

The Regulatory and Environment Status of Tetrabromobisphenol-A In Printed Wiring Boards

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Abstract

Tetrabromobisphenol-A (TBBPA) is the predominant flame retardant used in rigid FR-4 printed wiring boards (PWB). In this application, the TBBPA is fully reacted into the epoxy resins that form the base material of the PWB. TBBPA's leadership position in the rigid printed wiring board market is due to several factors, which include reliable performance over time. This paper will look at the benefits of TBBPA as a flame retardant in epoxy resin PWBs. It will also address the current regulatory status of TBBPA. An update will be given on the regulatory and environmental status of TBBPA and other industry assessments that compare TBBPA to alternative flame retardants for PB will be included.

Introduction

In a world where electronic equipment is frequently going through technological advances and changes, we are now experiencing a shift in chemical regulations and increase in market pressure. Many of the items we use on a daily basis, including electrical equipment, automobiles, and aircraft, are undergoing intense examination and scrutiny. The implications of the worldwide swing of regulatory programs impacts a broad range of materials, including flame retardants.

The use of flame retardants has had a positive impact on the overall safety of homes, hotels, hospitals, nursing homes, offices, automobiles, and public transportation. Lives have been saved by the use of flame retardants [1]. Flame retardants are used to delay the spread of fires or delay the time of flashover to enable people time to escape. While fire continues to be an ever-present threat to society, chemicals, including flame retardants, have been the object of considerable scrutiny. These concerns stem from the fact that low levels of particular materials can and have been detected in the environment and, in some cases, in animals and humans. Unfortunately, this can result in marketing pressure to eliminate specific chemicals or classes of chemicals, even without scientific justification or legislation to restrict these materials being in place.

TBBPA Flame Retardant - Used in Printed Wiring Boards

Tetrabromobisphenol A (TBBPA) is the major flame retardant used in laminates for FR4 printed wiring boards (PWB) for electrical and electronic equipment. A smaller use of TBBPA is as an additive flame retardant in some applications. In FR4 PWB applications, TBBPA is reacted with epoxy resin to form part of the polymeric backbone of the resin. FR4 PWB hold microchips and other electronic components used to run computers, telecommunications equipment, industrial controls and other devices. Because the very function of circuit boards is to transmit electrical charges, flame retardants are an absolute necessity. Exposed to constant heat and electrical current, PWB base laminates can be made of either epoxy or phenolic (thermoset) resins, rigid or flexible that are required to meet certain flammability standards. (FR-4 boards, for example, must meet UL94 V-1 ratings). Approximately 90 percent of the FR-4 PWB produced meet the UL 94 V-0 standard for fire safety [2]. TBBPA has been the flame retardant of choice in PWB applications for around 30 years and no regulations currently exist worldwide to restrict its continued use.

Flame Retardant Regulatory Activity

The pressure that chemicals have come under has led to a patchwork of worldwide chemical regulations. Evaluation of the risks presented by the use of chemicals is the current focus of many regulatory programs. This approach takes into account the hazard of a substance, plus the exposure to the substance to determine the risk. The European Union (EU) Risk Assessment program ("Council Regulation [EEC] 793/93 of 23 March 1993") is one process that was in place for over fifteen years and was used to evaluate the characteristics of a variety of high production volume chemicals. In July 1, 2007 the EU Risk Assessment process was replaced by the EU Registration, Evaluation and Authorization of Chemicals (REACH) Regulation. The principle of REACH is "no data, no market." This approach is welcomed, as the importance to ensure that all flame retardants are safe for use, now and in the future is well recognized. In order to do this, regulatory decisions need to be based on sound science. These decisions also need to be made from a specific chemical's risks, not simply hazards. The regulation system in place also needs to be adhered to and accepted by everyone. For our society to operate effectively and efficiently, then acceptance of good regulatory programs is of the utmost importance. No regulations exist that prohibit the use of TBBPA anywhere in the world. It is one of the most scientifically tested and most cost effective flame retardant available on the market.

EU Risk Assessment

The European Union (EU) Risk Assessment [3] was well recognized as being the leading independent, transparent, and science-based system for assessing chemicals and substances in everyday use [4]. It was in place for many years and was used to evaluate the characteristics of a variety of high production volume chemicals. It was the most comprehensive of current global assessment programs for human health and environmental characteristics. Several flame retardants went through EU Risk Assessments. Each flame retardant was assessed individually, not as specific classes. This process examined critical aspects of a chemical, including mammalian and environmental toxicology, environmental fate and releases (to water, soil, air, and from all operations throughout the lifecycle), and risk (exposures versus limits). After all this information was generated, a hazard assessment, exposure assessment, risk identification, and risk management was generated. This determined whether there was a need for more testing or whether there was a need for risk reduction. The risk assessment was the basis for the future legislation on the use of these substances in the European Union. This process was revoked in June 1, 2007 and replaced by the REACH Regulation (see next section) [5].

The EU Risk Assessment on TBBPA was completed, and the conclusions were that it presents no risks to human health and no risks to the environment were identified for reactive use of TBBPA in printed circuit board applications or in any applications. There are no restrictions for use in any applications [6, 7]. It is not a PBT (persistent, bioaccumulative, and toxic) material. It was classified R50/53 (Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment). Risk was identified at one specific additive user plant, so an active emissions control program has been put into place to help insure that emissions do not occur. The EU Scientific Committee on Health & Environmental Risks (SCHER) Opinion for TBBPA considered that the human health and environmental parts of the risk assessment of TBBPA to be of acceptable and of good quality [8, 9]. This scientific expert panel reporting to the EU Commission was always consulted after the finalization of EU risk assessments. The EU Commission used the SCHER Opinion in the conclusion of no restrictions for use in any applications.

The EU-funded cluster of research projects into endocrine disrupting chemicals (CREDO) found “no cause for concern” for TBBPA. Within the CREDO cluster, the FIRE Project (Flame retardants Integrated Risk assessment for Endocrine effects) studied 3-month exposure to TBBPA of estuarine flounders (flat fish). Despite the significantly higher exposure levels than those found in the natural environment, the CREDO report concludes that for TBBPA “general health and toxicity parameters (behavior, survival, growth rate, and relative liver and gonad weight) were not affected” [10].

