An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD)

By Gregory Morose

A Publication
Of the Lowell Center
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University of
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Prepared for
The Jennifer
Altman Foundation

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Purpose of this Study

The Jennifer Altman Foundation has commissioned the Lowell Center for Sustainable Production (LCSP) of the University of Massachusetts Lowell to conduct a study of potential alternatives to TBBPA and HBCD.

The Lowell Center for Sustainable Production

The Lowell Center for Sustainable Production develops, studies, and promotes environmentally sound systems of production, healthy work environments, and economically viable work organizations. The Center operates on the premise that environmental quality, safe and healthy workplaces, and social accountability can be achieved while at the same time enhancing the economic life of firms and communities. This is accomplished by broadening the fundamental design criteria for all productive activities to include an explicit and comprehensive commitment to sustainability.

The Center is composed of faculty and staff at the University of Massachusetts Lowell who work directly with industrial firms, social services institutions, citizen organizations, and government agencies to promote sustainable production. The LCSP is based at the University of Massachusetts Lowell, where it works closely with the Massachusetts Toxics Use Reduction Institute (TURI) and the Department of Work Environment.

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INTRODUCTION

Objectives and Scope

The Jennifer Altman Foundation has commissioned the Lowell Center for Sustainable Production to review available information relative to the uses and potential alternatives for two brominated flame retardants, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane HBCD. The objective of this study is to accomplish the following:

- Investigate TBBPA and HBCD product and application information that is available in the public domain.
- Identify potential alternatives to the products identified.
- Conduct a preliminary and qualitative review of potential alternatives.

This study presents a high level overview of the findings. No chemical analyses, toxicological studies, performance evaluations, or economic assessments were included as part of this study.

This paper is organized into three major sections as follows:

Section I: *TBBPA & HBCD Uses*
The various applications and uses of TBBPA and HBCD are described.

Section II: *Potential Alternatives & Initial Assessment*
The potential alternatives for the various TBBPA and HBCD uses are identified, as well as an initial identification of the key health, environmental, and performance concerns for these alternatives.

Section III: *Recommendations and Conclusions*
The overall conclusions from this study are provided, as well as recommendations for further research of TBBPA and HBCD alternatives.

The information for this report was generated by the following methods:

- Literature search of publicly available information, and
- Information requests and discussions with manufacturers of products containing HBCD and TBBPA flame retardants, as well as manufacturers of products containing alternative flame retardant materials.

Because the study does not include an in-depth evaluation of the environmental, technical performance, or economic impact for these alternatives. This study will not recommend specific alternatives for TBBPA and HBCD. Instead it will discuss additional steps to be taken before specific recommendations can be made for viable alternatives. It is outside of the scope of this report to assess the possible environmental and human health risks associated with TBBPA and HBCD.

Background

In 2003, fire departments responded to 1,584,500 fires in the United States. Every 20 seconds a fire department responds to a fire somewhere in the nation. In 2003, there were 3,925 deaths, 18,125 injuries, and approximately $12 billion in property damage as a result of these fires (Karter, 2004). In order to reduce the risks of fires and provide adequate time for egress during building fires, governments, product manufacturers, and professional associations have promoted the use of flame retardants in products and building materials likely to burn. This is particularly true for polymeric materials.

Flame retardants can be added to polymer materials to enhance their flame retardancy. Flame retardant polymer materials are used in various commercial products to protect people and property from potential fire hazards. Flame retardants used in polymer materials are added in order to accomplish one or more of the following functions during the course of a fire:

- Raising the ignition temperature of the polymer;
- Reducing the rate of burning;
- Reducing flame spread; or
- Reducing smoke generation.

There are four main types of flame retardants used with polymeric materials:

Inorganic: Includes flame retardants such as antimony trioxide, alumina trihydrate, and magnesium hydroxide. When heated, the hydroxides release water vapor that helps cool the substrate and perform other flame retardant functions. Antimony trioxide is typically used as a synergist in combination with other flame retardants.

Halogenated: These flame retardants are primarily based on chlorine and bromine substances such as halogenated paraffins, chlorinated alicyclic compounds, and brominated aromatic compounds. These flame retardants act primarily by chemically interfering with the radical chain mechanism that occurs in the gas phase during combustion. These flame retardants prevent or delay the onset of ignition, and slow the rate of burning once a fire is initiated.

Phosphorus-based: These flame retardants include organophosphates, halophosphates, phosphine oxides, and red phosphorus. The flame retardancy mechanism varies depending on the polymer type and the particular phosphorus compound. These flame retardants can function in the condensed phase, the gas phase, or both phases.

Nitrogen-based: These flame retardants, including melamine and melamine derivatives, are often used in combination with other flame retardants.

Of particular interest for this study is the use of brominated flame retardants. Certain brominated flame retardants are persistent in the environment and have been found in the food chain, and in the bodies of animals and humans. Research has shown that one type of brominated flame retardants, polybrominated diphenyl ethers (PBDEs), is often found in various environmental media, throughout the food chain, and in human breast milk, serum, and adipose tissue. Tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) are two brominated chemicals that are used as flame retardant materials in a variety of products. These flame retardants have desirable properties, and have proven to be successful flame retardant materials during years of use for a variety of applications. For example, HBCD combines high effectiveness with very low loading levels which enable polystyrene insulation products used in the building industry to meet required flame retardancy standards, while maintaining their insulation properties.

There are several studies underway investigating the possible environmental and human health effects of TBBPA and HBCD. The OSPAR Commission's List of Chemicals for Priority Action includes both HBCD and TBBPA. (OSPAR, 2004) The OSPAR Commission was formed for the protection of the marine environment of the Northeast Atlantic. The OSPAR Commission's list identifies hazardous substances based on their persistence, bioaccumulativeness, and toxicity.

Global Market and General Characteristics of TBBPA and HBCD

During 2001, the global market demand for the major brominated flame retardants was 203,790 metric tonnes. TBBPA is the most widely used brominated flame retardant, and accounted for 58.7% of total market demand of brominated flame retardants in 2001. HBCD is the third most widely used brominated flame retardant, accounting for 8.2% of total market demand in 2001. The total market demand estimated by the Bromine Science and Environmental Forum (an industry trade organization) for TBBPA, HBCD, and other major brominated flame retardants in 2001 is provided in the table below:

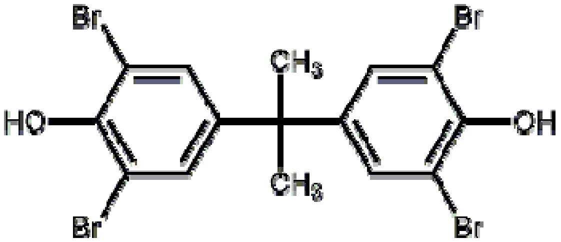
Table 1: Brominated Flame Retardant Global Market Demand in 2001 (BSEF-1)

Brominated Flame Retardant	Market Demand (Metric Tonnes)	Percent of Total
Tetrabromobisphenol A (TBBPA)	199,700	58.7%
Decabromodiphenyl ether (deca-BDE)	56,100	27.5%
Hexabromocyclododecane (HBCD)	16,700	8.2%
Pentabromodiphenyl ether (penta-BDE)	7,500	3.7%
Octabromodiphenyl ether (octa-BDE)	3,790	1.9%
Totals:	203,790	100.0%

TBBPA

TBBPA is a crystalline solid and has the chemical formula: $C_{15}H_{12}Br_4O_2$. The configuration of the TBBPA molecule is shown in Figure 1:

Figure 1: TBBPA Molecule



TBBPA is introduced into polymer applications in either a reactive or an additive form. When TBBPA is used as an additive component, it does not become part of the polymer structure. When TBBPA is used as a reactive flame retardant, the phenolic hydroxyl group reacts covalently and the TBBPA is incorporated into the polymer matrix.

