequate, methodological deficiencies (lack of analysis of the test atmosphere and stability of the test compound) raise uncertainties as to the reliability of this study.
		Rat, mouse, guinea pigs 8-hour aerosol inhalation LC_{50} >0.5 mg/L (Measured)	Int. Bio-Res., 1967b	Inadequate, due to short observation period and because the particle size of the aerosol was not measured.
Other Acute Effects	**Eye Irritation**	Minimal irritation, rabbits (Measured)	Hill Top, 1966	Adequate
		Non-irritating, rabbits (Measured)	Int. Bio-Res., 1967c	Adequate
		Non-irritating, rabbits (Measured)	Pharmakon et al., 1981c	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Dermal Irritation	Non-irritating, humans (Measured)	Jessup et al., 1978; Submitted confidential study	Adequate
		Irritating, rabbits, 21-day repeated dermal toxicity assay, dermal erythema (Measured)	IRDC, 1979	Adequate
		Non-irritating, rabbits (Measured)	Pharmakon et al., 1981d	Adequate
		Non-irritating, rabbits (Measured)	Hill Top, 1966	Adequate
	Skin Sensitization	**LOW: Negative for skin sensitization in humans and guinea pigs.**		
		Non-sensitizing, humans (Measured)	Jessup et al., 1978; Submitted confidential study	Adequate
		Non-sensitizing, guinea pigs (Measured)	Pharmakon et al., 1981e	Adequate
		Non-sensitizing, guinea pigs (Measured)	IRDC, 1978b	Adequate
Reproductive Effects		**LOW: An experimental study indicates TBBPA, administered orally to rats, produces no adverse effects on reproductive performance or outcomes at levels up to 1000 mg/kg/day.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects	20-Week, 2-generation reproductive assay, rats, oral gavage, no effects on reproductive performance or outcomes, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002b	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Developmental Effects		**MODERATE: Nonstandard experimental studies indicate TBBPA, administered orally to mice, produces adverse hepatic effects at 140.5 mg/kg/day during gestation and 379.9 mg/kg/day during lactation.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Prenatal Development	Negative in 10-day (GD 6-15) developmental study, rat, oral gavage, fetal NOAEL = 10,000 mg/kg/day (Measured)	IRDC, 1978c	Adequate
		Negative in 19-day (GD 0-19) developmental study, rat, oral gavage, fetal NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2001	Adequate
		Positive in nonstandard assay for gestational plus lactational exposure, mouse, diet, focal hepatocyte necrosis and enlargement of hepatocytes in female pups exposed at LOAEL of 140.5 mg/kg/day during gestation and 379.9 mg/kg/day during lactation. (Measured)	Tada et al., 2006	Adequate
	Postnatal Development	Positive in nonstandard assay for postnatal exposure (PND 4-21), rat, oral gavage, kidney effects, newborn rats LOAEL = 200 mg/kg/day, NOAEL = 40 mg/kg/day; In 5-week old rats dosed for 18 days, no effects were observed at 6000 mg/kg/day. (Measured)	Fukuda et al., 2004	Adequate. While renal effects were noted in offspring, similar effects were not noted in rats of the same species during a 2-generation reproductive toxicity assay at doses up to 1,000 mg/kg-bw/day. The NOAEL for offspring postnatal

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				development should be considered to be 1,000 mg/kg-bw/day (See Reproduction and Fertility Effects above).
Carcinogenicity		**LOW: Based on structure-activity relationships and functional properties, OncoLogic estimates indicate a low carcinogenicity hazard.**		
	OncoLogic Results	Marginal (Estimated)	OncoLogic	
	Carcinogenicity (Rat and Mouse)			No data
	Combined Chronic Toxicity/ Carcinogenicity			No data
Immunotoxicity		**LOW: Experimental studies indicate TBBPA, administered orally to rats, produces no adverse effects on the thymus or spleen at levels up to 1,000 mg/kg/day.**		
	Immune System Effects	90-Day, rat, oral gavage, no histopathology of thymus or spleen, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002a	Adequate
Neurotoxicity		**LOW: Experimental studies indicate TBBPA, administered orally to rats, produces no adverse neurotoxic effects in adults or during development at levels up to 1,000 mg/kg/day.**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)			No data
	Neurotoxicity Screening Battery (Adult)	90-Day repeated-dose study, rat, oral gavage, no clinical signs or neurohistopathology, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002a	Adequate
	Developmental Neurotoxicity	Developmental neurotoxicity and neuropathology assay, rats, oral gavage, no significant effects in F2 pups, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002b	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		20-Week 2-generation reproductive toxicity assay, rat, oral gavage, no clinical signs and no brain weight effect, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002b	Adequate
		Single neonatal dose, mice, no significant effects, NOAEL = 0.75 mg/kg (Measured)	Eriksson et al., 2001	Inadequate, methodological deficiencies (single dose, use of only males, use of non-standard test species) raise uncertainties as to the reliability of this study.
Genotoxicity		**LOW: Experimental studies indicate that TBBPA is not genotoxic to bacterial, mammalian, or yeast cells in vitro.**		
	Gene Mutation in vitro	Negative, Ames Assay (Measured)	Microbiological Associates, 1981	Adequate
		Negative, Ames Assay (Measured)	SRI et al., 1976	Adequate
		Negative, Ames Assay (Measured)	Litton Bionetics, 1977	Adequate
		Negative, Ames Assay (Measured)	Litton Bionetics, 1976	Adequate
		Negative, mitotic gene conversion assay in yeast (*Saccharomyces cerevesiae* D3) (Measured)	SRI et al., 1976	Adequate
		Negative, mitotic gene conversion assay in yeast (*S. cerevesiae* D4) (Measured)	Litton Bionetics, 1977	Adequate
		Negative, mitotic gene conversion assay in yeast (*S. cerevesiae* D4) (Measured)	Litton Bionetics, 1976	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	Gene Mutation in vivo			No data
	Chromosomal Aberrations in vitro	Negative, chromosomal aberration in human lymphocytes (Measured)	Gudi and Brown, 2001	Adequate
	Chromosomal Aberrations in vivo			No data
	DNA Damage and Repair			No data
	Other (Mitotic Gene Conversion)			No data

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Systemic Effects	**LOW: Experimental studies indicate that TBBPA, administered orally to rats, produces decreased body weight and mortality at levels of 10,000 mg/kg/day.**		
	10-Day developmental study, rat, oral gavage, maternal clinical signs, mortality, reduced body weight gain, NOAEL = 3000 mg/kg/day, LOAEL = 10,000 mg/kg/day (Measured)	IRDC, 1978c	Adequate
	21-Day repeated-dose study, rabbit, dermal, no systemic effects (NOAEL = 2500 mg/kg/day), but dermal erythema, NOAEL = 100 mg/kg/day, LOAEL = 500 mg/kg/day (Measured)	IRDC, 1979	Adequate
	28-Day repeated-dose study, rat, diet, no treatment-related effects, NOAEL = 98 mg/kg/day (0.1%) (Measured)	IRDC, 1972	Inadequate, the high dose was relatively low and failed to elicit toxicity.
	90-Day repeated-dose study, rat, gavage, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002a	Adequate
	90-Day repeated-dose study, rat, diet, no systemic effects, NOAEL = 100 mg/kg/day (Measured)	Quast and Humiston, 1975	Inadequate, the highest dose tested was relatively low.
	20-Week reproductive toxicity assay, rat, oral gavage, no systemic effects in P or F1 males and females, NOAEL = 1000 mg/kg/day (Measured)	MPI Research and Schroeder, 2002b	Adequate
	18-Day repeated-dose study, rat, oral gavage, no kidney effects, NOAEL = 6,000 mg/kg/day (Measured)	Fukuda et al., 2004	Adequate
	14-Day repeated-dose study, rat, aerosol inhalation, salivation, and nasal discharge, LOAEL = 2 mg/L (Measured)	IRDC, 1975	Inadequate, particle diameters were not measured.

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Endocrine Disruption	**Several studies were found related to endocrine disruption; however, they were not reviewed as part of this assessment. EPA is not making a judgment as to endocrine disruption potential. Citations for these studies are included at the end of the reference list found at the end of this table. These studies are provided for stakeholders to review and consider as appropriate.**		

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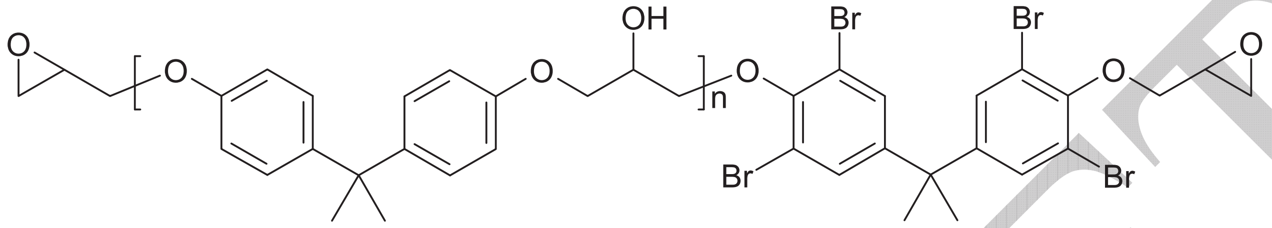
4.2.2 D.E.R. 538

Record ID: D.E.R. 538	**CAS No.** 26265-08-7
	**MW:** 900 (Measured) **MF:** $C_{39}H_{40}Br_4O_7$ as shown with n = 1 (MW = 940) **Physical Forms:** Solid **Use:** Flame-retardant resin, Reactive
SMILES: O1CC1COc2ccc(cc2)C(C)(C)c3ccc(cc3)OCC(O)COc4c(Br)cc(cc4Br)C(C)(C)c5cc(Br)c(c(Br)c5)OCC6CO6 as shown with n = 1	
Name: Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol] (The reaction product of TBBPA)	
Synonyms: D.E.R. 538	
Life-Cycle Considerations: A life cycle assessment of D.E.R. 538 suggests that potential releases to the environment from its use in PCBs may occur during 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. 538 present in the laminate and subsequently, the PCBs produced. The amount of free D.E.R. 538 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.	

D.E.R. 538			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)			No data
Boiling Point (°C)	>400 (Estimated)	EPI	
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	EPI	
Water Solubility (g/L)	$<10^{-6}$ (Estimated)	EPI	
Log K_{ow}	11 (Estimated)	EPI	
Flammability (Flash Point)			No data
Explosivity			No data
pH			No data
Dissociation constant in water			No data

D.E.R. 538				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility, the estimated negligible vapor pressure and the estimated K_{oc} of >100,000 indicate that this polymer is anticipated to partition predominantly to soil and sediment. The estimated Henry's Law Constant of <10^{-8} atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. The estimated K_{oc} of >100,000 indicates that it is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm-m^3/mole)	<10^{-8} (Estimated)	EPI	
	Sediment/Soil Adsorption/Desorption Coefficient – K_{oc}	>100,000 (Estimated)	EPI	
Bioaccumulation		**LOW: The estimated BCF in fish is less than 500.**		
	Fish BCF	3.2 (Estimated)	EPI	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**MODERATE: Although experimental data are not available, estimates indicate that the half lives for primary and ultimate aerobic biodegradation are expected to be greater than 60 days. The estimated degradation half life by hydrolysis is also expected to be greater than 60 days. Degradation of this polymer by direct photolysis is not expected to be significant as the functional groups present do not tend to undergo these reactions under environmental conditions. The atmospheric half life is estimated to be less than 2 days; however, it is not anticipated to partition significantly to air.**		
Water	**Aerobic biodegradation**	Primary: Months (Estimated) Ultimate: Recalcitrant (Estimated)	EPI	
		Water-leachates of the polymer inhibited bacterial growth by 8% (Measured).	Shell Oil Co., 1990	Inadequate. The study was performed on water-leachates of the polymer, and not on the polymer itself. Given the low water solubility of the polymer, it is not anticipated to be present in

D.E.R. 538				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				the leachate.
	Anaerobic biodegradation			No data
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI	
	Ready Biodegradability	Not ready biodegradable (Estimated)	EPI	
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**	1.4 hours (Estimated)	EPI	Given that this compound is anticipated to exist as a solid particulate in the atmosphere, degradation by gas-phase reactions are not expected to be important removal processes. (Professional judgment)
Reactivity	**Photolysis**			No data
	Hydrolysis	Half-life = months (Estimated)	Professional judgment	
	Pyrolysis			No data
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class		Diepoxides		
Acute Toxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
Fish LC_{50}		NES (Estimated)	Professional judgment	
Daphnid LC_{50}		NES (Estimated)	Professional judgment	
Green Algae EC_{50}		NES (Estimated)	Professional judgment	

D.E.R. 538				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Chronic Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. Due to the low water solubility of this polymer, there are expected to be no effects at saturation.**		
Fish ChV		NES (Estimated)	Professional judgment	
Daphnid ChV		NES (Estimated)	Professional judgment	
Green Algae ChV		NES (Estimated)	Professional judgment	
HUMAN HEALTH EFFECTS				
Absorption		Absorption is expected to be poor by all routes for the low molecular weight fraction. (Estimated)	Professional judgment	
Acute Toxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
Acute Lethality	**Oral**	Rat oral LD_{50} > 3663 mg/kg (Estimated, Confidential Analog)	Submitted Confidential Estimation	
	Dermal	Rabbit LD_{50} > 2000 mg/kg (Estimated, Confidential Analog)	Submitted Confidential Estimation	
	Inhalation			No data
Other Acute Effects	**Eye Irritation**			No data
	Dermal Irritation			No data
	Skin Sensitization	**MODERATE: Positive for skin sensitization in guinea pigs.**		
		Strong sensitizer, guinea pigs (Measured)	Shell Oil Co., 1990	Adequate
Reproductive Effects		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)**		
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/develop-mental toxicity screen			No data

D.E.R. 538				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Reproduction and fertility effects			No data
Developmental Effects		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)**		
	Reproduction/developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Prenatal development			No data
Carcinogenicity		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)**		
	OncoLogic Results			No data
	Carcinogenicity (rat and mouse)			No data
	Combined chronic toxicity/ carcinogenicity			No data
Immunotoxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
	Immune system effects			No data
Neurotoxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data

D.E.R. 538				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**MODERATE: Weight of evidence suggests that the polymer will exhibit genotoxicity based on a positive Ames Assay, Mouse Lymphoma Test and Sister Chromatid Exchange Assay submitted for a closely related analog, despite a negative Ames Assay for the polymer.**		
	Gene mutation in vitro	Negative, Ames Assay (Measured)	Shell Oil Co., 1991	Adequate
		Positive, Ames Assay (Measured, Confidential Analog)	Submitted Confidential Study	Inadequate, sufficient study details were not available.
		Positive, mouse lymphoma test (Measured, Confidential Analog)	Submitted Confidential Study	Inadequate, sufficient study details were not available.
	Gene mutation in vivo			No data
	Chromosomal aberrations in vitro	Positive, sister chromatid exchange assay (Measured, Confidential Analog)	Submitted Confidential Study	Inadequate, sufficient study details were not available.
	Chromosomal aberrations in vivo			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
				No data
Endocrine Disruption				No data

References for D.E.R. 538

EPA (2002). TSCA New Chemicals Program (NCP) Chemical Categories. Washington, DC, http://www.epa.gov/oppt/newchems/pubs/cat02.pdf. Accessed on October 9, 2008.

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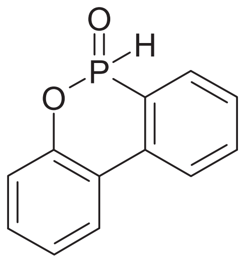
Shell Oil Co. *Bacterial mutagenicity studies with epikote 1145-B-70 with cover letter sheets and letter dated 010891*; Fiche OTS0528781; Shell Oil Company: Submitted January 15, 1991 to TSCA section 8D.

Shell Oil Co. Toxicolgy of resins: The skin sensitizing potential of "epikote" 1120-B-80. In *Letter from Shell Oil Company to US EPA regarding the submission of multiple 8D studies (30 studies enclosed) with attachments*; Fiche OTS0526023; Shell Oil Company: Submitted May 25, 1990 to TSCA section 8D.

4.2.3 DOPO

Record ID: DOPO	**CAS No.** 35948-25-5
	**MW:** 216.18 **MF:** $C_{12}H_9O_2P$ **Physical Forms:** Solid
	Use: Flame retardant, Reactive
SMILES: O=P1c2ccccc2c3ccccc3O1	
Name: 6H-Dibenz[c,e][1,2]oxaphosphorin, 6-oxide	
Synonyms: DOP; DOPPO; 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	
Life-Cycle Considerations: Potential human and environmental exposure to DOPO may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations during its manufacture or formulation. As reactive flame retardant, it is not anticipated to be released from laminates and PCBs through extractive or destructive (e.g., shredding) processes. Its extrapolated vapor pressure suggests that DOPO has at least some potential to volatilize at elevated temperatures. Its estimated water solubility suggests that it may migrate with the movement of water and has some potential to enter groundwater.	

	DATA	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	117 (Measured)	Chernyshev et al., 1972	Adequate
	122 (Measured)	Chang et al., 1998	Adequate
Boiling Point (°C)	200 at 5 torr (Measured)	International Resources, 2001	Adequate
	359 at 760 mm Hg (Extrapolated)	McEntee	The boiling point at 760 mm Hg was extrapolated from the measured boiling point at reduced pressure using NOMO5.

DOPO			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	354 (Estimated)	EPI	
Vapor Pressure (mm Hg)	5 at 200°C (Measured)	International Resources, 2001	Adequate
	2.2×10^{-5} at 25°C (Extrapolated)	McEntee	The vapor pressure at 25°C was extrapolated from the measured vapor pressure at elevated temperature using NOMO5.
	1.3×10^{-5} (Estimated)	EPI	
Water Solubility (g/L)	0.51 (Estimated)	EPI	
Log K_{ow}	1.87 (Estimated)	EPI	
Flammability (Flash Point)			No data
Explosivity			No data
pH			No data
Dissociation constant in water			The substance does not contain functional groups that would be expected to ionize.
ENVIRONMENTAL FATE			
Transport	**The estimated water solubility of 0.51 g/L and the extrapolated vapor pressure of 2.2×10^{-5} mm Hg indicate that DOPO will partition predominantly to soil and water. The estimated Henry's Law Constant of 5.4×10^{-8} atm-m^3/mole indicates that DOPO does not significantly volatilize from water to the atmosphere. The estimated K_{oc} of 45.6 indicates that DOPO has the potential to migrate from soil into groundwater and is not anticipated to strongly adsorb to sediment.**		
Henry's Law Constant – HLC (atm-m^3/mole)	5.4×10^{-8} (Estimated)	EPI	
Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}	45.6 (Estimated)	EPI	

DOPO				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Bioaccumulation		**LOW: The estimated BCF in fish is less than 500.**		
	Fish BCF	5.4 (Estimated)	EPI	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**LOW: Estimates indicate that the half-life for primary and ultimate aerobic biodegradation of DOPO in water is less than 60 days. Although experimental data are not available for other removal processes or environmental compartments, degradation of DOPO by hydrolysis or direct photolysis are not expected to be significant as the functional groups present on this molecule do not tend to undergo these reactions under environmental conditions. The atmospheric half-life for DOPO is estimated at <2 days although it is not anticipated to partition significantly to air.**		
Water	**Aerobic Biodegradation**	Primary: Days-weeks (Estimated) Ultimate: Weeks-months (Estimated)	EPI EPI	
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI	
	Ready Biodegradability	Not ready biodegradable (Estimated)	EPI	
Soil	**Anaerobic Biodegradation**			No data
	Soil Biodegradation w/ Product Identification			No data
	Sediment/Water Biodegradation			No data
Air	**Atmospheric Half-life**	1.8 days (Estimated)	EPI	

DOPO				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Biomonitoring				No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	The substance does not contain functional groups that would be expected to hydrolyze readily under environmental conditions.
	Pyrolysis			No data
ECOTOXICITY				
ECOSAR Classes		Esters, Esters (phosphate)		
Acute Toxicity		**MODERATE: The estimated LC_{50} for green algae, the most sensitive species, is between 1 mg/L and 100 mg/L.**		
Fish LC_{50}		96-hour LC_{50} = 20 mg/L (Estimate)	EPI	
		48-hour LC_{50} = 370 mg/L (Measured)	Wetton, 1999	Adequate
Daphnid LC_{50}		48-hour LC_{50} = 230 mg/L (Estimate)	EPI	
Green Algae EC_{50}		96-hour EC_{50} = 3.0 mg/L (Estimate)	EPI	
Chronic Toxicity		**MODERATE: The estimated chronic value for green algae, the most sensitive species, is between 0.1 mg/L and 10 mg/L.**		
Fish ChV		16 mg/L (Estimate)	EPI	
Daphnid ChV		23 mg/L (Estimate)		Acute to chronic ratio of 10
Green Algae ChV		2.4 mg/L (Estimate)	EPI	

DOPO				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Absorption		Absorption of neat solid negligible through skin. Absorption in solution moderate through skin. Absorption moderate through lungs and GI tract. (Estimated)	Professional judgment	Estimated based on physical/chemical properties
Acute Toxicity		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
Acute Lethality	**Oral**	Mouse (male) oral LD_{50} = 6490 mg/kg, Mouse (female) oral LD_{50} = 7580 mg/kg (Measured)	International Resources, 2001	Inadequate, study details and test conditions were not available.
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**			No data
	Dermal Irritation			No data
	Skin Sensitization	**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
		Non-sensitizing	Leisewitz et al., 2000	Inadequate, study details and test conditions were not available
Reproductive Effects		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects			No data

DOPO				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Developmental Effects		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Prenatal Development			No data
Carcinogenicity		**LOW: Based on structure-activity relationships and functional properties, OncoLogic estimates low carcinogenicity for the nearest analog it could assess, phenylphosphinic acid, phenyl ester.**		
	OncoLogic Results	Low (Estimated)	OncoLogic	Estimated for the analog phenylphosphinic acid, phenyl ester.
	Carcinogenicity (Rat and Mouse)			No data
	Combined Chronic Toxicity/ Carcinogenicity			No data
Immunotoxicity		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
	Immune System Effects			No data
Neurotoxicity		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)			No data
	Neurotoxicity Screening Battery (Adult)			No data

DOPO				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Developmental Neurotoxicity			No data
Genotoxicity		**LOW: Experimental studies indicate that DOPO is not genotoxic to bacteria or mammalian cells *in vitro*.**		
	Gene Mutation in vitro	Negative in Ames assay	Hachiya, 1987	Adequate
	Gene Mutation in vivo			No data
	Chromosomal Aberrations in vitro	Negative in Chinese hamster lung cells with and without activation	Ryu et al., 1994	Adequate
	Chromosomal Aberrations in vivo			No data
	DNA Damage and Repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: Based on closely related analogs with similar structures, functional groups, and physical/chemical properties. (Professional judgment)**		
		Unspecified duration repeated-dose study, rat, oral diet, effects on “feed requirement ratio,” LOAEL = 1.5% diet, NOAEL= 0.6% diet	Otaki et al., 1974	Inadequate, study details and test conditions were not available.
Endocrine Disruption				No data

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Boethling, R. S.; Mackay, D. *Handbook of property estimation methods for chemicals: Environmental and health sciences*. Lewis Publishers: Boca Raton, FL, 2000.