EU REACH

The REACH Regulation (Registration, Evaluation, Authorization and Restriction of Chemical substances) is a European Community Regulation on chemicals and their safe use (Regulation EC No 1907/2006) that entered into force on June 1, 2007 [5]. It is the central act of the new European chemicals policy. At this time, Council Regulation (EEC) 793/93 on Existing Substances (EU Risk Assessment Regulation) was revoked and replaced by REACH establishing a European Chemicals Agency. All manufacturers and importers of chemicals must identify and manage risks linked to the substances they manufacture and market. Also, article producers or importers are also impacted by this regulation. The principle of REACH is “no data, no market.” This approach is welcomed, as the importance to ensure that all chemicals, including flame retardants, are safe for use, now and in the future. TBBPA was registered under the REACH process prior to the December 2010 deadline, and there are no restrictions on its use.

Pre registration of substances under REACH was completed in December 2008. The first round of substance Registration (Art. 23) was completed on December 1, 2010. This was for existing substances >1,000 tons, > 1 ton carcinogenic, mutagenic, or toxic for reproduction substances (CMR) substances, and > 100 tons very toxic & R50/53 (per year/substance/any manufacturer). The timeline for additional existing substances to go through Registration is as follows (per year/substance/any manufacturer):

- | | |
|------------|---------------|
| > 100 tons | June 1, 2013 |
| > 1 ton | June 1, 2018. |

Consortia formation and registration dossiers gathering is currently ongoing for the additional existing substances due for Registration in June 1, 2012. The substances that have gone through the European Union (EU) Risk Assessment (“Council Regulation [EEC] 793/93 of 23 March 1993”) are already data-rich, so the process should be quicker for these substances.

The identification of a substance as Substance of Very High Concern (SVHC) and its inclusion in the SVHC Candidate List is the first step of the Authorization procedure. SVHCs include the following substances:

- CMR (Carcinogen, Mutagen, Reprotoxic) cat. 1 and 2
- PBT (Persistent, Bioaccumulative, and Toxic)
- vPvB (very Persistent and very Bioaccumulative)
- Substances with equivalent concern (e.g. endocrine disruptors)

The SVHC Candidate List was published by the European Chemicals Agency on October 28, 2008, and has since been updated to include 53 substances [11]. Inclusion in the list generates immediate new legal obligations for communication in the supply chain. These obligations are linked to the listed substances themselves, in preparations, and in articles. Two of the most common flame retardants included in the SVHC Candidate List are Hexabromocyclododecane (HBCD) and all major diastereoisomers and Tris (2-chloroethyl)phosphate (TCEP) [11]. Neither of these two flame retardants are used in PWB applications.

EU RoHS Directive

The Directive of the European Parliament and of the Council 2002/95/EC on the Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) was put into effect on July 1, 2006 and has recently been recast [12, 13]. It states that Member States shall ensure that new electrical and electronic equipment (EEE) put on the market shall not contain Pb, Hg, Cd, Cr (VI), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) above de minimus levels. All other flame retardants are compliant with the provisions of the RoHS Directive and can hence be used in EEE. The RoHS recast went into effect on July 1, 2011. It promotes science-based legislation, underlines the importance of coherence of RoHS with other chemicals legislation (particularly the REACH Regulation), and includes a clear methodology for possible future restrictions of substances in electrical and electronic equipment [14]. The recast RoHS will gradually open the scope of application to all electrical and electronic equipment over an 8-year period, from 2011 to 2019. TBBPA is not included or restricted under the current or recast RoHS Directive.

EU WEEE Directive

The EU legislation promoting the collection and recycling of Waste of Electrical and Electronic Equipment (WEEE Directive) has been in force since February 2003 (EU Directive 2002/96/EC). This directive calls for selective treatment of plastics containing brominated flame retardants, as stated in Annex II [15]. Also required within the directive is the separation of PWB of mobile phones (regardless of PWB size) and of other devices if the surface of the PWB is greater than 10 cm², regardless of what flame retardant is contained. The reason is to recover the valuable extractable metals (Ag, Au, Cu, Zn, Al, Ni) from the PWB.

The selective treatments of flame retardant plastics are fulfilled when the WEEE plastics are treated (recovered, recycled, thermally disposed) together with other wastes, as is the case with energy recovery processes that are currently practiced in Europe [16]. In this scenario, the joint recovery of plastics containing brominated flame retardants with other materials complies with the purpose of the WEEE Directive without the removal requirement of Annex II. Recent technical studies and legal reviews demonstrate that WEEE plastics containing brominated flame retardants, including TBBPA, are compatible with the EU WEEE Directive without separation and removal prior to the waste treatment. This has been confirmed by the 2006 EU Member States' guidance on the separation requirements of the WEEE Directive. The EU WEEE Directive is currently undergoing Recast.

North American Regulations

The Canadian federal government announced a new *Chemical Substances Plan* in December 2006 to prioritize chemicals targeted for risk assessment and risk management [17]. The first step of the Chemical Substances approach in Canada is categorization, followed by risk assessment and risk management. By 2006 some 23,000 chemical substances had been categorized to identify those that were:

- Inherently toxic to humans or to the environment and that might be:
 - Persistent (take a very long time to break down), and/or
 - Bioaccumulative (collect in living organisms and end up in the food chain)
- Substances to which people might have greatest potential for exposure.

A screening risk assessment is underway in Canada for TBBPA.

The EPA's Design for the Environment (DfE) Program focuses on the environmental, health, and safety aspects of flame retardants used in PWB [18]. It is a multi-stakeholder partnership with the goal to identify and evaluate commercially available flame retardants and their environmental and human health and safety aspects in FR-4 boards. The DfE project will try to determine the potential hazards associated with various flame retardants and potential exposures throughout the life cycle of flame retardants used in electronic FR-4 PWB. Consideration of exposures from manufacturing, use, and

incineration or burning at the end of life will be included. In addition, understanding the combustion products that could be formed during certain end of life scenarios will also be evaluated. The project began in February 2006. The Phase 1 report is complete and Phase 2 testing is in progress. The results show that once reacted with an epoxy to form the laminate, TBBPA had as good or better Human Health and Environmental properties than the alternatives.