TBBPA is most commonly used as a reactive flame retardant in epoxy resins for printed wiring boards (PWB). One study extracted and analyzed filings from a printed wiring board made with reactive TBBPA. The study found that only 4 micrograms of TBBPA was unreacted for each gram of TBBPA used to make the printed wiring board. (Sellstrom)

TBBPA is also used as an additive flame retardant for other polymer applications such as acrylonitrile butadiene styrene (ABS). One study measured the TBBPA emissions from computer monitors containing additive TBBPA in the housing. The study found low emissions of approximately 1 ng/m3, and these emissions decreased over time. (Herrmann) TBBPA has been detected in various environmental media and is considered persistent because it meets certain standard tests for persistence.

The largest manufacturers of TBBPA in the United States with their trade names/product names include the following:

Company, Location	Tradename
Albemarle, Louisiana	Saytex CP-2000
Dead Sea Bromine Group, New Jersey	FR-1524
Great Lakes Chemical/Chemtura, Connecticut	BE-59

HBCD

HBCD is a colorless solid with the chemical formula: $C_{12}H_{18}Br_6$. The configuration of the HBCD molecule is shown in Figure 2.

The primary use of HBCD is as a flame retardant additive in expanded polystyrene (EPS) and extruded polystyrene (XPS) applications. EPS and XPS are typically used for thermal insulation foams for applications in the building and construction industry. HBCD is also used for textile and high impact polystyrene (HIPS) applications. There are four types of commercial HBCD mixtures produced, each with different melting points. All mixtures contain the isomers alpha-HBCD, beta-HBCD, and gamma-HBCD (Zegers, 2004). HBCD is a lipophilic compound with a log K_{ow} of 5.6, and is considered bioavailable and bioaccumulative based on studies of fish and fish eating animals.

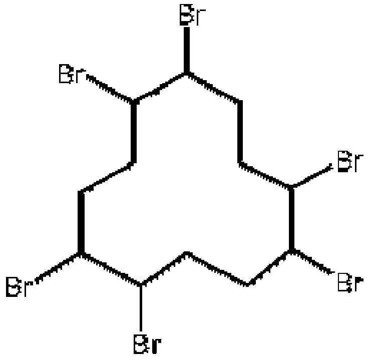


Figure 2: HBCD Molecule Configuration

The largest U.S. manufacturers of HBCD as well as trade names/product names include the following:

Company, Location	Tradename
Albemarle, Louisiana	Saytex HP-900)
Dead Sea Bromine Group, New Jersey	FR-1206
Great Lakes Chemical/Chemtura, Connecticut	CD-75P

Section I: TBBPA and HBCD Uses

TBBPA: Applications

Epoxy resin

Epoxy resin is used for a variety of applications including encapsulation of electronic components and printed wiring board laminates. TBBPA is commonly used as a reactive flame retardant for epoxy resin applications such as printed wiring board laminates and encapsulation of electronic components. Epoxy resin applications are the primary use of TBBPA.

Epoxy resin is made from epichlorohydrin and bisphenol A. First, epichlorohydrin and bisphenol A are combined to form BPA dichlorohydrin ether. Then sodium hydroxide and BPA dichlorohydrin ether are combined to form diglycidyl ether of bisphenol A (DGEBA).

Printed Wiring Boards

During 2003 in the U.S., approximately 22 million pounds (9,979 metric tonnes) of epoxy resin was used in the manufacture of laminates for use in rigid printed wiring boards. Printed wiring boards are used in a wide variety of end-use markets as illustrated in the table below.

Due to their excellent thermal, electrical, and flame retardant properties, relatively low cost, and good processability, epoxies containing TBBPA are widely accepted as a flame retardant material in the electronics industry. It is estimated that TBBPA is used as a reactive flame retardant in more than 90% of printed wiring boards (BSEF-3, 2004). The functional reliability of PWBs made with TBBPA has been demonstrated during years of actual use.

Dow Chemical, Resolution Performance Products LLC, and Huntsman International are the leading suppliers of brominated epoxy resins. The major manufacturers of printed wiring boards using epoxy resin laminates in 2003 include:

- Arlon
- Dynamic Details, Inc.
- Electroply, Inc.
- Hitachi
- Isola
- LG Chem
- MGC
- Nelco Products
- Polyclad Laminates
- Sumitomo Bakelite
- TTM Technologies, Inc

Table 2: Major End-Use Markets for Rigid Printed Wiring Boards (Greiner, Elvira 2004)

End-use Market	% Use of Printed Wiring Boards
Computers and peripherals	35%
Communication systems	20%
Automotive	15%
Consumer electronics	10%
Military	10%
Other applications such as business machines and industrial equipment	10%
Total	100%

Electronic Component Encapsulates

Epoxy embedding compounds are used to enclose, encapsulate, or seal an electrical or electronics component in a protective matrix. This matrix protects the component from environmental hazards such as moisture, dirt, and oxygen. The matrix can also provide enhanced mechanical strength and dielectric insulation. Approximately 12 million pounds (5,443 metric tones) of basic epoxy resins were consumed in the embedding market in 2003. There are hundreds of suppliers of epoxy embedding resins, but the major suppliers in the U.S. include Ablestik Laboratories (California) and Loctite Corporation (Connecticut).

Other Applications

TBBPA can be used as an additive flame retardant material for acrylonitrile butadiene styrene (ABS) products to meet Underwriters Laboratories (UL) 94 fire safety standards. ABS applications include various electrical and electronic equipment applications. It is estimated that ABS is used for approximately 2% of all television enclosures and for 34% of all computer monitor enclosures. (Pure Strategies, 2005) The primary flame retardants for these ABS applications are TBBPA and brominated epoxy oligomers (BEO).

