

# IPC-WP/TR-584A

## IPC White Paper and Technical Report on the Use of Halogenated Flame Retardants in Printed Circuit Boards and Assemblies (Correcting the Misunderstandings on “Halogen-Free”)

[This document, in its initial release, was titled:  
IPC White Paper and Technical Report on Halogen-Free  
Materials used for Printed Circuit Boards and Assemblies]

NOTE: The proposed resolutions to the Technical Comments submitted on the Final Draft in April 2007 are shown in the following document. These are indicated in lined-out **red** (deletions) and **blue** (additions). The proposed resolutions will be approved during a Subcommittee teleconference on June 6, 2007.

**FINAL DRAFT – May 2007**  
**By the IPC 4-33 Halogen-Free Materials Subcommittee**



ASSOCIATION CONNECTING  
ELECTRONICS INDUSTRIES®

## EXECUTIVE SUMMARY

### SCOPE

This document summarizes the IPC position on the subject of “halogen-free” materials for the electronics industry. Its initial release was developed over a period of three years and this revision was also worked upon for another 3 years by a team representing every level of the electronics supply chain. This document is applicable to materials for interconnecting electronics including, but not limited to, copper-clad laminates and prepregs, resin coated copper foils, flexible materials and solder masks. This document reflects the state of the information and technology as of May 2007.

### INTRODUCTION

Across a variety of industries, consideration is being given to the use of alternatives to halogenated flame retardants. Thus, the use of non-halogenated flame retardants in polymer applications is currently an area of much research and discussion. Halogens are the Group 7 elements in the periodic table and include fluorine, chlorine, bromine, iodine and astatine. Electrical and electronic products may be considered “halogen-free” if they are assembled without the intentional use of these elements in the raw materials and these elements are not intentionally present in the end product. Even when halogenated flame retardants are not added to the polymer formulations, the finite levels of these elements may be present as impurities in the raw materials and as an unintentional by-product of the polymerization process employed. The proposed industry standard for incidental occurrence of chlorine and bromine in electronic base materials is **0.09% maximum chlorine, 0.09% maximum bromine and 0.15% maximum total chlorine plus bromine** as defined by the international industry standard IEC 61249. **There is no mention of restrictions on the other halogen elements of fluorine, iodine and astatine.**

Due to the nature of their (flammable components) composition and function (transmission of electrical charges), printed circuit boards (PCBs) require ignition protection. Flame retardant materials, which prevent ignition and spread of flames should ignition occur, present a number of manufacturing challenges in terms of cost, performance, fire safety as well as health, environmental, and regulatory issues.

Tetrabromobisphenol A (TBBPA) is the primary flame retardant used in PCBs. TBBPA is an organic molecule whose composition includes approximately 59% bromine and thus falls under the broad classification of halogenated flame retardants. It is cost effective, compatible with PCB components, qualified in use on a worldwide basis, and has no health, environmental, or regulatory issues that exclude its use. Still there exist a number of activities that are being driven by marketing strategies and not scientific data which call for its reduction or elimination from PCBs. Clearly there is no legislation or regulations, pending or otherwise, calling for the removal of TBBPA.

This document serves as a historical perspective and status of industrial, environmental, and legislative programs. It also provides information on cost, performance, product reliability, consumer safety, and end-of-life issues of common and alternative flame retardants used in PWBs.

### RESEARCH

A shift from TBBPA to non-halogenated flame retardants in printed circuit boards would have a profound impact upon the PWB industry, thus this position paper was commissioned by IPC to

examine the need for such a shift. The exhaustive review is summarized in the appendices as shown below:

- APPENDIX 1: Fire Safety and Electronics**
- APPENDIX 2: Flame Retardants used in the PWB Industry**
- APPENDIX 3: Halogens in Non-Brominated Epoxy Resins and Their Electrical Laminates**
- APPENDIX 4: Toxicological, End-of-Life, and Recycling Issues**
- APPENDIX 5: Political and Marketing Driver and Organizational Efforts**
- APPENDIX 6: IEC 61249-2-21, Specification for Non-Halogenated Epoxide/Woven E-glass Laminates of Defined Flammability.**
- APPENDIX 7: Test Method for Total Halogen Content in Base Materials**
- APPENDIX 8: Final Report of the European Union Assessment of Tetrabromobisphenol-A Project – Human Health**

From the vast amount of information reviewed, a confident conclusion may be reached as to the use of TBBPA as a flame retardant in printed circuit boards. The resulting position of IPC is as stated below.

## **CONCLUSION**

There is no data indicating that the halogen flame retardants presently used in printed circuit boards present any significant environmental or health hazard. Although halogenated flame retardants have been in use in electronic products for many decades, there have been no reports of illness or death attributable to their use and in fact injuries and/or death are known hazards of the fires associated with non-flame retarded electronic equipment. There is also no data indicating that any of the materials currently being considered as replacements for these halogenated flame retardants are any better or worse for the environment.

Until relevant data is presented proving the current flame retardants incorporated into the polymeric structure have an adverse environmental impact and the alternatives are better, IPC will not support any reduced ppm level or recommend specific alternative chemistries. It is IPC's position that these reduced levels do not ensure product reliability and may exclude certain laminate and prepreg base materials from the market.

IPC, IEC and Underwriters Laboratories have chosen to segregate halogen-free materials from their halogen-containing counterparts. The basis for these decisions was, in part, due to the differences in thermal stability, physical performance such as moisture absorption and the PCB processing. The "halogen-free" materials are not direct replacements for halogen-containing grades with similar target performance. For Underwriters Laboratories, "halogen-free" materials must undergo Long Term Thermal Aging (LTTA), full index testing and Metal Clad Industrial Laminate (MCIL) testing in order to fully characterize these products before listing.

IPC documents will provide the electronics community with a test method for standardizing the analysis for halogens in base materials as well as defining maximum levels of chlorine and bromine for these newly developed grades of base materials. The purpose of this activity is standardization and consistency within the supply chain and is not considered an endorsement by IPC of these materials. IPC does encourage continued research in both base materials development and the study of the impact of these materials on health, safety and environmental concerns.

The use of the term 'halogen-free' as part of a marketing or other product campaign refers to the use of chlorine and bromine in electronics. The European Union Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) directives restrict the use and handling of certain brominated flame retardants in electronics. The IEC and IPC definitions of halogen-free pertain specifically to chlorine and bromine content in PCB base materials. Although fluorine is also a member of the halogen family, polytetrafluoroethylene

(PTFE)-based materials that are used as PCB base materials, are not included in any current or known pending regulatory guidelines or bans.

In light of this data, IPC recognizes the term "halogen-free" as a marketing term only and **does not support or advocate**~~will not advocate~~ a conversion from a known safe method of generating flame resistance for base materials. **In fact, all base materials and solder masks have some halogen content, so there are "low halogen", but no truly "halogen-free" materials.**

## APPENDICES

### APPENDIX 1: Fire Safety and Electronics

Maintaining and improving levels of fire safety are vital. Despite modern advances in building construction codes, sprinkler and fire alarm systems, and fire fighting capabilities, fire takes a tremendous toll on humanity.

The primary focus of fire hazard and risk reduction is to decrease the seriousness of the fire itself. This can be achieved by suppressing or delaying ignition and by avoiding or delaying flashover. Flashover can be avoided or delayed by reducing the rate of heat release rate and flame spread.

Flame retardants can reduce the seriousness of a fire because they decrease the probability of ignition and, if ignition occurs, limit the rate of fire growth. Thus, flame retardants reduce the incidence and developmental rate of fires. Fire performance testing and analysis of fire statistics indicate significant benefits in terms of reduction in the number of fire deaths and property losses can be achieved by using flame retardants. This is especially true with respect to consumer products in the high fire risk category; e.g., upholstered furniture, space heating, and textiles. The fire statistics analysis suggests that the risk of death or injury from fires involving consumer products such as upholstered furniture can be reduced by 30 to 90 percent or more by using flame retardants.

It can thus be concluded that most printed circuit boards must be flame retarded in order to assure public safety.

**1.1 Health and Monetary Costs** Research carried out in 19 countries by the World Fire Statistics Centre showed that 11,500 fire deaths occur annually, and that although deaths in the U.S. fell from 5880 in 1989 to 4860 in 1991, deaths in France, Germany, Japan, and Hungary rose (*Lloyd's List, 2 Aug 1995, p.3*). The total number of fire fatalities in seven countries (Japan, U.S., Canada, U.K., Germany, France, and Italy) exceeds 8800 each year according to recent statistics from the World Health Organization (WHO) (*as cited in Tsuda, Y. J. Med. Soc. Toho, Japan, 1996, 43,3: 188-192*). In the U.K., 900 people die annually, and the direct costs of fire losses increased to £1.3 billion in 1991 (*Lloyd's List, 2 Aug 1995, p.3*).

For the most recent year's data available in the United States (1994), the total dollar value either lost to fire, spent to avoid or deal with fire, or donated to avoid or deal with fire in the U.S. was \$115-154 billion (*Hall, J. R. The Total Cost of Fire in the United States Through 1994. National Fire Protection Agency, Quincy, MA, 1997*). Fire costs the EU around one percent of its Gross Domestic Product (GDP) each year and, despite this, according to Lloyd's List, in 1995, little was being done to either monitor or tackle the problem. In 2001, 388 deaths and 2310 injuries were attributed to fires in Canada.

**1.2 Results of Fires Due to Electronics** Electronic equipment is a part of the fire problem worldwide. The U.S. arguably has some of the highest standards for fire safety for electronic equipment, including voluntary UL compliance (UL 94 V-0) for plastics used in these applications. Yet even in the U.S., more than a thousand structure fires a year are reported to fire departments as originating in electronic equipment rooms or areas. Civilian deaths have been rare but have occurred in three of the last four years in the period from 1990 to 1994. Direct property damage averaged roughly \$30 million a year in recent years (*Hall, J.R. Special Analysis Package Computer Equipment and Computer Areas, National Fire Protection Agency, Quincy, MA, 1996*).

The risk of death or injury for consumer product-related fires is highest for upholstered furniture. Upholstered furniture fires account for 40 deaths and 4133 nonfatal injuries per 1000 product fires in the UK. In the US, upholstery related fire deaths are even higher - up to 86 deaths per 1000 upholstery fires. Other consumer-related high-risk sources or products include space heating, textiles and furnishings and, historically, televisions.

In the U.S. from 1989 to 1993, fires due to televisions, radios, VCRs, and phonographs accounted for the largest number of civilian fire deaths and placed third in the number of civilian fire injuries and dollar loss in all appliance or tool fires. There was an average of 35 civilian deaths, 166 civilian injuries and \$34.8 million in direct property damage per year resulting from an estimated 2400 home fires per year starting in this type of equipment. Short circuits or ground faults were the leading cause of ignition, and electrical wire or cable insulation was the leading form of material first ignited. Appliance housings or casings were the second leading form of material first ignited and was associated with more civilian fire deaths and injuries than any other form of material. (*Slayton, D. M. The U.S. Home Product, 1989-1993 (Appliance and Equipment), National Fire Protection Agency, Quincy, MA, 1996.*)

**1.3 Costs of Fires in the U.S.** Other U.S. data for the years 1990 to 1994 show there were an average of 1179 structure fires originating per year in electronic equipment rooms or areas, with an annual average of one civilian death, 36 civilian injuries and \$28.9 million in direct damages. Dwellings, duplexes, and manufactured homes collectively ranked first among properties with these fires. General business offices ranked second. Most of these fires began with electrical distribution system equipment vs. 'other equipment,' a large category that includes electronic equipment. Electronic equipment specifically was involved in the ignition of 148 fires (annual average from 1990 to 1994) at a direct property damage cost of \$7.29 million. Office machines vs. the combination of consumer electronics (televisions, radios, VCRs, or phonographs) were involved in the ignition of 21 and 15 fires, respectively at a direct property cost of \$0.27 or \$0.12 million, respectively. (*Hall, J. R. The Total Cost of Fire in the United States Through 1994. National Fire Protection Agency, Quincy, MA, 1997, and Hall, J.R. Special Analysis Package Computer Equipment and Computer Areas, National Fire Protection Agency, Quincy, MA, 1996.*)

The growth in the total cost of fire in the U.S. has been led not by the fire losses themselves but by other cost components. These 'other' costs totaled about \$30 billion in 1991. The largest share of this \$30 billion was associated with the manufacturing costs of equipment meeting UL or other fire safety standards (especially important in electrical systems equipment and other equipment using computer components). Manufacturing costs in this area accounted for \$18 billion or 12 to 15 percent of the total cost of fires in the U.S. In contrast, costs associated with fire retardants and all product testing for fire safety were only about \$2.5 billion or about two percent of the total fire costs. Reducing U.S. fire losses and achieving equivalent fire safety at lower costs are both important goals. (*Hall, J. R. The Total Cost of Fire in the United States Through 1994. National Fire Protection Agency, Quincy, MA, 1997.*)

**1.4 Human Health Fire-Related Issues** The numbers of fire deaths and injuries are a significant world-wide problem, particularly in dwellings and the home environment, despite a declining trend over the years. The major hazards of most fires arise from the existence of the fire itself and not from the materials burned. This is because most fire deaths are attributable to carbon monoxide poisoning, and carbon monoxide is produced in all fires, regardless of the source.