Additional Evaluations

In a recent study commissioned by the European Commission (DG Health and Consumers / Consumer Affairs) and performed by Arcadis Belgium, 42 different flame retardants in consumer products in domestic environments were evaluated [19]. The results of the study had flame retardants classified in categories as follows:

- “No Need For Immediate Risk Management” - Six flame retardants identified (had no risks identified)
 - Brominated Flame Retardants 2 (TBBPA was one of these)
 - Chlorophosphate Flame Retardants 2
 - Phosphorus Flame Retardants 1
 - Chloroparaffin (MCCP) Flame Retardant - 1
- “Inconclusive” - Ten flame retardants identified
 - Brominated Flame Retardants 1
 - Phosphorus Flame Retardants 9
- “Data Gaps” - Twenty-two flame retardants identified
 - Brominated Flame Retardants 4
 - Mineral Flame Retardants 3
 - Chlorophosphate Flame Retardants 1
 - Phosphorus Flame Retardants 14
- “Risk” - One flame retardant identified
 - Phosphorus Flame Retardants 1

Some of the major significant points of this study are:

- ❖ Substituting one particular flame retardant “class” or “family” is not a method to eliminate Environmental or Human Health risks
- ❖ Each specific flame retardant has its own unique set of properties (chemical, physical, human health, environmental, etc...) and must be evaluated individually

TBBPA was in the “No Need for Immediate Risk Management” class.

Recycle

For PWB, the main end-of-life outlet is to smelters. Copper smelters, as well as precious metal smelters, are able to use PWB as a source for energy recovery (replacing cokes) and as a reducing agent for the metals. By smelting, the copper and precious metals can be recovered in the most economical and environmental safe manner. To produce copper from recycled material rather than from ore, means that only one-sixth of the energy is needed [20].

Smelting can safely be practiced using proper conditions. Research and many years of operation have conclusively shown this to be the case. Pyrolytic treatment (typical method for smelting) involves the ignition and melting of ground feedstock in a furnace at ~1200°C via air injection. The organic constituents are destroyed at these high temperatures and emissions are addressed via afterburners [21].

It is estimated that out of a 50-75% recycling target, 55% can be achieved through the metal (smelting) recovery process. An eco-efficiency study carried out by PlasticsEurope in Belgium showed that a metal smelter provided the highest recovery rate for handling mobile phones, without high dismantling costs [20].

As an example of this process, the Swedish company, Boliden, has developed a metals recycling process for WEEE that is in compliance with European regulation. The plastics provide energy for the smelting process. A trial was recently carried out at a precious metal smelter in Antwerp to assess the feasibility of using mixed waste WEEE plastics to replace coke as a reducing agent and energy source for the smelter [22]. Approximately 150 tonnes of E-waste was fed into the smelter. A comparison was made of the operation with zero plastics input (treating wastes other than PWB and 4.5% coke) to 6% E-Waste plastics and 1% coke. Results available to date show similar smelter operation and performance (metal recovery rates, operating stability) between the two input schemes. This trial suggests that the Umicore Hoboken integrated smelter alone offers >15,000 tonnes/year capacity to treat WEEE plastics plus >40,000 tonnes/year capacity for PWB (which include around 25% plastic). Moreover, the Flemish Waste Administration granted Umicore a permit for handling WEEE plastics and agreed that this should be part of recycle quota in the WEEE directive

Product Stewardship

Sustainability has become the goal for many companies and industries. The three aspects of sustainability (environmental, societal, and economic concerns) must be reconciled for sustainable development to be achieved. The chemical industry views sustainability as a challenge put before all parts of society. Advances made in industrial operations, improved performance, and improvements to society (by the use of flame retardants) all help to improve living standards and the environment. Reducing or eliminating emissions of chemicals to air and water can further minimize exposure to humans.

To address emissions of plastics additives, including TBBPA, a Voluntary Emissions Control Action Plan (VECAPTM) was initiated [23]. The VECAP Pilot program was initiated in the UK textiles industries in 2004 to reduced emissions of flame retardants to air and water in line with the Code of Good Practice. After one year of implementation, the UK Pilot Program was able to achieve an estimated 75% reduction in emissions to water [24]. The second year, a total estimated reduction of 97% in emissions was then realized.

VECAP has seen significant successes and was subsequently implemented in five other European Member States, North America, Japan, China, and other parts of Asia. VECAP has expanded to include other materials, including phosphorus flame retardants and polymer additives that are not flame retardants. This program is not only a flame retardant program; it is a model program for all plastics additives. Companies participating in VECAP follow a cycle of continuous improvement. This starts with a commitment to the Code of Good Practice and verification of the actual working procedures with those required according to the Code of Good Practice. Then the company then critically analyzes its product flow and processes to identify the potential for emissions. Measuring and recording the relevant data will identify the actual emissions baseline throughout the entire production process. Once this emissions balance is known, an emissions report can be drawn up which will enable closure of the mass balance. The methodology and discipline of the VECAP mass balance assumes that material not accounted for during this process is an "emission." This has led to an exhaustive examination of the process and has resulted in the discovery of new potential emission sources. An improvement plan is implemented, operational results are evaluated, and potential for further emission reductions investigated to ensuring effective continuous improvement.

By committing to applying pro-active product stewardship practices, the safe and environmentally friendly use of plastic additives can continue. VECAP provides both a practical and cost-effective means of controlling emissions. This program is a potential model for chemical management that could be applied to other chemicals. Users and producers applying the principles of VECAP have demonstrated that by undertaking a series of simple and low cost measures at the production level, significant levels of emissions can be reduced. As global producers of chemicals, the flame retardant manufacturers that initialed the VECAP program are deeply committed to protecting the environment, ensuring the safety and security of our operations, and safeguarding the health and safety of employees and of the communities in which we live and work. In addition to reducing emissions of flame retardants from all stages of all processes, VECAP results in cost savings via recovered product and demonstrates leadership in a self-regulated stewardship program. This program will help to insure a sustainable future for plastic additives, including flame retardants.