TBBPA can be used as an additive flame retardant for casing materials made from high impact polystyrene (HIPS) (Leisewitz et al, 2001), and used in combination with antimony tri-oxide to provide flame retardancy. TBBPA is also used as an intermediate for the production of other brominated flame retardants such as TBBPA derivatives and brominated epoxy oligomers.

TBBPA: Global use

The total worldwide market demand for TBBPA in 2001 was 119,700 metric tonnes. The following table illustrates the use of TBBPA by region (BSEF-1) in 2001. The region with the highest demand for TBBPA is Asia, due to the high volume of printed wiring boards and electronics components manufactured in that region.

Total global demand for TBBPA increased over 25% in 2002 to 150,603 metric tonnes, but fell slightly in 2003 to 145,113 metric tonnes. (BSEF-1)

Table 3: TBBPA Market Demand by Region (BSEF-1)

Region	Market Demand (metric tonnes)	Percentage of Total
Asia	89,400	74.7%
Americas	18,000	15.0%
Europe	11,600	9.7%
Rest of the World	600	0.5%
Total	119,700	100%

TBBPA: TRI Reporting

The U.S. Toxics Release Inventory (TRI) has provided annual release data for TBBPA used in manufacturing since the chemical was first listed in 2000. The reporting threshold is 100 pounds (45.5 kilograms). The following table depicts the total on and off-site disposal or other releases of TBBPA in the U.S.

Table 4: TBBPA Annual Releases (TRI)

Year	Total Annual Releases of TBBPA (lbs.)	% Change from Previous Year
2000	794,981	Not applicable
2001	876,340	10.2%
2002	1,054,297	20.3%
2003	643,250	39.0%

In 2003, 48 facilities in the U.S. reported releases of TBBPA. The following table shows the reported releases and the Standard Industrial Codes (SIC) from all facilities that released more than one thousand pounds (454.5 kilograms) of TBBPA. These facilities are involved in manufacturing either TBBPA, printed wiring boards, or materials for encapsulating electronics components.

Table 5: Facility Releases of TBBPA in 2002 (TRI)

Company	Facility Location	Total Releases (lbs.)	SIC	SIC Description
Albemarle Corp.	Columbia, AR	417,660	2819, 2869	Industrial inorganic chemicals Industrial organic chemicals
Great Lakes Chemical	Union, AR	214,658	2819, 2869	Industrial inorganic chemicals Industrial organic chemicals
Henkel Corp.	Cattaraugus, NY	5,079	3087	Custom compound purchased resin
Isola	Maricopa, AZ	3,833	3679	Electronic components

HBCD: Applications

Expanded Polystyrene and Extruded Polystyrene

The primary use of HBCD is as a flame retardant material in expanded polystyrene (EPS) and extruded polystyrene (XPS) products. HBCD can be used in combination with dicumylperoxide for these applications. EPS and XPS are used for thermal insulation boards and laminates for sheathing products for use in the building and construction industry. In most cases, the polystyrene foam is laminated to another material in sheet form and sometimes is also used in combination with fiberglass. These foams can be used for roofing insulation products, wall insulation, cold storage, garage door insulation, foundation insulation, and exterior siding underlay.

EPS is derived mainly from styrene monomer and expanded to form a cellular structure of closed cells. Pentane is used as the blowing agent to expand the polystyrene into EPS. EPS is comprised of 98% air by volume. EPS is available with or without the flame retardant HBCD. If HBCD is used, it constitutes approximately 0.5% of the final product by weight (EUMEPS-1, 2002)

There are numerous properties that are important for evaluating the performance of foam used for thermal insulation. These properties include density, thermal resistance (R- Value), compressive resistance, flexural strength, water vapor permeance, water absorption, dimensional stability, maximum use temperatures, and fungus/bacterial resistance.

The use of HBCD is advantageous in EPS and XPS applications because it has high effectiveness for flame retardancy and requires low loading levels. This helps to maintain the thermal insulation and other properties of EPS and XPS products. The forecast for U.S. consumption of polystyrene in building and construction applications is illustrated in the following table.

Table 6: U.S. Consumption of Polystyrene in Building and Construction (Ring, 2001)

Material	2000 (millions of pounds)	2005 (millions of pounds)	Average Annual Growth Rate (2000 – 2005)
XPS foam board and sheathing	140	160	2.7%
XPS architectural moldings	70	75	1.4%
EPS board and sheathing	420	485	2.9%

EPS is a versatile material that performs well in many building applications. EPS can be used for not only insulation, but also for providing a moisture barrier, protection against damage from freezing, providing a stable fill material, and creating high-strength composite materials.

EPS bead board is cut from molded blocks and is usually provided at a density of 1 – 2 pounds (0.45 – 0.91 kilograms) per cubic foot. The major EPS board manufacturers in the U.S. include:

- CelloFoam North America Inc.
- Atlas Roofing
- Insulfoam Corp.
- BASF

The key performance requirements for EPS bead board include density, R-value (resistance to heat flow), compressive strength, flexural strength, water vapor transmission rate, water absorption, and oxygen index.

Extruded polystyrene (XPS) foam board is typically supplied in densities from 1.8 to 2.0 pounds (0.82 – 0.91 kilograms) per cubic foot. XPS foam board is used primarily for roofing and various architectural molding applications in the building and construction industry. The major manufacturers of XPS foam board in the U.S. are Dow Chemical Company, Owens-Corning, and BASF.

Other Applications

HBCD can be used for textile backcoating. It is mainly used for upholstery furniture in order to meet the strict fire safety standards in place in the United Kingdom and California. It is also used for upholstery seating in transportation vehicles, draperies, and wall coverings. HBCD is used in combination with antimony trioxide for textile back coatings. HBCD is also sometimes used as a flame retardant in High Impact Polystyrene (HIPS) for electrical and electronic appliances such as audio-visual equipment, as well as for certain wire and cable applications.

HBCD: Global Use

The total worldwide market demand for HBCD in 2001 was 16,700 metric tonnes. The following table illustrates the use of HBCD by region (BSEF-1).

Table 7: HBCD Market Demand by Region (BSEF-1)

Region	Market Demand (metric tonnes)	Percentage of Total
Europe	9,500	56.9%
Asia	3,900	23.3%
Americas	2,800	16.8%
Rest of the World	500	3.0%
Total	16,700	100%

Total global demand for HBCD increased over 28% in 2002 to 21,447 metric tonnes, and rose again slightly in 2003 to 21,951 metric tonnes. (BSEF-1)

HBCD: TRI Reporting

HBCD is not a listed chemical for the U.S. Toxics Release Inventory (TRI) program, and therefore there is no release data available.

Section II: Potential Alternatives & Initial Assessment

There is a range of approaches available to reduce the use of TBBPA and HBCD in various applications. These approaches can be grouped into the following three categories:

A. *Flame Retardant Substitution*: This approach involves identifying a drop-in chemical substitute for TBBPA and HBCD. The drop-in chemical would ideally be cost and performance comparable to TBBPA and HBCD. It is the simplest approach because it typically does not require changes to the polymer material or to the design of the product. This change could be implemented by the polymer processor or compounder.