The risk of human death and injury in fires is directly related to the rate of fire development; e.g., the rate of heat release and flame spread. The toxicity of fire atmospheres is a function of the production rate of a few key fire gases, with those concerns leading to toxicity and content. The greatest hazards occur in well-developed fires and with increasing duration of exposure to the fire atmosphere. Most fire deaths are due to carbon monoxide poisoning. The major hazard to human health from a fire is directly related to the fact that a fire exists, and not to what materials are burning.

Thus, the most effective method to reduce fire deaths and injuries is to decrease the seriousness of the fire itself. This can be achieved by suppressing or delaying ignition and by avoiding or delaying flashover. Flashover, the point at which all materials spontaneously burst into flames, can be avoided or delayed by reducing the rate of heat release and flame spread.

One means of reducing fire hazard and risk is through the use of flame retardants. Further to their abilities to prevent ignition, their overall effect is to reduce the rate of heat release, consumption of substrate, and consequently the evolution of toxic gases. In addition, flame retardants reduce exposure to toxic gases by increasing escape time; e.g., the time before flashover or the occurrence of an incapacitating atmosphere. No evidence indicates flame retardants contribute to the direct human health risks due to toxic fire gases.

**1.5 Future Strategies to Lower Fire Risk in Consumer Products** Flame retardants in consumer products are a very important part of any overall strategy to reduce the impact of fires. Risk assessments showing the balance of risk advantage, taking into account product life-cycle and the environment, need to be carried out on the more common flame retardants used in consumer products and when new flame retardant compounds are being considered. The more research that is done to assess these risks, the greater the opportunity will be to exploit the benefit of these compounds to improve consumer safety while safeguarding public health and the environment. Equally important is further research demonstrating that significant fire loss reduction, including loss of life, can be achieved by using flame retardants. The best example to date is the huge savings achieved by using flame retardants in upholstered furniture in the UK to meet the Furniture and Furnishing (Fire Safety) regulations of 1988. In 1997, an estimated 354 lives were saved as a result of these regulations. The total number of lives saved since 1988 could be as high as 1860.

In summary, a UK Department of Trade and Industry (DTI) report found: Despite falls in the numbers of fire deaths over the years, losses from fire are still a significant world-wide problem, particularly in dwellings and the home environment. The major hazards of most fires arise from the existence of the fire itself and not from the materials burned. There is no evidence that flame retardants contribute to the direct human health risks arising from toxic gas effects.

Toxicology data on flame retardants commonly used in consumer products suggest the benefits derived in reducing the risk from fire outweigh any risks to human health for many of the flame retardants. Further, many flame retardants do not pose a significant threat to human health and the environment. Continued reduction of fire losses can be achieved using a number of complementary tools. These include mandatory or voluntary fire safety controls, active promotion of fire safety devices such as smoke alarms and sprinklers, general education of consumers in fire prevention and escape, and designing out fire risk by reducing inherent fire risk of consumer products through product modification (e.g., using flame retardants or low flammability materials), particularly for higher fire risk items such as furniture and televisions.

## APPENDIX 2: Flame Retardants Used In The PCB Industry

There are four main families of flame-retardant chemistries:

- Inorganic flame retardants, including aluminum trioxide, magnesium hydroxide, ammonium polyphosphate, and red phosphorus.
- Halogenated flame retardants, primarily based on chlorine and bromine. The brominated flame retardants are included in this group, which represents about 25 percent by volume of the global production.
- Organophosphorus flame retardants are primarily phosphate esters and represent about 20 percent by volume of the global production; they may contain bromine or chloride.
- Nitrogen-based organic flame retardants, which are used for a limited number of polymers.

Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid, or gas phase. They interfere with combustion during a particular stage of this process; e.g., during heating, decomposition, ignition or flame spread. Substituting one type of flame retardant with another consequently means a change in the mechanisms of flame retardancy.

There are eight ANSI laminate classifications that require flame retardancy:

FR-1: phenolic resin /paper, general purpose

FR-2: phenolic resin /paper, higher quality, tested for electrical properties

FR-3: epoxy resin /paper

FR-4: epoxy resin /glass cloth, higher peel strength

FR-5: epoxy resin /glass cloth, higher heat resistance

FR-6: polyester resin /glass cloth

CEM-1: epoxy resin /glass cloth / cellulose core

CEM-3: epoxy resin /glass cloth / glass fiber core

N/A: Woven E-Glass/Hydrocarbon/ Ceramic

N/A: CRM-5: Woven E-Glass Face Sheets, Non-Woven E-Glass Core/Polyester/ Kaolin

N/A: Woven E-Glass/Polyester/ None

All of the above must pass NEMA LI-1, Flammability Classification 1, except the CEM grades that must pass classification 0. Classification 1 is essentially equal to UL-94 V-1, classification 0 is equal to V-0.

In addition, UL94 ratings can be and have been granted to a variety of other laminate materials on a specific product or product category basis not covered by the above ANSI grades.

UL-746E also specifies flame retardant performance for PCBs.

**2.1 Brominated Flame Retardants** Brominated flame retardants can be divided into three classes:

- Aromatic, including TBBPA, polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls (PBBs).
- Aliphatic, which are in general used in relatively small quantities.
- Cycloaliphatic, including hexabromocyclododecane (HBCD).

**2.1.1 Polybrominated Diphenyl Oxides or Ethers (PBDEs)** Brominated diphenyl oxides or ethers are a group of aromatic brominated compounds in which one to ten hydrogens in the diphenyl oxide structure are replaced by bromine. Three commercial PBDE products are had historically been manufactured : DBDPO (also abbreviated DBDPE), OBDPO (also OBDPE), and PeBDPO (also PeBDE). Since 2004, DBDPO is the only PBDE made commercially and available on a global basis. DBDPO is greater than or equal to 97% DBDPO decabromodiphenyl oxide (ether); OBDPO contained hexabromo- to decabromo-diphenyloxides and PeBDPO contained tribromo- to hexabromo-diphenyloxides.

The family of PDBEs is recommended for substitution by the EU's in the Official Restriction of Hazardous Substances (RoHS) Directive. ~~proposal and this recommendation is currently being debated in Europe~~ However, while both OctaBDO- and pentaBDO-types of PDBEs remain as prohibited substances under RoHS in electrical and electronic equipment, such is not the case with DBOPO. ~~these substances are currently undergoing risk assessments and these results will be taken into account before any decisions on substitution are reached. Based on the completion of the PeBDPO risk assessment, PeBDPO will be substituted. Only PeBDPO and DBDPO are commercial, and the DBDPO risk assessment is not yet complete.~~ Following the completion of the risk assessment of DBOPO, the EU has exempted this substance from the provisions of the RoHS Directive (Commission Decision 717/2005/EC published in the EU's Official Journal on 10/15/2005), and therefore, DBDPO can continue to be used in RoHS-compliant products.

**2.1.2 Polybrominated Biphenyls (PBBs)** PBBs are a group of halogenated hydrocarbons that are formed by substituting bromine for hydrogen in biphenyl. The bromine content can vary between two and ten. PBBs are a moot issue, as they have not been used in commercial production to any significant extent since the late 1970s and were never used in PCBs.

PBB is targeted for elimination in the ~~Official Proposal of the WEEE~~ EU's RoHS Directive.

**2.1.3 Tetrabromobisphenol A (TBBPA)** TBBPA is the major flame retardant used in circuit PCBs because it increases  $T_g$  of the epoxy resins and allows the resin to pass the UL-94 flammability test. It is also used to flame retard acrylonitrile-butadiene-styrene (ABS) resins used in electronic housings. One of the advantages of brominated flame retardants is that they can be used at relatively low concentrations because their mode of action is a free radical mechanism, which allows resins to maintain their physical properties.

**2.1.4 Hexabromocyclododecane (HBCD)** HBCD is the flame retardant for expanded and extruded polystyrene used in thermal insulation of buildings, and is also used to a lesser extent to flame retard upholstery textiles. In that use, HBCD is applied as a backcoat to the fabric that is, in turn, encapsulated in a polymer.

**2.1.5 Other Industrial Uses for Bromine** Further to serving as a flame retardant, bromine serves several other industries.

It is used as an active ingredient in over-the-counter and prescription medications, such as analgesics and anesthetics. Some new cancer drugs also contain bromine.

Brominated biocides are used in recreational swimming pools and industrial water treatment facilities to control algae, bacteria growth, and odor. Brominated pesticides are used for soil and grain storage and for high value crops, such as tomatoes, melons, and tobacco.

To reduce volatile organic emissions (VOCs), and due to concerns with ozone depletion, many solvent users are switching from chlorine- to bromine-based solvents.

Bromine compounds are also used to make the light-sensitive component of photographic emulsion and in photo developing compounds.

**2.2 Bromine Alternatives** Halogen-containing flame retardants are effective due to their interference with the radical chain mechanism in the combustion process of the gas phase. Bromine, in particular, is especially favored due to its ideal timing for interference attributed to the particular bonding strength to carbon. Other halogens including fluorine and iodine are not ideal, as they do not interact at the appropriate time in the combustion process due to their strong and weak bonding respectively. These bonding strengths also tend to cause these halogens to unfavorably impact the polymer properties.

As described by choice of halogen, a flame retardant should be carefully chosen not only for flame retardancy effectiveness but also for its effects on the overall properties of the polymer system. Two other considerations should also be made when identifying possible flame retardants due to their impact on the overall system: the mode of flame retardancy and its means of interaction into the polymer system.

The mode of fire retardancy can act either physically or chemically. Possible physical interactions by the flame retardant include cooling the polymer below necessary combustion temperatures, forming a char layer over the polymer to not allow oxygen in the system (intumescence), and diluting the amount of fuel in the system by the presence of an inert material. Chemical interaction includes mechanisms taking place in the gas phase, interfering and prohibiting the continuation of the combustion process, and mechanisms occurring in the solid phase, which can either break down the polymer or chemically form a carbon layer on the surface. In general, chemical interactions have been deemed most effective for fire retardancy due to their consistent and aggressive means.

Also important to the polymer system is the interaction of the flame retardant; be it reactive or additive. This is important to distinguish as it affects not only polymer properties but also processing and environmental repercussions. Reactive flame retardants are chemically built into the polymer structure and are usually more beneficial as they provide a consistent structure for fire retardancy and substrate properties. Additives flame retardants, however, are incorporated by mechanical means and have the unfavorable chance of not being uniform in the system and the potential for blooming out of the system, causing not only inconsistent properties, including flame retardancy, but also adverse environmental effects.

It should be noted that the combined use of flame retardants, reactive or additive, could sometime provide a synergistic effect to the polymer system. This is especially true for the synergistic effect of antimony in combination with halogens. When used alone, the primarily used antimony compound  $Sb_2O_3$  is believed to perform no fire retardancy mechanisms, however, improved flame retardancy properties are achieved when used along with halogen compounds. Despite this, antimony is a **very moderately** toxic metal and a **known suspected** carcinogen along with its oxides.

**2.2.1 Inorganic Flame Retardants** The majority of components in this class of flame retardants act in the physical means for fire retardancy and are incorporated into the polymer system as an additive. Under the combustion conditions of the substrate, the inorganics decompose to non-flammable gases that can perform the several physical interactions mentioned in 5.2. There are few available to be used for fire retardancy purposes, as they must sustain their effectiveness in the decomposition temperatures of polymers, 150°C to 400°C. Although these compounds are the most environmentally friendly, they provide difficult processing due to their additive nature. With proper dispersing and utilizing the proper particle size, these compounds can be used effectively.

**2.2.1.1 Aluminum Trihydroxide (ATH)** ATH is low cost filler that begins to break down at 180°C to 200°C. The decomposition is an endothermic reaction that releases water and performs all three physical interactions for fire retardancy: cooling of the polymer, forming a charred insulation layer over the substrate, and diluting the fuel remaining in the system. The disadvantage of using

this material is that very high levels of loading are required to achieve the desired flame retardancy.

Aluminum hydroxide and other hydroxides act in a combination of various processes. When heated, the hydroxides release water vapor that cools the substrate to a temperature below that required for sustaining the combustion processes. The liberated vapor also has a diluting effect in the gas phase and forms an oxygen-displacing protective layer. Additionally the oxide (e.g.  $\text{Al}_2\text{O}_3$ ) forms together with the charring products as an insulating protective layer.

**2.2.1.2 Magnesium Hydroxide  $\text{Mg}(\text{OH})_2$**  Magnesium hydroxide also decomposes in the same manner as ATH, yet at a higher temperature ( $330^\circ\text{C}$ ). It also chars to form an insulation layer but produces less smoke than ATH.

**2.2.1.3 Boron-Containing Compounds** Boron-containing compounds used as flame retardants act by an endothermic mechanism and stepwise release of water. They also aid in fire retardancy by forming a glassy coating protecting the substrate. The most common substance is zinc borate, which is usually used in combination with other flame retardants due to the synergistic effects, especially ATH.

**2.2.2 Nitrogen-Based Organic Flame Retardants** Nitrogen based fire retardants form an intumescent coating over the polymer due to gases released during decomposition. Nitrogen compounds are usually used as a synergist to phosphorus flame retardants, as the thermal decomposition or formation of phosphoric acid is accelerated, where after it esterifies, dehydrates, and then forms the intumescent coating. The result is a layer of liquid polyphosphoric acid, a glassy and temperature-resistant layer of PNO, and a layer of cross-linked polyphosphazenes.