Conclusions

Printed wiring boards (PWB) are an integral part of the electrical and electronic equipment that has helped to improve our quality of life. Tetrabromobisphenol-A (TBBPA) is a valuable flame retardant that has been used extensively in rigid FR-4 PWB for over 30 years to insure fire safety. It has had a long history of reliable use in this application. PWB containing TBBPA have an efficient and economical end-of-life option that is already in place. At end-of-life, PWB can be treated by smelting to remove copper and precious metals that are present.

There are no prohibitions on the use of TBBPA anywhere in the world. It has undergone extensive human health and environmental testing, in which other flame retardants used in this application have not. The EU Risk Assessment on TBBPA was completed, and the conclusions were that there are no restrictions for use in any applications. TBBPA has been registered under the REACH process. The conclusions of the EU Risk Assessments on TBBPA were key to the outcome under REACH. TBBPA is not categorized as dangerous, or a PBT, or a vPvB, or a CMR category 1 or 2.

Excellent product stewardship under the Voluntary Emissions Control Action Plan (VECAPTM) program will help to insure that TBBPA is kept out of the environment. By committing to applying pro-active product stewardship practices, the safe and environmentally friendly use of plastic additives, including TBBPA, can continue. VECAP encourages companies to critically analyze product flow and processes to identify the potential for emissions. It provides both a practical and cost-effective means of controlling emission, and is a potential model for chemical management that could be applied to all chemicals.

References

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The Regulatory and Environment Status of Tetrabromobisphenol-A In Printed Wiring Boards

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Why are Flame Retardants Needed?

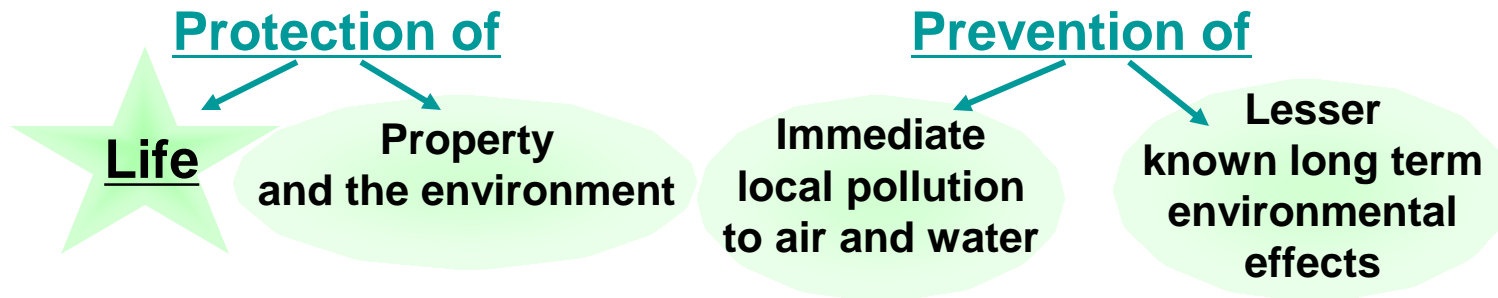
- **Flame retardants are used to help:**

Prevent ignition

Delay the
Spread of fires

Delay the time of flashover
to enable people time to escape

- **Fire prevention is essential from a number of perspectives:**



Pollutants generated in fires:

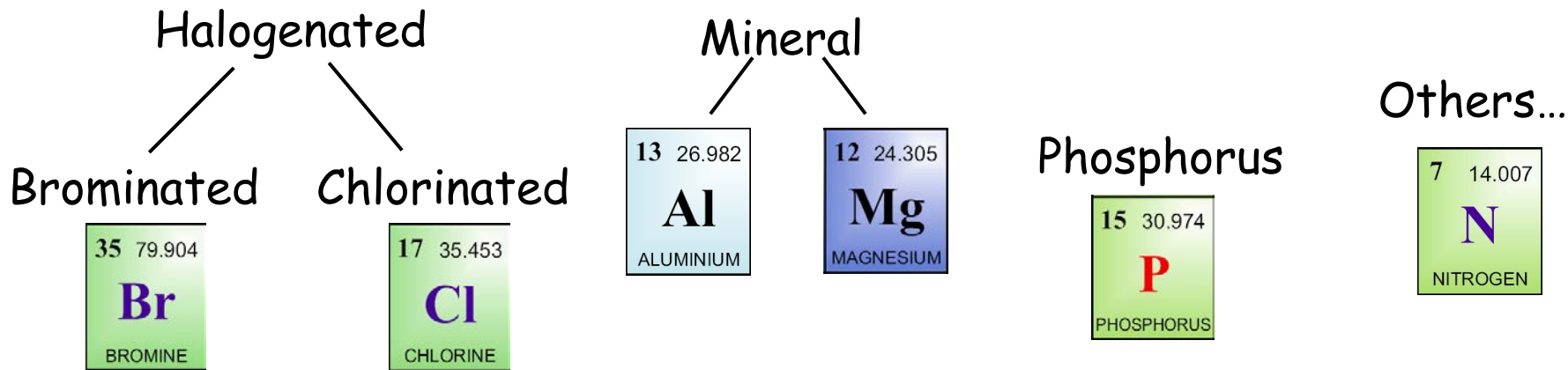
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Polyhalogenated dibenzodioxins and furans (PHDDs/PHDFs)
- Measurements in large fires have shown:
 - PAHs have an up to 500 times higher cancer risk than PHDDs/PHDFs
 - PAHs are generated in all fires and many are carcinogenic compounds.*

Combustion gases generated during fires that contribute to acute toxicity:

CO, HCN, HCl, and acrolein
Carbon monoxide is responsible for > 90% of all fire deaths *

* Troitzsch, J, "Fire Gas Toxicity and Pollutants in Fires – The Role of Flame Retardants," FR2000 Conference, London, 8th-9th February 2000

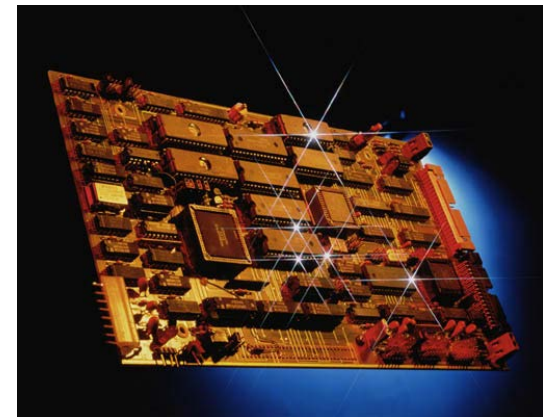
Common Flame Retardants Classes



- Based on natural elements
- There are many different flame retardants in each of these classes
- Each individual flame retardant has it's own unique set of environmental, human health, physical, and chemical properties
- The distinct nature of individual flame retardants requires that each be treated on it's own merits

Why use Flame Retardants in Printed Wiring Boards (PWBs)?