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Ryu, J. C.; Lee, S.; Kim, K. R.; Park, J. Evaluation of the genetic toxicity of synthetic chemicals (I). Chromosomal aberration test on Chinese hamster lung cells in vitro. *Environ. Mutag. Carcinog.* **1994,** *14* (2), 138-144.

Wetton, P. M. Acute Toxicity to Killifish (*Oryzias latipes*); SPL Project No. 1139/072; Unpublished report prepared by Safepharm Laboratories Limited. Sanko Co., Ltd.: 1999.

4.2.4 Dow XZ-92547

Record ID: Dow XZ-92547	**CAS No.**
	MW: >1,000 (Estimated)
	MF:
	Physical Forms: Solid
	Use: Flame-retardant resin, Reactive
SMILES:	
Name: The reaction product of an epoxy phenyl novolak with DOPO	
Synonyms:	
Life-Cycle Considerations: Potential releases of Dow XZ-92547 to the environment from its use in PCBs may occur as fugitive emission from dust-forming operations during its manufacture or subsequent loading/unloading, transfer, or mixing operations during the production of resins or laminates. The amount of Dow XZ-92547, a flame-retarded epoxy resin, that may be released from laminates or PCBs during their production and operational stages has not been determined quantitatively; however, its low vapor pressure indicates that 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. Dow XZ-92547 may be released from PCBs during its disposal or recycling, potentially through dust-forming operations (such as the shredding of PCBs). Leaching from PCBs deposited in landfills is not likely given its low water solubility.	

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	89 (Measured, Confidential)	Submitted confidential study	Adequate
Boiling Point (°C)	> 400 (Estimated)	Professional judgment	
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	$<10^{-6}$ (Estimated)	Professional judgment	
Log K_{ow}			No data
Flammability (Flash Point)			No data
Explosivity			No data
pH			No data
Dissociation constant in water			This polymer does not contain functional groups that would be expected to ionize.

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility and estimated negligible vapor pressure indicate that this polymer is anticipated to partition predominantly to soil and sediment. The estimated Henry's Law Constant of <10^{-8} atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. The estimated K_{oc} of >10,000 indicates that it is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm- m^3/mole)	<10^{-8} (Estimated)	Professional judgment	
	Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}	>10,000 (Estimated)	Professional judgment	
Bioaccumulation		**LOW: By analogy to similar polymers, the large size, negligible water solubility and poor bioavailability indicate that this polymer should be of low hazard for bioaccumulation.**		
	Fish BCF	<100 (Estimated)	Professional judgment	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**HIGH: Although experimental data are not available, by analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation. Degradation of this polymer by hydrolysis or direct photolysis is not expected to be significant as the functional groups present do not tend to readily undergo these reactions under environmental conditions.**		
Water	**Aerobic biodegradation**	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
	Anaerobic biodegradation	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
	Volatilization Half-life for Model River	>1 yr (Estimated)	Professional judgment	

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model Lake	>1 yr (Estimated)	Professional judgment	
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and MacKay, 2000; Professional judgment	This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	>1 mo (Estimated)	Professional judgment	While this polymer contains a functional group with the potential to hydrolyze, this group does not readily hydrolyze under environmental conditions. The low water solubility of this polymer will further decrease the rate of hydrolysis.
	Pyrolysis			No data
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class				No data
Acute Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic to aquatic species unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. For such particles, toxicity typically occurs at high concentrations. Due to the low water solubility of this polymer, there are expected to be no effects at saturation (NES).**		

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Fish LC_{50}		>100 mg/L or NES (Estimated)	Professional judgment	
Daphnid LC_{50}		>100 mg/L or NES (Estimated)	Professional judgment	
Green Algae EC_{50}		>100 mg/L or NES (Estimated)	Professional judgment	
Chronic Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic to aquatic species unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. For such particles, toxicity typically occurs at high concentrations. Due to the low water solubility of this polymer, there are expected to be no effects at saturation.**		
Fish ChV		>10 mg/L or NES (Estimated)	Professional judgment	
Daphnid ChV		>10 mg/L or NES (Estimated)	Professional judgment	
Green Algae ChV		>10 mg/L or NES (Estimated)	Professional judgment	
HUMAN HEALTH EFFECTS				
Absorption		Typically, polymers with molecular weights greater than 1,000 are considered to be of limited bioavailability. Based on the physical/chemical properties, absorption is expected to be negligible by all routes for the neat material and poor by all routes for the low molecular weight fraction if in solution. (Estimated)	Professional judgment	
Acute Toxicity		**LOW: Though the available experimental studies are not sufficient to assess acute toxicity, the weight of evidence indicates that when administered orally and dermally to rats, this polymer does not produce substantial mortality at levels up to 2,000 mg/kg.**		
Acute Lethality	**Oral**	Rat, oral LD_{50} >2000 mg/kg (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available.
	Dermal	Rat, dermal LD_{50} >2000 mg/kg (Measured, Confidential)	Submitted confidential study	Adequate
		Rat, dermal LD_{50} >2000 mg/kg (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available.
	Inhalation			No data

Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Other Acute Effects	**Eye Irritation**	Negative, rabbits (Measured, Confidential)	Submitted confidential study	Adequate
		Negative, rabbits (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available.
	Dermal Irritation	Negative, rabbits (Measured, Confidential)	Submitted confidential study	Adequate
		Positive, rabbits (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available.
	Skin Sensitization	**MODERATE: Positive for skin sensitization in guinea pigs.**		
		Sensitizing, guinea pigs (Measured, Confidential)	Submitted confidential study	Adequate
Reproductive Effects		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups. (Professional judgment)**		
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Reproduction and fertility effects			No data
Developmental Effects		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups. (Professional judgment)**		
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Prenatal development			No data

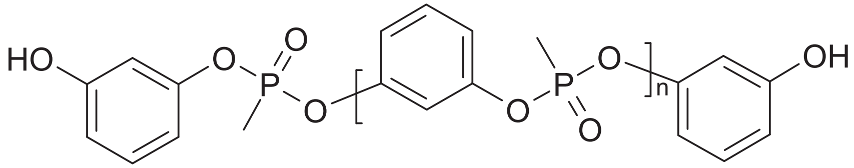
Dow XZ-92547				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Carcinogenicity		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups. (Professional judgment)**		
	OncoLogic Results			No data
	Carcinogenicity (rat and mouse)			No data
	Combined chronic toxicity/carcinogenicity			No data
Immunotoxicity		**LOW: By analogy to structurally similar polymers. (Professional judgment)**		
	Immune system effects			No data
Neurotoxicity		**LOW: By analogy to structurally similar polymers. (Professional judgment)**		
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data
Genotoxicity		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to confidential studies submitted on a closely related analog. (Professional judgment)**		
	Gene mutation in vitro			No data
	Gene mutation in vivo			No data
	Chromosomal aberrations in vitro			No data
	Chromosomal aberrations in vivo			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: By analogy to structurally similar polymers. (Professional judgment)**		
				No data

Dow XZ-92547			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Endocrine Disruption			No data

References for Dow XZ-92547

Boethling, R. S.; Mackay, D. Handbook of property estimation methods for chemicals: Environmental and health sciences. Lewis Publishers: Boca Raton, FL, 2000.

4.2.5 Fyrol PMP

Record ID: Fyrol PMP	**CAS No.**
	**MW:** >1,000 (Measured) **MF:** **Physical Forms:** Solid **Use:** Flame retardant, Reactive
SMILES:	
Name: Aryl alkylphosphonate, Poly(*m*-phenylene methylphosphonate)	
Synonyms: Fyrolflex PMP	
Life-Cycle Considerations: Potential releases of Fyrol PMP to the environment from its use in PCBs may occur as fugitive emission from dust-forming operations during its manufacture or subsequent loading/unloading, transfer, or mixing operations during the production of resins or laminates. The amount of Fyrol PMP, an additive flame retardant, which may be released from resins, laminates, or PCBs during their production and operational stages, has not been determined quantitatively; however, its low vapor pressure indicates that is not likely to undergo direct volatilization. This assessment considered lower molecular weight (<500) components that may be present in the polymeric mixture. Fyrol PMP may be released from PCBs during its disposal or recycling, potentially through dust-forming operations (such as the shredding of PCBs). Leaching from PCBs deposited in landfills is not likely given its low water solubility.	

Fyrol PMP			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	52 (Measured, Confidential)		Adequate
Boiling Point (°C)	>400 (Estimated)	Professional judgment	
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	$<10^{-6}$ (Estimated)	Professional judgment	
Log K_{ow}			No data
Flammability (Flash Point)			No data
Explosivity			No data
pH			No data
Dissociation Constant in Water			No data

Fyrol PMP				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility and estimated negligible vapor pressure indicate that this polymer is anticipated to partition predominantly to soil and sediment. The estimated Henry's Law Constant of <10^{-8} atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. The estimated K$_{oc}$ of >10,000 indicates that it is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm-m^3/mole)	<10^{-8}	Professional judgment	
	Sediment/Soil Adsorption/ Desorption Coefficient – K$_{oc}$	>100,000	Professional judgment	
Bioaccumulation		**LOW: By analogy to similar polymers, the large size, negligible water solubility and poor bioavailability indicate that this polymer should be of low hazard for bioaccumulation.**		
	Fish BCF	<100	Professional judgment	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in Fish			No data
Persistence		**HIGH: Although experimental data are not available, by analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation. Degradation of this polymer by hydrolysis or direct photolysis is not expected to be significant as the functional groups present do not tend to undergo these reactions under environmental conditions.**		
Water	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
	Anaerobic Biodegradation	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.

Fyrol PMP				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
Soil	**Soil Biodegradation w/ Product Identification**			No data
	Sediment/Water Biodegradation			No data
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	>1 year (Estimated)	Professional judgment	This polymer does not contain functional groups that would be expected to hydrolyze under environmental conditions.
	Pyrolysis			No data
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class				No data
Acute Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. For such particles, toxicity typically occurs at high concentrations. Due to the low water solubility of the polymer, there are expected to be no effects at saturation.**		
Fish LC_{50}		>100 mg/L (Estimated)	Professional judgment	

Fyrol PMP				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid LC_{50}		>100 mg/L (Estimated)	Professional judgment	
Green Algae EC_{50}		>100 mg/L (Estimated)	Professional judgment	
Chronic Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. For such particles, toxicity typically occurs at high concentrations. Due to the low water solubility of the polymer, there are expected to be no effects at saturation.**		
Fish ChV		>10 mg/L (Estimated)	Professional judgment	
Daphnid ChV		>10 mg/L (Estimated)	Professional judgment	
Green Algae ChV		>10 mg/L (Estimated)	Professional judgment	
HUMAN HEALTH EFFECTS				
Absorption		Typically, polymers with molecular weights greater than 1000 are considered to be of limited bioavailability. Based on the physical/chemical properties, absorption is expected to be negligible by all routes for the neat material and poor by all routes for the low molecular weight fraction if in solution. (Estimated)	Professional judgment	
Acute Toxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
Acute Lethality	**Oral**			No data
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**	Negative, rabbits (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available.
	Dermal Irritation			No data
	Skin Sensitization	**LOW: Negative for skin sensitization in guinea pigs.**		
		Non-sensitizing, guinea pigs (Measured, Confidential)	Submitted confidential study	Adequate

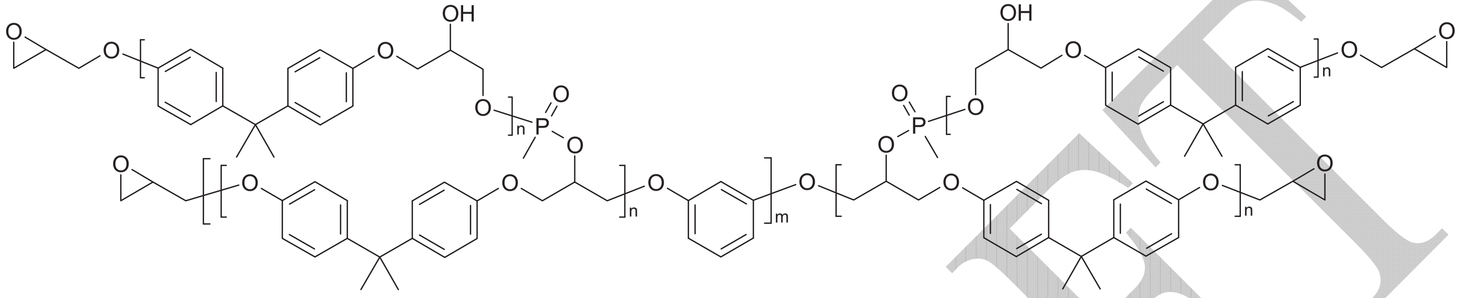
Fyrol PMP				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Reproductive Effects		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects			No data
Developmental Effects		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Prenatal Development			No data
Carcinogenicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	OncoLogic Results			No data
	Carcinogenicity (Rat and Mouse)			No data
	Combined Chronic Toxicity/ Carcinogenicity			No data

Fyrol PMP				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	Immune System Effects			No data
Neurotoxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)			No data
	Neurotoxicity Screening Battery (Adult)			No data
	Developmental Neurotoxicity			No data
Genotoxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
	Gene Mutation in vitro			No data
	Gene Mutation in vivo			No data
	Chromosomal Aberrations in vitro			No data
	Chromosomal Aberrations in vivo			No data
	DNA Damage and Repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
				No data
Endocrine Disruption				No data

References for Fyrol PMP

Boethling, R. S.; Mackay, D. *Handbook of property estimation methods for chemicals: Environmental and health sciences*; Lewis Publishers: Boca Raton, FL, 2000.

4.2.6 Reaction Product of Fyrol PMP with Bisphenol A, Polymer with Epichlorohydrin

Record ID:	**CAS No.**
	**MW:** >1000 (Estimated) **MF:** **Physical Forms:** Solid **Use:** Flame-retardant resin, Reactive
SMILES:	
Name: Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin (Representative Fyrol PCB Resin)	
Synonyms: Representative Fyrol PCB Resin	
Life-Cycle Considerations: A life cycle assessment of the reaction product of this representative resin suggests that potential releases to the environment from its use in PCBs may occur during 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 reaction product of this representative resin present in the laminate and subsequently, the PCBs produced. The amount of free reaction product of this representative resin 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.	

Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)			No data
Boiling Point (°C)	>400 (Estimated)	Professional judgment	
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	$<10^{-6}$ (Estimated)	Professional judgment	
Log K_{ow}			No data
Flammability (Flash Point)			No data
Explosivity			No data
pH			No data

Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The estimated negligible water solubility, the estimated negligible vapor pressure and the estimated K_{oc} of >100,000 indicate that this polymer is anticipated to partition predominantly to soil and sediment. The estimated Henry's Law Constant of $<10^{-8}$ atm-m^3/mole indicates that it is not expected to volatilize from water to the atmosphere. The estimated K_{oc} of >100,000 indicates that it is not anticipated to migrate from soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm- m^3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	
	Sediment/Soil Adsorption/Desorption Coefficient – K_{oc}	>100,000 (Estimated)	Professional judgment	
	Dissociation constant in water			This polymer does not contain functional groups that would be expected to ionize.
Bioaccumulation		**LOW: By analogy to similar polymers, the large size, negligible water solubility and poor bioavailability indicate that this polymer should be of low concern for bioaccumulation.**		
	Fish BCF	<100 (Estimated)	Professional judgment	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**HIGH: Although experimental data are not available, by analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation. Degradation of this polymer by hydrolysis or direct photolysis is not expected to be significant as the functional groups expected to be present do not tend to readily undergo these reactions under environmental conditions.**		
Water	**Aerobic biodegradation**	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
	Anaerobic biodegradation	Recalcitrant (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.

Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	By analogy to similar polymers, this polymer is expected to be recalcitrant to biodegradation.
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mackay, 2000; Professional judgment	This polymer does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	Half-life = months (Estimated)	Professional judgment	
	Pyrolysis			No data
Endocrine Disruption				No data
ECOTOXICITY				
ECOSAR Class		Epoxides		No data
Acute Toxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
Fish LC_{50}		NES (Estimated)	Professional judgment	
Daphnid LC_{50}		NES (Estimated)	Professional judgment	
Green Algae EC_{50}		NES (Estimated)	Professional judgment	
Chronic Toxicity		**LOW: Insoluble nonionic polymers are not expected to be toxic unless the material is in the form of finely divided particles. Most often, the toxicity of finely divided polymer particles does not depend on specific reactive structural features, but occurs from occlusion of respiratory organs such as gills. Due to the low water solubility of this polymer, there are expected to be no effects at saturation.**		
Fish ChV		NES (Estimated)	Professional judgment	

Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV		NES (Estimated)	Professional judgment	
Green Algae ChV		NES (Estimated)	Professional judgment	
HUMAN HEALTH EFFECTS				
Absorption		Absorption is expected to be negligible through the skin as the neat material and poor through the skin as a solution. Absorption is expected to be poor through the lungs and GI tract for any low molecular weight species based on the physical/chemical properties. (Estimated)	Professional judgment	
Acute Toxicity		**LOW: Based on the molecular weight and by analogy to structurally similar polymers. (Professional judgment)**		
Acute Lethality	**Oral**			No data
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**			No data
	Dermal Irritation			No data
	Skin Sensitization	**LOW: Poor absorption indicates that this polymer should be of low concern for skin sensitization. However, this polymer may have the potential for skin sensitization if it is absorbed through the skin; significant amounts of low molecular weight species increases the probability that the polymer will be absorbed through the skin.**		
				No data
Reproductive Effects		**MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)**		
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/ developmental toxicity			No data

Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	screen			
	Reproduction and fertility effects			No data
Developmental Effects		MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)		
	Reproduction/developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Prenatal development			No data
Carcinogenicity		MODERATE: For the low molecular weight oligomers of the polymer (<1,000), by analogy to compounds with similar functional groups as described in the EPA Chemical Categories document. (Professional judgment)		
	OncoLogic Results			No data
	Carcinogenicity (rat and mouse)			No data
	Combined chronic toxicity/ carcinogenicity			No data
Immunotoxicity		LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)		
	Immune system effects			No data
Neurotoxicity		LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)		
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data

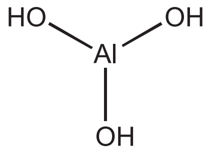
Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrin				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**MODERATE: Weight of evidence suggests that the polymer will exhibit genotoxicity based on a positive Ames Assay, Mouse Lymphoma Test and Sister Chromatid Exchange Assay submitted for a closely related analog, despite a negative Ames Assay for the polymer. Analogy to compounds with similar functional groups also suggests that the low molecular weight oligomers of the polymer (<1,000) may exhibit mutagenicity as described in the EPA Chemical Categories document. (Professional judgment)**		
	Gene mutation in vitro			No data
				No data
				No data
	Gene mutation in vivo			No data
	Chromosomal aberrations in vitro			No data
	Chromosomal aberrations in vivo			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: Based on the molecular weight and by analogy to structurally similar polymers as described in the EPA Chemical Categories document. (Professional judgment)**		
				No data
Endocrine Disruption				No data

References for Reaction product of Fyrol PMP with bisphenol A, polymer with epichlorohydrins

Boethling, R. S.; Mackay, D. *Handbook of property estimation methods for chemicals: Environmental and health sciences*; Lewis Publishers: Boca Raton, FL, 2000.

EPA (2002). TSCA New Chemicals Program (NCP) Chemical Categories. Washington, DC, http://www.epa.gov/oppt/newchems/pubs/cat02.pdf. Accessed on October 9, 2008.

4.2.7 Aluminum Hydroxide

Record ID: Aluminum Hydroxide	**CAS No.** 21645-51-2
	**MW:** 78.01
	MF: AlH_3O_3
	Physical Forms: Solid
	Use: Flame retardant, additive
SMILES: O[Al](O)O	
Name: Aluminum hydroxide	
Synonyms: Aluminum trioxide, Gibbsite, Bayersite, Nordstrandite, Aluminum trihydrate	
Life-Cycle Considerations: Potential releases of aluminum hydroxide to the environment from its use in PCBs suggests that it may occur as a fugitive emission through dust-forming operations resulting from its manufacture or during loading/unloading, transfer, or mixing operations. After incorporation into the 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			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes at approximately 200 (Measured)	European, 2000	Adequate
	Decomposes at approximately 150-220 to Al_2O_3 and H_2O (Measured)	European, 2000	Adequate
	Decomposes (loses water) at 300 (Measured)	Lewis, 2000	Adequate
Boiling Point (°C)	The substance is expected to decompose before boiling. (Estimated)	Professional judgment	
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	Insoluble in water (Estimated)	Lide, 2005-2006	
	Practically insoluble in water	Merck, 2001	

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		(Estimated)		
		Practically insoluble in water (Estimated)	Lewis, 2000	
		0.0015 g/L at 20 ˚C (Measured)	European, 2000	Adequate
		0.015 mg/L at 20 ˚C (Measured)	European, 2000	Adequate
Log K_{ow}				No data
Flammability (Flash Point)		Not flammable (Estimated)	European, 2000	
Explosivity		Not explosive (Estimated)	European, 2000	
pH				No data
Dissociation Constant in Water				No data
ENVIRONMENTAL FATE				
Transport		**Although the behavior of aluminum salts under environmental conditions is dependent on the characteristics of the local environment (predominately pH), transport of the aluminum (III) species is anticipated to be dominated by leaching through soil, runoff to aqueous environments; adsorption and/or precipitation of the metal ion onto soil or sediment; and wet and dry deposition dust particulates in air to land or surface water. Volatilization of this ionic compound from either wet or dry surfaces is not expected to be an important fate process. Nevertheless, the environmental fate of this compound will be dependent on its pH dependent dissociation, and these data are not available.**		
	Henry's Law Constant – HLC (atm-m^3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	
	Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}	$>10^{5}$ (Estimated)	Professional judgment	
Bioaccumulation		**LOW: Aluminum hydroxide is not expected to be bioaccumulative.**		
	Fish BCF	<500 (Estimated)	Professional judgment	
	Daphnids BCF			No data

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**HIGH: As a fully oxidized inorganic material, aluminum hydroxide is not expected to biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Aluminum hydroxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for aluminum hydroxide under typical environmental conditions were identified.**		
Water	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	
Soil	**Anaerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Soil Biodegradation w/ Product Identification			No data
	Sediment/Water Biodegradation			No data
Air	**Atmospheric Half-life**	>1 year (Estimated)	Professional judgment	
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Aluminum hydroxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Hydrolysis	>1 year (Estimated)	Professional judgment	Aluminum hydroxide is a fully oxidized inorganic material and is not expected to undergo hydrolysis.
	Pyrolysis	Not a significant fate process (Estimated)	Professional judgment	Aluminum hydroxide is a fully oxidized inorganic material and is not expected to undergo pyrolysis.
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class				No data
Acute Toxicity		**HIGH: The measured daphnid and green algae EC_{50} values, not including those that are above the water solubility limit, are <1.0 mg/L.**		
Fish LC_{50}		*Salmo trutta* 96-hr NOEC > 100 mg/L (Measured)	European, 2000	Inadequate, the effect concentration is greater than the measured water solubility.
Daphnid LC_{50}		*Daphnia magna* 48-hr EC_{50} = 0.8240 mg/L (Measured)	TSCATS, 1996	Adequate
		Daphnia magna 48-hr NOEC > 100 mg/L (Measured)	European, 2000	Inadequate, study details and test conditions were not available, and the effect concentration is greater than the measured water solubility.
Green Algae EC_{50}		*Selenastrum capricornutum* 96-hr EC_{50} = 0.6560 mg/L (Measured)	TSCATS, 1996	Adequate
		Selenastrum capricornutum 72-hr NOEC > 100 mg/L (Measured)	European, 2000	Inadequate, the effect concentration is greater than the measured water solubility.
Chronic Toxicity		**MODERATE: The measured fish and daphnid chronic values are between 0.1 and 10 mg/L.**		
Fish ChV		*Pimephales promelas* 42-da NOEC = 0.102 mg/L, LOEC = 0.209 mg/L (Measured)	TSCATS, 1996	Adequate