B. *Resin/Material Substitution*: This approach involves changing the resin system, for example, from ABS to HIPS, while also changing the chemical used as the flame retardant. This is a more complex approach than simple flame retardant substitution because it has a greater effect on overall product cost and performance. This change could be implemented by the polymer processor/compounder or the end-product manufacturer.

C. *Product Redesign*: This approach involves changes to the actual product design to minimize or eliminate the need for flame retardant chemicals. Examples of product redesign include using fire barrier material, as well as separating or reducing the source of heat from the product. This change could be implemented by the end-product manufacturer.

This report will focus on the first two approaches when identifying potential alternatives for TBBPA and HBCD.

Alternatives to TBBPA: Epoxy Resin for PWB Laminate

In selecting an epoxy resin laminate for printed wiring boards, several properties need to be considered including thermal, mechanical, electrical, and other properties. Some of the key performance requirements for epoxy laminate applications are listed below.

Thermal properties: glass transition temperature (Tg), degradation temperature, and delamination temperature.

Mechanical properties: flexural strength, flexural modulus, coefficient of thermal expansion (CTE), tensile strength, Young's modulus, Poisson's ratio, peel strength, and z-axis expansion.

Electrical properties: surface resistivity, volume resistivity, insulation resistance, dielectric constant, and dissipation factor.

Other properties: flame resistance and water absorption.

The acceptable values and relative importance of these properties is determined by the particular design requirements (e.g. board thickness), processing capabilities (e.g. multiple lamination cycles), and performance requirements (e.g. extended thermal cycling) for each printed wiring board application. For example, it is desirable for surface mount PWB designs to have a coefficient of thermal expansion (CTE) of the laminate similar to the CTE for the components in order to minimize strain on solder joints. Therefore, the ideal properties will vary by application. The flame retardant material can have an effect on many of these properties.

In addition, there are industry-wide market and regulatory forces that further determine the importance of various properties. For example, in January 2003, the European Union (EU) published the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (RoHS). The Directive does not restrict the use of TBBPA, although it may have indirect effects. For instance, the Directive has been a primary driver for a global movement toward lead-free electronics assembly.

The RoHS directive prohibits products that contain lead to be sold in the EU after July 2006, unless the use is specifically exempted. The electronics industry is currently working to transition from lead to lead-free soldering materials to meet the RoHS requirements. Since the lead-free alloys used to replace lead have higher melting temperatures, there is a need to select laminate materials that perform well under higher operating temperature. For lead-free applications, properties such as glass transition temperature, degradation temperature, and coefficient of thermal expansion are critical.

Fire safety standards in the U.S. for electronics products are developed by the Underwriter's Laboratory (UL). UL has developed several performance standards for electronics products and components regarding their resistance to ignition and flame propagation. The chief fire safety standards for electronic enclosures are the UL 94 component standards. The UL 94 Tests for Flammability of Plastic Materials for Parts in Devices and Appliances is the relevant standard for printed wiring boards. The UL 94 component standards range from UL94 HB (the lowest standard), which involves a horizontal burn, to successively more stringent vertical burning tests (Class UL 94 V-2, V-1, V-0 and 5V).

There are several National Electrical Manufacturers Association (NEMA) classes of fire retardant laminate materials used for printed wiring boards. For example, FR-1 is made from a phenolic resin with paper reinforcement. FR-4 is made from an epoxy resin with glass cloth reinforcement. FR-4 printed wiring boards are widely used in the electronics industry. In general, when using TBBPA alternatives for printed wiring boards it is a challenge to achieve the UL 94 V-0 rating for FR-4 type printed wiring boards because thermal stability, moisture resistance, and other properties may be compromised. In addition, the potential alternatives are typically more expensive.

A. Flame Retardant Substitutes

Alternative Brominated Compounds

TBBPA is the only brominated flame retardant that has significant use in epoxy resin printed wiring boards. Brominated chemicals other than TBBPA are commercially available as flame retardant materials for epoxy resin printed wiring boards. However, further research is required to determine if these other brominated chemicals are practical and reliable alternatives for TBBPA. For example Great Lakes Chemical supplies a flame retardant product, Model PH-73FF. This product contains 2,4,6-tribromophenol and can be used for epoxy circuit board applications.

Key Health, Environmental, and Performance Concerns

2, 4, 6-tribromophenol is considered a toxic substance by the oral route of administration, but not considered toxic by the dermal or inhalation routes (Great Lakes Chemical 2002).

Red Phosphorus

Red phosphorus is a relatively stable form of phosphorus that is commercially available as a powder with added stabilizers. It is very effective as a flame retardant, and can be used in combination with alumina trihydrate or magnesium hydroxide. For example, Italmatch Chemicals provides red phosphorus products, Model 70450 and 71450. These products can be used for electronics applications and must be combined with aluminum hydroxide.

Key Health, Environmental, and Performance Concerns

Red phosphorus is typically available in a powder form. The powder is highly flammable and is difficult to handle until it is incorporated into the plastic. There is also the slow attack of moisture on red phosphorus that generates traces of phosphine and corrosive phosphorus acids. Red phosphorus is toxic to aquatic organisms. Although unlikely, red phosphorus can be acutely toxic if contaminated with yellow phosphorus (Weil, 2004).

Other Phosphorus Based Compounds

Several phosphorus based compounds have been used as additive or reactive flame retardants for epoxy resins. For example, dihydrooxaphosphaphenanthrene (DOPO) has been used as a flame retardant for certain types of printed wiring boards. This is a cyclic hydrogenphosphinate made from o-phenylphenol and phosphorus trichloride. Isola makes a DURAVER product that is a phosphorus modified epoxy resin, and also utilizes metal hydroxides. Manufacturers often list their products as containing phosphorus based chemicals, without disclosing the exact chemical name. The following table illustrates examples of commercially available products containing phosphorus compounds.

Table 8: Manufacturers of Phosphorus Based Printed Wiring Boards Epoxies

Manufacturer	Model	Properties	Applications
Akzo Nobel	Fyrol PMP	Thermal stability to 300 degrees C	FR-4 Laminates
Isola	DURAVER-E-Cu quality 156	Has a higher time to delamination than standard FR-4. Tg = 160 degrees C.	FR-4 Laminates
Park/Nelco	N4000-7 EF	Tg = 165 degrees C UL 94 V-0 Thermal stability Moisture resistance	Lead-free assemblies, Fine Line Multilayers, Automotive Electronics, Wireless Communications, Telecommunications
Park/Nelco	High Speed EF	Tg = 180 degrees C	Anticipated to be available in Q3/Q4 2005 timeframe
Polyclad Laminates	PCL-HF-541 Laminate	Tg = 145 degrees C	Multilayer printed wiring boards
Polyclad Laminates	PCL-HF-571 Laminate	Tg = 165 degrees C	Multilayer printed wiring boards

Key Health, Environmental, and Performance Concerns

The Institute of Microelectronics conducted a comparison of standard FR-4 laminates versus phosphorus based halogen-free FR-4 laminates. The focus of the study was on moisture sensitivity performance. Low moisture absorption is a desirable laminate property for environmental stability and enhanced reliability. The results of this study indicate that phosphorus based laminates absorb more than two times as much moisture as conventional laminates (Rajoo, 2002). While no significant health or environmental issues were identified for these compounds, aquatic toxicity is a likely problem for certain other phophorus compounds.