- The function of a PWB is to transmit electrical charges - they are exposed to constant heat and electrical current
- PWBs are required to meet flammability standards
 - FR-4 boards must be UL-94 V-1 rated
- More than 90% of PWBs are UL-94 V-0 rated



Flame Retardant Selection

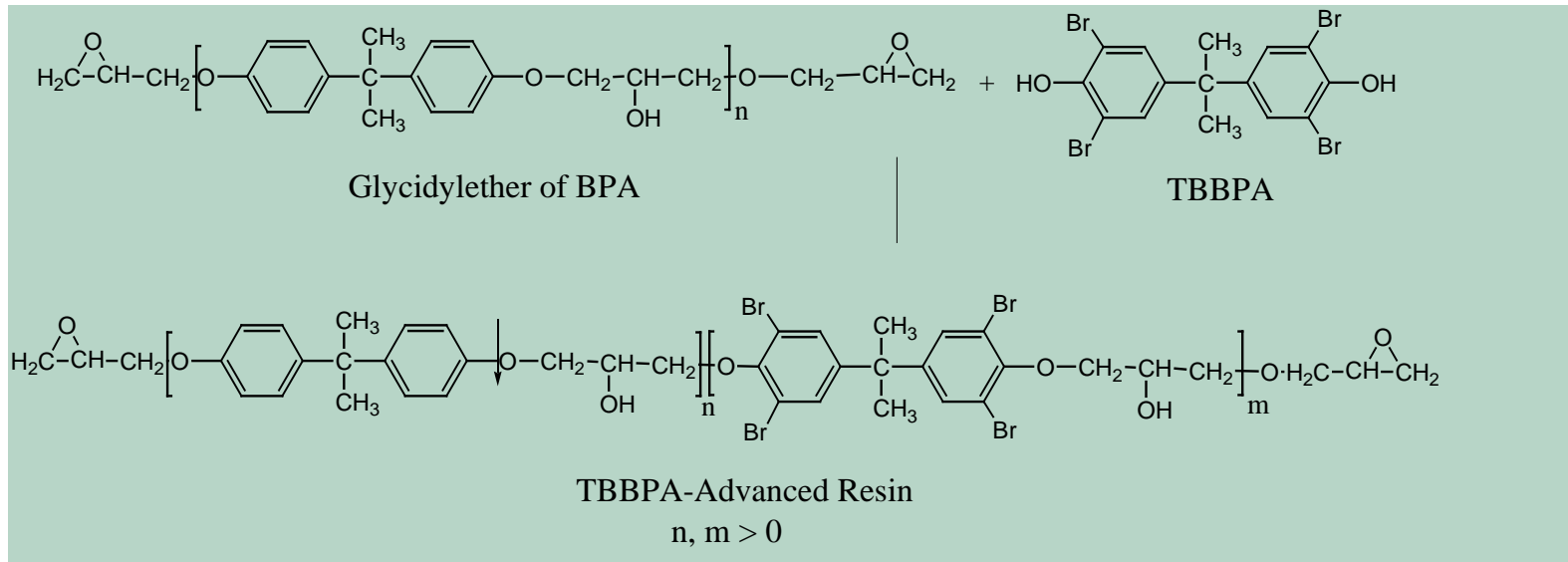
- Choosing the most suitable flame retardant solution needs to take into account multiple factors
 - Electrical properties
 - Assembly temperatures
 - Moisture uptake and soldering reliability
 - Mechanical performance
 - Reliability

Flame Retardant Selection

- One single criterion can't be the basis for material selection
 - Brominated formulations - the most common solution in wiring board laminates
 - In high and ultra-high end applications where low Dk and Df are required, additive brominated flame retardants perform better than the usual brominated epoxies based on TBBPA
 - Phosphorus formulations - epoxy resins can also incorporate phosphorus as a flame retardant
 - About 6-7% of the FR-4 printed wiring boards currently on the market are partly based on this technology
 - Metal hydroxides - phosphorus resins are used in combination with metal oxides
 - Tend to face technical challenges, such as higher water uptake, increased brittleness, higher Dk, and higher failure rate at assembly stage, making them unsuitable for high-reliability battery-powered consumer electronics

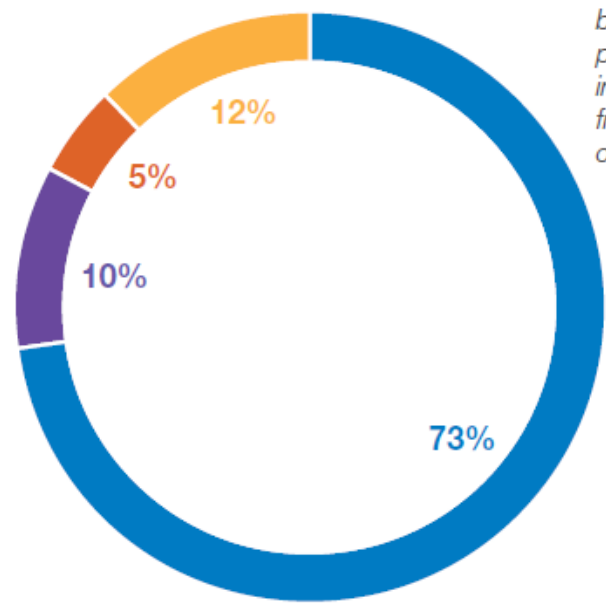
Tetrabromobisphenol A Flame Retardant (TBBPA)

- Flame retardant of choice for more than 30 years
- Used in epoxy-based PWBs
- A reactive flame retardant
- Incorporated into the epoxy resin backbone



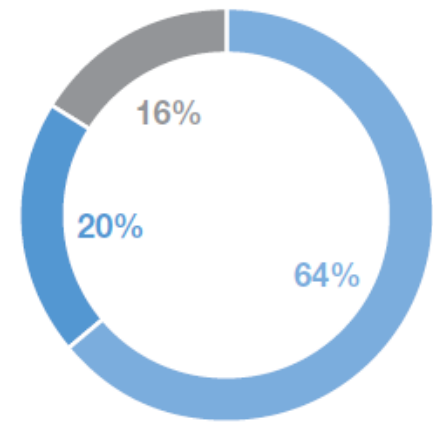
Rigid PWB Market

In 2009, about 84% of the FR-4 printed circuit boards market is based on brominated materials, with the remaining share based on phosphorous formulations and metal hydroxides. The latest trends in electronics (lower prices, higher computing frequencies, lead-free soldering) will put additional technical and economic pressure on the various formulations.