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid ChV		*Daphnia magna* 21-da NOEC = 0.091 mg/L, LOEC = 0.197 mg/L (Measured)	TSCATS, 1996	Adequate
Green Algae ChV				No data
HUMAN HEALTH EFFECTS				
Absorption		After rats were exposed to aluminum hydroxide in drinking water for 10 weeks, aluminum accumulated in intestinal cells but not in other tissues. (Measured)	National, 2006	Secondary source, study details and test conditions were not provided.
		In metabolic studies in humans, 12% of an oral load of aluminum hydroxide was retained, but absorption was not calculated. (Measured)	National, 2006	Secondary source, study details and test conditions were not provided.
		The absorbed fraction of aluminum hydroxide in two human males dosed orally was 0.01%. (Measured)	National, 2006	Secondary source, study details and test conditions were not provided.
		Adult humans with renal failure who ingested 1.5 – 3.0 g aluminum hydroxide per day for 20-32 days absorbed between 100 and 568 mg aluminum per day (7-19% of the dose, Measured)	National, 2006	Secondary source, study details and test conditions were not provided.
Acute Toxicity		**LOW: Aluminum hydroxide is estimated to be of low hazard for acute toxicity based on professional judgment, comparison to analogous aluminum compounds, and the results of an inadequate experimental study suggesting an LD_{50} > 1,000 mg/kg.**		
Acute Lethality	**Oral**	Rat oral LD_{50} > 5000 mg/kg bw (Measured)	European, 2000	Secondary source, study details and test conditions were not provided.
	Dermal			No data
	Inhalation			No data

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Other Acute Effects	**Eye Irritation**	Not irritating, rabbits (Measured)	European, 2000	Secondary source, study details and test conditions were not provided.
	Dermal Irritation	Not irritating, rabbits (Measured)	European, 2000	Secondary source, study details and test conditions were not provided.
	Skin Sensitization	**LOW: Aluminum hydroxide is not estimated to cause skin sensitization based on professional judgment and comparison to analogous aluminum compound.**		
				No data
Reproductive Effects		**LOW: Aluminum hydroxide is estimated to be of low hazard for reproductive effects based on professional judgment and comparison to analogous aluminum compounds.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects			No data
Developmental Effects		**LOW: Aluminum hydroxide does not show developmental toxicity when administered orally to rats or mice at dose levels up to 266 mg/kg/day.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Prenatal Development	Mouse, oral, no developmental effects, NOAEL = 266 mg/kg/day (Highest dose tested, Measured)	Domingo et al., 1989	Adequate

Aluminum Hydroxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Mouse, oral, NOAEL = 268 mg/kg/day (Highest dose tested, Measured)	Gomez et al., 1989	Inadequate, abstract only
		Mouse, oral, NOAEL = 300 mg/kg/day (Only dose tested, Measured)	Colomina et al., 1994	Inadequate, abstract only
		Rat, oral, NOAEL = 768 mg/kg/day (Highest dose tested, Measured)	Gomez et al., 1990	Inadequate, abstract only
		Rat, oral, NOAEL = 384 mg/kg/day (Only dose tested, Measured)	Llobet et al., 1990	Inadequate, abstract only
Carcinogenicity		**LOW: Aluminum hydroxide is estimated to be of low hazard for carcinogenicity based on professional judgment and comparison to analogous aluminum compounds.**		
	OncoLogic Results			No data
	Carcinogenicity (Rat and Mouse)			No data
	Combined Chronic Toxicity/ Carcinogenicity			No data
Immunotoxicity		**MODERATE: Aluminum hydroxide is estimated to be of moderate hazard for immunotoxicity based on professional judgment and comparison to analogous aluminum compounds.**		
	Immune System Effects	6-Week Human, oral, LOAEL = 25 mg Al/kg/day (Reduction in primed cytotoxic T-cells, only dose tested, Measured)	ATSDR, 2006	Inadequate, the toxicological significance of the finding is unknown.
Neurotoxicity		**MODERATE: Aluminum hydroxide is estimated to be of moderate hazard for neurotoxicity based on available experimental data.**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)			No data
	Neurotoxicity Screening Battery (Adult)	30-day Rat, oral diet, no significant effects noted, NOAEL = 1,252 mg Al/kg/day (Measured)	ATSDR, 2006	Adequate

Aluminum Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		90-day Rat, oral gavage, impaired learning in a labyrinth maze test, LOAEL = 35 mg Al/kg/day as aluminum hydroxide with citric acid (Measured)	ATSDR, 2006	Adequate
	Developmental Neurotoxicity			No data
Genotoxicity		**LOW: Aluminum hydroxide is estimated to be of low hazard for genotoxicity based on professional judgment and comparison to analogous aluminum compounds.**		
	Gene Mutation in vitro			No data
	Gene Mutation in vivo			No data
	Chromosomal Aberrations in vitro			No data
	Chromosomal Aberrations in vivo			No data
	DNA Damage and Repair			No data
	Other (Sister Chromatid Exchange, Cell Transformation, etc.)			No data
Systemic Effects		**LOW: An experimental study indicates that, administered orally to rats, aluminum hydroxide does not show adverse effects at levels up to 14,470 ppm/diet.**		
		28-day Rat (male), oral diet, no systemic effects noted, NOAEL = 14,470 ppm/diet (Measured)	Hicks et al., 1987	Adequate
Endocrine Disruption				No data

References for Aluminum Hydroxide

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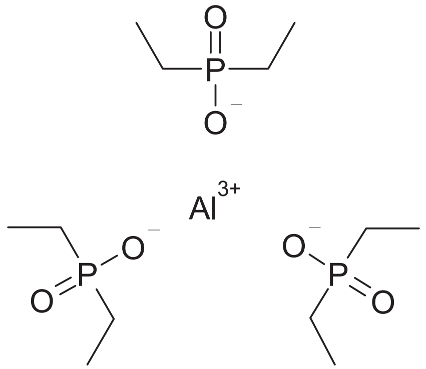
4.2.8 Exolit OP 930

Record ID: Exolit OP 930	**CAS No.** 225789-38-8
	**MW:** 390.27 g/mole
	MF: 3 $C_4H_{11}PO_2$. Al
	Physical Forms: Solid
	Use: Flame retardant, additive
SMILES: CCP(=O)(CC)O[Al](OP(=O)(CC)CC)OP(=O)(CC)CC	
Name: Phosphinic acid, diethyl-, aluminum salt	
Synonyms: Exolit OP 930, Aluminium Diethylphosphinate, Aluminium tris(diethylphosphinate)	
Life-Cycle Considerations: Potential human and environmental exposure to Exolit OP930 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. After incorporation into the resin and/or the laminate, potential releases of Exolit OP930 during the useful life cycle of PCBs is not anticipated, except by an extractive processes upon contact with water. Potential releases of Exolit OP930 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.	

Exolit OP 930			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes 315 (Measured, Confidential)	Submitted confidential study	Adequate
	Decomposes 300 (Measured, Confidential)	Submitted confidential study	Adequate
	Decomposes 330 (Measured)	De Boysère and Dietz, 2005	Inadequate, study details and test conditions were not available.

Exolit OP 930			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Decomposes >300 (Measured)	Clariant, 2007	Inadequate, study details and test conditions were not available.
	>400 (Measured)	NICNAS, 2005; Submitted confidential study	Inadequate, study details and test conditions were not available.
Boiling Point (°C)	As an organic salt, the substance is expected to decompose before boiling (Estimated)	Professional judgment	
Vapor Pressure (mm Hg)	<0.000001 (Estimated)	Professional judgment	
Water Solubility (g/L)	2.5 (Measured, Confidential)	Submitted confidential study	Inadequate, study details and test conditions were not available. Exolit OP 930 has low wettability and very slow dissolution. This gives a kinetically controlled solubility of < 1 mg/L by guideline 92/69/EEC A.6. If Exolit OP 930 is formed by precipitation of a soluble salt, the remaining equilibrium solubility of 2.5 g/L is found, which can be assumed to be the true limit of solubility under ideal conditions.
	<0.001 (Measured)	NICNAS, 2005; Submitted confidential study	Adequate, Exolit OP 930 has low wettability and very slow dissolution. This gives a kinetically controlled solubility of < 1 mg/L by guideline 92/69/EEC A.6. If Exolit OP 930 is formed by precipitation of a soluble salt, the remaining equilibrium solubility of 2.5 g/L is found, which can be assumed to be the true limit of solubility under ideal conditions.
Log K_{ow}	-0.44 (Estimated)	Stuer-Lauridsen et al., 2007; Beard and Marzi, 2005	

Exolit OP 930			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Flammability (Flash Point)	Not readily combustible according to guideline 96/69/EEC, test A. 10. (Measured, Confidential)	Submitted confidential study	Adequate
	No self-ignition below 402°C (Measured, Confidential)	Submitted confidential study	Adequate
Explosivity			No data
pH	4.0 (Measured)	Beard and Marzi, 2005	Inadequate, study details and test conditions were not available.
Dissociation Constant in Water	Dissociates within 24 hours at pH 4.5 during MITI test (Measured)	NICNAS, 2005; Submitted confidential study	Inadequate, available data suggest that this compound is likely to dissociate under environmental conditions. However, its potential for dissociation as a function of pH will have a significant influence on its environmental fate. Available data are not adequate to assess its dissociation under typical environmental conditions.
ENVIRONMENTAL FATE			
Transport	**Although the behavior of metal salts under environmental conditions is dependent on the characteristics of the local environment (predominately pH), transport of both the metal species and the organic anion is anticipated to be dominated by leaching through soil, runoff to aqueous environments; adsorption and/or precipitation of the metal ion onto soil or sediment; and wet and dry deposition dust particulates in air to land or surface water. Volatilization of this ionic compound from either wet or dry surfaces is not expected to be an important fate process. Nevertheless, the environmental fate of this organic salt will be dependent on its pH dependent dissociation, and these data are not available.**		
Henry's Law Constant – HLC (atm-m^3/mole)	$<10^{-7}$ (Estimated)	Professional judgment	Based on analogy to metal salts that dissociate under environmental conditions.

Exolit OP 930				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}			No data
Bioaccumulation		**Given the ubiquitous presence of metal salts in the environment, and the ionic nature of this compound, it is not anticipated to appreciably bioconcentrate.**		
	Fish BCF	<1000 (Estimated)	Professional judgment	Based on analogy to metal salts that dissociate under environmental conditions and the ubiquitous nature of such salts in the environment.
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in Fish			No data
Persistence		**HIGH: For the organic counter ion, estimates indicate that the half-life for ultimate aerobic biodegradation in water is less than 60 days. However, the metal ion is expected to be recalcitrant to biodegradation or other typical environmental removal processes.**		
Water	**Aerobic Biodegradation**	**Organic counter ion:** Primary: days-weeks (Estimated) Ultimate: weeks (Estimated)	EPI	
		Metal ion: Recalcitrant (Estimated)	Professional judgment	
		Not inherently biodegradable (Measured)	Stuer-Lauridsen et al., 2007	Inadequate, study details and test concentrations were not available.
	Anaerobic Biodegradation	Did not biodegrade (Measured)	Stuer-Lauridsen et al., 2007	Inadequate, study details and test conditions were not available.
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI	Estimate was obtained for the neutral form of the organic counter ion although the other ionic species

Exolit OP 930				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
				arising from ionization are also not anticipated to volatilize from environmental waters (Professional judgment).
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI	Estimate was obtained for the neutral form of the organic counter ion although the other ionic species arising from ionization are also not anticipated to volatilize from environmental waters (Professional judgment).
	Ready Biodegradability	Not readily biodegradable (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
		Not readily biodegradable (Measured)	Stuer-Lauridsen et al., 2007	Inadequate, study details and test concentrations were not available.
Soil	**Aerobic Biodegradation**	Respiration inhibition of activated sludge microorganisms LC_{50} = 1968 mg/L, NOEC = 483 mg/L. (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Soil Biodegradation w/ Product Identification			No data
	Sediment/water Biodegradation			No data
Air	**Atmospheric Half-life**	4.6 days (Estimated)	EPI	Estimate obtained for the gas-phase reaction of the neutral form of the organic counter ion with hydroxyl radicals. Given that this compound is anticipated to exist as a solid particulate in the atmosphere,

Exolit OP 930				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				degradation by gas-phase reactions are not expected to be important removal processes (Professional judgment).
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mackay, 2000	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths (Professional judgment).
	Hydrolysis	Stable to hydrolysis (Measured)		Inadequate, study details and test conditions were not available.
		Metal salts form a variety of hydroxylation products as a function of pH. Hydrolysis of the organic counter ion is not expected to be a significant fate process (Estimated)	Boethling and Mackay, 2000	Estimates based on analogy to similar metal salts containing organic counterions (Professional judgment).
	Pyrolysis	Major products are diethylphosphinic acid, ethylphosphonic acid, phosphoric acid, and their respective salts (Measured)	Beard and Marzi, 2005	Inadequate, study details and test conditions were not available.
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class				No data
Acute Toxicity		**MODERATE: The measured green algae EC_{50} is between 1 and 100 mg/L. For fish and daphnia, no lethality was observed up to the limit of solubility for the study.**		
Fish LC_{50}		Zebra fish 96-hour LC_{50} >11 mg/L (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
		Zebra fish 96-hour LC_{50} >9.2 mg/L (Measured, Confidential)	Submitted confidential study	Adequate

Exolit OP 930			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Daphnid LC_{50}	Daphnia magna 48-hour LC_{50} >33.7 mg/L (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Daphnia magna 48-hour LC_{50} >33 mg/L (Measured, Confidential)	Submitted confidential study	Adequate
Green Algae EC_{50}	*Scenedesmus subspicatus* 72-hour E_bC_{50} of 60 mg/L (Measured) *Scenedesmus subspicatus* 72-hour E_rC_{50} of 76 mg/L (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	72-hour EC50 = 50mg/L (Measured, Confidential)	Submitted confidential study	Adequate
Chronic Toxicity	**MODERATE: The estimated green algae ChV is between 0.1 mg/L and 10 mg/L.**		
Fish ChV	48 mg/L (Estimated, Confidential)		
Daphnid ChV	*Daphnia magna* 21-day EC_{50} = 22.3 mg/L for immobility (Measured) *Daphnia magna* 21-day EC_{50} = 46.2 mg/L for reproduction (Measured) *Daphnia magna* 21-day LOEC = 32 mg/L for immobility and reproduction (Measured) *Daphnia magna* 21-day NOEC = 10 mg/L for immobility and reproduction (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
Green Algae ChV	1.4 mg/L (Estimated, Confidential)		
	1.8 mg/L (Measured, Confidential)	Submitted confidential study	Adequate

Exolit OP 930				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Absorption		Absorption as neat solid negligible through skin. Absorption good through lungs. Absorption good through GI tract. (Estimated)	Professional judgment	Estimates based on physical/chemical properties and analogs.
Acute Toxicity		**LOW: Experimental studies indicate that Exolit OP 930, administered orally and dermally to rats, does not produce substantial mortality at levels up to 2,000 mg/kg.**		
Acute Lethality	**Oral**	Rat oral LD_{50} >2000 mg/kg (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Dermal	Rat dermal LD_{50} >2000 mg/kg (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Inhalation			No data
Other Acute Effects	**Eye Irritation**	Slightly irritating, rabbits (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
		Not irritating, rabbits (Measured, Confidential)	Submitted confidential study	Adequate
	Dermal Irritation	Non-irritating, rabbit (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Skin Sensitization	**LOW: Negative for skin sensitization in guinea pigs.**		
		Non-sensitizing, guinea pigs (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
Reproductive Effects		**LOW: Exolit OP 930 is estimated to be of low hazard for reproductive effects resulting from the presence of a bioavailable metal species, by professional judgment based on a comparison to analogous metal salts.**		
	Reproduction/ Developmental Toxicity Screen			No data

Exolit OP 930				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects			No data
Developmental Effects		**MODERATE: Exolit OP 930 is estimated to be of moderate hazard for developmental effects resulting from the presence of a bioavailable metal species, by professional judgment based on a comparison to analogous metal salts.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Prenatal Development			No data
Carcinogenicity		**LOW: Exolit OP 930 is estimated to be of low hazard for carcinogenicity based on comparison to analogous metal salts and professional judgment.**		
	OncoLogic Results			No data
	Carcinogenicity (Rat and Mouse)			No data
	Combined Chronic Toxicity/ Carcinogenicity			No data

Exolit OP 930				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Immunotoxicity		**MODERATE: Exolit OP 930 is estimated to be of moderate hazard for immunotoxicity, due to the presence of a bioavailable metal species, based on comparison to analogous metal salts and professional judgment.**		
	Immune system effects			No data
Neurotoxicity		**MODERATE: Exolit OP 930 is estimated to be of moderate hazard for neurotoxicity, due to the presence of a bioavailable metal species, based on comparison to analogous metal salts and professional judgment.**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)	Rat NOAEL = 1000 mg/kg (Measured)	Beard and Marzi, 2005	Inadequate, study details and test conditions were not available.
	Neurotoxicity Screening Battery (Adult)			No data
	Developmental Neurotoxicity			No data
Genotoxicity		**LOW: Experimental studies indicate that Exolit OP 930 is not genotoxic to bacterial or mammalian cells *in vitro*.**		
	Gene Mutation in vitro	Negative, Ames Assay (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Gene Mutation in vivo			No data
	Chromosomal Aberrations in vitro	Negative, chromosomal aberrations in CHL cells (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
	Chromosomal Aberrations in vivo			No data
	DNA Damage and Repair			No data
	Other (Mitotic Gene Conversion)			No data

Exolit OP 930			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Systemic Effects	**LOW: Experimental studies indicate that Exolit OP 930, administered orally to rats, produces no adverse effects at levels up to 1,000 mg/kg/day.**		
	28-day NOAEL = 1000 mg/kg/day, rats (Measured)	NICNAS, 2005; Submitted confidential study	Adequate
Endocrine Disruption			No data

References for Exolit OP 930

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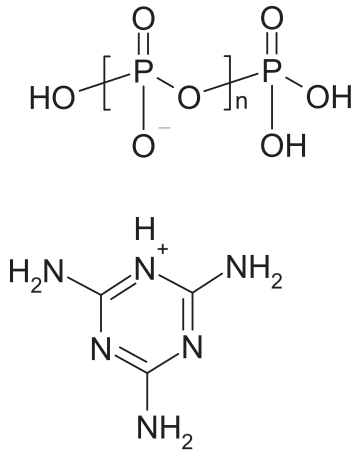
4.2.9 Melapur 200

Record ID: Melapur 200	**CAS No.** 218768-84-4
	**MW**: >1,000 (Measured, Confidential) **MF:** H, O, P . x $C_3H_6N_6$ **Physical Forms:** Solid **Use:** Flame retardant, additive

SMILES:

Name: Polyphosphoric acids, compounds with melamine

Synonyms: Melapur 200

Life-Cycle Considerations: Potential human and environmental exposure to Melapur 200 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. After incorporation into the resin and/or the laminate, potential exposure potential releases of Melapur 200 during the useful life cycle of PCBs is not anticipated, except by an extractive processes upon contact with water. Potential releases of Melapur 200 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.

Melapur 200			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melapur 200			
Melting Point (°C)	> 400 (Measured, Confidential)	Submitted confidential study	Adequate
	> 400 (Measured)	Australia, 2006	Adequate
Boiling Point (°C)	As an organic salt, the polymer is expected to decompose before boiling (Estimated)	Professional judgment	

Melapur 200			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	20 (Measured, Confidential)	Submitted confidential study	Adequate
	20 (Measured)	Australia, 2006	Adequate
Log K_{ow}			No data
Flammability (Flash Point)	Not highly flammable (Measured, Confidential)	Submitted confidential study	Adequate
Explosivity	Not a potential explosive (Measured, Confidential)	Submitted confidential study	Adequate
	Not a potential explosive (Measured)	Australia, 2006	Adequate
pH			No data
Dissociation constant in water	**Melapur 200**		
			No data
	Polyphosphoric acid		
			No data
	Melamine		
	$pK_a = 5.00$ (Measured)	Lide, 2000	Adequate
ENVIRONMENTAL FATE			
Transport	**Melapur 200 has a high measured water solubility of 20 g/L and contains aromatic amines, which tend to bond with humic matter in soil. Therefore, it can be expected to partition predominately to water, soil and sediment. It is not anticipated to migrate from soil into groundwater. As a polymer salt, volatilization from either wet or dry surfaces is not expected to be an important fate process.**		
Melapur 200			
Henry's Law Constant – HLC (atm- m^3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	
Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}	<1,000 (Estimated)	Professional judgment	Aromatic amines form covalent bonds to humic matter in soils and sediments, binding irreversibly.
Bioaccumulation	**LOW: Based on the relatively high water solubility of Melapur 200 (20g/L), the BCF is expected to be <1000. (Professional judgment)**		
Melapur 200			
Fish BCF	<1000	Professional judgment	

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
	Polyphosphoric acid			
	Fish BCF			No data
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
	Melamine			
	Fish BCF	<3.8 for 0.2 mg/L melamine and <0.38 for 2 mg/L melamine (*Cyprinus carpio*) (Measured)	SIDS, 1999; IUCLID, 2000a	Secondary source, study details and test conditions were not provided.
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**MODERATE: Melapur 200 is expected to show moderate persistence in the environment based on the data for melamine. The weight of evidence suggests that melamine will not biodegrade rapidly. Degradation of melamine by hydrolysis or direct photolysis is not expected to be significant as the functional groups present on this molecule do not tend to undergo these reactions under environmental conditions. Polyphosphoric acid is expected to show low persistence in the environment. The weight of evidence suggests that polyphosphoric acid will hydrolyze under environmental conditions.**		
	Melapur 200			
Water	**Aerobic biodegradation**			No data
	Anaerobic biodegradation			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Volatilization Half-life for Model River			No data
	Volatilization Half-life for Model Lake	>1 yr (Estimated)	Professional judgment	
	Ready Biodegradability	>1 yr (Estimated)	Professional judgment	
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**			No data
	Hydrolysis			No data
	Pyrolysis			No data
	Polyphosphoric acid			
Water	**Aerobic biodegradation**			No data
	Anaerobic biodegradation			No data
	Volatilization Half-life for Model River	>1 yr (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 yr (Estimated)	Professional judgment	
	Ready Biodegradability			No data
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	The half-life for the formation of phosphoric acid is several days at 25°C. (Measured)	Kirk-Othmer, 2005	Secondary source, study details and test conditions were not provided.
		At neutral pH, the hydrolysis of linear long-chain polyphosphates to shorter chains has a half-life around 20 days. (Measured)	Spanggord et al., 1985	Inadequate, study details and test conditions were not available.
		Hydrolysis occurs in 2 months at 20°C. (Measured)	IUCLID, 2000b	Secondary source, study details and test conditions were not provided.
	Pyrolysis			No data
	Melamine			
Water	**Aerobic biodegradation**	Primary: days-weeks (Estimated)	EPI	
		Ultimate: weeks-months (Estimated)	EPI	
		16% removal after 20 days with activated sludge, 14% removal after 10 days with adapted sludge (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
		0% removal after 28 days with activated sludge (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
		0% removal after 14 days with activated sludge (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
		<30% removal after 14 days with activated sludge (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
		<1% removal after 5 days with an adapted inoculum (Measured)	IUCLID, 2000a	Secondary source, study details and test conditions were not provided.
		0% removal after 14 days with activated sludge (Measured)	IUCLID, 2000a	Secondary source, study details and test conditions were not provided.