Metal Hydroxides:

Aluminum hydroxide is the largest volume flame retardant used in the world. It is commonly referred to as alumina trihydrate (ATH), and its chemical formula is $Al(OH)_3$. When heated to 220 degrees C, ATH decomposes into 66% alumina and 34% water. This irreversible process helps make ATH an effective flame retardant.. High loadings of ATH (combined with other flame retardant materials) and sometimes magnesium hydroxide, $Mg(OH)_2$, have been used as alternatives to TBBPA.

To be effective as a flame retardant, ATH has to be used in high loadings, typically 40% to 60% by weight. ATH is relatively low in cost. However, there can be processing issues during the laminating process because of the high viscosity and aggregation of the filler. Consequently, microstructural defects may remain in the printed wiring board, thereby increasing moisture absorption and decreasing mechanical strength. Hitachi has improved the thermal stability of formulations of ATH above 20% by weight by adding polysiloxanes (Weil, 2004).

Magnesium hydroxide undergoes an endothermic reaction that releases its water at approximately 330 degrees C. Therefore, it can be used when processing temperatures are too high for use of ATH. The following table provides examples of commercially available flame retardant products containing metal hydroxides.

Table 9: Manufacturers of Metal Hydroxide Products

Manufacturer	Model	Properties	Applications
Albemarle	Martinal TS-601, Martinal TS-610, Martinal TS-702, Martinal OL-104/WE	Increased thermal stability, aluminum hydroxide	CEM-3 and FR-4 printed wiring boards
Mitsubishi Gas Chemical Company, Inc. (MGC)	Copper clad laminate: CCL-EL150 Prepregs: GEPL-150	UL 94 V-0 rating, Lower CTE (z-direction than standard FR-4	Computer motherboards, consumer electronic devices, communication systems.
Mitsubishi Gas Chemical Company, Inc. (MGC)	Copper clad laminate: CCL-EL150 Type HT Prepregs: GEPL-150 Type HT	UL 94 V-0 rating	Motherboards for routers, servers, and IC testers.

Key Health, Environmental, and Performance Concerns

Since ATH requires high loadings, it cannot be used in applications where the high loadings may affect critical polymer processing and physical properties. In addition, because of the relatively low decomposition temperature of ATH, it cannot be used when processing temperatures exceed 180 degrees C. No significant environmental or health issues were identified for ATH or magnesium hydroxide.

B. Resin/Material Substitution

Non-Flammable Resins

Modifying the epoxy resin with more thermally stable inflexible structures, such as biphenyl of naphthalene groups between glycidoxyphenyl groups, can significantly improve the inherent flame retardancy of the epoxy resin. Hitachi offers a laminate product that is based on a new flame retardant resin system. This resin system contains a large quantity of nitrogen-containing aromatic coreactant and a high inorganic filler content. The following table provides examples of suppliers of commercially available non-flammable resins

Key Health, Environmental, and Performance Concerns

There is limited data available for the health and environmental effects for these modified resins.

Polyimide Resin

Polyimide resin is an alternative to epoxy resin for making printed wiring board laminates. High temperature resins such as polyimides and blends with epoxy are used for high performance boards primarily for chip packaging and military applications. Polyimide printed wiring boards are usually inherently flame retardant. The market for polyimide laminates is estimated at 660 thousand pounds (300,000 kilograms) for 2003. The anticipated growth rate for polyimide laminates is anticipated to average 2.5% annually through 2008. (Ring, 2004)

There are several manufacturing processes used for making polyimides. For example, polyimides can be made from condensation reactions between aromatic dianhydrides and aromatic diamines. Some polymides made from condensation reactions use methylenedianiline (MDA) in the manufacturing process.

Table 10: Flame Retardant Resin System

Manufacturer	Model	Properties	Applications
Hitachi Chemical	MCL-BE-67G(H)	CTE is lower than conventional FR-4. Elastic modulus at high temperature is higher than conventional FR-4.	Includes lead-free solder applications and high density interconnection technology. Applications include camera phones, PDAs, 2-way pagers, and hand-held devices. (DDI)
Shengyi Corp.	S1165	High CAF function, low water absorption, low z-axis CTE	Lead-free solder applications, and can be applied in thin layers for multi-layer PWBs

Key Health, Environmental, and Performance Concerns

A drawback to using polyimide laminates has been difficulty in processing, due to low moisture resistance and other properties. Most polyimide resins do not present a health hazard under conditions of normal use. (Ring, 2004) However, one of the raw materials used for some polyimide resins is MDA. This chemical is listed by the International Agency for Research on Cancer (IARC) as a Group 2B, possible human carcinogen.

Other Resins Available for Printed Wiring Board Laminates

Approximately 85% of all printed wiring boards manufactured in the U.S. are made from epoxy resin. There are a number of other resins currently used in rigid printed wiring boards. For low-end applications, less expensive resins such as phenolics, melamines, vinyl esters, and polyesters are used. For high frequency applications, poly(tetrafluoroethylene) (PTFE) can be used. For high temperature applications, PTFE, other fluoropolymers, cyanates and epoxy-PPE blends, and even ceramics can be used. Cyanates, PTFE, and inorganic substrates are usually inherently flame retardant.

Injection-molded three-dimensional circuit boards are used in certain niche applications in the automotive, communications, and consumer electronics industries. High-temperature thermoplastics are generally used in these products.