PWB Laminates - \$ 7,66 Bn (2007)

- FR-2 Paper Phenolic
- Composite Epoxy materials
- Others
- FR-4 Epoxy



FR-4 - \$ 4,6 Bn (2009)

- Standard FR-4 brominated epoxies
- High Tg FR-4 brominated epoxies
- FR-4 phosphorus-based formulations

Source: Inoguchi et al., *Electronic chemicals Part 2: Printed circuit board chemicals and semiconductor packaging materials*, SRI Consulting, Dec. 2007

Source: *Global Market Share and Global Laminate Production per Prismark - PCB laminate market by material type (2009)*

Some of the Chemical Regulations

Country / jurisdiction	Chemical control - product safety laws	Regulations on electronics recycling / take-back
EU	REACH	ROHS / WEEE
USA	TSCA / Chemical Substances Inventory	Resource Conservation and Recovery act
Canada	CEPA / Chemical Control Regulations	E-waste regulations
Rep. of Korea	Toxic Chemicals Control Act	Resource recycling of EEE and vehicles
China	New / Existing Chemicals Management Regulations	Discarded appliances and electronic products
Japan	Law on Control of Examination and Manufacture of Chemical Substances	Home appliances recycling law
Australia	NICNAS / Industrial Chemicals Notification and Assessment	Hazardous Waste Act
Taiwan	Toxic Chemical Substances Control Act	Waste Disposal Act

TSCA
Reform

State-by-State
activity on a limited
number of flame
retardants

CA
Green Chemistry
Focus – Alternatives
Assessment

Canada
Chemical Substances Plan
~22,000 substances

EPA

- “Chemicals of Concern” Action Plan (Dec 2009)
- High Production Volume (HPV) Challenge (~2,200 chemicals)
- Design for Environment (DfE)
 - Hazard based
 - Broad range of stakeholders
 - Various substances evaluated
 - Three DfE projects in progress on flame retardants

➤ DfE in progress to review tetrabromobisphenol-A (TBBPA) alternatives in printed boards

➤ DfE in progress to review decabromodiphenyl ether (Deca-BDE) alternatives in many different applications (~30 alternatives)

➤ DfE upcoming to review hexabromocyclododecane (HBCD) alternatives in XPS & EPS foam

North American Regulatory Activity - EPA DfE

- US EPA DfE Electronics Partnership, “Flame Retardants in Printed Circuit Boards”
 - Identify and evaluate environmental and human health and safety aspects of commercially available flame retardants used in FR-4 PWB, including TBBPA
 - Determine the potential hazards and potential exposures throughout the life cycle - manufacture, use, and incineration or burning at EOL (also understand combustion products)

REACH

Registration, Evaluation,
Authorization and Restriction
of Chemical Substances
EU Regulation EC No 1907/2006
June 1, 2007
Replaced EU risk assessment
regulation 793/93 (EC)

RoHS

Restriction of Certain
Hazardous Substances in
Electrical and Electronic Equipment
Directive 2002/95/EC
July 1, 2006

WEEE

Waste Electrical and
Electronic Equipment
Directive 2002/96/EC
February 2003
Promoting the collection
and recycling of EEE

TBBPA Risk Assessment

- Human Health Section
 - Risk Assessment was concluded in December 2004
 - Final conclusion: no risks identified and no need for risk reduction measures
 - Final report on Human Health RA published in 2006 on ECB website: <http://ecb.jrc.it/esis/esis.php?PGM=org>
- Environmental Section
 - Last discussion completed in March 2007
 - TBBPA is classified R50/53, very toxic to aquatic organisms
 - This classification does not affect the reactive use of TBBPA; only applies to additive use of TBBPA
- **EU Authorities agreed that TBBPA is not a Persistent, Bioaccumulative, Toxic (PBT) chemical**

TBBPA Additional Study

- CREDO Study
 - The EU Research Cluster on endocrine disruption, CREDO, announced results of long-term exposure studies on fish.
 - Three studies on estuarine flounders with long-term exposure to TBBPA were performed.
 - The conclusion was:
“no major endocrine effects found in fish”

- Registration, Evaluation, Authorization and Restriction of Chemical Substances (REACH) - EU Regulation EC No 1907/2006
 - Provides a lead in determining substances of very high concern based on:
 - Persistence, Bioaccumulation, Toxicity, Carcinogenicity, Mutagenicity, Reproductive effects, and Substances of Equivalent Concern
 - Hazard based characterization followed by risk and socio-economic analysis



73 substances on the SVHC's Candidate List, 5 can be used as flame retardants

- Substances targeted by authorization are Substances of Very High Concern (SVHCs):

CMR

(Carcinogen, Mutagen, Reprotoxic)
cat. 1a or 1b*

PBT

(Persistent, Bioaccumulative, and Toxic)

vPvB

(very Persistent and very Bioaccumulative)

Substances with equivalent concern
(e.g. Endocrine disruptors)

* <http://echa.europa.eu>

HBCD (Hexabromocyclododecane) CAS# 25637-99-4, 3194-55-6

TCEP (Tris(2-chloroethyl) phosphate) CAS# 115-96-8)

Boric Acid (CAS# 10043-35-3, 11113-50-1)

Disodium tetraborate, anhydrous (CAS# 1303-96-4, 1330-43-4, 12179-04-3)

Tetraboron disodium heptaoxide, hydrate (CAS# 12267-73-1)