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		<30% removal after 14 days with activated sludge (Measured)	IUCLID, 2000a	Secondary source, study details and test conditions were not provided.
		<20% removal after 20 days, 14% removal after 10 days with adapted inoculum (Measured)	IUCLID, 2000a	Secondary source, study details and test conditions were not provided.
	Anaerobic biodegradation	0-8.9% nitrification was observed after 28 days incubation with bacteria in Webster silty clay loam under anaerobic conditions (Measured)	IUCLID, 2000a	Secondary source, study details and test conditions were not provided.
	Volatilization Half-life for Model River	>1 yr (Estimated)	EPI	
	Volatilization Half-life for Model Lake	>1 yr (Estimated)	EPI	
	Ready Biodegradability	Not ready biodegradable (Estimated)	EPI	
Soil	**Soil biodegradation w/ product identification**			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**			No data
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	The substance does not contain functional groups that would be expected to absorb light at environmentally significant wavelengths.
	Hydrolysis	Not a significant fate process (Estimated)	Boethling and Mckay, 2000; Professional judgment	The substance does not contain functional groups that would be expected to hydrolyze readily under environmental conditions.
	Pyrolysis			No data
Biomonitoring				No data

Melapur 200			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class			No data
Acute Toxicity	**LOW: Melapur 200 is expected to be of low hazard for low acute toxicity to aquatic organisms based on the data for melamine. For melamine, the weight of evidence suggests that the acute values are > 100 mg/L. For Melapur 200, no effects were observed at the highest concentration tested (3.0 mg/L). Melapur 200 does not cause eutrophication.**		
	Melapur 200		
Fish LC_{50}			No data
Daphnid LC_{50}			No data
Green Algae EC_{50}	*Selenastrum capricornutum* 96-hour $EC_{50} > 3.0$ mg/L (Measured, Confidential); 96-hour NOEC = 3.0 mg/L (Measured, Confidential)	Submitted confidential study	Adequate
	Selenastrum capricornutum 96-hour $EC_{50} > 3.0$ mg/L (Measured); 96-hour NOEC = 3.0 mg/L (Measured)	Australia, 2006	Secondary source, study details and test conditions were not provided.
	In a 96-hr control growth test (*Selenastrum capricornutum*), Melapur 200 causes increased algal growth, but growth is 95% less than growth in standard medium with adequate P. This indicates that Melapur 200 is not a good source of P for algal growth and does not cause eutrophication. (Measured, Confidential)	Submitted confidential study	Adequate
	Polyphosphoric acid		
Fish LC_{50}			No data
Daphnid LC_{50}			No data
Green Algae EC_{50}			No data
	Melamine		
Fish LC_{50}	*Leuciscus idus melanotus* 48-hour $LC_{50} > 500$ mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.

Melapur 200			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Oryzias latipes 48-hour $LC_{50} = 1000$ mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
	Poecilia reticulata 96-hour $LC_{50} >$ 3000 mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
	Poecilia reticulata 4400 mg/L dose lethal to <10% (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
Daphnid LC_{50}	*Daphnia magna* 48-hour $LC_{50} > 2000$ mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
Green Algae EC_{50}	*Scenedesmus pannonicus* 4-day EC_{50} = 940 mg/L (Measured); 4-day NOEC = 320 mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
Chronic Toxicity	**LOW: Melapur 200 is expected to be of low hazard for chronic toxicity to aquatic organisms based on the data for melamine. For melamine, the weight of evidence suggests that the chronic values are > 10 mg/L.**		
	Melapur 200		
Fish ChV			No data
Daphnid ChV			No data
Green Algae ChV			No data
	Polyphosphoric acid		
Fish ChV			No data
Daphnid ChV			No data
Green Algae ChV			No data
	Melamine		
Fish ChV	*Jordanella floridae* 35-day NOEC ≥ 1000 mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
	Salmo gairdneri NOEC (macroscopic) = 500 mg/L (Measured); NOEC (microscopic) < 125 mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
Daphnid ChV	*Daphnia magna* 21-day LC_{50} = 32-56 mg/L, 21-day LC100 = 56 mg/L, 21-day NOEC = 18 mg/L (Measured)	SIDS, 1999	Secondary source, study details and test conditions were not provided.
Green Algae ChV			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Absorption		Low for all routes. (Estimated)	Professional judgment.	Estimates based on physical/chemical properties.
Acute Toxicity		**LOW: Melapur 200 is expected to be of low hazard for acute toxicity based on evidence measured for Melapur 200, phosphoric acids and melamine. The weight of evidence indicates that when administered orally and dermally to rats, mice and rabbits, Melapur 200, polyphosphoric acid and melamine do not produce substantial mortality at levels up to 1,000 mg/kg.**		
	Melapur 200			
Acute Lethality	**Oral**	Rat (Gavage) LD_{50} >2,000 mg/kg b.w. (Measured)	RCC Ltd, 2005	Adequate
		Rat LD_{50} >2000 mg/kg b.w. (Measured)	NOTOX B.V., 1998	Inadequate, sufficient study details were not available.
		Rat (Gavage) LD_{50} >2,000 mg/kg b.w. (Measured, Confidential)	Submitted confidential study	Adequate
		Rat LD_{50} >2000 mg/kg b.w. (Measured, Confidential)	Submitted confidential study	Inadequate, sufficient study details were not available.
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**	Slightly Irritating (Measured)	NOTOX B.V., 1998	Inadequate, sufficient study details were not available.
		Slightly Irritating (Measured, Confidential)	Submitted confidential study	Inadequate, sufficient study details were not available.
	Dermal Irritation	Not Irritating (Measured)	NOTOX B.V., 1998	Inadequate, sufficient study details were not available.
		Not Irritating (Measured, Confidential)	Submitted confidential study	Inadequate, sufficient study details were not available.
	Skin Sensitization	**LOW: Melapur 200 is not expected to be a skin sensitizer based on the data for melamine.**		
				No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Polyphosphoric Acid			
Acute Lethality	**Oral**	An oral acute toxicity test was conducted that resulted in a LD_{50} of 4000 mg/kg. The test substance was identified as polyphosphates, and was described as containing 1/3 Kurrol's potassium salt and 2/3 pyrophosphate (Measured)	ARZNAD, 1957	Inadequate, sufficient study details were not available.
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**			No data
	Dermal Irritation			No data
	Skin Sensitization			
				No data
	Melamine			
Acute Lethality	**Oral**	Rat LD_{50} = 3,161 mg/kg (male), 3,828 mg/kg (females) (Measured)	NTP, 1983; Melnick et al., 1984	Adequate
		Mouse LD_{50} = 3,296 mg/kg (male), 7,014 mg/kg (female) (Measured)	NTP, 1983; Melnick et al., 1984	Adequate
		Mouse LD_{50} = 4550 mg/kg (Measured)	Trochimowicz et al., 2001; American Cyanamid Company, 1955; May, 1979	Inadequate, sufficient study details were not available.
		Rat LD_{50} = 3160 mg/kg (male) and 3850 mg/kg (female) (Measured)	Trochimowicz et al., 2001	Inadequate, sufficient study details were not available.
		Rat LD_{50} >6400 mg/kg b.w. (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.
		LD_{50} ≈ 4800 mg/kg b.w. (Measured)	Hoechst AG, 1963	Inadequate, sufficient study details were not available.
	Dermal	Rabbit LD_{50} > 1,000 mg/L (Measured)	Unknown, 1990	Inadequate, sufficient study details were not available.
	Inhalation	Rat LC_{50} > saturated vapor (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.
		Rat LC_{50} > melamine dust enriched air (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Rat LC_{50} = 3.248 mg/L (Measured)	Ubaidullajev et al., 1993	Inadequate, the study details, if present, were not translated into English.
	Intraperitoneal	Mice LD_{50} = 112 mg/kg b.w. (Measured)	Rutty and Connors, 1977	Inadequate, sufficient study details were not available.
		Mice LD_{50} = 800 mg/kg b.w. (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.
Sub-Acute Lethality	**Oral**	Rat 14-day dietary sub-acute LOAEL = 10000 ppm (500 mg/kg/day)[1] in males based on crystal formation in the urinary bladder, and 15000 ppm (750 mg/kg/day) [7] in females based on mean bodyweight depression (Measured)	NTP, 1983; Melnick et al., 1984	Adequate
		Mice 14-day dietary sub-acute LOAEL = 30000 ppm (3,900 mg/kg/day) [1] based on crystal formation in the urinary bladder (Measured)	NTP, 1983; Melnick et al., 1984	Adequate
		Rat 14-day dietary sub-acute LOAEL = 1.2% (12000 ppm; 600 mg/kg/day)[1] based on unquantifiable calculi in the urinary bladder (Measured)	RTI, 1983	Inadequate, the dose levels were insufficient for endpoint determination.
	Intraperitoneal	Mouse 5-day LD_{10} = 762 mg/kg/day (male) (Measured)	Lake et al., 1975	Inadequate, sufficient study details were not available.
		Rat, Mouse LD_{50} > 500 mg/kg/day (Measured)	Philips and Thiersch, 1950	Adequate
Other Acute Effects	**Eye Irritation**	Non- irritating to rabbit eyes (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.

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[7] Based on a food factor reference value of 0.05 for rats and 0.13 for mice.

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Non- irritating to rabbit eyes following 0.5 mL of 10% melamine (Measured)	Trochimowicz et al., 2001; American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
		Mild irritant to rabbit eyes following exposure to 30 mg of dry powder (Measured)	Trochimowicz et al., 2001; American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
		Slightly irritating to rabbit eyes (Measured)	Marhold, 1972	Inadequate, sufficient study details were not available.
	Dermal Irritation	Not irritating to rabbit skins according to OECD TG 404 (Measured)	Rijcken, 1995	Adequate
		Not irritating to rabbit skins (Measured)	BASF, 1969	Inadequate, sufficient study details were not available.
		Not irritating to rabbit skins (Measured)	Trochimowicz et al., 2001; American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
		Not irritating to rabbit skins (Measured)	Trochimowicz et al., 2001; Fasset, et al., 1963/1981	Inadequate, sufficient study details were not available.
	Skin Sensitization	**LOW: Weight of evidence suggests that melamine is not sensitizing to guinea pigs or humans.**		
		No evidence of primary dermal irritation or sensitization in a human patch test (Measured)	Trochimowicz et al., 2001; American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
		Non-sensitizing to guinea pigs (Measured)	Trochimowicz et al., 2001; Fasset et al.,1963/1981	Inadequate, sufficient study details were not available.
	Acute Metabolism/ Excretion	Melamine was found to be a potent diuretic in rats. At doses greater than 1 mM/kg, 140% to 160% of fluid fed was excreted along with crystaluria. (Measured)	Lipschitz and Hadidian, 1944	Adequate, non-guideline study
	Acute Metabolism/ Excretion	Increased output of both water and NaCl was noted in dogs receiving 125 mg/kg melamine, as well as an increase in the amount of red cells per volume of blood the day after dosing. Crystalluria was noted (Measured)	Lipschitz and Stokey, 1945	Inadequate, sufficient study details were not available.

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Rats excreted slightly acidic urine, equal to 131.6% of the fluid administered, 6-hours following dosing of 250 mg/kg melamine. Crystalluria was noted, and crystals were composed of an insoluble dimelamine monosphophate that equated to approximately 50 percent of the melamine fed. (Measured)	Lipschitz and Stokey, 1945	Inadequate, sufficient study details were not available.
		No significant difference in the fatal dose of digitalis standard powder was found between cats fed 250 mg/kg and dogs fed 125 mg/kg melamine. (Measured)	Lipschitz and Stokey, 1945	Inadequate, sufficient study details were not available.
		The elimination phase half-life calculated from plasma data was 2.7-hours, and the urinary half-life was 3.0-hours. The renal clearance was determined to be 2.5 mL/min. (Measured)	Mast et al., 1983	Adequate, non-guideline study
Reproductive Effects		**Low: By analogy to structurally similar polymers. (Professional judgment)**		
	Melapur 200			
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Reproduction and fertility effects			No data

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	Polyphosphoric Acid			
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Reproduction and fertility effects			No data
	Melamine			
	Reproduction/ developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Reproduction and fertility effects	Reproductive dysfunction was observed at 0.5 mg/m^3 and included effects on spermatogenesis (genetic material, sperm morphology, motility, and count), effects on the embryo/fetus (fetal death), pre-implantation mortality (reduction in the number of implants per female), and total number of implants per corpora lutea. (Measured)	Ubaidullajev et al., 1993	Inadequate, the study details, if present, were not translated into English.
Developmental Effects		**LOW: Melapur 200 is expected to be of low hazard for developmental effects based on the data for melamine. For melamine, no adverse effects on gestational parameters and no signs of developmental toxicity, and only minor effects on the fetuses or litters were noted.**		

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Melapur 200			
	Reproduction/developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Prenatal development			No data
	Polyphosphoric Acid			
	Reproduction/developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Prenatal development			No data
	Melamine			
	Reproduction/developmental toxicity screen			No data
	Combined repeated dose with reproduction/developmental toxicity screen			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Prenatal development	Signs of maternal toxicity at 136 mg/kg b.w. included decreased body weight and feed consumption, hematuria (23/25 rats), indrawn flanks (7/25 rats), and piloerection (1/25 rats). No adverse effects on gestational parameters and no signs of developmental toxicity were noted. (Measured)	Hellwig et al., 1996	Adequate
	Nonstandard developmental toxicity	Only minor effects on the fetuses or litters, including a non-significant increase in adsorptions in the group treated on the 4th and 5th days of gestation, were observed. (Measured)	Thiersch, 1957	Inadequate, sufficient study details were not available.
Carcinogenicity		**LOW: Melapur 200 is expected to be of low hazard for carcinogenicity based on the data for melamine. For melamine, FDA's Cancer Assessment Committee, in conjunction with the U.S. EPA, concluded that melamine was not a carcinogen, and that incidence of bladder neoplasia was a result of mechanical damage due to the production of stones in the bladder (The Federal Register of April 27, 1984 (49 FR 18120)); however, this conclusion is based on test data that indicated melamine was non-genotoxic. In contrast to the negative findings for genotoxicity that were available at the time of publication of the 2-year bioassay of melamine (1983) and the FDA/EPA conclusion about the mechanism of melamine bladder carcinogenicity, subsequent studies conducted by NTP (1988 and 1989) reported positive results for an *in vivo* chromosomal aberration assay and an *in vivo* sister chromatid exchange assay. These positive data, and the absence of *in vitro* genotoxicity testing using a metabolic activation system from bladder epithelial cells (refer to the genotoxicity conclusion), introduce uncertainty in the conclusion of low potential for carcinogenicity.**		
	Melapur 200			
	OncoLogic Results			No data
	Carcinogenicity (rat and mouse)			No data
	Combined chronic toxicity/ carcinogenicity			No data
	Polyphosphoric Acid			
	OncoLogic Results			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Carcinogenicity (rat and mouse)			No data
	Combined chronic toxicity/ carcinogenicity			No data
	Melamine			
	OncoLogic Results	Marginal (Estimated)	OncoLogic	
Carcinogenicity (cont.)	**Carcinogenicity (rat and mouse)**	Significant formation of transitional cell carcinomas in the urinary bladder of male rats and significant chronic inflammation in the kidney of dosed female rats were observed. Carcinoma formation was significantly correlated with the incidence of bladder stones. A transitional-cell papilloma was observed in the urinary bladder of a single high dose male rat, and compound related lesions were observed in the urinary tract of dosed animals. Based on the mechanical nature of tumor formation, FDA and EPA considered melamine non-carcinogenic. (Measured)	NTP, 1983; Melnick et al., 1984; Huff, 1984	Adequate
		Increased incidence of acute and chronic inflammation and epithelial hyperplasia of the urinary bladder was observed in male mice. Bladder stones and compound related lesions were observed in the urinary tract of test animals. Melamine was not considered carcinogenic. (Measured)	NTP, 1983; Melnick et al., 1984; Huff, 1984	Adequate

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Melamine-induced proliferative lesions of the rat urinary tract were directly due to the irritative stimulation of calculi, and not to molecular interactions between melamine or its metabolites with the bladder epithelium. (Measured)	Okumura et al., 1992	Adequate
		Water intake, used as an index of urinary output, was increased by NaCl treatment. Calculus formation resulting from melamine administration was suppressed dose-dependently by the simultaneous NaCl treatment. The main constituents of calculi were melamine and uric acid (total contents 61.1–81.2%). The results indicate that melamine-induced proliferative lesions of the urinary tract of rats were directly due to the irritative stimulation of calculi, and not molecular interactions between melamine itself or its metabolites with the bladder epithelium. (Measured)	Ogasawara et al., 1995	Adequate
		As an initiator, melamine caused no significant increase in papillomas per mouse when compared to controls. (Measured)	Perrella and Boutwell, 1983	Adequate, non-guideline study

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Diffuse papillary hyperplasia of the bladder epithelium and bladder calculi were observed in all melamine treated rats. Elevated spermidine/spermine N^1-acetyltransferase (SAT) activity following melamine treatment was considered to be an indicator of cell proliferation. (Measured)	Matsui-Yuasa et al., 1992	Adequate, non-guideline study
		Decreased antitumor activity was correlated with increasing demethylation; melamine was considered inactive as an antitumor drug. (Measured)	Rutty and Connors, 1977	Inadequate, sufficient study details were not available.
		In an *in vitro* cytotoxicity study in cultured ADJ/PC6 plasmacytoma ascites tumor cells the ID_{50} was 470 ug/mL after 72-hours of treatment. (Measured)	Rutty and Abel, 1980	Inadequate, sufficient study details were not available.
	Combined chronic toxicity/ carcinogenicity	No effects were observed in rats fed 1000 ppm of melamine. Four of the 10 rats fed 10,000 ppm melamine had bladder stones associated with the development of benign papillomas. (Measured)	Anonymous, 1958	Inadequate, sufficient study details were not available.
		Increased incidence of urinary bladder stones (6/20 rats) was noted in the 10000 ppm dose group, and was associated with an increase in benign papillomata. The NOAEL was determined to be 1000 ppm (67 mg/kg). (Measured)	American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
Immunotoxicity		**LOW: By analogy to structurally similar polymers. (Professional judgment)**		
	Melapur 200			
	Immune system effects			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Polyphosphoric acid			
	Immune system effects			No data
	Melamine			
	Immune system effects			No data
Neurotoxicity		**LOW: By analogy to structurally similar polymers. (Professional judgment)**		
	Melapur 200			
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data
	Polyphosphoric acid			
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data
	Melamine			
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Genotoxicity		**MODERATE: Melapur 200 is expected to be of moderate hazard for genotoxicity based on the data for melamine. For melamine, positive results were observed in *in vivo* chromosome aberration and sister chromatid exchange assays conducted by NTP in 1988 and 1989. Available *in vitro* genotoxicity testing was conducted with metabolic activation systems from the liver. NTP suggests this may not account for potential activation from bladder epithelial cells, which is the target organ. Proposed genotoxicity testing using a metabolic activation system from bladder epithelial cells (NTP, 1983) was never conducted (Personal Communication, 2007a,b).**		
	Melapur 200			
	Gene mutation *in vitro*			No data
	Gene mutation *in vivo*			No data
	Chromosomal aberrations *in vitro*			No data
	Chromosomal aberrations *in vivo*			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
	Polyphosphoric Acid			
	Gene mutation *in vitro*			No data
	Gene mutation *in vivo*			No data
	Chromosomal aberrations *in vitro*			No data
	Chromosomal aberrations *in vivo*			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
	Melamine			
	Gene mutation *in vitro*	Bacterial forward mutation assay: Negative with and without liver activation (Measured)	Haworth et al., 1983; NCI/NTP, 2007	Adequate

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Bacterial forward mutation assay: Negative (Measured)	Seiler, 1973	Inadequate, sufficient study details were not available.
		Bacterial reverse mutation assay: Negative with and without liver activation (Measured)	Lusby et al., 1979	Inadequate, sufficient study details were not available.
		Bacterial reverse mutation assay: Negative with and without unspecified metabolic activation (Measured)	Mast et al., 1982a	Inadequate, sufficient study details were not available.
		In vitro mouse lymphoma test: Negative with and without liver activation (Measured)	McGregor et al., 1988; NCI/NTP, 2007	Adequate
		CHO/HGPRT forward mutation assay: Negative with and without liver activation (Measured)	Mast et al., 1982a	Inadequate, sufficient study details were not available.
	Gene mutation *in vivo*	*In vivo* mouse micronucleus test: The initial test gave a positive trend (P=0.003) for chromosomal damage; however, both peripheral blood smears and the repeat bone marrow test were negative. The overall conclusion was that melamine does not induce chromosomal damage. (Measured)	Shelby et al., 1993; NTP, 1983	Adequate
		In vivo mouse micronucleus test: Negative without activation (Measured)	Mast et al., 1982b	Inadequate, sufficient study details were not available.
	Chromosomal aberrations *in vitro*	*In vitro* chromosomal aberrations test: Negative in Chinese hamster ovary cells (CHO) with and without liver activation (Measured)	NCI/NTP, 2007; Galloway et al., 1987	Adequate
		In vitro sister chromatid exchange assay: Negative in Chinese hamster ovary cells (CHO) with and without	NCI/NTP, 2007; Galloway et al., 1987	Adequate

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		liver activation (Measured)		
		In vitro sister chromatid exchange assay: Negative in Chinese hamster ovary cells (CHO) with and without liver activation (Measured)	Mast et al., 1982a	Inadequate, sufficient study details were not available.
	Chromosomal aberrations *in vivo*	*In vivo* chromosome aberrations test in mice: Positive (Measured)	NCI/NTP, 2007	Adequate
		In vivo sister chromatid exchange assay in mice: Positive (Measured)	NCI/NTP, 2007	Adequate
	DNA damage and repair	*In vivo* and *in vitro* unscheduled DNA synthesis (UDS) test: None of the tested chemicals, including melamine, were genotoxic hepatocarcinogens in the *in vivo* assay, and melamine was negative for UDS in the *in vitro* assay (Measured)	Mirsalis et al., 1983	Inadequate, sufficient study details were not available.
		SOS/*umu* test: Negative for its ability to result in DNA damage and induce the expression of the *umu* operon (Measured)	Reifferscheid and Heil, 1996	Adequate, non-guideline study
		DNA synthesis-inhibition test in Hela S3 cells: Inhibits DNA synthesis by 50% (DI_{50}) at greater than 300 µM (Measured)	Heil and Reifferscheid, 1992	Inadequate, sufficient study details were not available.
	Other (Mitotic Gene Conversion)	Sex-linked recessive lethal/reciprocal translocation: Results were considered equivocal based on 0.18% and 0.36% total lethals following oral and injection exposure, respectively, compared to control total lethals of 0.07% for oral and 0.09% for injection (Measured)	NCI/NTP, 2007	Adequate