**2.2.3 Phosphorus-Containing Flame Retardants** Phosphorus-containing flame retardants are very diverse as they not only exist in additive and reactive means, but also can act physically or chemically in the mode of fire retardancy. Acting in the physical mode, the material is thermally decomposed to form phosphorus acid, which extracts water from the substrate, thus forming a char. In the chemical mode of fire retardancy, the phosphorus compound can interfere with the radical mechanisms of the gas phase just like that of halogen flame retardants.

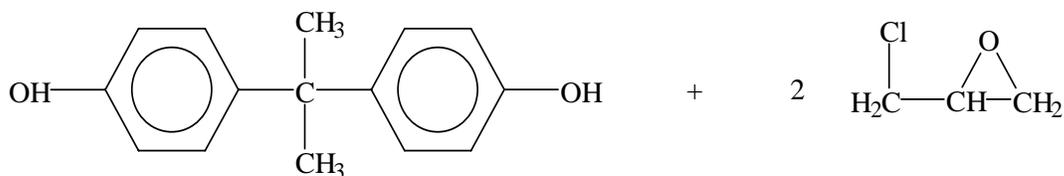
**2.2.3.1 Red Phosphorus** Red phosphorus can be used by additive means and achieves fire retardancy in the same manner as other phosphorus compounds, by forming a protective char due to phosphorus' affinity for oxygen. There are several human health risks associated with the material including flammability and autoignition. Red phosphorus as a filler will create red and black laminates due to the opaque nature of the material.

**2.2.3.2 Organo-Phosphorus** These products react with epoxy resins. This reacted material is hydrophilic, which results in high water absorption, which is a useful property for a flame-retardant material. However, the compounds do poorly in pressure cooker tests, and even worse, unfortunately, produce carbon monoxide when burned.

### APPENDIX 3: Halogens in Non-Brominated Epoxy Resins and Their Electrical Laminates

**3.1 The Source of Halogens in Non-Brominated Epoxy Resins** Virtually all non-brominated epoxy resins contain small amounts of residual halogen-containing compounds that were produced during the epoxy resin's manufacturing process. These halogens are in the form of chlorine-containing organic and inorganic compounds. The source of these chlorinated compounds usually originated with epichlorohydrin (2,3-epoxypropylchloride). It is one of the two primary starting reactants used in almost all of the commercial epoxy resin manufacturing processes.

Typically, epoxy resins are manufactured using the reaction between one molecule that contains two or more phenolic hydroxyl groups with an equivalent number of epichlorohydrin molecules. This reaction is conducted in the presence of a base such as sodium hydroxide. The following chemical reaction is representative of those used to manufacture the most common, commercially available epoxy resins.



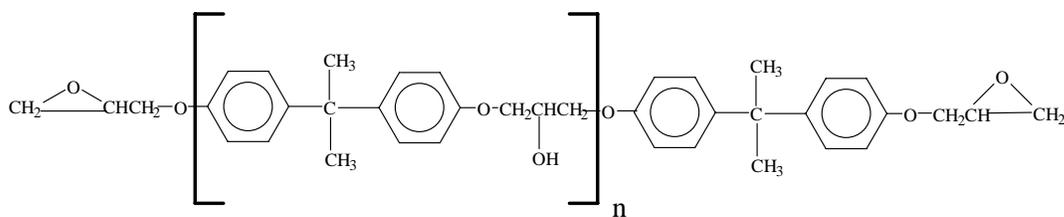
Bisphenol of Acetone (BPA)

Epichlorohydrin

[4, 4'-isopropylidenediphenol]

[2,3-epoxypropylchloride]

The resulting epoxy resin has a chemical structure as follows:



where  $n = 0, 1, 2, 3, \dots$

During this reaction, two by-products are produced:

$(n + 2)$  NaCl  
Sodium Chloride

and

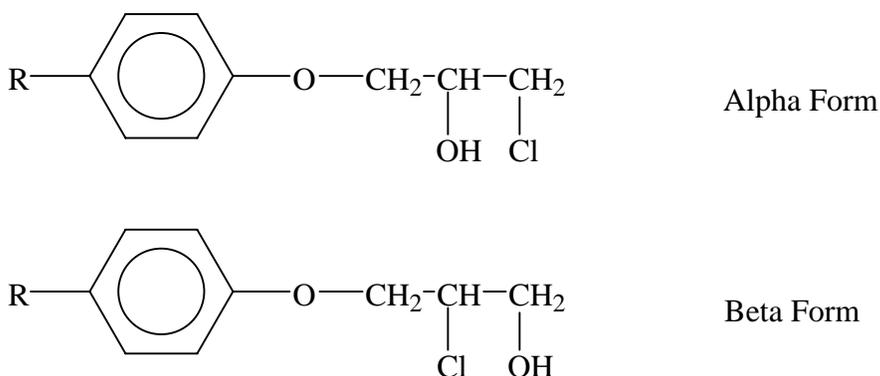
$(n + 2)$  H<sub>2</sub>O  
Water

In a subsequent purification step, the brine (sodium chloride/water) solution is removed from the product mixture yielding the epoxy resin. The epoxy resin that is made using BPA and epichlorohydrin reactants is known as the diglycidyl ether of the bisphenol of acetone; it is usually abbreviated as either DGEBA or BADGE. A wide range of products composed of this type of epoxy resin are commercially available where  $0 \leq n_a \leq 14$ , with  $n_a$  being the average number of structural units in the DGEBA molecule. Since there are two epoxy groups per DGEBA molecule, this type of resin is designated as a difunctional epoxy resin.

When materials that contain more than two phenolic hydroxyl groups per molecule are reacted with equivalent amounts of epichlorohydrin, epoxy resins are produced that have more than two epoxy groups per repeating unit of the polymer molecule. These materials are designated as multifunctional epoxy resins. A wide range of these epoxy resins is also commercially available. Both difunctional and multifunctional epoxy resins can be used to prepare non-brominated epoxy laminating resins. The specific epoxy resin that is used depends upon the desired laminate properties.

Not all of the chemical compounds found in commercial epoxy resins contain only epoxy groups. During the commercial manufacturing of epoxy resins, side reactions between epichlorohydrin and other organic compounds yield molecules that do not necessarily contain just epoxy groups. These molecules often contain chlorine atoms and can exist as a wide variety of different chemical compounds. The most familiar of these compounds, in the electrical laminating industry, are those classified as hydrolyzable chlorides.

**3.2 Hydrolyzable Chlorides** During the reaction of a phenolic hydroxyl group with epichlorohydrin, an intermediate chlorohydrin chemical molecule is formed. While almost all of these molecules are converted into epoxy molecules during the commercial epoxy resin manufacturing process, a few usually remain unconverted. These chlorohydrin compounds can exist in two different chemical isomeric forms.



where R signifies the presence of another chemical molecular fragment.

While structurally very similar, these compounds chemically react very differently. The alpha chlorohydrin is much more reactive than the beta chlorohydrin. The chlorohydrins that can be readily hydrolyzed are commonly called hydrolyzable chlorides or occasionally saponifiable chlorides. Their average concentration and variation around this average concentration are tightly controlled in most commercial epoxy resins. This is done to minimize the effect of their potential reaction with organic bases. Organic bases are frequently used as epoxy curing agents or epoxy curing accelerators.

In the laminating industry, dicyandiamide (DICY, cyanoquanidine) is the most widely used epoxy resin curing agent. The epoxy resin curing accelerator commonly used in most laminating resin formulations is an imidazole type compound. Both of these materials are also organic bases. These organic bases can react with the alpha chlorohydrins and under some conditions potentially with the beta chlorohydrins. Should these organic bases be "neutralized" by varying concentrations of the hydrolyzable chlorides in epoxy resins (i.e., on an epoxy resin lot-to-lot basis), then the epoxy resin polymerization rate, even under constant processing conditions, would vary widely. Thus, maintaining a relatively constant hydrolyzable chloride content in an epoxy resin is important to ensure their consistent reactivity. This is especially critical in the preparation of electrical laminates where controlled resin flow is important in the manufacture of copper clad laminates. As a consequence, historically the hydrolyzable chloride content has

been the major chlorine-containing epoxy resin compound of interest in the electrical laminating industry.

There are a number of different chemical tests that can be used to determine the hydrolyzable chloride content in epoxy resins. Unfortunately, each of these tests yield slightly different results, depending upon the severity of the chemical test conditions employed. Thus, hydrolyzable chloride content can be defined variously as:

The alpha chlorohydrin content.

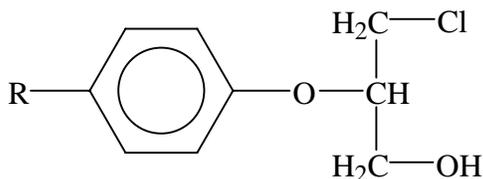
The alpha chlorohydrin content, plus some of the beta chlorohydrin content.

The alpha and beta chlorohydrin content.

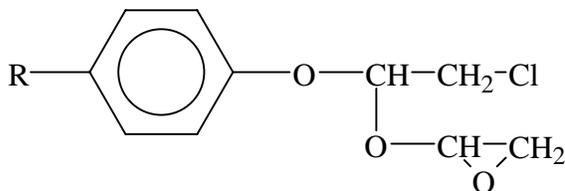
Typically, the sum of the alpha and beta chlorohydrins is designated as the harsh chloride content. When these terms are used in connection with reported Chloride Content values, it is important to understand which test method was used in their measurement in order to understand the meaning of the test result.

**3.3 Fixed Chlorides** While not commonly realized in the electrical laminating industry, other chlorine-containing compounds than just the alpha and beta chlorohydrins also exist in most commercial epoxy resins. The concentration of these fixed chlorides is almost always higher than that of the hydrolyzable (harsh) chloride content. The fixed chlorides are organic compounds that contain chlorine atoms, which cannot be hydrolyzed. They are usually designated by the terms fixed chlorides, inactive chlorides, or bound chlorides. Chemically, they are composed of a number of different chlorine-containing organic compounds. In the following paragraphs the most common of the fixed chlorides will be briefly described.

**3.3.1 1, 3-Chlorohydrins** A 1,3-chlorohydrin family of compounds (where R varies) is very difficult to hydrolyze. Their representative chemical structure is illustrated below:



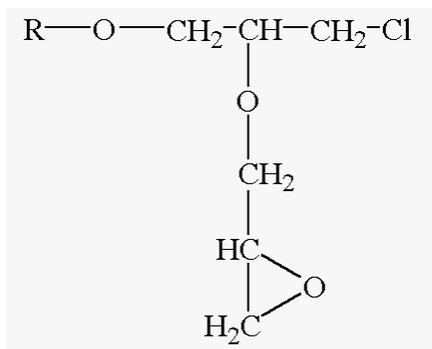
**3.3.2 Fixed Chlorides Formed by Abnormal Epichlorohydrin Reaction with BPA** Another of the fixed chlorides are those formed by the abnormal addition of epichlorohydrin with BPA. They have chemical structures of the following type:



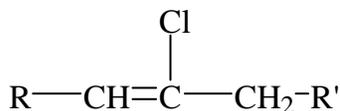
**3.3.3 Fixed Chlorides Formed by Oligomeric Epoxy Reaction with Epichlorohydrin**

The secondary alcohols on oligomeric epoxy molecules can react with epichlorohydrin yielding structurally complex, branched chlorine-containing molecules. These compounds are also

difficult to hydrolyze and thus are members of the fixed chlorides. They have chemical structures as represented below:



**3.3.4 Chloropropenes** Impurities in epichlorohydrin can lead to the formation of chlorine-containing compounds that are called chloropropenes. They have the following general chemical structure:



where R and R' designated different (or possibly the same) chemical structural fragments.

**3.4 Ionic Chlorides** During the commercial manufacturing of epoxy resins, it is difficult to remove all of the sodium chloride that is formed when the epoxy group is produced. While the sodium chloride concentration is greatly reduced during the purification stage of epoxy resin manufacturing, minor quantities of sodium chloride are usually found in most commercial epoxy resins. Generally, they are present in concentrations of less than 100 ppm and frequently less than one quarter of this value.

**3.5 Total Chlorine Concentration in Epoxy Resins** The concentration of all of the chlorine-containing compounds found in epoxy resins varies widely based upon the type of epoxy resin being produced, the manufacturing process that is being used, the purity of the starting materials and either specific end-use or regional epoxy resin standards. In general, for typical non-brominated epoxy resins, the range of chloride compound concentrations found in commercially available epoxy resins is:

<u>Chlorine Type</u>	<u>Percent Chlorine by Weight</u>
- Hydrolyzable Chlorides	0.03 - 0.20
- Fixed Chlorides	0.13 - 0.50
- Ionic Chlorides	< 0.01

**Total Chlorides      0.16 - 0.70\***

\* The extremes are 0.06 up to one percent.