Currently restricted in Annex XVII (Regulation No 552/2009 (EC)) are the following flame retardants:
PeBDE - Pentabromodiphenyl ether (0.1% wt), TEPA – Tris(aziridinul)phosphinooxide (skin contact), TRIS – Tris (2,3 dibromopropyl) phosphate (skin contact), PBBs – Polybrominated biphenyls (0.1% wt)

- Restriction of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) Directive 2002/95/EC
- Since July 1, 2006, restricts the placing on the EU market new electrical and electronic equipment containing certain levels of:
 - Lead, Cadmium, Mercury, hexavalent chromium, polybrominated biphenyl (PBB), polybrominated diphenyl ether (PBDE) flame retardants
- The RoHS Recast:

Voted on Nov 24, 2010

Recast RoHS Directive 2011/65/EU to enter force on Jan 2, 2013

- The recast RoHS Directive text includes:

No additional restriction of substances in EEE

No blacklisting of substance for priority review

No mention of Additional BFRs, except HBCD, mentioned in recital

Methodology for future assessment of substances under RoHS - to be more coherent with REACH

“Open scope” that would extend to all EEE unless specifically exempted

TBBPA is NOT included in the RoHS Directive

- A 400-page study to provide up-to-date knowledge on flame retardants currently used in consumer products in the EU
- Commissioned by the EU Commission's Health and Consumers Directorate
- The Final Report, conducted by consultants Arcadis and EBRC Consulting, was recently published
- http://ec.europa.eu/consumers/safety/news/index_en.htm
- Pages 27-36 are Tables for the Flame Retardant Groupings according to their risks (various tables of "No Need for immediate Risk Management" to "Data Gaps")
- This gives you a good idea of known properties on many of the flame retardants that are commercially used
- ***“No Need For Immediate Risk Management”*** - Six Flame Retardants identified (had no risks identified)
 - Brominated Flame Retardants - 2 – **one of these is TBBPA**
 - Chlorophosphate Flame Retardants –2
 - Phosphorus Flame Retardants - 1
 - Chloroparaffin (MCCP) Flame Retardant - 1



- “Inconclusive” - Ten flame retardants identified
 - Brominated Flame Retardants - 1
 - Phosphorus Flame Retardants – 9
- “Data Gaps” - Twenty-two flame retardants identified
 - Brominated Flame Retardants - 4
 - Mineral Flame Retardants - 3
 - Chlorophosphate Flame Retardants - 1
 - Phosphorus Flame Retardants - 14
- “Risk” - One flame retardant identified
 - Phosphorus Flame Retardants – 1
- Some of the major significant points of this study are
 - Substituting one particular flame retardant “class” or “family” is not a method to eliminate Environmental or Human Health risks
 - Some of the alternative flame retardants being promoted today will fit in the “Inconclusive,” “Data Gaps,” or “Risk” categories
 - Each specific flame retardant has its own unique set of properties (chemical, physical, human health, environmental, etc...) and must be evaluated individually



End-of-Life (EOL)



- Main EOL outlet is to smelters
- PWB in Copper and Precious Metal Smelters
 - Source of energy recovery (replacing coke)
 - Reducing agent for the metals
 - Most economical EOL scenario
 - Currently practiced safety
 - One-sixth of energy needed to produce copper from recycled material rather than from ore
 - Several trials have shown the addition of PWBs to the smelting process provides energy for the smelting process with no problems

End-of-Life (EOL)

PWBs as feedstock for precious metals recycling in state-of-the-art metal smelters

A trial study conducted by PlasticsEurope in conjunction with Umicore and EFRA documented that brominated epoxies printed wiring boards present in the typical household WEEE can be safely used as metal smelter feedstock.

- *Organic compounds (such as brominated polymers, phosphorous flame retardants or melamine compounds) are destroyed at smelter operating temperatures (>1100°C);*
- *70% of the antimony (Sb) can be recovered as a metal and recycled as a commercial antimony salt for industrial applications;*
- *Aluminium, magnesium and phosphorus are primarily transferred to slags, which can then be reused in the concrete industry as a substitute for gravel;*
- *No increase in toxic emissions by the smelter have been observed during the large scale trial study. Actually, the presence of bromine in the smelter acted as a reducing agent for mercury and helped lower mercury emissions to air.*

EU **WEEE** Directive **W**aste **E**lectrical & **E**lectronic **E**quipment

*WEEE Directive **requires separation of All PWBs greater than 10 cm²**, regardless of whether they contain P, Al, Br, Cl, N, C or any other element*

TBBPA

- $C_{15}H_{12}Br_4O_2$
- 2,2',6,6'-Tetrabromo-4,4'-isopropylidenediphenol
- Reactive compound
- CAS# 79-94-7, EC # 201-236-9
- REACH (Regulation (EC) N° 1907/2006) Registration:
 - # 01-2119538800-42-0001
- Directive 67/548/EEC-1999/45/EC (DSD - DPD)
 - N - Dangerous for the environment
 - R50/53 - Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
- EC Regulation 1272/2008 (CLP)
 - Acute aquatic toxicity Category 1; H400
 - Chronic aquatic toxicity Category 1; H410
 - M Factor = 10

TBBPA

- A Risk Assessment has been performed
- Human Health Effects - Not expected to be acutely toxic
- Persistence/Degradability - Not readily biodegradable
- Mutagenic Effects - Not mutagenic in AMES Test, Chromosome aberration test in vitro negative
- Reproductive Effects - No indication of effects on developmental toxicity

- TBBPA is not classified as toxic for health and has little potential for bioaccumulation, as highlighted in the World Health Organization's International Program on Chemical Safety

Informed Substitution

From the
EPA's
perspective:

Informed Substitution Goals

- Minimize likelihood of unintended consequences
- Choose a course of action based on the best environmental and human health information that is available or can be modeled

Critical Decision Elements

Alternatives should:

- Be technologically feasible;
- Deliver the same or better value in cost and performance;
- Provide an improved profile for health and environmental issues;
- Account for economic and social considerations; and
- Have potential to result in lasting change.