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Drosophila Muller-5 test: Negative for mutagenicity (Measured)	Rohrborn, 1959	Inadequate, sufficient study details were not available.
		Drosophila melanogaster Sex-linked recessive lethal: No mutagenic effects were observed. (Measured)	Luers and Rohrborn, 1963	Inadequate, sufficient study details were not available.
		In vitro flow cytometric (FCM) DNA repair assay: Negative for genotoxic effects (Measured)	Seldon et al., 1994	Adequate, non-guideline study
		Microscreen assay: Positive for genetic toxicity in E.coli WP2s (Measured)	Rossman et al., 1991	Adequate, non-guideline study
		Growth and genotoxic effects to bacteria (*Salmonella typhimurium)* and yeast *(Saccharomyces cerevisiae): N*on-mutagenic in *S.typhimurium* with or without S-9 mix. The growth of eight out of nine strains tested was delayed by 10 mM melamine during 24 hr cultivation. *S.cerevisiae* strain was tested, and did not recover its growth following 48-hour cultivation. (Measured)	Ishiwata et al., 1991	Inadequate, sufficient study details were not available.
Systemic Effects		**MODERATE: Melapur 200 is expected to be of moderate hazard for systemic effects based on the data for melamine. For melamine, the determination is based on a dose-dependant incidence of urinary bladder calculi and urinary bladder hyperplasia, and clinical signs of pilo-erection, lethargy, bloody urine spots in the cage and on the pelage of animals, and chromodacryorrhea. The LOAEL was determined to be 475 mg/kg/day.**		
	Melapur 200			
				No data

Melapur 200			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Polyphosphoric Acid			
Repeated-Dose	Rat Repeated-Dose Toxicity Study: An oral repeated-dose toxicity test in rats resulted in a TDLo of 450 g/kg. The test substance was identified as polyphosphates, and was described as containing 1/3 Kurrol's potassium salt and 2/3 pyrophosphate. Toxic effects included changes in liver weight, changes in tubules (including acute renal failure, acute tubular necrosis), and weight loss or decreased weight gain. (Measured)	ARZNAD, 1957	Inadequate, sufficient study details were not available.
Melamine			
Repeated-Dose	Rat 28-Day Dietary Toxicity Study: Clinical signs included a dose-related increase in pilo-erection, lethargy, bloody urine spots in the cage and on the pelage of animals, and chromodacryorrhea. The incidence of urinary bladder calculi and urinary bladder hyperplasia in treated animals was dose dependant, with a significant relationship between the calculi and hyperplasia. Calculi composition indicated the presence of an organic matrix containing melamine, phosphorus, sulfur, potassium, and chloride. Crystals of dimelamine monophosphate were identified in the urine. The NOAEL was estimated to be 2000 ppm (240 mg/kg/day), excluding the observed increase in water consumption and the	RTI, 1983	Adequate

Melapur 200				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		incidence of crystalluria. The LOAEL was determined to be 4,000 ppm (475 mg/kg/day) based on the formation of calculus. (Measured)		
		Rabbit and Dog 28-Day Dietary Toxicity Study: No significant rise in the body temperature of rabbits was noted. Gross histological examination of the heart, lung, liver, spleen, thyroid, pancreas, intestines, kidneys and bladder did not show pathological changes. A zone of fat was found in the inner part of the renal cortex in two dogs, but also in the kidneys of 3 control dogs. (Measured)	Lipschitz and Stokey, 1945	Inadequate, sufficient study details were not available.
		Rat 28-day Dietary Toxicity Study: Incidence and size of bladder stones were directly related to the amount of substance administered. The larger stones were found to be unchanged melamine in a matrix of protein, uric acid and phosphate. The lowest effect dose (LED) was considered to be 1500 ppm (~125 mg/kg)[8] in males. (Measured)	American Cyanamid Company, 1984	Inadequate, sufficient study details were not available.

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[8] Calculated based on the highest dose level of 4280 ppm, which corresponded to 357 mg/kg.

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Rat 90-day Dietary Toxicity Study: One male rat receiving 18000 ppm and two males receiving 6,000 ppm died. Mean body weight gain and feed consumption were reduced. Stones and diffuse epithelial hyperplasia in the urinary bladders were observed. Focal epithelial hyperplasia was observed in only 1 male. A second and third 13-week repeated dose toxicity study was conducted in rats at a dose range of 750 to 18000 ppm in order to determine the No Observed Adverse Effect Level; however, bladder stones were observed at all dose levels. At 18000 ppm, stones occurred in diets with and without the addition of ammonium chloride. (Measured)	NTP, 1983; Melnick et al., 1984	Adequate

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Mouse 90-day Dietary Toxicity Study: A single female mouse died after receiving 9000 ppm. Mean body weight gain relative to controls was depressed. The incidence of mice with bladder stones was dose-related and was greater in males than in females. Sixty percent of mice having bladder ulcers also had urinary bladder stones. Bladder ulcers were multifocal or associated with inflammation (cystitis). Epithelial hyperplasia and bladder stones were observed together in 2 mice. Also, epithelial cell atypia was seen. No observed adverse effects were noted at 6000 ppm. (Measured)	NTP, 1983; Melnick et al., 1984	Adequate
	Chronic	Dog 1-Year Dietary Toxicity Study: Crystalluria started 60 to 90 days into treatment, and persisted during the study period. No other effects attributable to melamine were observed. (Measured)	American Cyanamid Company, 1955	Inadequate, sufficient study details were not available.
		Rat 30-Month Dietary Toxicity Study: Neither accumulation of calculi nor any treatment-related urinary bladder lesions were found. (Measured)	Mast et al., 1982c	Inadequate, sufficient study details were not available.

Melapur 200				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Rat 24 to 30-Month Dietary Toxicity Study: A dose related trend for dilated glands in glandular gastric mucosa and inflammation in non glandular gastric mucosa was observed. Urinary bladder calculi formation was not observed. (Measured)	American Cyanamid Company, 1983	Inadequate, sufficient study details were not available.
Endocrine Disruption				No data

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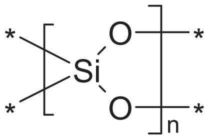
4.2.10 Silicon Dioxide

Record ID: Silicon Dioxide	**CAS No.** 112945-52-5
	**MW:** 60.09
	MF: $(SiO_2)_n$
	Physical Forms: **Neat:** Solid
	Use: Flame retardant, additive
SMILES:	
Name: Silicon dioxide (finely divided amorphous silica is typically used for flame retardants)	
Synonyms: Silica, amorphous, fumed (112945-52-5); Silica (7631-86-9); Silica, vitreous (60676-86-0); Silica, crystalline, cristobalite (14464-46-1), Silica, crystalline, tripoli (1317-95-9); Silica, crystalline, tridymite (15468-32-3); Silica, amorphous, silica gel (112926-00-8); Silica, amorphous, diatomaceous earth (61790-53-2); Silica, amorphous, flux-calcined diatomaceous earth (68855-54-9); Quartz (14808-60-7); Sand	
Life-Cycle Considerations: Potential health concerns for silicon dioxide are limited to effects on the lung and arise from the inhalation of finely divided particulates that are generally less than 10 microns in diameter. Other adverse effects are likely linked to the potential adverse lung effects from respirable, poorly soluble particulates. 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. 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).	

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	1710 (Measured)	Lewis, 1999	Adequate
Boiling Point (°C)	2230 (Measured)	Lewis, 1999	Adequate
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	0.12 for amorphous, finely divided silica (Measured)	Alexander et al., 1954	Adequate
	0.15 for quartz and amorphous, finely divided silica (Measured)	Flörke et al., 2000	Adequate

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	0.012 for quartz (Measured)	Verma, 2000	Adequate
	0.011 for quartz (Measured)	Verma, 2000	Adequate
	0.0066 for quartz (Measured)	Verma, 2000	Adequate
	0.070 for amorphous silica (Measured)	KEMI, 2006	Adequate
	0.006 for quartz (Measured)	KEMI, 2006	Adequate
	Practically insoluble (Estimated)	Merck, 1996	Adequate
	Insoluble for amorphous and crystalline (Estimated)	Lide, 2000	Adequate
	Insoluble for fumed, amorphous and crystalline silica (Estimated)	Lewis, 1999	Adequate
Log K_{ow}			No data
Flammability (Flash Point)	>1000 (Estimated)	Professional judgment	The flash point must be greater than the melting point.
Explosivity	Silicon dioxide is a fully oxidized inorganic material and is not expected to be explosive. (Estimated)	Professional judgment	
pH	3.6-4.5 for 4% aqueous suspension of fumed silica (Measured)	IUCLID, 2000	Adequate
	3.5-9 for 5% aqueous suspension of wet process silicas (Measured)	IUCLID, 2000	Adequate, the pH values of 20 different types of wet process silicas, identified only by trade names, fall within this range.
Dissociation Constant in Water			No data

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
ENVIRONMENTAL FATE				
Transport		**The low water solubility, the estimated vapor pressure of <10^{-6} torr, estimated K_{oc} of >10^5 and estimated Henry's Law Constant of <10^{-8} atm-m^3/mole indicate that silicon dioxide will be relatively immobile in the environment (with the exception of silicon dioxide dust in the atmosphere). Silicon dioxide is a component of sand, soil, and sediment.**		
	Henry's Law Constant – HLC (atm-m^3/mole)	<10^{-8} (Estimated)	Professional judgment	
	Sediment/Soil Adsorption/ Desorption Coefficient – K_{oc}	>10^5 (Estimated)	Professional judgment	
Bioaccumulation		**LOW: Silicon dioxide is not expected to be bioaccumulative.**		
	Fish BCF	<500 (Estimated)	Professional judgment	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**HIGH: As a fully oxidized inorganic material, silicon dioxide is not expected to biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Silicon dioxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for silicon dioxide under typical environmental conditions were identified.**		
Water	**Aerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	
Soil	**Anaerobic Biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Soil Biodegradation w/ Product Identification			No data
	Sediment/Water Biodegradation			No data
Air	**Atmospheric Half-life**	>1 year (Estimated)	Professional judgment	
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Silicon dioxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.
	Hydrolysis	>1 year (Estimated)	Professional judgment	Silicon dioxide is a fully oxidized inorganic material and is not expected to undergo hydrolysis.
	Pyrolysis	Not a significant fate process (Estimated)	Professional judgment	Silicon dioxide is a fully oxidized inorganic material and is not expected to undergo pyrolysis.
Biomonitoring				No data
ECOTOXICITY				
ECOSAR Class				No data
Acute Toxicity		**LOW: The estimated fish and daphnid LC_{50}s and the green algae EC_{50} are all >100 mg/L.**		
Fish LC_{50}		>100 mg/L (Estimated, Confidential)		Adequate
		Brachydanio rerio LC_{50} = 5000 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided.
Daphnid LC_{50}		>100 mg/L (Estimated, Confidential)		Adequate

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Ceriodaphnia dubia EC_{50} ca. 7600 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
Green Algae EC_{50}		>100 mg/L (Estimated, Confidential)		Adequate
		Selenastrum capricornutum EC_{50} = 440 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
Chronic Toxicity		**LOW: The estimated fish, daphnid, and green algae chronic values are all >10 mg/L.**		
Fish ChV		>10 mg/L (Estimated, Confidential)		Adequate
Daphnid ChV		>10 mg/L (Estimated, Confidential)		Adequate
Green Algae ChV		>10 mg/L (Estimated, Confidential)		Adequate
HUMAN HEALTH EFFECTS				
Absorption				No data
Acute Toxicity		**LOW: Weight of evidence and professional judgment suggest that neither amorphous nor crystalline silicon dioxide is acutely toxic when administered via oral, dermal, or inhalation routes.**		
Acute Lethality	**Oral**	LD_{50} (rat) >15,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_{50} (rat) >20,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_{50} (rat) >20,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		LD_{50} (male rat) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >3300 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >5110 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (male rat) >5620 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >3300 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >31,600 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		LD_0 (rat) >20,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >20,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >10,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >10,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >40,000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_0 (rat) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Dermal	LD_{50} (rabbit) >2000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		LD_{50} (rabbit) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_{50} (rabbit) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_{50} (rabbit) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		LD_{50} (rabbit) >5000 mg/kg (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Inhalation	4-Hour LC_0 (rat) >0.139 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		4-Hour LC_0 (rat) >0.691 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		7-Hour LC_0 (rat) >3.1 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		1-Hour LC_{50} (rat) >2.2 mg/L (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Other Acute Effects	**Eye Irritation**	Eleven study summaries indicating not irritating to the rabbit eye (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Slightly irritating, rabbits (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Slightly irritating, humans (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Dermal Irritation	Nine study summaries indicating not irritating to rabbit skin (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Not irritating, humans (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Skin Sensitization	**LOW: An unpublished study and professional judgment indicate that neither amorphous nor crystalline silicon dioxide will cause skin sensitization in guinea pigs.**		
		Not sensitizing in a guinea pig maximization test (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Reproductive Effects		**LOW: An unpublished study and professional judgment indicate that neither amorphous nor crystalline silicon dioxide is likely to produce reproductive effects.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects	One-generation oral dietary reproductive toxicity study, rats, NOAEL (parental and offspring) >497 mg/kg/day, no clinical symptoms, behavior or developmental changes, or changes in pups were observed. (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
Developmental Effects		**LOW: Weight of evidence and professional judgment suggest that neither amorphous nor crystalline silicon dioxide is a developmental toxicant when administered orally.**		
	Reproduction/ Developmental Toxicity Screen			No data.
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data.
	Prenatal Development	Oral gavage developmental toxicity study, rats, NOAEL (maternal and fetal) >1350 mg/kg/day, no observable effects on maternal or fetal survival or development (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Oral gavage developmental toxicity study, mice, NOAEL (maternal and fetal) >1340 mg/kg/day, no observable effects on maternal or fetal survival or development (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Oral gavage developmental toxicity study, rabbits, NOAEL (maternal and fetal) >1600 mg/kg/day, no observable effects on maternal or fetal survival or development (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Oral gavage developmental toxicity study, hamster, NOAEL (maternal and fetal) >1600 mg/kg/day, no observable effects on maternal or fetal survival or development (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
Carcinogenicity		**HIGH: Exposure to crystalline silica has been associated with increased carcinogenic potential in several epidemiological investigations.**		
	OncoLogic Results	High-moderate (Estimated)	OncoLogic	
	Carcinogenicity (Rat and Mouse)	**Amorphous Silica**		
		Slightly increased incidence of intra-abdominal lymphosarcomas was reported after intraperitoneal injection of diatomaceous earth to mice. Subcutaneous and oral administration in mice produced no increase in tumors (Measured)	IARC, 1997	Adequate
		Oral administration of food-grade, micronized, amorphous silica to rats and mice was negative for tumorigenesis. (Measured)	IARC, 1997	Adequate

Silicon Dioxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Intrapleural implantation of synthetic amorphous silica was negative for tumorigenesis. (Measured)	IARC, 1997	Adequate
		Crystalline Silica		
		Several epidemiological investigations have shown an excess cancer risk following workplace inhalational exposure to quartz and cristobalite. (Measured)	IARC, 1997	Adequate
		Thoracic and abdominal malignant lymphomas, primarily of the histiocytic type (MLHT) were found following intrapleural or intraperitoneal injections of several types of quartz to rats. (Measured)	IARC, 1997	Adequate
		Four experiments in rats by inhalation of quartz and four experiments in rats by intratracheal instillation of quartz produced increased incidences of adenocarcinomas and squamous-cell carcinomas of the lungs. (Measured)	IARC, 1997	Adequate
		Unspecified Silica		
		Negative 103-week oral dietary carcinogenicity study in rats, NOAEL = 5% diet (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Negative 93-week oral dietary carcinogenicity study in mice, NOAEL = 5% diet (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Combined Chronic Toxicity/ Carcinogenicity			No data
Immunotoxicity		**HIGH: Subjects that develop silicosis following exposure to crystalline silica have increased numbers of macrophages in the lungs.**		
	Immune System Effects	**Crystalline Silica**		
		Human subjects with silicosis have increased macrophages and lymphocytes in the lungs, but minimal increases in neutrophils. (Measured)	IARC, 1997	Adequate
		Crystalline silica deposited in the lungs causes macrophage injury and activation (species not stated). (Measured)	IARC, 1997	Adequate
		Crystalline silica results in inflammatory cell recruitment in a dose-dependent manner (species not specified). (Measured)	IARC, 1997	Adequate
		In vitro studies show that crystalline silica can stimulate the release of cytokines and growth factors from macrophages and epithelial cells; some evidence exists that these effects occur *in vivo* (species not specified). (Measured)	IARC, 1997	Adequate

Silicon Dioxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Exposure of rats to high concentrations of quartz leads to recruitment of neutrophils, marked persistent inflammation, and proliferative responses of the epithelium. (Measured)	IARC, 1997	Adequate
Neurotoxicity		**LOW: For all potential routes of exposure by analogy to similar materials (Professional judgment).**		
	Acute and 28-day Delayed Neurotoxicity of Organophosphorus Substances (Hen)			No data
	Neurotoxicity Screening Battery (Adult)			No data
	Developmental Neurotoxicity			No data
Genotoxicity		**HIGH: In vivo exposure to crystalline silica dust induced chromosomal aberrations and sister chromatid exchange in peripheral blood lymphocytes. Crystalline silica also induces sister chromatid exchange in co-cultures of human lymphocytes and monocytes.**		
	Gene Mutation in vitro	**Amorphous Silica**		
		Negative in *Salmonella typhimurium* and *Escherichia coli* mutagenicity assay (Measured)	IARC, 1987	Adequate
		Crystalline Silica		
		Direct treatment of epithelial cells with quartz *in vitro* did not cause HPRT mutation. (Measured)	IARC, 1987	Adequate
		Negative in *Salmonella typhimurium* and *Escherichia coli* mutagenicity assay (Measured)	IARC, 1997	Adequate

Silicon Dioxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Unspecified Silica		
		Negative in five *Salmonella typhimurium* and *Escherichia coli* mutagenicity assays (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Negative in *Saccharomyces cerevisia* mutagenicity assay. (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Negative in HGPRT assay in Chinese hamster ovary cells (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Gene Mutation in vivo	**Crystalline Silica**		
		Epithelial cells from the lungs of rats intratracheally exposed to quartz showed HPRT gene mutations. (Measured)	IARC, 1997	Adequate
	Chromosomal Aberrations in vitro	**Amorphous Silica**		
		Positive for micronuclei formation in mammalian cells *in vitro* (Measured)	IARC, 1987	Adequate

Silicon Dioxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		Crystalline Silica		
		Induces micronuclei in Syrian hamster embryo cells, Chinese hamster lung V79 cells, and human embryonic lung Hel 299 cells *in vitro*, but negative for inducing chromosomal aberrations (Measured)	IARC, 1997	Adequate
		Unspecified Silica		
		Negative for chromosomal aberrations in Chinese hamster ovary cells (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Negative for chromosomal aberrations in human embryonic lung cells (Wi-38) (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Chromosomal Aberrations in vivo	**Crystalline Silica**		
		Induced chromosomal aberrations in human peripheral blood lymphocytes following *in vivo* exposure to dust containing crystalline silica (Measured)	IARC, 1997	Adequate
		Quartz did not induce micronuclei in mice *in vivo*. (Measured)	IARC, 1997	Adequate
		Unspecified Silica		
		Negative for chromosomal aberrations in two assays following single and subacute oral gavage administration to rats (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	DNA Damage and Repair			No data

Silicon Dioxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	Other (Sister Chromatid Exchange, Cell Transformation, etc.)	**Crystalline Silica**		
		Tridymite induced sister chromatid exchange in co-cultures of human lymphocytes and monocytes. (Measured)	IARC, 1997	Adequate
		Induced sister chromatid exchange in human peripheral blood lymphocytes following *in vivo* exposure to dust containing crystalline silica (Measured)	IARC, 1997	Adequate
		Two quartz samples induced morphological transformation in Syrian hamster cells *in vitro*. (Measured)	IARC, 1997	Adequate
		Five quartz samples induced transformation in BALB/c-3T3 cells *in vitro*. (Measured)	IARC, 1997	Adequate
		Unspecified Silica		
		Negative in two dominant lethal assays in rats following oral gavage administration (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
		Negative unscheduled DNA synthesis assay in primary rat hepatocytes (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Systemic Effects	**HIGH: Extended workplace exposure to amorphous and crystalline silica induced silicosis in humans.**		
	Amorphous Silica		
	Silicosis in humans following extended workplace exposure (Measured)	NIOSH, 1978b	Adequate
	13-Week inhalation study, rats, LOAEL = 1 mg/m^3, increased lung weight, focal interstitial fibrosis, pulmonary inflammation, and pulmonary granulomas (Measured)	Reuzel et al., 1991	Adequate
	Biogenic silica fibers induced ornithine decarboxylase activity of epidermal cells in mice following topical application (Measured)	IARC, 1997	Adequate
	1-Year inhalation study, rabbits, LOAEL <53 mg/m^3, progressive functional incapacitation, emphysema, pulmonary vascular obstruction, blood pressure changes, mural cellular infiltration, peribronchiolar cellular catarrh, perivascular cellular nodules, ductal stenosis (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	27-Month inhalation study, rabbit, LOAEL = 28 mg/m^3, dyspnea, cyanosis, shortness of breath, emphysema, vascular stenosis, alveolar cell infiltration, sclerosis, granulomatosis, lesions in the liver, spleen, and kidney (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Crystalline Silica		
	Silicosis in humans following extended workplace exposure (Measured)	NIOSH, 1978a	Adequate

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	2-Year inhalation study, rats, LOAEL = 1 mg/m^3, subpleural and peribronchial fibrosis, focal lipoproteinosis cholesterol clefts, enlarged lymph nodes, granulomatous lesions in the walls of large bronchi (Measured)	Rice, 2000	Adequate
	6-Month inhalation study, rats, LOAEL = 2 mg/m^3, increased collagen and elastin content in the lungs, induced type II cell hyperplasia in alveolar compartment and intralymphatic microgranulomas around bronchioles (Measured)	Rice, 2000	Adequate
	6-Month inhalation study plus 6-month recovery/incubation period, rats, LOAEL = 2 mg/m^3, increased lung weight, increased collagen, elastin, DNA, and protein content of lungs following incubation/recovery period (Measured)	Rice, 2000	Adequate
	Unspecified Silica		
	14-Day inhalation study, rats, LOAEL <0.017 mg/L, respiratory distress, increased lung weight, decreased kidney and liver weights, dose-dependent changes in lung characteristics (pale, spotted, spongy, alveolar interstitial pneumonia, early granulomata) (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	13-Week inhalation study, rats, LOAEL <0.001 mg/L, increased respiration rate, hematological effects, swollen and spotted lungs, increased lung weight, increased collagen content in lungs, enlarged mediastinal lymph node, accumulation of alveolar macrophages, granular material, cellular debris, focal interstitial fibrosis, cholesterol clefts, and ganuloma-like lesions (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	13-Week inhalation study, rats, LOAEL = 0.035 mg/L, decreased body weight, increased lung and thymus weight, swollen and spotted lungs, enlarge medistinal lymph node, increased numbers of alveolar macrophages, intra-alveolar leukocytes, and septal cellularity, focal necrosis, and slight atrophy of nasal epithelium (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	14-Day inhalation study, rats, LOAEL <0.046 mg/L, respiratory distress, increased lung weight, decreased liver weights, dose-dependent changes in lung characteristics (pale, spotted, spongy, alveolar interstitial pneumonia, early granulomata), accumulation of alveolar macrophages and particulate material in lungs (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	Up to 1 year inhalation study, rats, LOAEL <0.045 mg/L, enlarged and discolored lymph nodes, perivascular and peribronchiolar dust cell granuloma, necrotic cells (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.