**3.6 Sources of Halogens in Non-Brominated Flame Retarded Epoxy Resins (Other than the Epoxy Resin Itself) and Their Laminates** To achieve flame retardancy in non-brominated epoxy resins and their laminates, it is necessary to add other substances to the epoxy resin to achieve the UL V-0 or V-1 Flammability Rating (visit [www.ul.com](http://www.ul.com) for more information). These non-halogenated flame retardants (both man-made and naturally occurring products) frequently contain small amounts of halogens (typically residual chlorine compounds).

Hence, the amount of halogens present in a flame retarded, non-brominated epoxy resin is proportional to the product of the weight fraction of the halogen present in the epoxy resin times the weight fraction of the epoxy resin in the total composition plus the weight fraction of the halogen present in the flame retardant times the weight fraction of the flame retardant present in the total composition.

Specific information describing the non-halogenated flame retardant agents commonly used with epoxy resins can be found elsewhere in this report.

Other potential sources of halogens in laminates include the fiberglass sizing, resin defoaming agents, resin wetting agents, epoxy curing agents, and epoxy curing accelerators. In general, it is commonly assumed that all of these potential halogen sources add < 0.01 weight percent halogen to those in the epoxy resin. Depending upon the choice of these non-epoxy materials, this assumption may not necessarily be valid.

**3.7 Total Chlorine Content Test Methods for Electrical Laminates** Numerous wet chemical and instrumental methods can be used to measure the halogen content of either organic or inorganic materials. There also exist a large number of analytical tests to measure the various types of chlorides found in epoxy resins. However, to determine the total chlorine content in epoxy resins and their composites, there is generally one preferred method.

In this test, a sample is first combusted in an oxygen-rich environment and the residual charred material is used to measure the halogen content. This measurement is then conducted using either a wet chemical method or a potentiometric titration method. This test procedure can be used to measure the total halogen content of organic materials, inorganic materials and their combinations.

ASTM-D-1847 describes the test procedures to use for measuring the total chlorine content in epoxy resins. The Japan Printed Circuit Association (JPCA) developed a similar test for analyzing halogen content of PCBs (JPCA-ES-01-1999). The sample used in the JPCA test is prepared by first removing any copper foil on the PCB, combusting the resulting sample, and then analyzing its halogen content as described in the preceding paragraph. The halogen content of the electrical laminate is reported as the weight percent halogen (either bromine or chlorine) in the laminate (i.e., fiberglass plus the epoxy resin).

## APPENDIX 4: Toxicological, End-Of-Life, and Recycling Issues

- DecaBDE

European scientists have evaluated Deca-BDE's potential effects in the framework of a European Risk Assessment, which reviewed around 550 studies. This assessment identified no significant risk from Deca-BDE to human health or the environment.

- TBBPA

TBBPA is being evaluated in the framework of an EU risk assessment, the human health part of the risk assessment has been finalized identifying no risk to human health. The environment part of the risk assessment will be finalized by June 2007. So far this part of the assessment has identified no risk from the reactive use of TBBPA and a risk for the additive use. The BFR industry believes this risk can be controlled through working with users of TBBPA to help them control their emissions of TBBPA into the environment.

- HBCD

HBCD is being evaluated in the framework of an EU risk assessment The Human Health part has been finalised and identified no risk to consumers and to workers when standard industrial hygiene measures are applied. Draft reports on Environment part are currently under review and expected to be concluded in June 2007.

### 4.1 Indoor and Outdoor Effects of Bromine

**4.1.1 Indoor Emissions** Since 1995, indoor emissions of flame retardants have been the focal point of several studies.

Although currently available data do not show detailed estimates of emissions from specific products, the Danish Environmental Protection Agency (EPA) reviewed products used in Denmark.

In its studies, it found that there were significant emissions from office machines through detection of compounds in office spaces, computer halls, and control rooms. The most obvious emissions came from products using additive flame retardants, such as phenol-paper-based laminate and thermoplastic components.<sup>1</sup>

**4.1.1.1 Chamber Experiments** In the chamber experiments, final products, such as televisions and VCRs, are placed in an enclosure and forced to succumb to three days of air flushing while maintaining a consistent operating temperature. For televisions, the temperature would be 36°C to 39° for televisions and 46°C to 48° for VCRs.

The Danish EPA found that the televisions and computer monitors it tested emitted primarily tetra-BDE and penta-BDE, but it did not analyze emissions for TBBPA.

**4.1.2 Outdoor Emissions** ~~There currently are no data showing any environmental effects of emissions from brominated flame retardants, or that they leach from end products into the environment. There is also no data showing adverse effects of brominated flame retardants leaching into the water table, eventually making its way and causing harm to humans and animals. Environmental and health effects of brominated flame retardants are minimal and manageable<sup>2</sup>. There is no evidence that brominated flame retardants leach from end products into the environment.~~ The effects on the environment of the main commercial flame retardants have been assessed as part of the EU's risk assessments. This has concluded that there is no identified risk for Deca-BDE. The assessments of TBBPA use as an additive and HBCD have identified a risk to the environment. For both these flame retardants the industry has started a

<sup>1</sup> Brominated Flame Retardants, Danish Environmental Protection Agency (EPA) Web site.

<sup>2</sup> ~~Bromine Science and Education Forum (BSEF) Web site.~~

voluntary program of emissions reductions (Voluntary Emissions Controls and reductions Action Program - VECAP) designed to address these concerns.

According to the Bromine Science and Environmental Forum (BSEF), concerns over dioxin and furan formation during incineration have been rendered a thing of the past by the advanced incinerator technology that is now available. ~~As to any potential risk due to exposure to dioxins and furans from accidental fires, studies have shown that even firefighters who face a high number of accidental fires are not adversely affected.~~

According to BSEF, it is highly unlikely that significant amounts of brominated flame retardants will enter the environment.

**4.2 Toxicology** The toxicology of a number of the more common flame retardants used in consumer products indicates that most do not pose any significant threats to human life or the environment. Any risks associated with these products are very small in comparison with the risk of death in an unrestrained fire. ~~Further, the limited data available suggests that exposures to flame retardants in consumer products are unlikely to be greater than a few ug/kg body weight/day, thus further reducing the possibility of any adverse effects.~~

**4.2.1 Toxicology of Tetrabromobisphenol A (TBBPA)** The toxicology of TBBPA has been tested on an acute and subchronic basis in mammalian, aquatic and environmental systems.

TBBPA's toxicology data show the product does not pose a health hazard to mammals. TBBPA has been tested in rats in 28- and 90-day studies by oral administration. Oral doses as high as 100 mg/kg for 90 days produced no significant adverse effects. Total bromine content in tissues of the rats was not affected. Inhalation doses of 18,000 mg/m<sup>3</sup> to rats for two weeks produced no significant adverse effects. Doses of up to 2500 mg/kg body weight dermally applied to rabbits for three weeks produced no significant adverse effects. TBBPA was not teratogenic, maternally toxic or embryotoxic to rats in oral doses up to 3000 mg/kg during gestation. Fish with continual exposure may take up TBBPA, however, because of TBBPA's short half-life in fish (t<sub>1/2</sub> <one day), residues will be rapidly lost from fish once exposure ends. Effective levels in aquatic acute and repeated dose studies are greater than TBBPA's water solubility. Tests in sediment-residing organisms show TBBPA is not detrimental to these organisms.

**4.2.1.1 Mammalian Toxicology** TBBPA produced minimal effects in mammals when tested in acute and subchronic studies; TBBPA is not acutely toxic. The oral LD50 in the rat is >5000 mg/kg, and the dermal LD50 in rabbits is >2000 mg/kg. TBBPA was also not acutely toxic on inhalation; the inhalation LC50 in rats is >2550 mg/m<sup>3</sup> for a two-hour exposure. TBBPA is not irritating to the skin or eye. TBBPA did not induce chloracne on skin exposure and did not induce skin sensitization in guinea pigs. Testing in human volunteers showed no evidence of irritation or induction of skin sensitization; TBBPA was negative in the Ames Salmonella mutagenicity test. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

In a 14-day inhalation study, no systemic toxicity was observed in rats treated with up to 18 mg/L. Rats were exposed to an atmosphere of 0, 2, 6, or 18 mg micronized TBBPA/L air (0, 2000, 6000, or 18,000 mg/m<sup>3</sup>) for four hours daily, five days a week for two weeks. Mortality, body weight gain, food consumption, hematological, biochemical, or urinary parameters were not affected by treatment. No gross or microscopic lesions were detected in any dosage. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

In a 21-day dermal study, no systemic toxicity was observed in rabbits treated with 0, 100, 500, or 2500 mg TBBPA/kg body weight for six hours daily, five days per week for three weeks. No mortality or overt signs of toxicity were observed. Body weight gain, hematological parameters, urinalysis, organ weights, and gross and microscopic examinations did not reveal any compound-related changes. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

In a 28-day oral study, no toxicity was observed in rats treated with up to 1000 ppm TBBPA in their diet. Rats were fed at dietary dose levels of 0, 1, 10, 100 or 1000 ppm TBBPA for 28 days after which one group was sacrificed and the remaining rats placed on untreated diets for two, six, or 12 weeks. No effects on general appearance, behavior, body weight, food consumption, or mortality were observed. No compound related gross or microscopic lesions or variations in organ weights were observed at any dose level. Liver and adipose bromine levels were similar in rats of the control and high dose groups sacrificed at the end of the 28-day treatment period. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

In a 90-day oral study, no toxicity was found in rats treated with up to 100 mg/kg in the feed. Rats were fed a diet supplying 0, 0.3, 3, 30, or 100 mg TBBPA/kg body weight for 90 days. No toxicological effects were detected at any dose level for appearance, demeanor, body weight gain, food consumption, hematology, clinical chemistry values, urinalysis, organ weights, and gross and microscopic examinations. The total bromine content in liver, kidney, skeletal muscle, fat, and serum of rats in the 3 mg/kg dose group did not differ from that of the controls. (The 3 mg/kg group was the only group tested for total bromine content.) (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

In another 90-day study, a no adverse effect level of 4900 mg/kg diet (~700 mg/kg body weight) was determined in mice. (*Tobe M et al, 1986 as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

TBBPA was not teratogenic in rats. TBBPA was administered to pregnant rats by gavage at dosages of 0, 30, 100, 300, 1000, 3000, or 10,000 mg/kg body weight on gestation days for six through 15. No signs of toxicity were observed in rats receiving doses of 3000 mg/kg or less. No differences in the mean numbers of viable or nonviable fetuses, resorption, implantations, or corpora lutea were detected between treated and control rats. In another study, female rats were treated with 0, 280, 830, or 2,500 mg/kg body weight from day 0-19 of gestation. Birth rate was not impaired by the treatment. No toxic effects were observed on the embryo or fetus. No skeletal or visceral abnormalities were detected, and postnatal development was not impaired. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

TBBPA's lack of toxicity in mammals is likely related to its pharmacokinetics. In rats, after oral dosing, approximately 95 percent of the administered material was found in the feces and <1.1 percent in the urine within 72 hours. Blood and tissue levels were extremely low at all time points measured. The half-life in the blood was about 20 hours; the maximum half life in any tissue was less than 3 days. Because of the short half-life, the small amounts of TBBPA absorbed would have relatively little persistence or accumulation in mammalian systems. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

A second study of the metabolism and disposition of TBBPA in the rats also showed rapid elimination by the rat. Seventy-one percent of a single dose was excreted in the bile in 72 hours with 48 percent excreted in the first 24 hours. Ninety-five percent of the dose was excreted without metabolism, although biliary metabolites were identified (primarily glucuronide conjugates). About two percent of the dose remained in the rat 72 hours after dosing. (*Larsen, G. et al, Organohalogen Compounds, 31, 413-416, 1998*)

**4.2.1.2 Aquatic Toxicology** In addition to mammalian tests, aquatic and environmental tests have been conducted on TBBPA. TBBPA's water solubility is estimated to be 0.001 mg/L using Syracuse Research Corporation's modeling software (*EPAwin V3.04*). Its estimated octanol water partition coefficient is 7.20 using the same software. TBBPA's measured water solubility is  $\leq 0.08$  mg/L (*BSEF, 2000*).

All LC50 and EC50 values derived from acute tests in aquatic species are greater than TBBPA's estimated and measured water solubility. The 96 hour LC50 values for bluegill sunfish, rainbow

trout, and fathead minnow are 0.51, 0.40 and 0.54 mg/L, respectively. The 48-hour LC50 for daphnia magna is 0.96 mg/L. The 96-hour EC50 for the eastern oyster was 0.098 mg/L. The growth of freshwater green algae was not affected by 5.6 mg/L, the highest level tested. The 96-hour EC50 in <1, 5, or 10 day old Mysid shrimp was 0.86, 1.1, and 1.2 mg/L, respectively. *(Studies performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995)*

In an early life stage test, fathead minnow embryos and larvae were continuously exposed for five days to TBBPA concentrations 0, 0.024, 0.04, 0.084, 0.16, or 0.31 mg/L. Survival of embryos to doses less than 0.31 mg/L was unaffected; survival at 0.31 mg/L was less than controls. Growth was not affected at any dose level. The maximum acceptable toxicant concentration (MATC), the range encompassing the highest test concentration that had no significant effect and the lowest concentration that had a significant effect, was 0.22 mg/L for fathead minnow embryos and larvae exposed continuously for 35 days. *(Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995.)* The MATC in these fish's early life stage test was greater than TBBPA's estimated and measured water solubility.