U.S. Environmental Protection Agency

From a **Supply Chain perspective**, substitutes must at least meet:

- Health and environmental hazard and risk considerations
- Chemical compatibility with the process and other materials
- Compliance with standards
- Functionality in end use – some parts will need to be tested under actual operating conditions, must be reliable
- Some parts will need material changes as well as flame retardant changes



Voluntary Emissions Control Action Program - **VECAP**TM

- **V**oluntary – user and producer implemented
 - **E**missions – identify sources of BFR emissions
 - **C**ontrol – develop procedures to better manage chemicals and minimize emissions
 - **A**ction – dynamic, continuous process
 - **P**rogram – focus on Best Practices
- To increase awareness of chemical handling processes throughout the value chain
- **VECAP** is an innovative and excellence-driven way of doing business, based on ISO 14001 principles

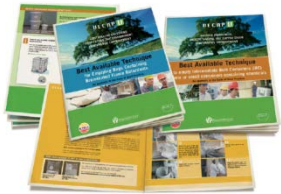


www.vecap.info

VECAPTM is a voluntary Industry initiative applicable to all polymer additives



VECAP's Success – Continuous Improvement



MANUFACTURING

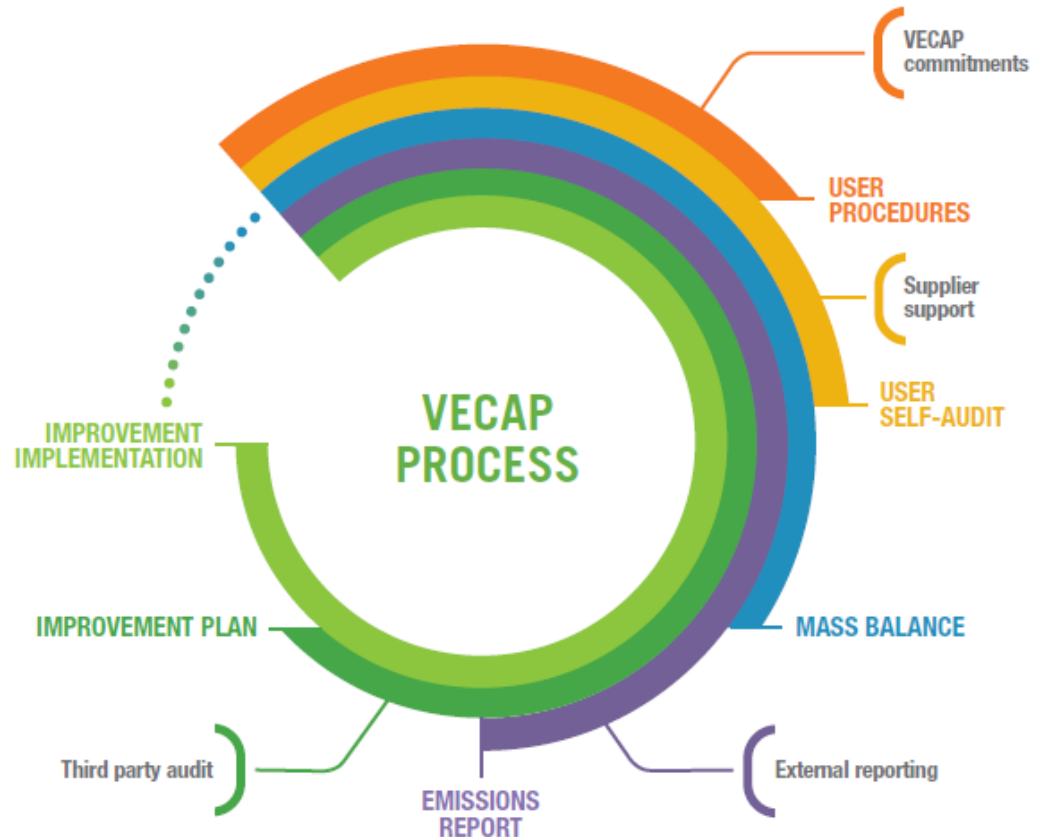
- 1 Production
- 2 Packaging
- 3 Shipping

PROCESSING

- 1 Dust from unloading and feed operations
- 2 Leaks in feed equipment on production lines
- 3 Inadequate or missing air filters
- 4 Improper clean-up of spills

WASTE DISPOSAL

- 1 Residues in packaging
- 2 Poorly treated wastewater from system wash-outs
- 3 Waste not reprocessed
- 4 Use of uncontrolled landfills



Conclusions

- Base decisions on good quality science
- Reward data and Penalize lack of data
- Minimize Risk (Reduce hazard and Reduce exposure)
- Understand total implications of substitution in terms of life cycle (Production, Use, and End of life)
- Science available on TBBPA
 - EU Risk Assessment/Health: no human health hazard identified
 - EU Risk Assessment/Environment: no risks are identified for TBBPA use in epoxy resins
 - EU Authorities agreed that TBBPA is not a Persistent, Bioaccumulative, Toxic (PBT) chemical
 - EU REACH Directive: TBBPA has been registered
 - TBBPA is NOT included in the EU RoHS Directive



Thank You!

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Flame retardant product selector

Fire safety solutions
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2010-11 PRODUCT SELECTOR GUIDE

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Product advocacy

Tetrabrom - Facts on use

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Literature

- Fire safety solutions product selector brochure
- Fire safety solutions for electronics brochure
- Fire safety solutions for automobiles brochure
- Fire safety solutions for public transportation brochure

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Home > Polymer solutions > Flame retardants

Flame retardants



Albemarle flame retardants save lives.

We've designed several Albemarle flame retardants to improve electrical properties of wire and cable applications. Others resist blooming, plate-out and UV light in HIPS and ABS. Still others improve the "green strength" or reduce fogging of urethane foams. In fact, we offer additives that can improve virtually any polymer you can name.

But what we're most proud of at Albemarle is that, by helping plastic molders, compounders, and foamers meet or exceed stringent legal and regulatory requirements to protect property, every one of our flame retardants also helps save lives.

Learn more about Albemarle flame retardants for your industry or market. If you don't find what you're looking for here, contact us anyway. Our technical application and development experts around the world are always looking for a new challenge, and can probably help you with yours.

> Markets	> Flame retardant product selector	> Flame retardant application selector
Select the market that is right for you	Find the product that is right for you	Select an application for your flame retardant

**A member of
NAFRA - North
American Flame
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