Silicon Dioxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	13-Week oral dietary study, rats, LOAEL >8% diet (highest dose tested), no clinical signs or other findings (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	6-Month oral dietary study, rats, LOAEL >497 mg/kg/day (highest dose tested), no clinical signs or other findings (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	14-Day oral dietary study, rats, LOAEL >24,200 mg/kg/day (highest dose tested), no clinical signs or other findings (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
	4-Week oral dietary study, dog, LOAEL >800 mg/kg (highest dose tested), no clinical signs or other findings (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided. The original study was in an unpublished report.
Endocrine Disruption			No data

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4.2.11 Magnesium Hydroxide

Record ID: Magnesium Hydroxide	**CAS No.** 1309-42-8
HO−Mg−OH	**MW:** 58.32 **MF:** MgH_2O_2 **Physical Forms:** Solid **Use:** Flame retardant, additive
SMILES: O[Mg]O	
Name: Magnesium hydroxide	
Synonyms: Brucite, Milk of Magnesia	
Life-Cycle Considerations: Potential releases of magnesium hydroxide to the environment from its use in PCBs suggests that it may occur as a fugitive emission through dust-forming operations resulting from its manufacture or during loading/unloading, transfer, or mixing operations. 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).	

Magnesium Hydroxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	Decomposes at 350 ˚C to MgO and H_2O (Measured)	Lewis, 2000	Adequate
	Decomposes at 350 ˚C (Measured)	Lewis, 1997	Adequate
	Decomposes at 350 ˚C (Measured)	Hodgman, 1959	Adequate
	Decomposes at 380 ˚C (Measured)	IUCLID, 2000	Adequate
	350 (Measured)	Aldrich, 2006	Adequate
	350 (Measured)	Lide, 2000	Adequate
Boiling Point (°C)	The substance will decompose before boiling. (Measured)	IUCLID, 2000	Adequate
Vapor Pressure (mm Hg)	$<10^{-6}$ (Estimated)	Professional judgment	
Water Solubility (g/L)	0.009 at 18 °C (Measured)	Hodgman, 1959	Adequate
	0.04 at 100 °C (Measured)	Hodgman, 1959	Adequate
	0.009 at 18 °C (Measured)	IUCLID, 2000	Adequate

Magnesium Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		0.001 at 20 °C (Measured)	IUCLID, 2000	Adequate
		0.006 at 20 °C (Measured)	IUCLID, 2000	Adequate
		<0.008 at 20 °C (Measured)	IUCLID, 2000	Adequate
Log K_{ow}				No data
Flammability (Flash Point)		Not flammable (Estimated)	IUCLID, 2000	
Explosivity		Not explosive (Estimated)	IUCLID, 2000	
pH		9.5-10.5 (Measured)	Merck, 1996	Adequate
ENVIRONMENTAL FATE				
Transport		**The low water solubility, the estimated vapor pressure of $<10^{-6}$ torr, estimated K_{oc} of $>10^{5}$ and estimated Henry's Law Constant of $<10^{-8}$ atm-m^3/mol indicate that magnesium hydroxide will be relatively immobile in the environment. Magnesium hydroxide is a mineral found naturally in the environment.**		
	Henry's Law Constant – HLC (atm-m3/mole)	$<10^{-8}$ (Estimated)	Professional judgment	
	Sediment/Soil Adsorption/Desorption Coefficient – K_{oc}	$>10^{5}$ (Estimated)	Professional judgment	
	Dissociation constant in water			No data
Bioaccumulation		**LOW: Magnesium hydroxide is not expected to be bioaccumulative.**		
	Fish BCF	<500 (Estimated)	Professional judgment	
	Daphnids BCF			No data
	Green Algae BCF			No data
	Oysters BCF			No data
	Earthworms BCF			No data
	Metabolism in fish			No data

Magnesium Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Persistence		**HIGH: As a fully oxidized inorganic material, magnesium hydroxide is not expected to biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Magnesium hydroxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for magnesium hydroxide under typical environmental conditions were identified.**		
Water	**Aerobic biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Volatilization Half-life for Model River	>1 year (Estimated)	Professional judgment	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	Professional judgment	
	Ready Biodegradability	Not ready biodegradable (Estimated)	Professional judgment	
Soil	**Anaerobic biodegradation**	Recalcitrant (Estimated)	Professional judgment	
	Soil biodegradation w/ product identification			No data
	Sediment/water biodegradation			No data
Air	**Atmospheric Half-life**	>1 year (Estimated)	Professional judgment	
Reactivity	**Photolysis**	Not a significant fate process (Estimated)	Professional judgment	Magnesium hydroxide does not absorb UV light at environmentally relevant wavelengths and is not expected to undergo photolysis.
	Hydrolysis	Not a significant fate process (Estimated)	Professional judgment	Magnesium hydroxide is a fully oxidized inorganic material and is not expected to undergo hydrolysis.
	Pyrolysis	Not a significant fate process (Estimated)	Professional judgment	

Magnesium Hydroxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class			
Acute Toxicity	**LOW: The estimated LC_{50} values for all of the species in the standard toxicity profile are greater than 100 mg/L.**		
Fish LC_{50}	96-hour LC_{50} = 1110 mg/L (Estimated)	Mount et al., 1997	Estimated from the measured LC_{50}s for $MgCl_2$ and $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$.
Daphnid LC_{50}	48-hour LC_{50} = 648 mg/L (Estimated)	Mount et al., 1997; Biesinger and Christensen, 1972	Estimated from the measured LC_{50}s for $MgCl_2$ and $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$.
Green Algae EC_{50}	96-hour EC_{50} = 2111 mg/L (Estimated)	Professional judgment	Estimated using an acute to chronic ratio of 4.
Other Invertebrate LC_{50}	*Gammarus lacustris* LC_{50} = 64.7 mg/L (Measured)	O'Connell et al., 2004	Secondary source, study details and test conditions were not provided.
Chronic Toxicity	**LOW: The estimated chronic values are all greater than 10 mg/L.**		
Fish ChV	403 mg/L (Estimated)	Professional judgment	Estimated using an acute to chronic ratio of 3.3. This ratio is for daphnids and has not been validated for use with fish.
Daphnid ChV	197 mg/L (Estimated)	Suter, 1996	Estimated from the measured ChV for Mg^{2+} ion, modified by a molecular weight adjustment for $Mg(OH)_2$.
Green Algae ChV	528 mg/L (Estimated)	ECOTOX database	Estimated from the measured NOEC and LOEC for $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$.

Magnesium Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
HUMAN HEALTH EFFECTS				
Absorption		About 5-15% of ingested magnesium is absorbed and this is readily excreted in the urine, if kidney function is normal. (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided.
Acute Toxicity		**LOW: Weight of evidence suggests that magnesium hydroxide is of low concern for acute toxicity. Magnesium hydroxide is categorized by the U.S. Food and Drug Administration (FDA) as a Generally Recognized As Safe (GRAS) food ingredient.**		
Acute Lethality	**Oral**	Rat oral LD_{50} = 8500 mg/kg bw (Measured)	Lewis, 2000	Secondary source, study details and test conditions were not provided.
		Mouse oral LD_{50} = 8500 mg/kg bw (Measured)	Lewis, 2000	Secondary source, study details and test conditions were not provided.
		Human infant oral TD_{Lo} (behavioral) = 2747 mg/kg bw (Measured)	Lewis, 2000	Secondary source, study details and test conditions were not provided.
		Probable human oral lethal dose = 5-15 g/kg bw (Estimated)	HSDB, 2008	Secondary source, study details and test conditions were not provided.
	Dermal			No data
	Inhalation			No data
Other Acute Effects	**Eye Irritation**	Moderately irritating to rabbit eyes. (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not provided.
		Administration of milk of magnesia twice a day for 3-4 days caused damage to corneal epithelium of rabbit eyes; however, effects disappeared within 2-3 days. (Measured)	HSDB, 2008	Secondary source, study details and test conditions were not provided.
	Dermal Irritation			No data

Magnesium Hydroxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	Skin Sensitization	**LOW: Magnesium hydroxide is not estimated to cause skin sensitization based on professional judgment.**		
				No data
Reproductive Effects		**LOW: Based a nonstandard experimental study indicating magnesium hydroxide produces no adverse effects on reproductive performance or outcomes at levels up to 96 mg/kg/day of Mg^{2+} ion and professional judgement, magnesium hydroxide is expected to be of low concern for reproductive effects.**		
	Reproduction/ developmental toxicity screen	10-day (GD 6-15) reproductive/developmental study on $MgCl_2$, rat, oral, no maternal or reproductive effects, NOAEL > 96 mg/kg/day for Mg^{2+} ion. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.
	Combined repeated dose with reproduction/developmental toxicity screen			No data
	Reproduction and fertility effects			No data
Developmental Effects		**LOW: Based on weight of evidence from a nonstandard experimental study indicating magnesium hydroxide produces no adverse effects on reproductive performance or outcomes at levels up to 96 mg/kg/day of Mg^{2+} ion and an experimental study from a secondary source showing no effect on human newborns, magnesium hydroxide is expected to be of low concern for reproductive effects.**		
	Reproduction/ developmental toxicity screen	10-day (GD 6-15) reproductive/developmental study on $MgCl_2$, rat, oral, no maternal or reproductive effects, NOAEL > 96 mg/kg/day for Mg^{2+} ion. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.
	Combined repeated dose with reproduction/ developmental toxicity screen	Repeated-dose/developmental study (3rd trimester), humans, no effect on newborns except slightly increased body weight and hypermagnesiumemia. Cord serum Mg levels reported to be	HSDB, 2008	Secondary source, study details and test conditions were not provided.

Magnesium Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		70-100% of maternal levels (potentially causing neurological depression in neonate, characterized by respiratory depression, muscle weakness, decreased reflexes). Prolonged magnesium treatment during pregnancy may be associated with maternal and fetal hypocalcemia and adverse effects on fetal bone mineralization. (Measured)		
	Prenatal development			No data
Carcinogenicity		**LOW: Experimental studies and structure-activity relationships indicate that magnesium hydroxide is of low concern for carcinogenicity.**		
	OncoLogic Results	Low for magnesium (Estimated)	OncoLogic	
	Carcinogenicity (rat and mouse)	5-week, repeated-dose/carcinogenicity study, diet, rat, decreased carcinogen-induced increase in DNA synthesis in the large bowel epithelial cells, NOAEL > 2000 ppm (approximately 100 mg/kg/day). (Measured)	BIBRA, 1993	Secondary source, study details and test conditions were not provided.
	Combined chronic toxicity/ carcinogenicity	96-week chronic toxicity/carcinogenicity study on $MgCl_2$, oral, mouse, no significant differences in tumor incidence between treated and control animals except for dose-related decrease in the incidence of hepatocellular carcinomas in males. (Measured)	Kurata et al., 1989	Adequate
		227-day, chronic toxicity/ carcinogenicity study, diet, rat, decreased number of colon tumors in rats pretreated with a known colon carcinogen, NOAEL > 50 mg/kg/day. (Measured)	BIBRA, 1993	Secondary source, study details and test conditions were not provided.

Magnesium Hydroxide				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
		16-week carcinogenicity study, diet, rat, inhibitory effects on colon carcinogenesis, carcinogen-induced expression of *c-myc* proto-oncogene and cell proliferation, NOAEL = 0.2%. (Measured)	Wang et al., 1993	Adequate
		Inhalation exposure of male rats to short (4.9 x 0.31 mm) or long (12 x 0.44 mm) $MgSO_4/5Mg(OH)_2\ 3H_20$ filaments for 6 hr/day, 5 day/wk for up to 1 year did not increase the incidence of any tumor types in animals sacrificed 1 day or 1 year after cessation of exposure. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.
Immunotoxicity		**LOW: Magnesium hydroxide is expected to be of low hazard for immunotoxicity based on professional judgment.**		
	Immune system effects			No data
Neurotoxicity		**LOW: Magnesium hydroxide is expected to be of low hazard for neurotoxicity based on professional judgment.**		
	Acute and 28-day delayed neurotoxicity of organophosphorus substances (hen)			No data
	Neurotoxicity screening battery (adult)			No data
	Developmental neurotoxicity			No data
Genotoxicity		**LOW: An experimental study from secondary sources indicates that magnesium hydroxide is not genotoxic to bacteria.**		
	Gene mutation in vitro	Negative, Ames Assay in *Salmonella* and *E. coli* (Measured)	BIBRA, 1993	Secondary source. Only 3 strains of *Salmonella* were tested; current regulatory guidelines suggest that

Magnesium Hydroxide				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
				at least 4 strains be used in Ames tests. Study details and test conditions were not provided.
	Gene mutation in vivo			No data
	Chromosomal aberrations in vitro			No data
	Chromosomal aberrations in vivo			No data
	DNA damage and repair			No data
	Other (Mitotic Gene Conversion)			No data
Systemic Effects		**LOW: Experimental studies indicate magnesium ions produce no adverse systemic effects in rats or mice at magnesium levels equivalent to over 1,000 mg/kg/day magnesium hydroxide.**		
		96-week repeated-dose study for $MgCl_2$, mouse, oral, decreased body weight gain, increased food/water consumption and increased relative brain, heart and kidney weights in high dose females, no effects in males, female LOAEL = 470 mg/kg/day for Mg^{2+} ion. (Measured)	Kurata et al., 1989	Adequate
		90-day repeated-dose study for $MgCl_2$, mouse, oral, decreased body weight gain in males and females, renal tubular vacuolation in males, LOAEL = 650 mg/kg/day for Mg^{2+} ion. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.

Magnesium Hydroxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	90-day repeated-dose study for $MgCl_2$, mouse, oral, decreased body weight gain, renal tubular vacuolation in males, female NOAEL = 587 mg/kg/day for Mg^{2+} ion, male NOAEL = 420 mg/kg/day for Mg^{2+} ion. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.
	32-week repeated-dose study, rat, oral (dietary), no effects on body weight or liver weight when administered at 1000 ppm (approximately 50 mg/kg/day). (Measured)	BIBRA, 1993	Secondary source, study details and test conditions were not provided.
	Inhalation exposure of male rats to short (4.9 x 0.31 mm) or long (12 x 0.44 mm) $MgSO_4/5Mg(OH)_2$ $3H_20$ filaments for 6 hr/day, 5 day/wk for up to 1 year exhibited a slight increased in the incidence of pulmonary lesions 1 year after cessation of exposure. Histopathological examination revealed a slight increase in segmental calcification of the pulmonary artery and thickening of the lung pleura in rats exposed to both short and long filaments for 4 weeks or 1 year. There were no effects on survival or body, lung, liver, kidney and spleen weights of animals sacrificed 1 day or 1 year following a 1-year exposure period. (Measured)	NAS, 2000	Secondary source, study details and test conditions were not provided.
	4-week repeated-dose study, oral, human, 400 mg/day, diarrhea, abdominal discomfort, increased serum magnesium levels. (Measured)	BIBRA, 1993	Secondary source, study details and test conditions were not available.

Magnesium Hydroxide			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
	Human Systemic Effects: chlorine level changes, coma, somnolence. (Measured)	Lewis, 2000	Secondary source, study details and test conditions were not available.
	Repeated use in humans may rarely cause rectal stones composed of magnesium carbonate and magnesium hydroxide. (Measured)	IUCLID, 2000	Secondary source, study details and test conditions were not available.
Endocrine Disruption			No data

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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 PCBs. In Sections 5.1 through 5.4, this chapter provides general background regarding potential exposure pathways that can occur during different life-cycle stages, discusses factors that affect exposure potential in an industrial setting, provides process descriptions for the industrial operations involved in the PCB manufacturing supply chain (identifying the potential primary release points and exposure pathways) and discusses potential consumer and environmental exposures. Following this general discussion, Section 5.5 highlights life-cycle considerations for the seven 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 analysis 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-retarded 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 TBBPA as reactive FR)

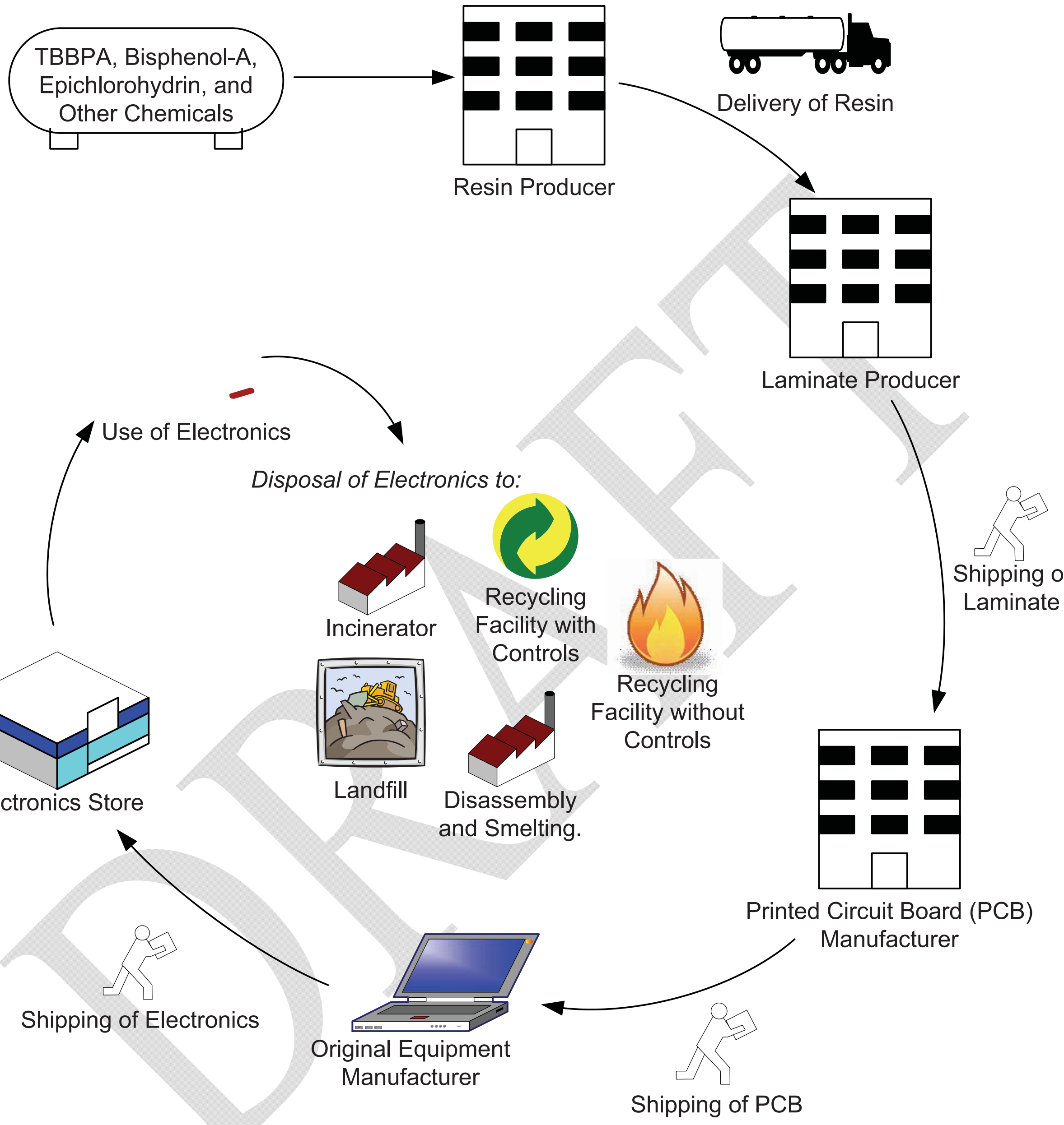


Table 5-1: Potential Exposure to Flame-Retardant Chemicals throughout Their Life Cycle in PCBs

Reactive FRs	
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. Reactive FRs are part of the polymer (chemically bound), and only trace amounts of unreacted FR 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	*Disassembly / Recycling:* Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Reactive FRs 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 FRs may become mobilized through direct intervention processes, such as shredding, are unknown. *Landfill*: Testing needs to be conducted to determine exposure potential from leaching from PCBs. *Incineration*: Combustion byproducts need to be considered (see combustion experiments). *Smelting*: Combustion byproducts need to be considered (see combustion experiments). *Open Burning*: Combustion byproducts need to be considered (see combustion experiments).
Additive FRs	
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 FRs 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 FRs are embedded in the polymer matrix.
End of Life	*Disassembly/Recycling:* Disassembling electronics and shredding PCBs can release dust that contains epoxy resin. Additive FRs 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. *Landfill*: Testing needs to be conducted to determine exposure potential from leaching from PCBs. *Incineration*: Combustion byproducts need to be considered (see combustion experiments). *Smelting*: Combustion byproducts need to be considered (see combustion experiments). *Open Burning*: Combustion byproducts need to be considered (see combustion experiments).

*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, dispersibility, log K_{ow}, BCF, 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 Section 4.1.2, Physical/Chemical Property Endpoints. More detailed information on physical, chemical, and fate properties of each flame-retardant chemical can be found in the full chemical summary assessments in Section 4.2.