In a chronic study on an aquatic invertebrate species, daphnia magna were continuously exposed (flow-through) for 21 days to mean measured concentrations of 0.056, 0.1, 0.19, 0.30, 0.98 mg 14C-TBBPA/L. Nominal concentrations were 0.31, 0.25, 0.5, 1.0, 2.0 mg/L. After 21 days, daphnia survival ranged from 95-100 percent in all treatment groups and was statistically comparable to control survival. Organism growth; e.g., individual body length in all treatment groups, was also comparable to the control means and was not affected by treatment at any dose level. Reproduction at the highest dose level (0.98 mg/L measured or 2 mg/L nominal) was approximately one-third of that in the control groups and was statistically significantly different from controls. Reproduction at all other dose levels was statistically comparable to controls. The maximum acceptable toxicant concentration (MATC) for reproduction was > 0.3 and < 0.98 mg/L (measured concentration) or > one and < 2 mg/L (nominal concentration). The MATC for survival and growth was  $\geq$  0.98 mg/L (measured) or  $\geq$  2 mg/L (nominal). Survival and growth were not affected by chronic exposure of Daphnia to TBBPA. Reproduction in Daphnia was not affected by doses < 0.98 or 2 mg/L, measured or nominal, respectively. The MATC for chronic exposure of Daphnia to TBBPA was > 0.98 or 2 mg/L, measured or nominal, respectively. All of these doses are greater than TBBPA's estimated or measured water solubility. *(Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995)*

The subchronic effects of the sediment-bound form of TBBPA to a representative benthic invertebrate species, the midge chironomus tentans were determined. The study consisted of a series of three 14-day (partial life cycle) tests. Each test was conducted with sediment-containing different organic carbon levels. The three sediments were of high (6.8 percent organic carbon), mid (2.7 percent), or low (0.25 percent) organic carbon content. The sediments were physically characterized with a high sand content, 2-8 percent silt, and were slightly acidic (pH 5.4-5.5). The sediment concentration of TBBPA ranged between 13 and 200 mg/kg (nominal). The test systems achieved and maintained equilibrium between sediment and water for the duration of the tests. The highest mean interstitial water concentrations of TBBPA were measured in the nominal 200 mg/kg treatments as expected and midges were continuously exposed to interstitial water concentrations of 0.046 mg/L (HOC), 0.045 mg/L (MOC) and 0.039 mg/L (LOC) TBBPA. Sediment/interstitial water partitioning coefficients (Kd) were 7349, 5378, and 5816, in the HOC, MOC, and LOC groups, respectively, at the highest dose tested. These Kd values indicate TBBPA preferentially partitions to sediment rather than water. Midge survival in all TBBPA-treated sediments ranged from 44 to 96 percent and was statistically comparable to control organisms. Midge growth in the treatment groups also was statistically comparable to controls. The no effect sediment concentrations were 228 to 341 mg TBBPA/kg sediment, corresponding to 0.039 to 0.046 mg TBBPA/L interstitial water. The NOEC in interstitial water was greater than TBBPA's estimated water solubility. The NOECs in both sediment and interstitial water were

independent of the total organic carbon content of the sediments. (*Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995.*)

Under the EU's Directive 67/548/EEC on the Classification and Labeling of Chemicals, TBBPA has been classified with the Risk Phases R50-53. This classifies TBBPA as toxic to the aquatic environment and it should be labeled appropriately.

**4.2.1.3 Bioconcentration Studies** Bioconcentration studies with aquatic invertebrates and vertebrates indicate bioconcentration factors (BCF) ranging from 20 up to 3200. In fish, the BCF range from 20 to 1200. The half life in fish is < one day, and in oysters < five days. During depuration, most of the TBBPA (and any metabolites) are eliminated within 3-7 days. Therefore, TBBPA's relatively high bioconcentration factor in some species is balanced by a rapid excretion. TBBPA has not been detected in biological samples collected in the environment. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

Fathead minnows were exposed to 4.7 ug/L 14C-TBBPA (flow through conditions) for a 24 day exposure period followed by a six-day depuration period. One-Four-C activity remained below the limit of radiometric detection in water during depuration. The concentration of 14C in fish tissue reached a steady- state level on day four of the exposure. The mean steady-state concentration on a whole body basis was 5800 ug/Kg or a BCF of 1200 (mean equilibrium tissue concentration = 5800 ug/kg; mean water concentration = 4.7 ug/L). This BCF value was based on 14C residues and therefore represents the sum total of parent compound, any retained metabolites and assimilated carbon. The BCF of the parent compound (TBBPA) may be lower. Rapid elimination of the radio-label was observed. The whole-body half-life in the fish was < one day. Ninety-eight percent of the 14C activity was eliminated by six days of depuration; elimination of 95 percent occurred between days one and four of depuration. Therefore, 14C TBBPA residues did not appear to persist in fish tissue to any significant extent. (*Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995.*)

The results of this study indicated ready uptake in continuously exposed fathead minnows with steady state reached within four days. Extending the period of continuous exposure up to 24 days did not increase the levels in fish. During depuration, the fathead minnows rapidly and nearly completely eliminated the 14C-residue. The whole body half- life was < 24 hours and by day 6 of the elimination period only two percent of the 14C residue remained in the exposed fish. Therefore, these residues should not persist once the fish are no longer continuously exposed. Intermittent exposures should not result in any significant TBBPA tissue residues because of the short half-life (<24 hours) of TBBPA and its metabolites.

Blue gill sunfish were exposed to 14C TBBPA for 28 days to 0.0098 mg/L followed by a 14-day withdrawal period. The bioconcentration factor (BCF) in edible tissue was 20, and 170 in visceral tissue. These BCF values were based on 14C residues and therefore represent the sum total of parent compound, any retained metabolites and assimilated carbon. A BCF based on total amount of radio-label retained may not be comparable to the BCF derived for the parent compound only. Plateau levels were reached within three to seven days. The whole body half-life was <24 hours. The radiocarbon dissipation to <0.01 mg/kg in fish tissue occurred within three to seven days of the beginning of the withdrawal phase. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

The bioconcentration of TBBPA was evaluated in Japanese carp following an eight-week exposure period at concentrations of 8 or 80 ug/L. The BCF was 30~341 at 80 ug/L and 52~485 at 8 ug/L. The LD50 in killifish was determined to be 8.2 mg/L at 48 hours. (*Data of Existing Chemicals Based on the CSCL Japan, CITI, 1992, Tokyo*)

**4.2.1.4 Biodegradation** TBBPA is estimated to partition in the environment as follows: air -  $4.34 \times 10^{-7}$  percent, water - 1.13 percent, soil - 44.9 percent, and sediment - 53.9 percent (*Syracuse Research Corporation EPIWIN modeling software, V3.04*).

TBBPA is not readily biodegradable by sewage sludge, according to a 28-day study. In a wastewater treatment plant, TBBPA is estimated to be removed mainly by sludge adsorption (93.14 percent) and 0.78 percent by biodegradation. Removal by a wastewater treatment plant is estimated at 93.92 percent. (*Syracuse Research Corporation EPIWIN modeling software, V3.04*)

Other test results indicate TBBPA has potential for degradation in the environment. TBBPA's degradation has been studied in the following prolonged studies:

Sixty-four-day aerobic soil  
Sixty-four-day anaerobic soil  
Fifty-six-day sediment/water biodegradation

TBBPA's estimated half-life in the 64-day aerobic and anaerobic studies is approximately 50 days. TBBPA's half-life in the sediment/water degradation study is 48 to 84 days.

The biodegradability of <sup>14</sup>C TBBPA was tested under aerobic conditions in three soil types, i.e., Massachusetts sandy loam, a California loam, and Arkansas silty loam. The three soil types contained:

Sand (83 percent) / Silt (13 percent) / Clay (four percent)  
Sand (16 percent) / Silt (58 percent) / Clay (26 percent)  
Sand (43 percent) / Silt (24 percent) / Clay (33 percent)

Thin-layer chromatography showed biodegradation of TBBPA in all soil types. 6 percent or less of the applied radioactive TBBPA was recovered in the volatile traps, indicating partial degradation to CO<sub>2</sub>. Results of the TLC analysis indicated variable degradation rates of TBBPA dependent on soil types. After 64 days, the amount of TBBPA remaining in the soils ranged from 36 to 82 percent, with the highest level in sandy loam soil and the lowest in the silty loam soil. (*Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995.*)

The biodegradability of <sup>14</sup>C TBBPA was also tested under aerobic conditions in a sediment/water microbial test system using natural river sediment and water. The test conditions were pH 5.5, field moisture capacity 15.9 percent, temperature 24°C to 26°C, and the composition of the soil (6.8 percent carbon) was 92.5% sand, 6% silt, and 2% clay. TBBPA biodegraded at all tested concentrations (0.01, 0.1 and one mg/L). Half-lives calculated for TBBPA in the sediment/water microbial test systems ranged between 48 days at 0.01 ug/L concentration and 84 days at the one mg/L concentration with apparent correlations between half-life and TBBPA concentration and half-life and microbial population. The half-life in sterile soil was extrapolated to be 1300 days, clearly indicating that the degradation observed in the active test systems was due to microbial degradation rather than physical processes. Less than eight percent of the applied radioactive carbon from TBBPA was recovered in the volatile traps indicating partial degradation to CO<sub>2</sub>. Filtered water contained less than five percent of the applied radioactivity. The amount of radioactivity observed to be remaining in the sediment at test termination, 44.7, 64.2, and 60.8 percent in the 0.01, 0.1 and one mg radioactive TBBPA/L treatments, respectively, was comparable to the amounts reported in the aerobic degradation study in soil. (*Study performed by the Brominated Flame Retardant Industry Panel, 1989, as reported in Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995.*)

The dimethyl derivative of TBBPA is reportedly a metabolite from microbial methylation. Because any toxicity cause in aquatic organisms is most likely related to the phenolic moiety of TBBPA, this metabolite is expected to be less toxic to aquatic species than the TBBPA parent molecule.

**4.2.1.5 Abiotic Degradation** TBBPA should also undergo abiotic degradation. TBBPA's calculated half life in water by UV radiation was 10.2 days in spring, 6.6 days in summer, 25.9 days in autumn, and 80.7 days in winter. Photolysis of TBBPA in the presence of UV light and hydroxyl radicals has also been reported; TBBPA was said to totally degrade within five to six days with an estimated 33-hour half-life. The half-life of TBBPA adsorbed onto silica gel and exposed to UV radiation was 0.12 days. (*Environmental Health Criteria Document # 172, World Health Organization, Geneva, 1995*)

**4.3 End-of-Life and Recycling** Consumers go through electronics at a higher rate than ever, with specific emphasis on hand-held, throw-away items such as mobile phones and pagers. Due to this, OEMs have a tremendous amount of focus on end-of-life considerations and how the materials used in the electronics may adversely affect the environment if not properly discarded.

A full scale trial to assess the technical feasibility of treating mixed WEEE materials with high plastics content in an integrated metal smelter has recently been completed<sup>2</sup>. Results confirm that integrated metal smelters represent an appropriate recycling route for WEEE materials as metals can be recovered and recycled and the plastic content can serve as an energy source and reducing agent<sup>3</sup>.

The trial also showed that the treatment of mixed WEEE materials in an integrated metals smelter does not cause any particular operating problems and that no emissions of brominated dioxin/furan congeners are detected.

This trial has been performed by PlasticsEurope in cooperation with the Umicore integrated metals smelter and the European Flame Retardant Association (EFRA), in the context of the implementation of the treatment requirements under the EU WEEE Directive and in particular of the provisions concerning plastics containing brominated flame retardants.

This trial demonstrates that economic and environmental appropriate routes exist to treat WEEE materials containing plastics with flame retardants without having to separate those plastics from the mix prior to the treatment and therefore that it is possible to comply with the provisions of the EU WEEE Directive.

**4.3.1 Dioxins** The term "dioxin" has evolved from the single chemical entity, 2-,3-,7-,and 8-tetrachlorodibenzodioxin (TCDD), to reference to a class of halogenated aromatic compounds that have "similar chemical structures, similar physical-chemical properties, and invoke a common battery of toxic responses"(General information on dioxin can be found in the U.S. EPA Information Sheet 1, Dioxin: Summary of the Dioxin Reassessment Science; [www.epa.gov/nceawww1/dioxreass.htm](http://www.epa.gov/nceawww1/dioxreass.htm)).

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<sup>2</sup> "Using metal-rich WEEE plastics as feedstock/fuel substitute for an integrated metals smelter", November 2006. Technical Report produced by: PlasticsEurope in cooperation with Umicore and EFRA

<sup>3</sup> 2/3 of the plastics' energy content was used to replace consumption of coke and fuel oil and approximately 1/3 was recovered as increased steam production.