Key Health, Environmental, and Performance Concerns

Perfluorooctanoic acid (PFOA) salts and tetrafluoroethylene are used in the production of PTFE. Tetrafluoroethylene is listed as "reasonably anticipated to be a human carcinogen". This listing is based on findings of elevated liver and biliary tract cancer rates in occupational groups exposed to tetrafluoroethylene, and evidence of cancer formation in experimental animal studies. (National Institute of Environmental Health Sciences)

Alternatives to TBBPA: Manufacturing Printed Wiring Boards with Halogen-free Materials

A cost analysis was conducted by IVR Industrial Research and the Technical University of Berlin to examine the impact of using halogen-free FR-4 materials versus traditional FR-4 materials (Bergendahl et al, 2004) The following twelve processing steps were identified for printed wiring board manufacturing for both traditional FR-4 and halogen-free FR-4 materials:

1) Photo resist, expose, develop
2) Etching, stripping
3) Deposition of bond or oxide layer
4) Pressing
5) Drilling
6) Desmearing
7) Cleaning and hole metallization
8) Photo resist, expose, develop
9) Copper and tin plating
10) Solder mask
11) Cleaning, oxide protection
12) Machining, electrical testing, final inspection

Of these twelve processing steps, differences were identified between manufacturing printed wiring boards with traditional FR-4 and halogen-free FR-4 materials for the following four process steps:

- Pressing
- Drilling
- Desmearing
- Solder mask

Two scenarios were examined for the impact of using halogen-free FR-4 materials instead of traditional FR-4 materials: “worst case” and “best case”. The worst case scenario describes a situation in which the worst case effects of the technology shift occur. The best case scenario outlines a situation where few or minor cost effects occur. The following table illustrates the comparison for both worst case and best case scenarios.

The life cycle analysis also identified additional costs to manufacture halogen-free printed wiring boards rather than traditional printed wiring boards. A shift to halogen-free printed wiring boards causes an increase in cost between approximately one to twelve dollars per panel. The cost increase is caused primarily by the drilling process, the desmearing process, and raw material costs.

Table 11: Impact of Transition to Halogen Free Printed Wiring Board

Process Step	Traditional PWB	Halogen-free PWB Worst Case	Halogen-free PWB Best Case
Pressing	Original process	Increased cycle time	Increased cycle time
Drilling	Original process	Reduction in the number of panels that can be drilled at the same time	No reduction in the number of panels that can be drilled at the same time
Desmearing	Original process	Increased cycle time	No increase in cycle time
Solder mask	Original process	Increased cycle time	Increased cycle time

Alternatives to TPPBA: Encapsulation of Electronics Components

Epoxy embedding compounds are used to encapsulate or seal electronics components in a protective matrix. This matrix protects the component from various environmental hazards.

A. Flame Retardant Substitution

Aluminum Hydroxide

Aluminum hydroxide is the largest volume flame retardant used in the world. As noted above, it is commonly referred to as alumina trihydrate (ATH), and its chemical formula is $Al(OH)_3$. To be effective as a flame retardant, ATH has to be used in high loadings, typically 40% to 60% by weight. Mitsubishi Gas Chemical Company, Inc. (MGC) provides products containing ATH, Models CCL-HL832NB and GHPL-830NB. These products can be used to achieve UL 94 V-0 rating for IC plastic package applications such as ball grid arrays.

Key Health, Environmental, and Performance Concerns

Since ATH requires high loadings, it cannot be used in applications where the high loadings may affect critical polymer processing and physical properties. In addition, because of the relatively low decomposition temperature of ATH, it cannot be used when processing temperatures exceed 180 degrees C. No significant environmental or health issues were identified for ATH.

Zinc Borate

Zinc borate is typically used as a synergist for halogen flame retardants such as TBBPA and decabromodiphenyl oxide. Zinc borate retains its water of hydration up to a temperature of 290 degrees C. In halogen-free applications, zinc borates are usually used with silica to provide flame retardancy for encapsulation of electronics components in low temperature environments. For example, Borax provides zinc borate products, Models Firebrake ZB and Firebrake 415. These products can be used for PWB laminates and component encapsulation applications and must be combined with aluminum hydroxide.

Key Health, Environmental, and Performance Concerns

The use of zinc borate and silica for flame retardancy is not recommended for high temperature applications for encapsulating electronics components. The low water solubility (<0.28% at 25 degrees C) and vapor pressure (negligible at 20 degrees C) of zinc borate makes it unlikely that it would be released from a polymeric matrix under normal use conditions. Zinc borate is toxic to aquatic organisms, but is not expected to bioconcentrate. At high concentrations, zinc borate can be harmful to boron sensitive plants. Zinc borate readily breaks down in the stomach to zinc oxide (ZnO) and boric acid (H_3BO_3). Zinc borate can slowly hydrolyze under certain environmental conditions to form zinc hydroxide and boric acid. There is little published information on the human toxicity of zinc borate (HDUGI, 2004), (Gardner et al, 2000).

B. Resin/Material Substitution

Non-flammable Resin

Modified epoxy resins with rigid groups between the glycidoxyphenyl groups as well as high loadings of silica, have been used for encapsulation of electronics components. For example, Sumitomo Bakelite Co. provides a flame retardant resin, Model LalphaZ. This product is used as a substrate material for semiconductor packages, and its properties include low chip warpage and improve package reliability.

Key Health, Environmental, and Performance Concerns

No data was identified for health and environmental concerns with these modified epoxy resins.

Other materials

Epoxies are the dominant plastic used in the semiconductor encapsulation and electrical power segments. Other materials used for these segments include ceramics as well as silicones and polyphenylene sulfide resins.

Ongoing Research and Product Development

Several other technologies to provide flame retardancy for epoxy resins are in the research or early commercialization phase. For example, the material 2-(6-oxido-6H-debenzo(c,e)(1,2)oxaphosphorin-6-yl)-1,4-benzenediol, known as ODOPB, was converted into a phosphorus-containing epoxy material for use in an electronic encapsulation application. An investigation in Taiwan has shown that incorporating silicon compounds, such as triglycidyl phenyl silane oxide (TGPSO) into epoxy resins improves their flame retardancy (Dufton, 2003).

Aluminum diethylphosphinate has been used as an additive flame retardant in epoxy resins in combination with alumina trihydrate. A desirable feature of this alternative is that it is hydrolysis resistant and has little moisture-absorbing tendency. Also, recent advances in biological science and polymer science have enabled efforts to generate new, robust, hybrid multifunctional materials with excellent flame retardant properties. Research is underway to develop a flexible method to use lipases for the synthesis of siloxane-based highly flame retardant hybrid polymers. (Kumar 2004)

Alternatives to TBBPA: ABS Applications

TBBPA and brominated epoxy oligomers (BEO) are the primary flame retardants used for ABS products. Several different resin systems can be used for enclosures for electrical and electronic products other than ABS. The following table provides estimates for current applications in various electrical and electronics products:

Key Health, Environmental, and Performance Concerns

Several studies show that levels of decabromodiphenyl ether (decaBDE) eixst in environmental media and in human tissue. Further information is needed to conclusively determine if a health threat exists, and numerous studies are underway to address data gaps on the toxicology and environmental fate of decaBDE.