Table 5-2: Key Physical/Chemical and Fate Properties of FR Chemicals

<table>
<tr><td colspan="11">Physical state of chemical</td></tr>
<tr><td colspan="11"><i>Relevance</i>: Indicates if the chemical substance is a solid, liquid, or gas under ambient conditions. Determined from its melting and boiling points.</td></tr>
<tr><td colspan="11"><i>Potential exposure</i>: One of the chemical properties used to determine the 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 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).</td></tr>
<tr><td>TBBPA</td><td>D.E.R. 538</td><td>DOPO</td><td>Dow XZ-92547</td><td>Fyrol PMP</td><td>Representative Fyrol PCB Resin</td><td>Aluminum Hydroxide</td><td>Exolit OP 930</td><td>Melapur 200</td><td>Silicon Dioxide</td><td>Magnesium Hydroxide</td></tr>
<tr><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td><td>Solid</td></tr>
<tr><td colspan="11">Vapor pressure at 25°C (mm Hg)</td></tr>
<tr><td colspan="11"><i>Relevance</i>: Indicates the potential for a chemical to volatilize to the atmosphere. If a chemical has a vapor pressure amenable to volatilization, then the chemical will evaporate and present the potential for a person to inhale the vapor.</td></tr>
<tr><td colspan="11"><i>Potential exposure</i>: For flame retardants, exposure may occur through inhalation of gas-phase chemicals if the chemical vapor pressure is greater than 1×10^{-6} mm Hg.</td></tr>
<tr><td>TBBPA</td><td>D.E.R. 538</td><td>DOPO</td><td>Dow XZ-92547</td><td>Fyrol PMP</td><td>Representative Fyrol PCB Resin</td><td>Aluminum Hydroxide</td><td>Exolit OP 930</td><td>Melapur 200</td><td>Silicon Dioxide</td><td>Magnesium Hydroxide</td></tr>
<tr><td>$<8.9 \times 10^{-8}$</td><td>$<1 \times 10^{-6}$</td><td>2.2×10^{-5}</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td></tr>
<tr><td colspan="11">Water solubility (g/L)</td></tr>
<tr><td colspan="11"><i>Relevance</i>: Indicates the potential of a chemical to dissolve in aqueous solutions. Chemicals with higher water solubility are more likely to be transported into groundwater, absorbed through gastrointestinal tract or lungs, partition to aquatic compartments, undergo atmospheric removal by rain washout, and present a higher potential for human and environmental exposure through the ingestion of contaminated drinking water.</td></tr>
<tr><td colspan="11"><i>Potential exposure</i>: In general, chemicals with water solubility less than 10^{-6} g/L have a low exposure potential to aquatic and human populations due to their low bioavailability.</td></tr>
<tr><td>TBBPA</td><td>D.E.R. 538</td><td>DOPO</td><td>Dow XZ-92547</td><td>Fyrol PMP</td><td>Representative Fyrol PCB Resin</td><td>Aluminum Hydroxide</td><td>Exolit OP 930</td><td>Melapur 200</td><td>Silicon Dioxide</td><td>Magnesium Hydroxide</td></tr>
<tr><td>1.2×10^{-6}</td><td>$<1 \times 10^{-6}$</td><td>0.51</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>$<1 \times 10^{-6}$</td><td>Insoluble in H_2O</td><td><0.001*
2.5**</td><td>20</td><td>0.12, amorphous</td><td>0.006</td></tr>
</table>

Table 5-2: Key Physical/Chemical and Fate Properties of FR Chemicals

Dispersibility										
Relevance: Indicates a chemical's potential to form a dispersion in an aqueous solution. Ideally, this information can be obtained from the scientific literature. In the absence of experimental data, dispersibility can be determined from chemical structure and/or comparison to closely related analogs. There are two general structural characteristics that lead to the formation of dispersions in water. The first type consists of those chemicals that have both a hydrophilic (polar) head and a hydrophobic (non-polar) tail. The second type consists of relatively large molecules that have a large number of repeating polar functional groups (e.g., polyethylene oxide).										
Potential exposure: Dispersibility should be considered when assessing a chemical's water solubility. The potential for a chemical to form a dispersion influences its potential for exposure, environmental fate, and toxicity. The potential for human and environmental exposure, leach ability, and aquatic toxicity of dispersible chemicals is greater than what might be anticipated based on the material's water solubility alone.										
TBBPA	D.E.R. 538	DOPO	Dow XZ-92547	Fyrol PMP	Representative Fyrol PCB Resin	Aluminum Hydroxide	Exolit OP 930	Melapur 200	Silicon Dioxide	Magnesium Hydroxide
None of the flame-retardant chemicals assessed in this project are anticipated to form dispersions.										
Log K_{ow}										
Relevance: Indicates the 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 than in water, while a low log K_{ow} value means that the chemical is more soluble in water than in octanol.										
Potential exposure: 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 not well absorbed, chemicals with a log K_{ow} of 5-6 tend to bioconcentrate, and chemicals with a high log K_{ow} tend to bind to organic matter in soils and in suspended sediment in water.										
TBBPA	D.E.R. 538	DOPO	Dow XZ-92547	Fyrol PMP	Representative Fyrol PCB Resin	Aluminum Hydroxide	Exolit OP 930	Melapur 200	Silicon Dioxide	Magnesium Hydroxide
5.90	11	1.87	No data	No data	No data	No data	-0.44	No data	No data	No data
BCF										
Relevance: Indicates the degree to which a chemical concentrates in an organism relative to its surroundings.										
Potential exposure: Chemicals that have the potential to bioconcentrate generally are anticipated to bioaccumulate in higher trophic levels. As chemicals bioconcentrate (or bioaccumulate), there is a higher potential for them to reach levels within an organism where toxic effects may be expressed.										
TBBPA	D.E.R. 538	DOPO	Dow XZ-92547	Fyrol PMP	Representative Fyrol PCB Resin	Aluminum Hydroxide	Exolit OP 930	Melapur 200	Silicon Dioxide	Magnesium Hydroxide
300	3.2	5.4	<100	<100	<100	<500	<500	<500	<500	<500

Table 5-2: Key Physical/Chemical and Fate Properties of FR Chemicals

Persistence										
Relevance: Indicates the length of time a chemical is anticipated to remain unchanged after it is released into the environment.										
Potential exposure: The longer a chemical lasts in the environment, the higher the likelihood for human or environmental exposure.										
TBBPA	D.E.R. 538	DOPO	Dow XZ-92547	Fyrol PMP	Representative Fyrol PCB Resin	Aluminum Hydroxide	Exolit OP 930	Melapur 200	Silicon Dioxide	Magnesium Hydroxide
Moderate Hazard (M) in all compartments (Experimental)	M in water, (EPI Estimate); M in other compartments (Professional Judgment)	Low Hazard (L) in water (EPI Estimate); L in other compartments (Professional Judgment)	High Hazard (H) in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)	M in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)	H in all compartments (Professional Judgment)
*GLP test conditions, Guideline 92/69/EEC A.6. For more information, see Section 4.2.6. **Ideal conditions, thermodynamic limit. For more information, see Section 4.2.6.										

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. Therefore, a risk evaluation should address occupational exposures separately from environmental and general population exposures.

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 non-volatile 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.

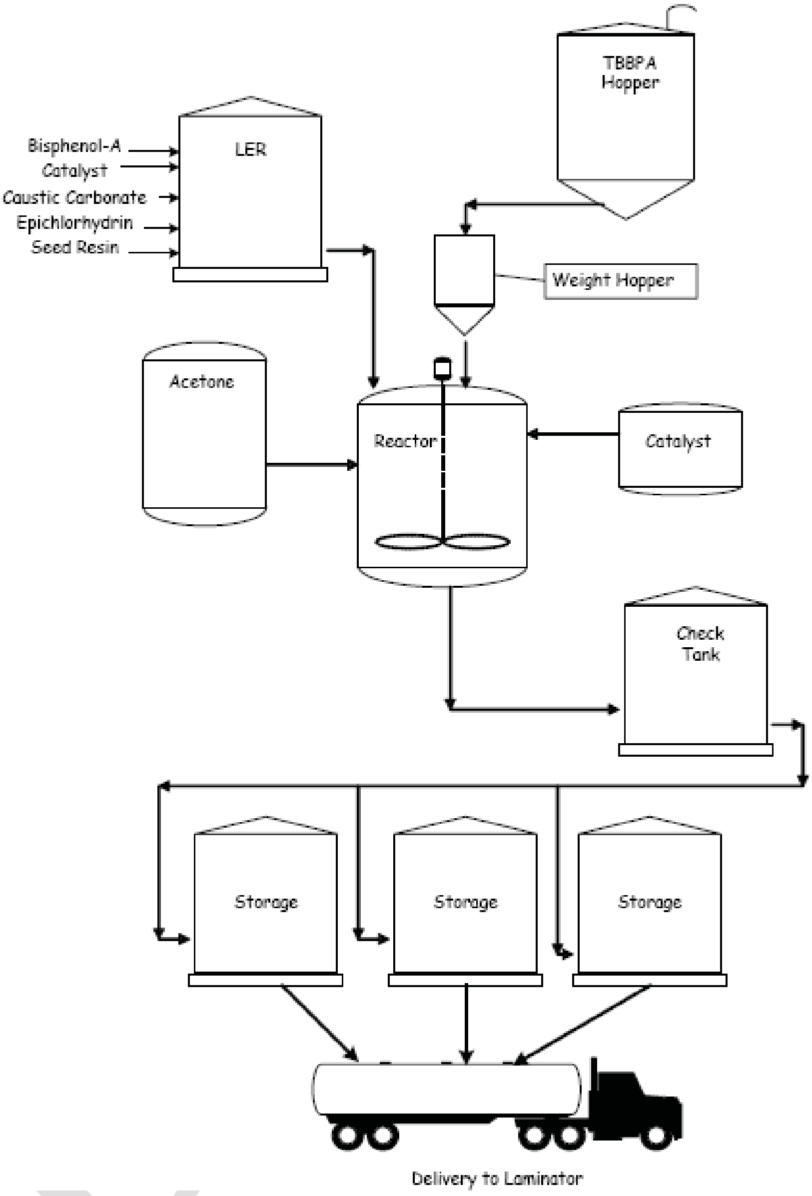
5.2.1 Flame Retardant and Epoxy Resin Manufacturing

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 FR-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 (LER) 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-retarded 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 Figures 5-3 and 5-4, can result in occupational exposures to process chemicals if protective measures are not put in place. The potential release of FR 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-retarded 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

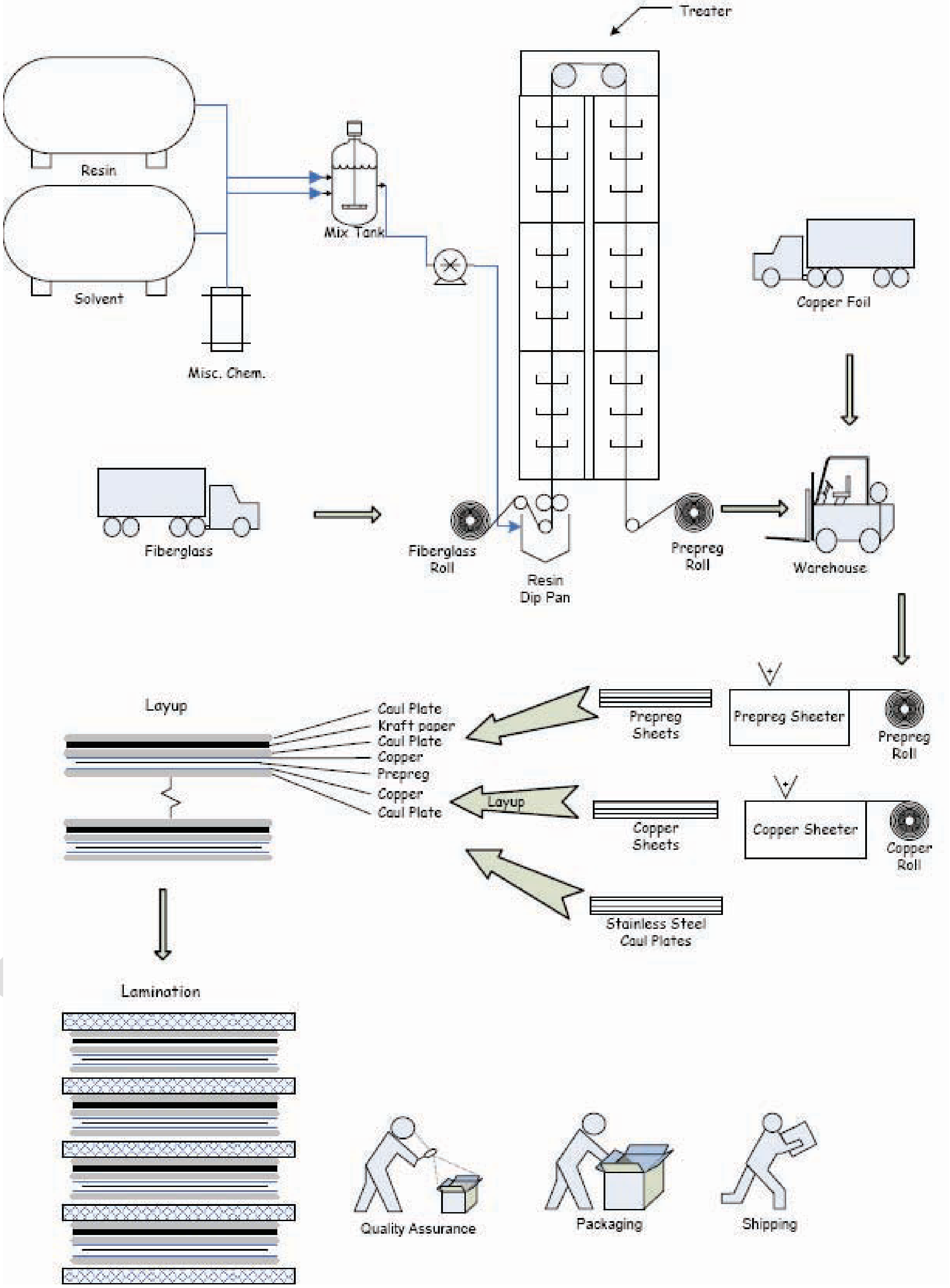
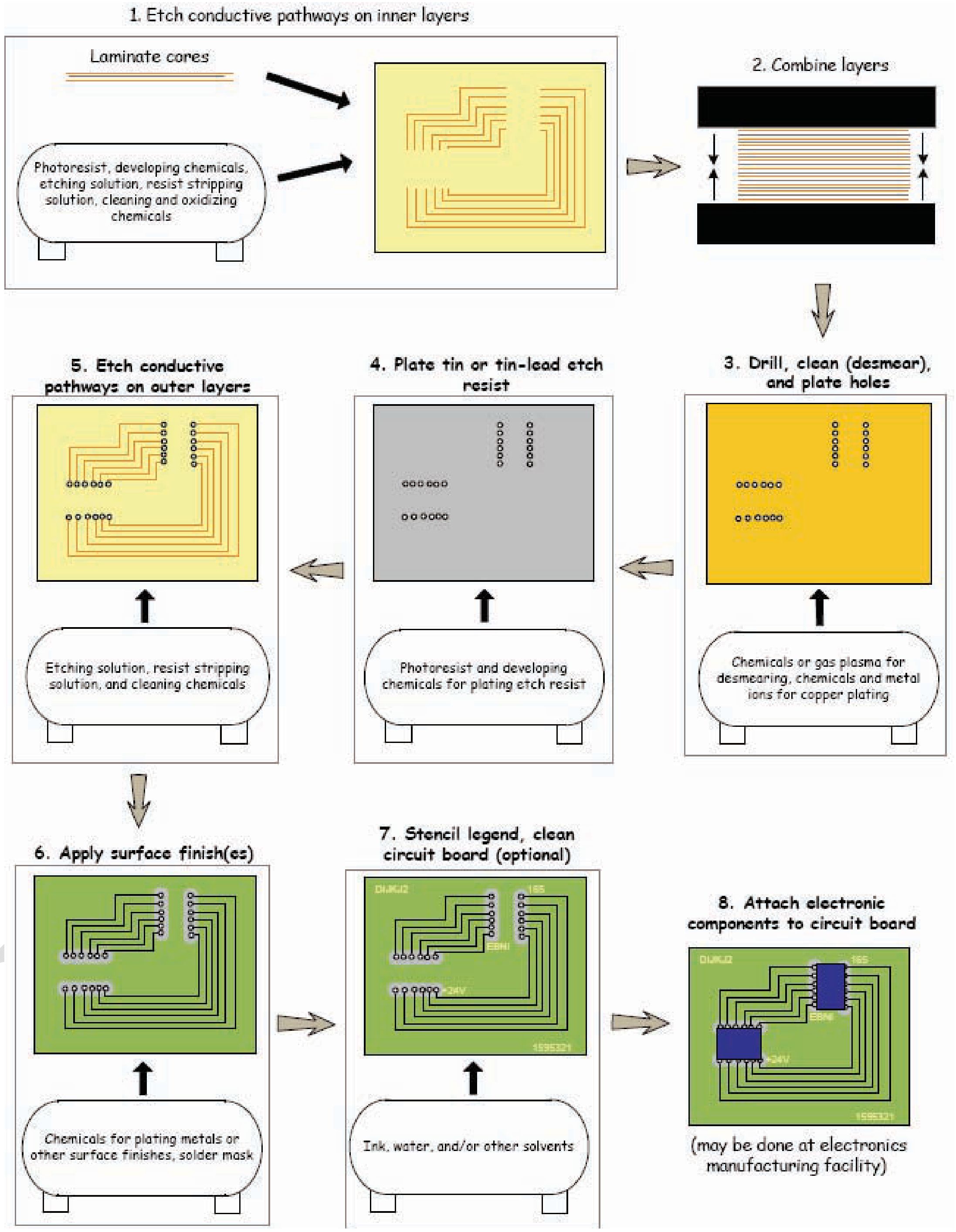


Figure 5-4: Printed Circuit Board Manufacturing Process



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 decabromodiphenylether 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-retarded 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.

Additive Versus Reactive Flame Retardants

As discussed in Chapter 3, flame-retardant chemicals can be classified as either additive or reactive. 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. Most PCBs currently 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 analogues 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).

Properties Affecting Transport in the Environment

If a chemical is released into the environment, either from the finished PCB or directly from an industrial facility, there still may not be significant exposures unless there is a potential for the chemical to travel from the source to the receptor. Primary mechanisms of transport include the water supply and air dispersion. Many factors affect movements of chemicals throughout these media. However, a few chemical properties can provide a good screening-level indication of which pathway(s) a chemical is likely to take.

Water Solubility

Water solubility is an indicator of the amount of chemical that will dissolve in aqueous solutions. Chemicals with high water solubility will readily dissolve. This indicates a potential for the chemical to be transported long distances in rainwater and surface water runoff from the point of release. High water solubility also means the chemical is less likely to settle or precipitate as a solid at the bottom of a receiving stream; it may become dispersed throughout a drinking water supply that is eventually ingested by the general population.

Octanol/Water Partition Coefficient (Log K_{ow})

The log K_{ow} is a chemical-specific parameter that reflects the hydrophobicity of the chemical, meaning the tendency for the chemical to partition from water to organic phases (e.g., organic matter in soil or water, or lipids in organisms like fish). A high partition coefficient value means that the chemical is more soluble in octanol than in water, while a low partition coefficient value means that the chemical is more soluble in water than in octanol. Some chemicals may initially be released on the ground; however, they are quickly absorbed by organic materials in the soil. In this instance, the chemical may never be transported to a water supply. Chemicals that readily dissolve in water are more likely to find their way to an underground water supply. The octanol/water partition coefficient can be used to evaluate potential aquatic exposure and potential exposure of the general population via ingestion.

Vapor Pressure

Vapor pressure can be used to assess the amount of chemical that vaporizes into the gas phase (from solution or from a finished article). Similarly, the Henry’s Law Constant indicates the amount of chemical that will volatilize from an aqueous solution. A high vapor pressure and

Henry's Law Constant indicates a higher potential for the chemical to enter the vapor phase and be transported long distances through ambient air. These parameters can be used to evaluate potential exposure of the general population via inhalation.

Persistence and Bioaccumulation

If a chemical is released, there still may be little or no potential for environmental and general population exposures. This potential is affected by the fate of the chemical in the environment and its ability for uptake by the receptor organism. Two parameters affecting fate components of the exposure pathway are persistence and bioaccumulation.

Persistence

Many natural phenomena can degrade or destroy chemicals. Factors that can contribute to degradation include exposure to light, reactivity with air and water, and microbial activity. The ability of a chemical to persist in the environment can be measured by its half-life. This is the amount of time required for half of the chemical to be degraded. The half-life can be measured (or estimated) for different media (e.g., half-life in air and half-life in water). Chemicals with a very long half-life are said to be persistent. Half-life can be used to describe the persistence of chemicals, as well as their expected degradation products.

Bioaccumulation

The toxicological effects exhibited for some endpoints depend on the ability of the chemical to be absorbed in tissue, and remain for extended periods of time. This general concept is referred to as bioaccumulation. Chemicals that are highly bioaccumulative pose greater concerns. Bioaccumulation can be measured or estimated by analyzing a number of parameters, including the fish bioconcentration factor (BCF). BCFs can be used to evaluate the bioaccumulation potential of chemicals.

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, at the moment little information exists in the literature 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 (Kemmlein et al., 2003). Beard and Marzi (2006) investigated the offgassing potential of thermoplastic polymers containing phosphorus-based and brominated FRs 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 generated annually in the United States is growing rapidly. According to a recent 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 United States, 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.[9] A recent 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 (CRTs) 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

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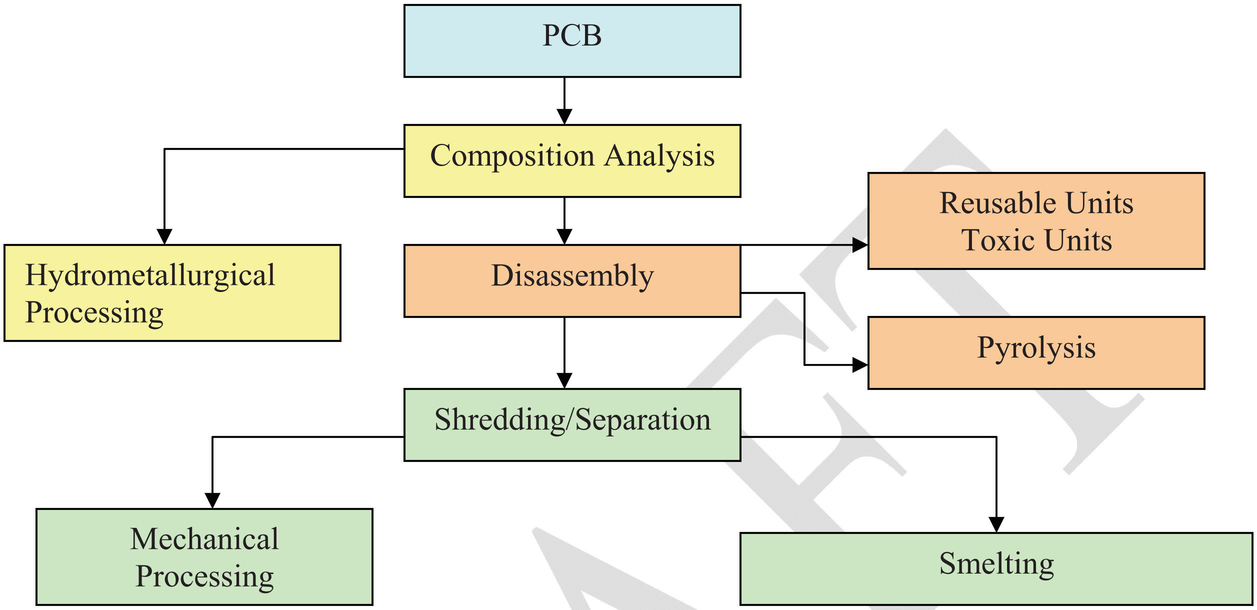
[9] According to a 2005 UN report, up to 50 million metric tons of e-waste is generated annually. In the United States, the amount of e-waste is increasing at three times the rate of general waste. http://www.rrcap.unep.org/policy2/13-Annex%204a-e-wastes%20SEPD2.pdf; http://news.yahoo.com/s/nm/20070611/lf_nm/china_ewaste_dc.

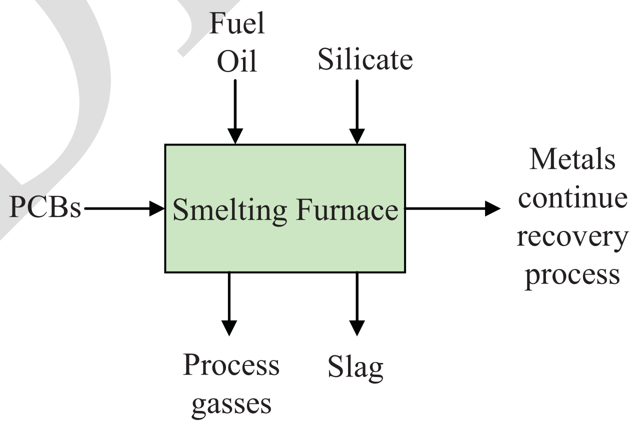
employed. Many recycling operations employ these methods in safe conditions that minimize the potential for exposure, and recover valuable metals that are part of finished boards.