The specific halogenated aromatic compounds designated dioxins are polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzodioxins (PCDDs). The analogous polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are also generally included in the description "dioxin." Within these classes, only 12 of the 209 PCBs are thought to have "dioxin-like" toxicity. These 12 are the only PCBs that can achieve a flat (coplanar) configuration, a necessary requirement to invoke "dioxin-like" biological activity. Similarly, only seven of the 75 possible PCDDs and seven of the 75 possible PBDDs are thought to have dioxin-like toxicity. These 14 all have halogen substituents at the 2-, 3-, 7-, and 8-positions, a necessary requirement for this class to fit the proper receptor site for biological activity. Only 10 of the 135 possible PCDFs and 10 of the 135 possible PBDFs are thought to have "dioxin-like" toxicity. These 20 also have halogen substituents at the 2-, 3-, 7-, and 8-positions. The non-planar PCBs and the non-2-, 3-, 7- and, 8-substituted PCDFs/PBDFs/PCDDs/PBDDs do not exhibit "dioxin-like" biological activity.

	<b>Dioxins</b>	<b>Non-Dioxins</b>
PCBs	12 Planar	197 Non-Planar
PCDDs	7 with 2-, 3-, 7-, and 8-Substitution	68 Without 2-, 3-, 7-, and 8-Substitution
PBDDs	7 with 2-, 3-, 7-, and 8-Substitution	68 Without 2-, 3-, 7-, and 8-Substitution
PCDFs	10 with 2-, 3-, 7-, and 8-Substitution	125 Without 2-, 3-, 7-, and 8-Substitution
PBDFs	10 with 2-, 3-, 7-, and 8-Substitution	125 Without 2-, 3-, 7-, and 8-Substitution

Exposure to dioxins can result in an overt effect, such as chloracne, and subtle effects such as increased risk of cancer (TCDD is characterized as a human carcinogen), suppression of the immune system and adverse changes in reproduction and development. Within the individual classes, the various components exhibit differing degrees of dioxin-like activity. For example, octachlorodibenzodioxin (OCDD) is considered to be much less potent than TCDD. The relative toxicity of the dioxins is generally referenced to TCDD. Several organizations have used a toxicity equivalence factor (TEF) to quantify the relationship. In general, the more halogens on the molecule, the lower the TEF. For example, TCDD has a TEF of one while OCDD has been assigned an international toxic equivalency factor (ITEF) of 0.001.

The 46 dioxins, particularly the PCDFs and PCDDs, are not all products of industrialization. Studies have shown that PCDDs and PCDFs can be formed during the combustion of practically any material containing a carbon source and a chlorine source. Forest fires and garden compost piles have been cited as sources of minor amounts of dioxin. Dioxin levels in the environment have declined significantly in recent years, mainly due to reduced emissions from combustion sources such as incinerators. Changes in chemical processes, such as pulp bleaching in the paper industry, have also contributed to the reduction in dioxin levels.

The man-made production of dioxin attracted an extraordinary amount of attention in July 1976, when a trichlorophenol production site in Seveso, Italy, experienced an uncontrolled reaction and released a substantial quantity of dioxin, particularly TCDD. Thousands of individuals were exposed to high to moderate levels of dioxin. The accident was given worldwide press coverage and moved dioxin from the scientific vocabulary and into the common vernacular. Prior to 1976, other occupational accidents in locations such as Nitro, West Virginia (1949), Ludwigshafen, Germany (1953), and Ufa, Russia (1965-67) exposed hundreds of workers to high levels of dioxins. In 1999, a contamination of chicken feed in Belgium exposed an indeterminate number of people to low levels of dioxin. The concern with human dioxin exposure has led governmental and regulatory bodies to undertake extraordinary measures to determine where dioxin is found and how it is produced. This has involved the academic, industrial, and governmental analysis of food, breast milk, certain synthetic organic chemicals, consumer products, air, water, soil, human fat tissue, human blood, and a variety of other media. Most studies agree that incinerators are the

primary dioxin source and that human exposure is primarily through food consumption. All humans have a certain level of dioxin in their body and intake a trace amount of dioxin (about one picogram per kilogram of body weight per day) through their food.

In the electronics area, most attention for potential human dioxin exposure has been focused on the halogen-containing parts of appliances such as television sets, computer monitors and the like. Analyses have been made during practically every facet of a typical appliance's life: birth (raw materials used to make appliances), use (analysis of the finished products and emissions from the finished product), reuse and disposal (analysis of products from the combustion of the halogen-containing raw materials and the halogen-containing polymers).

From these analyses, only two particular types of halogen-containing raw materials appear to be of concern to regulators: polyhalogenated biphenyls and some PBDEs. Of particular interest to information technology product manufacturers and users, the principal halogen-containing component of PCBs, TBBPA, has been thoroughly analyzed and has **not** been found to be a source of potential human dioxin exposure.

The following are some tests that have been performed to arrive at this conclusion:

1. Quantitative analysis of multiple samples of commercial TBBPA from three different manufacturers was carried out as required by a U.S. EPA TSCA, Section 4, Test Rule. None of the 15 dioxins (2-, 3-, 7-, and 8-substituted PBDDs/PBDFs) specified in the Test Rule were found at or below the target limits of quantitation [*Ranken et. al., Bull. Soc. Chim. Bel. 103 219-233 (1994)*].
2. Analysis of the workplace during processing of TBBPA-containing polymers showed that the investigated air samples contained no dioxin [*Thies, Neupert and Pump, Chemosphere 20 1921-1928 (1990)*; *Brenner and Knies, Toxicological and Environmental Chemistry 38 81-94 (1993)*]; analysis of air samples taken during the shredding of PCBs also showed that no dioxin was formed [*Lorenz and Bahadir, Chemosphere 26 2221-2229 (1993)*].
3. Analysis of PCBs before and after thermal stress (up to 300°C) showed no dioxins present and none formed [*Lorenz and Bahadir, Chemosphere 26 2221-2229 (1993)*].
4. Analysis of a typical office machine housing (ABS plastic containing TBBPA), before and after reprocessing and reuse, showed no that no dioxin was present [*Meyer, Neupert and Pump, Kunststoffe 83 253-257 (1993)*].
5. Laboratory pyrolysis studies of TBBPA and TBBPA-containing polymers demonstrated that, although non-dioxins such as non-2-, 3-, 7- and, 8-substituted PBDDs/PBDFs are formed, dioxin is either not produced or is present in the pyrolysis gas in trace amounts [*Luijk and Govers, Chemosphere 25 261-374 (1992)*; *Thies, Neupert and Pump, Chemosphere 20 1921-1928 (1990)*].
6. Analysis of the products from the laboratory pyrolysis of epoxy resins containing TBBPA and copper showed no dioxin [*Lahaniatis et. al., Toxicological and Environmental Chemistry, 31-32 521-526 (1991)*].

The data from the laboratory pyrolysis studies are the most interesting, since these investigations seem to be the source of the assumption that TBBPA can form dioxin. The confusion concerning the distinction between non-dioxin and dioxin within the same class of chemicals undoubtedly contributes to the misinformation regarding TBBPA and its potential for human dioxin exposure. It cannot be disputed that TBBPA, being an organohalogen, will provide a source of halogen for the ultratrace formation of dioxin in an incinerator, but it is erroneous to conclude that pyrolysis of TBBPA or common fires involving TBBPA will lead to another Seveso. One example has been reported of actual experience with a fire involving a TBBPA-containing polymer. Analysis of

burned plastic from a warehouse fire involving polybutyleneterphthalate (PBT) containing TBBPA oligomers did show detectable amounts of dioxin but not at a level requiring special worker protection. The ash/slag residue contained no dioxin and the TEF of soil 1300-1700 meters from the fire was indistinguishable from background levels.

These studies and others involving TBBPA and TBBPA-containing polymers support the conclusion that the manufacture, use, and disposal of information technology devices containing TBBPA flame retardant PCBs do not increase human dioxin exposure. A major driver for halogen free substitutes for TBBPA in PCBs is marketing and not based on any health or scientific basis.

Several studies have also been undertaken on the use of TBBPA in printed wiring boards and their subsequent behavior when smelted:

1. The Swedish IVF institute undertook a case study comparing the costs and environmental implications of using halogen-free flame retardants in the manufacture of printed wiring boards (PWB) instead of bromine-based fire safety systems. In the case study undertaken there was a cost increase ranging from almost zero to €10 per panel resulting from the move to halogen free flame retardant systems. These increases related to costs for panel drilling, desmearing and materials. Though experience is limited with regard to producing non-halogenated PWBs, the case study indicates that costs relating to panel drilling and desmearing would remain whereas other parameters used in the study, pressing, design, and solder mask, did not change depending on the flame retardant system used.<sup>4</sup>

2. A study entitled "Recycling of bromine from plastics containing brominated flame retardants in state-of-the-art combustion facilities" by Tamara, Vehlow, B. at the Forschungszentrum Karlsruhe Institut für Technische Chemie Bereich Thermische Abfallbehandlung, was done in 2002. The study showed that brominated flame retardants contained in WEEE plastics –including TBBPA in ABS- can be safely handled in modern household waste incinerators. The study concluded that up to 3% WEEE plastics containing BFRs can be safely added to the incinerator, the halogens have a positive cleaning effect on the heavy metals in the slag.

3. The Nordic Council of Ministers commissioned a study entitled "Emission measurement during incineration of waste containing Bromine" by Borgnes and Rikheim at the Kjelforeninge Norsk Energi, published in 2005. The study confirms that BFRs in waste decomposes in the incineration process and that increasing the content of BFRs in the waste gave no significant increase in the emissions of chlorinated dioxins, or either brominated and chlorinated/brominated dioxins.<sup>5</sup>

### 4.3.2 Recovery Methods

**4.3.2.1 Recovery Potential of Bromine Used in Electronics** Bromine sources, like the Dead Sea, salt lakes, or brines, or sea water contain from ca. 1.5 percent down to 65 ppm. Through the use of brominated flame retardants in electrical and electronic equipment (EEE) – the bromine content in a mixed waste electrical and electronic equipment (WEEE) plastic fraction might present on average 2.6 percent<sup>6,7,8</sup>, so it can be of economical interest to close the bromine loop.

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<sup>4</sup> [http://www.bsef.com/newsmanager/uploads/halogenfree\\_printed\\_wiring\\_boards.zip](http://www.bsef.com/newsmanager/uploads/halogenfree_printed_wiring_boards.zip)

<sup>5</sup> <http://www.norden.org/pub/miljo/miljo/sk/TN2005529.pdf>

<sup>6</sup> Kennedy & Donkin (1999): Recovery of Bromine & Energy from waste Electrical & Electronic Equipment in the European Union.- Unpublished project report.

<sup>7</sup> ECN (2000): Implementation of thermal processes for the feedstock recycling of bromine and antimony with energy recovery from Waste of Electrical and Electronic Equipment (WEEE).- Unpublished draft project report.

<sup>8</sup> APME (1997): Electrical and electronic plastics waste co-combustion with municipal solid waste for energy recovery.- Juergen Vehlow, Frank Mark.

To ascertain the potential for recovering bromine, an investigation has been conducted to calculate the volumes of WEEE generated in the EU. It was found that 95 percent of the brominated flame retardants used in EEE are contained in 273,000 metric tonnes of plastic. These values formed the basis for the elemental and energy calculations within the study and hence the technical, financial, and socioeconomic assessment. The main plastics identified were:

High impact polystyrene (HIPS) in brown goods.  
Styrene Copolymers (ABS) in data processing & office equipment.  
Epoxy resins in PCBs.

The major brominated flame retardants associated with these plastics are DecaBDE in brown goods, TBBPA in data processing & office equipment, and TBBPA in printed circuit PCBs. The volumes available correspond to ca. 10,000 tons of bromine and 2000 tons of antimony per year from WEEE<sup>3</sup>.

To improve the economic benefit, additional feed streams, like plastics from automotive shredder residues (ASR), packaging material with bromine residues, and other bromine-containing waste, are also taken into account.

ASR has similar characteristics as WEEE related to the aspects of heavy metals and halogen content. The ASR plastic fraction contains 180-3200 mg/kg of antimony and 0-3220 mg/kg of bromine. The typical bromine content is 300 mg/kg and for antimony 400 mg/kg. The amount of ASR available for Europe is 2.2 million tons per year<sup>9</sup>.

**4.3.2.2 Thermal Process Selection Criteria and Process Description** In thermal processes, bromine (Br) will form radicals that will then generally react to form HBr and Br<sub>2</sub>. The isolation of the bromine from the gas stream in a suitable form for re-use is based on absorption into an aqueous (hydroxide) solution. The bromine distribution in combustion depends in general on the amount of bromine; an indicative distribution is in the grate ash (two percent), fly ash (20 percent), and in the flue gas (78 percent). Under these conditions the distribution of antimony between the grate ash and the fly ash is approximately 2:1, accounting for ~95 percent of the mass. Under gasification conditions a similar partitioning of the bromine and the antimony is expected as for combustion conditions<sup>4</sup>.

Four processes have been identified and selected to be potentially suitable for the conversion of WEEE plastics. The criteria have been energy efficiency, bromine recovery, emissions, quality of secondary products, operational experience, and profit expectations. The four processes are:

- Austria Energy: fast internal circulating fluid bed technique, which is based on combustion, combined with the FUAPUR process to recover the metals.
- ABB/Ebara: TwinRec process, which is a fluidized bed gasifier with cyclonic combustion chamber. The process is combined with a smelter.
- Von Roll Recycling Clean Product (RCP): This process is a combination of grate furnace, smelter, slag treatment and circulating fluidized bed combustor.
- Gibros-PEC: pyrolysis technology developed by Pyrolyse Kraft Anlage (PKA). The process is built up by a pyrolysis step with a gasifier chamber plus a smelter unit to produce a basalt. The unit produces a syngas, which can be used in a gas turbine engine.