Table 12: Resin System and Flame Retardants used for Electrical/Electronics Enclosures (Pure Strategies, 2005)

Resin System	Primary Flame Retardant	Printers	Copiers	TVs	Scanners	Fax	Monitors
FR High Impact Polystyrene (HIPS)	DecaBDE			98%			3%
FR ABS	TBBPA, BEO			2%			34%
FR Polycarbonate/Poly-styrene (PC/PS)	-						<1%
FR PPO/HIPS	Resorcinol diphosphate						<1%
FR Polycarbonate (PC)	-						<1%
FR PC/ABS	Resorcinol diphosphate	6%	5%				61%
Non FR plastics	-	94%	95%		100%	100%	

Alternatives to HBCD: EPS and XPS for Building and Construction Industry

There are numerous regulations and standards that apply to insulation used for the building industry in the U.S. These regulations and standards may exist at the national, state, county, or municipal level. Examples include:

- California State Insulation Quality Standards and Title 25 Foam Flammability Criteria
- Factory Mutual (FM) Standard 4450/4470
- Underwriters Laboratories (UL) Standard 1256
- UL Standard 263 Fire Resistance
- American Society for Testing and Materials (ASTM) C 1289
- ASTM E 119
- Miami-Dade County Florida Product Control No. 00-0208.04

It was beyond the scope of this report to determine if the alternatives identified meet the requirements for all insulation regulations and standards.

A. Flame Retardant Substitutions

Alternative Brominated Flame Retardants

There is limited data supporting non-brominated drop-in flame retardant chemical substitutes for HBCD used in EPS and XPS applications. However, there are brominated chemicals other than HBCD that are commercially available as flame retardant materials for EPS and XPS applications. The following table provides examples of manufacturers that provided these other brominated chemicals.

Key Health, Environmental, and Performance Concerns

No data was identified for health and environmental issues for these brominated chemicals.

Table 13: Manufacturers of Other Brominated Chemicals

Manufacturer	Model	Properties	Applications
Albemarle	Saytex BC-48	Contains tetrabromo-cyclooctane	Expandable polystyrene (EPS)
Albemarle	Saytex BCL-462	Contains dibromoethyldibromo-cyclohexane	Expandable polystyrene (EPS)
Great Lakes Chemical	BE-51	Contains TBBPA	Expandable polystyrene (EPS)

B. Resin/Material Substitution

Polyurethane and Polyisocyanurate Products

In 2001, approximately 185 million pounds (84.1 million kilograms) of polyester polyols and approximately 10 million pounds (4.54 million kilograms) of polyether polyols were used in the production of boardstock made of rigid foam. Most rigid foam boardstock is characterized by a high polyisocyanurate content and is usually based on lower-cost polester polyols. These polyisocyanurate modified urethane foams are used in a variety of construction applications, and are commonly referred to as "polyiso" products.

Polyiso insulation products use the following flame retardant chemicals: tris monochloropropyl phosphate (TMCPP), tris chloroethyl phosphate (TCEP), and RB-79 (diol made from tetrabromo phthalic anhydride). The following table provides examples of manufacturers of polyisocyanurate modified foams.

Key Health, Environmental, and Performance Concerns

Chlorinated and brominated flame retardants are used in the manufacture of polyiso insulation products.

TMCPP is of low to moderate acute toxicity by the oral, dermal, and inhalation routes. TCEP is manufactured from ethylene oxide and phosphorus oxychloride. (International Programme on Chemical Safety, 2005) The Department of Human and Health Services has determined that ethylene oxide may reasonably be anticipated to be a human carcinogen. (Agency for Toxics Substances and Disease Registry, 1999) Several chlorophosphates are currently undergoing the EU risk assessment process.

Phenolic Foam

Closed cell phenolic foam has been used in the building industry for various applications such as roofing, cavity board, external wall board, and floor insulation. Phenolic resins are used to bind glass fiber, mineral wool, or shredded waste to make insulation products. Glass fiber is the most commonly used material, accounting for 88% of all phenolic insulation products. Phenol and formaldehyde are the raw materials used to make the phenolic resin monomer.

In 2001, the consumption of phenolic resins for insulation products was 106 thousand metric tonnes. This consumption is anticipated to increase to 115 thousand metric tonnes in 2006.

Table 14: Manufacturers of Polyisocyanurate Modified Urethane Products

Manufacturer	Model	Properties	Applications
Atlas Roofing	AC Foam-II	Zero HCFCs, long term thermal resistance values from 6.0 to 25.0	Single ply membrane systems and cold-applied modified bitumen applications
Dow Chemical Company	Thermax	Glass-fiber reinforced polyisocyanurate foam core with embossed aluminum covering	Insulation and interior finish system for walls and ceilings
Dow Chemical Company	TUFF-R	Closed cell polyisocyanurate core with polymer/foil facers	Commercial interior wall construction behind gypsum board
Isothane	LD40 LK	Good compressive strength and cell structure.	Thermal insulation of large panels, water heaters, and storage tanks.

Key Health, Environmental, and Performance Concerns

Formaldehyde is used as a raw material for making phenolic resins. Formaldehyde is listed by the International Agency for Research on Cancer (IARC) as a known human carcinogen.

Other Insulation Materials

There are several other materials that may be used as alternatives for EPS and XPS for certain insulation applications in the building and construction industry. The four major categories of building insulation are:

1) *Blankets (fiber batts or rolls)*: Blanket insulation is usually made of fiber glass or rock wool and can be fitted between studs, joists, and beams. They are available in widths suited to standard spacings between wall studs or floor joists. Continuous rolls can be hand cut and trimmed to fit various spaces. The blankets are available with or without vapor retardant facings. Batts with special flame resistant facing are available where the insulation will be left exposed. Fiberglass is a synthetic vitreous fiber.

2) *Loose-fill*: Loose-fill insulation is typically blown into place or spray-applied by special equipment. It can be used to fill existing wall cavities and for irregularly shaped areas. Materials used for blown-in or spray-applied insulation include rock wool, fiber glass, cellulose, or polyurethane foam. Loose-fill cellulose insulation is commonly manufactured from recycled newsprint, cardboard, or other forms of waste paper. The blown-in loose-fill insulation can provide additional resistance to air infiltration if the insulation is sufficiently dense. Loose-fill insulation can also be poured in place by using materials such as vermiculite or perlite. These materials are produced by expanding naturally occurring minerals in a furnace.

3) *Rigid insulation*: This insulation is used for various wall, roof, foundation, and other building applications. Materials typically used for rigid insulation include XPS, EPS, and polyisocyanurate. This rigid insulation may be faced with reflective foil that reduces heat flow when next to an air space. These materials were discussed in more detail previously in this report.

4) *Reflective insulation systems*: These insulation systems include foils, films, or papers that are fitted between studs, joists, and beams. Common reflective system materials include foil-faced paper, foil-faced polyethylene bubbles, foil-faced plastic film, and foil-faced cardboard. The resistance to heat flow depends on the heat flow direction, and this type of insulation is most effective in reducing downward heat flow.

When using alternative building insulation materials, the necessary flame retardancy is often provided by use of a thermal barrier. Thermal barriers are fire resistant coverings or coatings that separate the insulation material from the building interior. Thermal barriers can be used to increase the fire retardant performance for various types of insulation. Thermal barriers are subject to current building code requirements. Commonly used thermal barriers include: gypsum board, gypsum or cement plasters, perlite board, spray-applied cellulose, mineral fiber, or gypsum coatings, and select plywoods.