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 FRs 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, 2005). 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 (Umicore, 2006). However, the three primary smelters in the world – 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. Greenpeace recently 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, PBDEs, and polychlorinated biphenyls (Greenpeace, 2005).

In terms of the size of the population potentially at risk from open burning practices, the local government Web site 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 last year 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

Electronic 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.

To date, most leachability studies 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 (BFRs), and in general, have found either no or very small concentrations of brominated compounds in the leachate. When BFRs are added versus reacted into the resin system, the potential for the BFRs to leach from PCBs is much greater (KemI, 1995).

A recent 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’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 is currently 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, Tables 5-3 and 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	Inhalation exposure: 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. Dermal exposure: EASE model used to estimate "typical" and "worst-case" dermal values for bromination and other laminate production steps.	Sampling results from 2002 study at UK laminate manufacturing facility; EASE model
Computer recycling	Inhalation exposure: 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. Dermal exposure: EASE model used to estimate dermal exposure values. Predicted to be very low; consequently, dermal exposure values not used by EU in exposure assessment.	Sampling results from 2002 study at UK recycling facility; EASE model
PCB Assembly	Inhalation exposure: 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. Dermal exposure: Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.	Sjodin et al., 2001; professional judgment of risk assessors
Office environment	Inhalation exposure: 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. Dermal exposure: Dermal exposure assumed to be negligible given the low levels of free TBBPA in PCBs.	Sjodin et al., 2001; professional judgment of risk assessors
Plastic recycling	Inhalation exposure: EASE model used to predict "typical" and "worst-case" inhalation values. Dermal exposure: EASE model predicted dermal exposure to be very low; consequently, dermal exposure values not used by EU in exposure assessment.	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 lifecycle 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 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 EBFRIP
	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 FR 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 FRs volatilize at same release factor as additive FRs.	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 FR.	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 FR) 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 seven 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

Tetrabromobisphenol A (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 Stated 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 liquify, 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.

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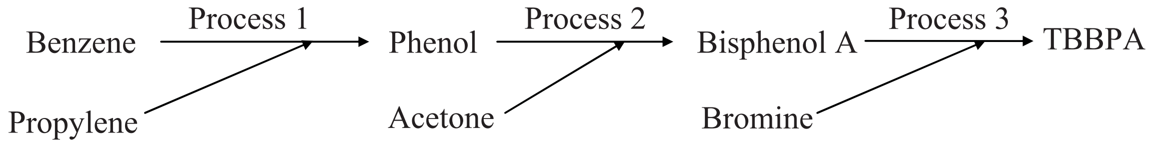
TBBPA is produced by brominating bisphenol A (BPA) in the presence of solvent. This reaction is highly exothermic, and no catalyst is required. Co-products will depend on the solvent used and the process conditions. The use of some solvents results in co-products, while the use of other solvents does 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.

TBBPA is commercially produced by Albemarle Corporation (Magnolia, AR) and Chemtura (El Dorado, AR). Both corporations use proprietary processes that do not yield methyl bromide (Haneke, 2002).

While commercially employed bromination processes are proprietary, most involve bromination of bisphenol A. 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.

Figure 5-7: Common Reactants and Processes Involved in TBBPA



Process (1): Cumene hydroperoxide rearrangement involving benzene and propylene to form phenol – this is the most common industrial process for producing phenol, accounting for approximately 97 percent of phenol production. Acetone is also formed as a coproduct (Plotkin 2006). Process (2): Condensation reaction between phenol and acetone to produce bisphenol A. Process (3): Bromination of bisphenol A to produce TBBPA. In the absence of an oxidant, HBr would be produced as a coproduct. Hydrogen peroxide can be used to convert HBr back to Br_2, forming water and avoiding this problem.

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 are currently limited. 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). Recent 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.438). 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. 538, 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. 538 present in the laminate and, subsequently, the PCBs produced. The amount of free D.E.R. 538 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.

Bisphenol A, the unbrominated precursor to TBBPA, may also pose potential hazards to human health and the environment. The European Union's risk assessment of bisphenol A 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).

Use and End of Life

Since TBBPA is reacted with an epoxy resin to form D.E.R. 538, which is then reacted with a hardener to form a crosslinked polymer low levels of unreacted TBBPA and D.E.R. 538 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 difunctional, 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 byproducts 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 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 P_4 molecule. P_4, 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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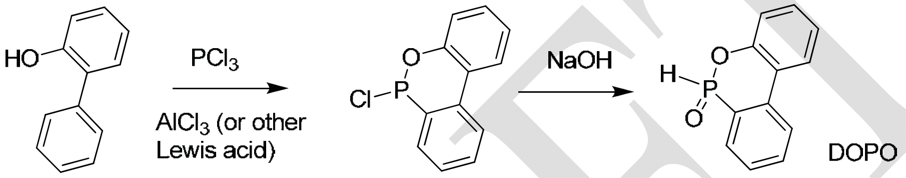
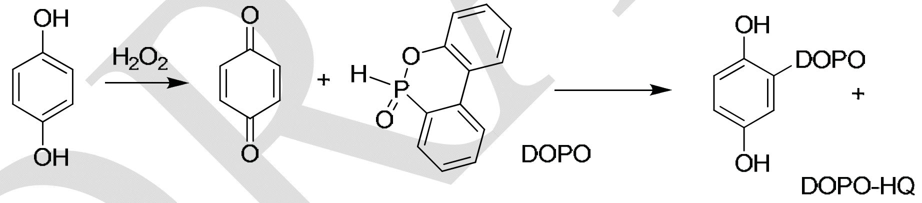
Chemistry that can be used to make DOPO is shown below. The byproducts of this chemistry are salts of the Lewis acid (such as aluminum chlorohydrates) and NaCl from the second step.



Further chemistry must be performed to react DOPO into the thermoset backbone. The largest manufacturer of organophosphorus flame retardants for electrical laminates is currently 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 molecular weight and functionality. Leaching of DOPO is more likely given its relatively low molecular weight 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.

Manufacture of Flame Retardant, Laminate, and PCB

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

The reaction product of Fyrol PMP with resin has the potential to be released to the environment as a result of 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). Unreacted reaction product may be present in the laminate and subsequently, the PCBs produced. The amount of free reaction product is generally anticipated to be low given that it is incorporated as a reactive flame retardant, but quantitative data on the amount of free material that may be present are currently not available. 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, 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. It is unlikely that the Fyrol PMP reaction product will leach from PCBs deposited in landfills given its low water solubility, high molecular weight, and hydrolytic instability. 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 Hydroxide

Raw Material Extraction

Aluminum is one of the most plentiful elements in the Earth's crust, and is usually present as bauxite ore. Bauxite can contain three different aluminum minerals, including gibbsite ($Al(OH)_3$), and böhmite and diaspore (different crystalline structures of AlO(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 United States 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 ($Al(OH)_3$) can be isolated following the precipitation step (see process steps below) (International Aluminium, 2000). More than 90 percent of domestic bauxite conversion to alumina occurs 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:

   Gibbsite: $Al(OH)_3 + NaOH \rightarrow Na^+\ Al(OH)_4^-$
   and
   Böhmite and Diaspore: $AlO(OH) + NaOH + H_2O \rightarrow Na^+\ Al(OH)_4^-$

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:

   $Na^+\ Al(OH)_4^- \rightarrow Al(OH)_3 + NaOH$

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.)

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

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 ≈ 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).

5.5.5 Exolit OP930

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 Exolit OP930 may occur through dust-forming operations from its manufacture or during loading/unloading, transfer, or mixing operations. No additional information regarding the manufacture of Exolit OP930 was available at the time of publication due to the chemical's proprietary nature.

Use and End of Life

As an additive flame retardant, Exolit OP930 may also be released from laminates and PCBs. After incorporation into the resin and/or the laminate, potential releases of Exolit OP930 during the useful life cycle of PCBs is not anticipated, except by an extractive processes upon contact with water. Potential releases of Exolit OP930 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.

5.5.6 Melapur 200

Raw Material Extraction

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

Manufacture of Flame Retardant, Laminate, and PCB

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 Melapur 200 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 Melapur 200 during the useful life cycle of PCBs is not anticipated, except by an extractive process upon contact with water. Potential releases of Melapur 200 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.

5.5.7 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). 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 pariciulate, 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 FRs are preferred since silicon dioxide is used as a flux in the process (Lehner, 2008).

5.5.8 Magnesium Hydroxide

Raw Material Extraction

There are several million tons of mineral magnesium hydroxide, called brucite, in the 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).

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Recovering magnesium hydroxide from brine and seawater typically involves the addition of lime calcined dolime ($CaO \cdot MgO$), which is obtained from a mineral source such as dolomitic limestone ($CaMg(CO_3)_2$). Magnesium-bearing brine and seawater contain varying concentrations of calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$), which are mixed with appropriate concentrations of calcined dolime and water (if necessary) to facilitate the following reaction (Martin, 2008):

$$CaCl_2 + MgCl_2 + (CaO \cdot MgO) + 2H_2O \rightarrow 2Mg(OH)_2 + 2CaCl_2 + H_2O$$

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):

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2$$

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).

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6 Combustion, Pyrolysis and Offgassing Testing of FR-4 Boards

As discussed in Section 5.3.2, little information exists about the combustion and pyrolysis products that could be formed during end-of-life scenarios. The stakeholders of this partnership have decided that testing of FR-4 laminates and PCB materials is warranted to learn more about potential byproducts during product use (e.g., leachability and offgassing) and thermal end-of-life processes (e.g., open burning, incineration, offgassing, and smelting).

This chapter describes the rationale and methods for offgassing, combustion, and pyrolysis testing of PCB materials. The University of Dayton Research Institute (UDRI), which has been involved in studying thermal processes for the last three decades and has experience with the brominated materials used as flame retardants in PCB manufacturing, will lead the testing. EPA's Office of Research and Development (ORD) will supplement UDRI's testing by directing the analysis for dioxins/furans and metals. Testing is scheduled to be completed in 2009. Leachability testing will not be conducted as part of this partnership project given the lack of suitable analytical methods to study the leachability potential of alternative flame retardants in landfill environments.

The following stakeholders are funding the combustion testing that will be conducted by UDRI:
- Boliden
- Supresta
- ITEQ
- Hewlett-Packard
- Clariant
- Ciba Specialty Chemicals
- Sony
- Intel
- Isola
- Dell
- Fujitsu-Siemens
- Bromine Science and Environmental Forum (BSEF)
- Matsushita Electric Industrial and Matsushita Electric Works
- IBM
- Nabeltec

6.1 Combustion and Pyrolysis Testing

This section explains the rationale for combustion testing, and describes test methods and materials.

6.1.1 Rationale

The overall goal of the combustion testing component of this partnership project is to compare the combustion byproducts from FR-4 laminates and PCB materials during potential thermal end-of-life processes, including open burning, incineration, and smelting. This testing will be a first step in providing industry with a comparative analysis of combustion byproducts from these materials, which will, in turn, help to identify what further studies are needed to better understand these byproducts in real-world scenarios. Moreover, this testing will help to advance decision making on the selection of flame-retardant materials and environmentally acceptable end-of-life thermal disposal process.

6.1.2 Methods

UDRI will lead the combustion and pyrolysis testing and analysis of byproducts, supplemented by EPA ORD-directed analysis for dioxins/furans and metals. The testing methodology was developed through an ongoing collaboration among UDRI and stakeholders of this partnership. The testing will take place in two phases: Phase 1 will evaluate the ability of proposed test methods to predict thermal decomposition products of a small number of laminates and establish experimental methods and conditions; Phase 2 will expand upon Phase 1 by testing both laminates and populated PCBs at experimental conditions established in Phase 1. The laminates in Phase 1 and the laminates and populated PCBs in Phase 2 will be tested under a number of different temperature and atmosphere conditions to predict combustion and pyrolysis products that could occur across various end-of-life scenarios.

Table 6-1 summarizes the methodology for both phases of the combustion and pyrolysis testing. A more detailed description of the methodology will be made available with the testing results in 2009.

6.1.3 Test Materials

The following laminates are being considered for testing under Phases 1 and 2. In addition, a non flame-retarded laminate will be tested in both phases to serve as a baseline.

- NanYa (NPG-TL, NPG-170TL)
- Hitachi BE-67G(R)
- Isola (DE156 and IS500)
- TUC (TU-862 and TU-742)
- MEW R1566W
- ITEQ (IT170G, IT140G, and IT155G)
- Nelco 4000-7EF
- Shengyi S1155
- Supresta FR Laminate

Before the combustion and pyrolysis testing begins, EPA ORD will conduct X-ray fluorescence (XRF) analysis of each laminate to determine its elemental composition. The subset of laminates for inclusion in Phases 1 and 2 will be selected to ensure a broad range of compositions. After Phase 1 is completed, UDRI will review the data with sponsors to determine the best way to proceed with Phase 2. In Phase 2, populated boards will be simulated by combining laminates with components removed from conventional boards.

Table 6-1: Summary of Combustion Testing Methodology

	Phase 1	Phase 2
Goal:	• To evaluate the ability of proposed test methods to predict thermal degradation products of laminates, and to establish experimental methods/conditions for Phase 2 testing	• To expand quartz tube and cone-calorimeter testing to other candidate laminates
Test Methods:	• XRF analysis to determine elemental composition (performed by EPA ORD) • TGA to determine pyrolysis temperatures • Pyrolysis/quartz tube reactor system • Cone calorimeter	• XRF analysis to determine elemental composition (performed by EPA ORD) • TGA to determine pyrolysis temperatures • Pyrolysis/quartz tube reactor system • Cone calorimeter
# of Test Vehicles:	• 3 laminates (TBBPA laminate, phosphorus-based laminate, and non-flame-retardant laminate)	• 6 laminates (2 from Phase 1, + 4 of varying composition) + 6 populated boards
Sample Size:	• 10 mg samples for quartz tube reactor • 3” x 3” x approximately 0.5” samples for cone calorimeter	• 10 mg samples for quartz tube reactor • 3” x 3” x approximately 0.5” samples for cone calorimeter
Test Conditions	• For quartz tube: 4 different temperature/atmosphere conditions • For cone calorimeter: 2 different temperature/atmosphere conditions: moderately high and highest possible temperatures (based on quartz tube results) and 2 combustion atmospheres (air or nitrogen)	• For quartz tube: 5 temperature/ atmosphere conditions • For cone calorimeter: moderately high and highest possible temperatures (based on quartz tube results) and 2 combustion atmospheres (air or nitrogen)
Replicates	• For quartz tube: 2 conditions with no replicates, and 2 conditions with 2 replicates each • For cone calorimeter: 1 condition with no replicates, and 1 condition with 2 replicates	• To be determined based on Phase 1 results
Analytical Method:	• Gas chromatography-mass spectrometry (GC-MS) analysis	• GC-MS analysis • Inductively coupled plasma-mass spectrometry methods for phosphorus or aluminum-containing compounds (performed by EPA ORD)

6.2 Offgassing

This section explains the importance of offgassing tests, and briefly discusses the assessment methods that will be used.

6.2.1 Rationale

Little information exists in the literature about the offgassing potential of alternative flame retardants from electronic products. Similarly, little to no research has addressed whether the type of flame retardants used in PCBs potentially affects offgassing of heavy metals during product use or thermal end-of-life treatment. Testing is needed to provide a comparative analysis of byproducts of concern that "offgas," or volatize, from FR-4 laminates and PCBs during product use and recycling processes.

The stakeholders of this partnership have worked collaboratively with UDRI to identify a testing approach for offgassing, which is presented below. As of the writing of this report, however, the offgassing testing has been put on hold due to a lack of sufficient funding.

6.2.2 Methods

If sufficient funds are raised, UDRI will conduct the offgassing testing at temperatures that approximate offgassing potential during product use and shredding of PCBs that often occurs as part of the recycling process. Table 6-2 summarizes the methodology for offgassing testing. A more detailed description of the methodology will be made available with the testing results in 2009.

Table 6-2: Summary of Offgassing Testing Methodology

	Offgassing
Goal:	• To run tests at temperatures that approximate offgassing during product use and shredding of PCBs
Test Methods:	• Place entire PCBs into sealed vessels that have septum sampling ports
# of Test Vehicles:	• 5 (brominated epoxy laminate + 4 halogen-free laminates and/or PCBs)
Sample Size:	• Full-size laminates and/or PCBs
Test Conditions	• 4 temperatures between 25 and 200°C
Analytical Method	• Solid phase microextraction with GC-MS analysis

6.3 Results (PENDING)

7 Considerations for Selecting Flame Retardants

Multiple factors must be considered when selecting an appropriate chemical flame retardant. In addition to flame retardancy properties and health and environmental considerations, the flame-retarded PCB must meet all required technical specifications. The epoxy resins used for PCBs are complex chemical formulations. Therefore, a drop-in exchange of flame retardant is usually not possible, and some adjustment of the overall formulation is required. Small changes in formulations can significantly affect the manufacturability and performance of PCBs. Additionally, the laminate containing the selected flame retardant should be compatible with existing PCB production and processing equipment. Finally, the resulting laminate formulation must be economically competitive. The cost comparison should not be limited to the flame retardant itself, but rather on the complete laminate formulation or the resulting PCB.

This partnership recognizes the significance of considering practical alternatives. The information in this report focuses on human health and environmental attributes and should be weighed with cost and performance information when selecting alternatives.

7.1 Positive Human Health and Environmental Attributes

This section identifies a set of positive attributes that companies should consider when formulating or selecting a flame retardant that will meet or exceed existing flammability standards. These attributes are linked to different aspects of what might happen to a chemical substance during its life cycle. While ensuring that fire-safety standards are met, the following desirable human health and environmental chemical characteristics and attributes, relevant to many flame-retardant chemicals, should be considered general "rules of thumb." These general rules of thumb should be applied to both flame retardant chemicals and any of their decomposition byproducts described in chapter 6.

7.1.1 Low Human Health Hazard and Low Exposure Potential

The overall risk posed to human health is a combination of hazard and exposure. Chemical hazards to human health include acute toxicity, skin sensitization, carcinogenicity, immunotoxicity, reproductive effects, developmental effects, neurological effects, systemic effects, and genotoxicity. Chemical exposure to humans can occur through the skin, inhalation, and ingestion, and is affected by several physiochemical factors, such as melting point, boiling point, vapor pressure, water solubility, octanol/water partition coefficient, and Henry's law constant.

7.1.2 Low Ecotoxicity

Ecotoxicity measures adverse effects observed in living organisms that typically inhabit the wild, specifically aquatic organisms (fish, invertebrates, algae). Toxic effects are generally expressed as the lethal concentration for 50 percent of the study sample (LC_{50}) or the lethal dose for 50 percent of the study sample (LD_{50}). Since chemicals can have different short-term and long-term affects, acute ecotoxicity (typically less than 96 hours) and chronic (repeated-exposure) ecotoxicity should both be considered in choosing a chemical flame retardant.

7.1.3 Readily Degradable: Low Persistence

Persistence describes the tendency of a chemical to resist degradation and removal from environmental settings, such as air, water, soil, and sediment. Chemical degradation in the environment either occurs through chemical reactivity with its surroundings or through biodegradation by microorganisms. Chemical reactivity is most commonly a result of hydrolysis (reactions with water), though photolysis (reactions with sunlight) and oxidative gas-phase processes may also play a role. In the absence of rapid chemical reactivity, biodegradation is the primary process that causes degradation. Biodegradation can occur in aerobic settings via oxidative processes and in anaerobic settings via reductive processes. Depending on the organism and chemical substrate combination, chemicals may degrade into other chemical substances or may be completely mineralized into small building blocks (e.g., CO_2 and water).

Typically, the environmental profile of a chemical improves with its rate of biodegradation. According to the OECD, a chemical is readily biodegradable if, in a 28-day test, it biodegrades 60 percent or more within 10 days of the time when degradation first reaches 10 percent (70 percent for DOC-based tests). There are two main features of readily biodegradable substances. Hydrophobic components composed of unsaturated linear alkyl chains (straight chain carbon molecules) biodegrade more rapidly under aerobic conditions in sewage treatment plants and the environment than highly branched chains. Also, hydrophobic and hydrophilic components that are linked by an easily biodegradable group like a carboxylic acid ester will separate the hydrophobe from the hydrophile during the first step through aerobic biodegradation (i.e., ester hydrolysis).

Keep in mind that while the rate of degradation is important, it is equally important to be aware of the byproducts formed through the degradation process. In some cases, the products of biodegradation might be more toxic and persistent than the parent compound. It is also important to note that the technical requirements for flame retardants in PCBs, mainly high temperature and hydrolysis stability, make it impossible to use flame retardants of low chemical stability (see Section 7.2).

7.1.4 Low Bioaccumulation: High Log K_{ow} (>8); Large Molecule

The ability of a chemical to accumulate in living organisms is often measured by the bioconcentration factor (BCF). A high BCF indicates a high potential to bioaccumulate. Quantified, chemical-specific BCFs are often not available; however, this property can be estimated by correlating it with another readily-available parameter – the octanol/water partition coefficient (K_{ow}). In general, a log K_{ow} of 3.5 to 5 corresponds to BCFs of approximately 1,000 to 5,000. Both ranges represent a moderate to high bioaccumulation potential. Note that as the log K_{ow} increases above 8, the bioaccumulation potential decreases.

The potential for a molecule to be absorbed and harm an organism is less when the molecule is larger than a certain size. Molecules with the following characteristics are not available for passive uptake through the respiratory membranes of aquatic organisms: (a) molecules with hydrophilic components having large cross-sectional diameters (larger than 10 Å), or (b) neutral and anionic surfactants with molecular weights greater than 1,000 Daltons. (Large diameters or high molecular weights will limit toxicity to surface effects only and will prevent systemic effects.)

In addition, high molecular weight molecules (greater than 1,000 Daltons) tend to be less volatile and therefore, may exhibit less of a potential for inhalation exposure to vapors during manufacturing and processing of PCB epoxies and laminates. If exposure occurs, high molecular weight molecules are less likely to be absorbed, therefore limiting potential for adverse effects to be expressed.

7.1.5 Reactive Flame Retardants

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 epoxy and laminate during the early stages of manufacturing, resulting in a loss of the chemical identity of the flame retardants. Additives are mixed throughout the formulation but are not chemically bound. Therefore, additives have a much higher potential to migrate, or leach, from the product into the environment under normal conditions.

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 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.

7.2.1 Flame Retardant Effectiveness and Reliability

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 United States 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 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 it can be equally viable to use a low amount of an expensive, highly efficient flame retardant or a higher amount of a less expensive, less efficient material.

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).

7.2.2 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.

Changes in these properties can affect the manufacturability and overall performance of the PCB. The glass transition temperature, 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 transition temperatures 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 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 Section 2.2, iNEMI is currently conducting performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties.

7.2.3 Economic Viability

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 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 FRs. In addition, daily operation costs may be different for the new process steps required to manufacture PCBs with alternative FRs.

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.

7.2.4 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., WEEE 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, although combustion and pyrolysis testing results described in chapter 6 may help elucidate possible impacts, and some predictions can be made based on past and current practices. 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 FRs, and acrolein, hydrogen cyanide, and PAH from nitrogen-based FRs, 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.

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