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<sup>9</sup> APME (1998): The role of plastics in automotive shredder residue (ASR). Characterization and environmental Assessment.- Frank E. Mark, Michael M. Fisher.

The final feedstock recycling process will operate according to the following steps:

Step 1: Pyrolysis - the plastic will be converted into hydrocarbon, hydrogen bromide, and antimony bromide.

Step 2: Gasification/incineration - the hydrocarbons will be mixed with air and converted into a syngas or CO<sub>2</sub>, water and heat.

Step 3: The slag from the pyrolysis will go to a molten metal bath where the metals are recovered. The remaining carbon fraction from the plastics will be used to heat the molten metal bath.

Step 4: The hydrogen bromide and the flue gas will be neutralized and converted into salt. Also a hydrobromic acid solution could be produced as an end product.

Step 5: The bromine salts or residues are converted by the bromine industry into bromine products – the bromine loop is closed.

The overall bromine recovery efficiency is estimated to be more than 90 percent, and overall antimony recovery efficiency is calculated to be between 50 percent and 90 percent, depending on the type of thermal process. The total plastic (hydrocarbon fraction) yield will be equivalent to 750 kg of oil, which will be used to produce electricity and energy. New studies are underway to find out the most optimal process and to investigate the resulting bromine salts.

**4.3.2.3 Conclusions on Bromine Recovery** It can be concluded that bromine recovery from WEEE and ASR is economically and ecologically feasible. Beside mechanical recycling and energy recovery, this feedstock recycling method could play an important role in an integrated waste management concept for plastics containing brominated flame retardants. The major advantages of this project would be the sustainable production of bromine while closing the bromine loop and providing a technically and environmentally sound way of recovering waste E&E plastics. The process would also result in low sorting/separation costs and would create an additional option to recover E&E plastics where a mechanical recycling market is not established. The project has the potential to reduce emissions of greenhouse gases in the form of CO<sub>2</sub> by more than 800,000 tons/year and provide bromine-producing companies with the opportunity of recycling a minimum of 10,000 tons of bromine annually in Europe. The approach for E&E waste could be equally plastics and jointly applicable for end-of-life vehicle (automotive) plastics which likewise contain bromine and antimony.

## APPENDIX 5: Political/Governmental and Marketing Drivers and Organizational Efforts

**5.1 Political/Governmental and Marketing Drivers** The advent of halogen-free materials used for PCBs began in the early 1990s in Europe, as companies began to research reduced chemistries and alternative solutions. At the time, there wasn't a push to provide these materials, from either a legislative/regulatory perspective or market gain.

Later that same decade, early drafts of the European Commission's (EC's) WEEE Directive and marketing schemes of European and Japanese OEMs initiated the drive to replace halogenated flame retardants.

**5.1.1 Legislative and Regulatory Drivers** There are no legislation or regulations, pending or otherwise, calling for the removal of TBBPA, but other brominated flame retardants ([Penta BDE](#), [Octa BDE](#) and [PBBs](#)) have been targeted by the EC.

**5.1.1.1 EU Restriction on Hazardous Substances Directive (RoHS) Waste Electrical and Electronics Environment (WEEE) Directive** ~~Although early drafts of the WEEE Directive called for the impending substitution of TBBPA, t~~The ~~ecurrent~~ ~~WEEE~~ Directive and the Restriction on Hazardous Substances (RoHS) ~~does~~ not contain any restriction on TBBPA.

~~The current~~ RoHS ~~still~~ calls for the elimination of two ~~other~~ classes of brominated flame retardants by July 1, 2006:

- Polybrominated biphenyls (PBB)
- Polybrominated diphenylether (PBDE) [with an exemption for DBDPE \(Deca\) since 15 October 2005](#)

PBBs are no longer manufactured. Of the family of PBDEs, only decabromo diphenylether (DBDPE) finds limited use in PCB, but is widely used in plastics. DBDPE ~~has is currently~~ ~~undergoing~~ a risk assessment in Europe [which did not identify a risk for human health and the environment from its continued use. Subsequently the EU has exempted it from the RoHS Directive since October 2005.](#) The restriction or elimination of DBDPE will be considered by the European Council pending the completion of this risk assessment activity.

**5.1.1.1.1 PBDEs Waste Electrical and Electronics Environment (WEEE) Directive** ~~WEEE Directive~~ According to the ~~draft~~ WEEE Directive, some PBDEs were found in the blood of workers in one recycling plant. [The WEEE Directive requires the separate treatment of plastics containing bromine and of printed wiring boards if the surface is greater than 10 square cm.](#)

**5.1.1.2 U.S. Environmental Protection Agency (US EPA)** The U.S. Environmental Protection Agency (US EPA) has not placed limits on the management of brominated flame retardants at their end-of-life state.

TBBPA is subject to reporting requirements under TRI. However, because TBBPA, when reacted with the resin, chemically bonds and forms to the backbone of the system, essentially disappearing, PCB shops will not have to report their release. If laminators don't have an MSDS from the resin manufacturer that includes TBBPA on the report, or if they maintain less than 100 pounds of TBBPA for use as an additive, they will not have to file a report.

**5.1.1.3 Ecolabels** Several agencies in U.S., Europe and Japan make available to OEMs ecolabels, which inform consumers that the product they are purchasing meets the agencies' requirements for environmentally friendly manufacture and consumption. The following sections detail some of the labels currently used and some of the requirements for using them on products.

**5.1.1.3.1 Germany's Blue Angel** Germany's **Blue Angel** ecolabel enables retailers and consumers to make a deliberate choice in favor of more environmentally sound product alternatives. The ecolabel also creates a competitive incentive for electronics manufacturers.

Currently over 71 product groups and 4000 products have been awarded the Blue Angel. The institution responsible for assessing proposals for new groups and products is the **Umweltbundesamt (German EPA)**. Twice a year, a Blue Angel jury meets and proposes product groups for potential ecolabels. The jury ensures that the interests of the various groups in society are taken into consideration. After that, the Umweltbundesamt examines the proposals and develops a preliminary draft of ecolabel criteria. After an expert hearing organized by the **Deutsches Institut für Gutesicherung und Kennzeichnung (RAL)** and revision of the criteria by the Umweltbundesamt, final criteria are agreed upon by the jury. Manufacturers who can prove their products comply with the ecolabel criteria can then apply for use of the Blue Angel label (see Figure 5-1).



**Figure 5-1 Blue Angel Ecolabel**

The **Blue Angel label for PCs** covers three main attributes:

- Power Consumption
- Recyclability
- Longevity

Power consumption of Blue Angel PCs is kept to a minimum, because major system components (monitors, hard disks, etc.) switch to low power-consumption modes after the computer is idle for a specified time. Manufacturers awarded the Blue Angel are obliged to take their products back after use. Due to the modular design of Blue Angel computers, parts can be easily exchanged, which extends the lifetime of a machine.

**5.1.1.3.2 The Netherlands, Milieukeur** Milieukeur is managed by an independent organization in which consumers, manufacturers, retail, government and environment organizations participate. Once a product has been awarded the Milieukeur, this means that it is less damaging to the environment compared to most similar products. The Milieukeur can be found on photocopying paper, stationary, labels, chairs, shoes, linoleum, writing pads, toilet paper, car polishing products, car-washes, cat litter, organic waste base plates, plants and flowers, bread, apples, pears, onions, barley, wheat, apple juice, potatoes and other things. Its requirements are:

- Low energy consumption
- No heavy metals and environmentally unfriendly fire retardants in the plastics
- Low sound levels
- Required acceptance of discarded computers
- Easy to repair
- Easy to expand/upgrade
- Safety

The Milieukeur label is shown in Figure 5-2.



**Figure 5-2 Milieukeur Ecolabel**

**5.1.1.3.3 TCO Ecolabel** TCO (The Swedish Confederation of Professional Employees) labeling started to take shape in the early 1980s. TCO'92 was the first international eco-labeling scheme to appear on the market. It contained emission and energy requirements for office computer displays. Currently the TCO certification scheme covers CRT displays, flat screens, system units, portable computers and keyboards as well as alternative keyboard designs. Recently, the possibility of certifying printers, faxes and copiers has been added.

The most important requirements of the TCO scheme are:

- Ergonomics: (visual ergonomic characteristics of displays and reducing ergonomic strain on such users).
- Emissions: (electric and magnetic fields generated by electrical equipment).
- Energy: (energy-saving functions, short restart times).
- Ecology: (Prohibitions on chlorinated solvents in production and on heavy metals in specified parts).

**5.1.1.3.4 EU Flower Eco-label** The EU flower eco-label is aimed at products and services with reduced environmental impacts, participation is voluntary. Criteria are established for individual product groups, such as paper products, textiles, detergents, paints, refrigerators or computers. Eco-label criteria for different products are periodically revised. Current criteria for computers are valid until April 2009 and covers:

- Substances used
- Energy efficiency
- User instructions
- Noise
- Electromagnetic emissions
- End of life issues

**5.1.2 Market Drivers and OEM Roadmaps** Although there are no legislative or regulatory pressures for the elimination of the most common flame retardants used in PCBs, OEMs in Europe and Japan continue to call for alternative materials. As a second step to what they market as "environmentally friendly" electronics (lead-free electronics serving as the precursor), these OEMs feel they can enjoy further market gain with the introduction of halogen-free electronics too.

It is common knowledge that people have very strong feelings about lead because they know of its toxicity and links to environmental and health concerns. Whether the OEM will be able to educate its consumer on the concerns with halogenated flame retardants remains to be seen. For now, the market activity remains between the OEM and its supply chain.

**5.1.2.1 Japan** Several Japanese OEMs have indicated activities planned or underway to reduce or remove halogenated flame retardants from their products.

**5.1.2.1.1 NEC** NEC is currently involved in the development of PCB technologies that it believes clears itself of current and possible environmental restrictions. It has incorporated halogen-free flame retardants into its products that not only eradicate the emission of toxic substances, but also retain the same level of flame resistance as common flame retardants.

In its long-term reliability tests, it has found the materials to be equivalent to its common flame-retardant-based products, all the while reducing the halogen content by 1/80<sup>th</sup>.

**5.1.2.1.2 Sony** As part of its *Green Management 2002: Medium Term Environmental Action Plan*, Sony indicated it was eliminating the use of halogenated flame retardants by 2000 in Europe, and by 2002 for products sold in all other areas.

**5.1.2.1.3 JVC** In March 2000, JVC certified a PCB that eliminated the use of halogenated materials from base materials and insulation layers. In its product, the amount of bromine is under the JPCA-ES-01 measurement limit, and the reliability of the product is equivalent to that of its conventional PCBs.

**5.1.2.2 Europe** ~~Although the requirements for the elimination of TBBPA in the WEEE Directive have been lifted,~~ Several European OEMs continue to require alternative chemistries for some their products. Products with significantly short life cycles, such as mobile phones, carry the most emphasis for the use of these materials. Incorporating the materials into these products enables the manufacturer to gather reliability data for these materials that can be used when incorporating them into products with longer life cycles.

**5.1.2.2.1 Nokia** Although Nokia has not yet announced plans for the introduction of one or more of its products incorporating alternative materials, it has indicated that it has been researching alternatives.

**5.1.2.2.2 Ericsson** Ericsson has pioneered processes for bromine-free PCBs for mobile phones. It has eliminated the use of PBB and PBDE, and efforts are now being concentrated on phasing out the other bromine-based flame retardants.

Its goal is to implement these environmental improvements in all of its phones after scientifically evaluating these processes and materials to ensure that there is no negative impact on the environment.

**5.1.2.3 United States** The main thrust of activity in the U.S. comes from the OEMs, primarily in Europe and Japan, who are requiring raw materials and laminate manufacturers to supply halogen-free systems or run the risk of losing their business.

## 5.2 Organizational Efforts

Resulting data from several studies have been referenced in this white paper. This section offers further information on the various institutes that have or are conducting studies on brominated flame retardants. IPC recommends consulting with these organizations for updates on their efforts.

**5.2.1 IPC** IPC's members have gathered data for this white paper and will continue to make available the most pertinent information on the issues and alternatives. The reader should check [www.halogenfree.org](http://www.halogenfree.org) for continual updates.

**5.2.2 European Brominated Flame Retardant Industry Panel (EBFRIP)** The European Brominated Flame Retardant Industry Panel (EBFRIP) acts as the main spokesperson for the bromine flame retardants industry within Europe on key issues such as fire safety, ecolabels,

electronic waste and risk assessments. In basing its position on science, EBFRIIP follows closely and encourages developments in the scientific understanding of brominated flame retardants as related to health and the environment.

**5.2.3 Bromine Science and Education Forum (BSEF)** The Bromine Science and Environmental Forum (BSEF) was formed by the bromine industry in 1997 and is dedicated to furthering the scientific understanding of bromine products. It works closely with both the BFRIP [in the US](#) and EBFRIIP [in Europe](#).