Insulation is rated in terms of thermal resistance, called R-value. This value indicates the resistance to heat flow. The R-value is a critical property considered by residential, commercial, and industrial consumers of insulation. The R-value of thermal insulation depends on the type of material, and the thickness of the material. The following table illustrates the R-value for several types of insulation materials that are currently commercially available.

Table 15: R-Values for Various Types of Insulation (Department of Energy, 2002)

Insulation Type	R-Value per inch of thickness
Fiber glass blanket or batt	2.9 – 3.8
High performance fiber glass blanket or batt	3.7 – 4.3
Loose-fill fiber glass	2.3 – 2.7
Loose-fill rock wool	2.7 – 3.0
Loose-fill cellulose	3.4 – 3.7
Perlite or vermiculite	2.4 – 3.7
EPS board	3.6 – 4.0
XPS board	4.5 – 5.0
Polyisocyanurate board (unfaced)	5.6 – 6.3
Polyisocyanurate board (foil faced)	7.0
Spray polyurethane foam	5.6 – 6.3

Another important consideration for selecting an insulating material is moisture control. An indoor relative humidity of about 50% is typically considered a healthy level because it is comfortable to humans, and also because may molds and mites are unlikely to thrive in that environment. The moisture performance of a building depends on the type and position of the insulation, and whether a vapor retarder is installed. The best insulation approach is dependent on the local climate, type of building construction, amount of indoor moisture produced, building ventilation, and indoor temperature conditions. Permeance is a measure of how much water vapor can travel through a material. Permeance is an important property for moisture control. The lower the permeance, the better the vapor retarder. The following table illustrates the permeance value for certain insulation types and other vapor retarder materials.

Key Health, Environmental, and Performance Concerns

The fiber glass blanket or batt, loose-fill fiber glass, perlite, and loose-fill rock wool have a much lower R-Value than XPS boards or polyisocyanurate boards and therefore may not be desirable for applications where high R-Value is a critical property.

Fiberglass, glass wool, and mineral wool are considered synthetic vitreous fibers. When these fibers are suspended in air they can cause irritation of the eyes, nose, throat, and parts of the lung. Animal studies show that repeatedly breathing air containing synthetic vitreous fibers can lead to inflammation and fibrosis of the lung. (Agency for Toxics Substances and Disease Registry, 2004)

Table 16: Permeance of Building Materials (Department of Energy, 2002)

Material	Permeance
Vapor retarder paper	0.45
EPS (1 inch)	2.0
XPS (1 inch)	1.2
Cellulose acetate (0.01 inches)	4.6
Polyester (.0032 inches)	0.23
Gypsum wall board	50

Section III: Recommendations & Conclusions:

On a global basis, the annual market demand in 2003 for TBBPA and HBCD was approximately 145,113 and 21,951 metric tonnes respectively. TBBPA and HBCD are used in a variety of applications. TBBPA is most commonly used as a reactive flame retardant in epoxy resins for printed wiring boards. HBCD is most commonly used for expanded polystyrene (EPS) and extruded polystyrene (XPS) insulation applications in the building and construction industry.

Manufacturers of end-products such as printed wiring boards and building insulation requiring flame retardance can employ one of three approaches to reduce or eliminate the use of TBBPA and HBCD in their products. These approaches are flame retardant substitution, resin/material substitution, and product redesign. This report has identified numerous potential alternatives for both TBBPA and HBCD that are commercially available. Most of the potential alternatives identified are flame retardant substitutes, and some are resin/material substitutes.

For TBBPA use in printed wiring boards, this report identified potential alternatives in the following categories: other brominated compounds, red phosphorus, other phosphorus based compounds, metal hydroxides, non-flammable resins, polyimide resin, and other resins. For HBCD use in EPS and XPS insulation applications, this report identified alternatives in the following categories: other brominated flame retardants, polyurethane and polyisocyanurate products, phenolic foam, and other insulation materials.

Manufacturers have identified certain requirements that should be met before these substitutions can be made. (Scheifers, 2004) These requirements include:

- ➢ Equal or better flame retardance for the product/part
- ➢ Equal or better performance and physical properties for the product/part
- ➢ Less risk to environment and human health
- ➢ Cost
- ➢ Commercial availability

This report identifies some key health, environmental, and performance concerns for each alternative. However, additional research needs to be conducted on the TBBPA and HBCD alternatives identified in this report. This research will help to better determine if the above substitution requirements are satisfied for the most common uses of TBBPA and HBCD and to determine if the materials discussed in fact represent safer alternatives.

The following areas of additional research would provide a better understanding of the adequacy of the alternatives:

- The various chemicals that are used for flame retardancy could be identified for each of the potential alternative materials. The percent composition for each of these chemicals can be determined, as well as the manner of incorporation, additive or reactant, into the product. Once this chemical information is obtained, a more detailed assessment of the environmental and human health risks associated with the TBBPA and HBCD alternatives can be performed. For many of the potential alternatives identified in this report, the existing health and environmental data may be more limited than for either TBBPA or HBCD. These data gaps should be identified and carefully considered before recommending specific alternatives. Sufficient care should be taken to ensure that the substitutes are less hazardous than the chemicals they are replacing.

- In this study we provided a nominal review of pertinent standards associated with the various uses of TBBPA and HBCD. To better understand the flame retardance requirements for products using HBCD and TBBPA, a more thorough review of the pertinent regulations and standards that apply to electronics and building insulation products regionally, nationally, and globally could be conducted. This could include UL standards, Factory Mutual Standards as well as various municipal, county, state, federal, and international regulations.

- Further research of TBBPA and HBCD alternatives could include a more detailed comparison of the flame retardancy as well as other key performance requirements for the various uses of TBBPA and HBCD. The alternatives could then be evaluated and compared as to how well they meet the various performance requirements for each use. It should be noted that TBBPA is used in some mission critical PWB applications such as military, aerospace, medical equipment, and telecommunications. Sufficient reliability data should be obtained for these alternatives before their use is recommended.

- A comparison could be conducted of costs associated with using TBBPA and HBCD versus costs for using alternatives. The commercial availability of the alternatives could also be determined. This comparison was outside the scope of this study.

- The U.S. Green Building Council (USG BC) has developed a system to rate the environmental design of buildings. The Leadership in Energy and Environmental Design (LEED) Green Building Rating System is a voluntary standard that recognizes the life cycle costing of building construction. Building insulation products are often evaluated based upon their ability to obtain LEED credits in several categories. HBCD alternatives could be evaluated with respect to attaining LEED credits.

- Additional factors that may be investigated for the potential alternatives include the raw materials and manufacturing processes used to make the chemical/material, as well as the recyclability of the material at product end of life.

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