**5.2.4 National Association of State Fire Marshals (NASFM)** The National Association of State Fire Marshals (NASFM) represents the most senior fire official of each of the 50 United States and District of Columbia. State Fire Marshals' responsibilities vary from state to state, but Marshals tend to be responsible for fire safety code adoption and enforcement, fire and arson investigation, fire incident data reporting and analysis, public education and advising Governors and State Legislatures on fire protection. Some State Fire Marshals are responsible for fire fighter training, hazardous materials incident responses, wildland fires and the regulation of natural gas and other pipelines.

This organization has been vocal regarding the impacts of removing flame retardants from the outer housings of computer equipment.

**APPENDIX 6: IEC 61249-2-21, Specification for Non-Halogenated Epoxide/Woven E-glass Laminates of Defined Flammability****MATERIALS FOR INTERCONNECTION STRUCTURES -  
Part 2: Sectional specification set for reinforced base  
materials clad and unclad - Section 21: Non-halogenated epoxide  
woven E-glass reinforced laminate sheets of defined flammability  
(vertical burning test), copper-clad.****Scope**

This specification gives requirements for properties of non-halogenated epoxide woven E-glass reinforced laminate sheets of defined flammability (vertical burning test), copper-clad of thicknesses 0,05 mm to 3,2 mm. The flammability rating is achieved through the use of non-halogenated inorganic and/or organic compounds acting as fire retardants. These fire retardants are contained as part of the polymeric structure or in addition to it. The glass transition temperature is defined to be 120°C minimum.

Some property requirements may have several classes of performance. The class desired must be specified on the purchase order otherwise the default class of material may be supplied.

**Normative References**

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of IEC 61249-2. At the time of publication, the editions indicated were valid. All normative documents are subject to revision, and parties to agreements based on this part of IEC 61249-2 are encouraged to investigate the possibility of applying the most recent editions of the normative documents listed below. Members of the IEC and ISO maintain registers of currently valid International standards.

IEC 60194: 1999, *Printed Board Design, Manufacture and Assembly, Terms and definitions*

IEC 61189-2: 1997, *Test methods for electrical materials, interconnection structures and assemblies – Part 2: Test method for interconnection structures.*

IEC 61249-1: 200X, *Materials for printed boards and other interconnection structures – Part 1: Generic specification.*

IEC 61249-5-1: 1995, *Materials for interconnection structures - Part 5: Sectional specification set for conductive foils and films with or without coatings - Section 1: Copper Foil (for the manufacture of copper-clad base materials).*

IEC 61249-6-3: 200X, *Materials for interconnection structures - Part 6: Sectional specification set for reinforcement materials - Section 3: Woven E-glass (for the manufacture of prepregs and copper-clad base materials).*

**Materials and construction**

The sheet consists of an insulating base with metal-foil bonded to one side or both.

**Resin system**

Non-halogenated epoxide with a glass transition temperature of 120°C minimum. The maximum total halogens contained in the resin plus reinforcement matrix is 1500 ppm with a maximum chlorine of 900 ppm and maximum bromine being 900 ppm.

Contrast agents may be added to enhance processing such as automated optical inspection (AOI). Its flame resistance is defined in terms of the flammability requirements of 7.3.

**Metal foil**

Copper as specified in IEC 61249-5-1, Copper foil (for the manufacture of copper-clad materials). The preferred foils are electrodeposited of defined ductility.

**Reinforcement**

Woven E-glass as specified in IEC 61249-6-3, Woven E-glass fabric (for the manufacture of prepreg and copper clad materials).

**APPENDIX 7:****IPC-TM-650, Method 2.3.41, Test Method for Total Halogen Content in Base Materials  
[Identical to: IEC 61189-2, Test 2C12; Total Halogen Content in Base Materials]****1 Object**

The purpose of this test method is to measure the amount of chlorine and bromine compounds in base materials. This test method is applicable to reinforced base materials with a minimum thickness of 0.3 mm and to un-reinforced base materials with a minimum thickness of 0.08 mm.

A combustion flask is used to extract ionic and covalent halogen from the specimen, and Ion Exchange Chromatography is used for the quantitative analysis of halogen content.

**2 Test Specimens**

- a) Rigid or flexible base materials shall be used for the test in accordance with the thickness requirements described in the scope. The copper foil (if applicable) shall be removed from the test specimens by etching by any industry acceptable etching method or by mechanical peeling before test.
- b) For reinforced base materials, the number of test specimens shall not be less than 5 with a minimum size of 1cm x 1cm. For un-reinforced base materials, the number of test specimens shall not be less than 5 with a minimum size of 1cm x 1cm.
- c) Wash the specimens thoroughly in distilled or de-ionized water.
- d) For reinforced base materials, dry the specimen at 105 °C +5/- 0 °C for 1 + 0,25/-0 h.
- e) For un-reinforced base materials, wipe off the water with a lint-free cloth or paper wiper and leave them to dry at room temperature for a minimum of 1 h.
- f) For reinforced base materials, the number of test specimens shall not be less than 5 with a minimum size of 1cm x 1cm.
- g) For un-reinforced base materials, the number of test specimens shall not be less than 5 with a minimum size of 1cm x 1cm.

**3 Apparatus & Materials**

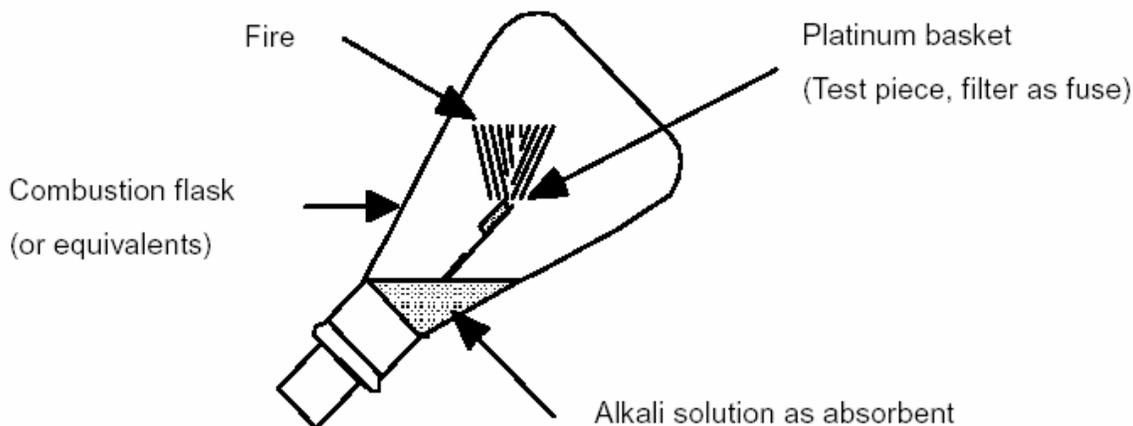
- a. Ion exchange chromatograph with a detection limit of 10 ppm or better.
- b. Analytical balance with an accuracy of approximately 1 mg or better.
- c. Knife
- d. Tweezers
- e. Vinyl gloves
- f. Lint-free cloth, paper wipers or equivalent.
- g. Quantitative filter paper.
- h. Combustion flask, or equivalent.
- i. Oxygen (99.9 % purity or better)
- j. Gas pressure regulator
- k. Flint striker, or another ignition device
- l. Wash bottle
- m. Beaker
- n. Micro-pipette
- o. Flasks (various sizes)
- p. Potentiometric titrator for silver nitrate, if necessary
- q. Platinum basket for holding sample
- r. Alkali solution
- s. Ethyl alcohol

- t. Chloride ion standard solution for chromatograph
- u. Bromide ion standard solution for chromatograph
- v. Silver nitrate, if potentiometric titration with silver nitrate is used

#### 4 Procedure

##### 4.1 Combustion Procedure

- a) Weigh the specimen using the analytical balance and record the result.
- b) Place approximately 50 ml alkali solution in a combustion flask to act as an absorbent of combustion gas.
- c) Fill the combustion flask with Oxygen.
- d) Insert a test specimen into the combustion flask as shown in Figure 1, below.
- e) Insert a piece of filter paper into the combustion flask as shown in Figure 1 to act as a flame starter.
- f) Apply several drops of ethyl alcohol on the test specimen for improving ignition of the specimen and ignite the specimen.



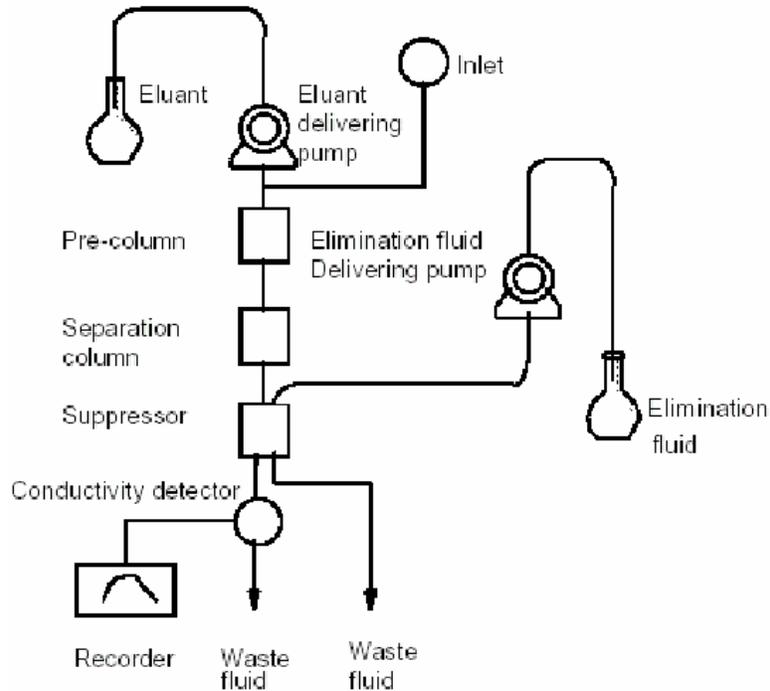
**Figure 1 - Combustion flask set up**

- g) Leave the flask at room temperature for 30 +/- 2 min after combustion. The generated gas is absorbed into the alkali solution to produce Cl-/Br- ion solution.
- h) Transfer the solution from the combustion flask to a volumetric flask. Add de-ionized water in the flask until the total amount is 100 ml of the test solution.
- i) Remove the suspended particles from the test solution by filtration or centrifugation, if necessary.
- j) Follow the same procedure outlined above without the test specimen to prepare a reference test solution (blank) without combustion of a test specimen.

Note - Chlorine and bromine contents shall be measured beforehand without any test specimen in the combustion flask to exclude any impurity contained in the filter from the test data.

## 4.2 Chemical characterization

- a) Inject the test fluid gathered from the flask in clause 4.1 into the inlet of an ion exchange chromatograph shown in Figure 2, below.



**Figure 2 Composition of ion exchange chromatograph**

- b) Analyze the peak area/height of the Cl-/Br- ions conductivity on the recorder and obtain Cl-/Br- concentration from a calibration curve.
- c) Obtain Cl-/Br- concentration of the reference by comparing its conductivity using the standard solution. The reference concentration will be subtracted from the test solution concentration to yield the final test result.
- d) Titrate test solution using silver nitrate if concentration of Cl-/Br- ion is high (higher than 1 wt%).
- e) An example of analyzing conditions for the ion exchange chromatography is given in Table 1, below.
- f) The analyzing conditions depend on the test devices, test specimens, their composition and environment.

**Table 1 Example of analyzing conditions for the ion exchange chromatography**

<u>Item/Material</u>	<u>Definition/Quantity</u>
Eluant	Alkali solution
Eluant delivering rate	1.0 ml/min to 2.0 ml/min
Elimination fluid	H <sub>2</sub> SO <sub>4</sub>
Elimination fluid and delivering rate	1.0 ml/min to 2.0 ml/min
Column	Pre-column, separation column
Suppressor	Suppression for anion
Detector	Conductivity meter

### 4.3 Calculation of halogen content

Substitute the concentration of halogen ion (Cl-/Br-) obtained in clause 4.2 in the following formula to obtain halogen contents in the specimens

$$\text{Chlorine (wt\%)} = \frac{\{[\text{Cl- concentration in the test fluid (ppm)} \times \text{Cl- Dilution ratio in the fluid}] - [\text{Cl- concentration in the reference (ppm)} \times \text{Cl- Dilution ratio in the reference}]\} \times \{\text{quantity of test solution (ml)} / \text{mass of the test specimen}\} \times 10^{-7}}$$

Note: For the Bromine content, use the same equation but Br- values in the place of Cl-.

Note: The 'dilution ratio' is the amount of added water compared to the original solution in the test flask. If the amounts used were each 50 ml, the dilution ratio would be 2.

## 5 Report

In addition to the general requirements for reporting, the report shall include:

- 1) The test method number and revision;
- 2) The date of the test;
- 3) The identification and description of the specimen;
- 4) The average chloride content of the 5 specimens in ppm;
- 5) The average bromide content of the 5 specimens in ppm;
- 6) The average total halogen content of the 5 specimens in ppm;
- 7) Any deviation from this test method;
- 8) The name of the person conducting the test.

Note: Observe all appropriate precautions on the Material Safety Data Sheets (MSDS) for the chemicals involved in this test method.

**APPENDIX 8:**

The final report (June 2006) of the European Union's human health assessment of TBBPA concludes as follows:

**“No health effects of concern have been identified for TBBP-A.”**

The full report is currently a .pdf file of 170 pages.