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# 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”)

### IPC-WP/TR-584A

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# 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]

Developed by the Halogen-Free Materials Subcommittee (4-33) of the Environment Health and Safety Steering Committee (4-30) of IPC

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Users of this publication are encouraged to participate in the development of future revisions.

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## Acknowledgment

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# 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”)

## 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 PCBs.

### RESEARCH

A shift from TBBPA to non-halogenated flame retardants in printed circuit boards would have a profound impact upon the PCB 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 PCB 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 are necessary

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 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.

## 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 of 148 fires).

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.



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

There are four main families of flame-retardant chemistries:

- Inorganic flame retardants, including aluminum trihydroxide, 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 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% decabromodiphenyl oxide (ether); OBDPO contained hexabromo- to decabromodiphenyloxides and PeBDPO contained tribromo- to hexabromo-diphenyloxides.

The family of PDBEs is recommended for substitution by the EU's Restriction of Hazardous Substances (RoHS) Directive. 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. 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 have not been used in PCBs.

PBB is targeted for elimination in the 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. Additive 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  $\text{Sb}_2\text{O}_3$  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 moderately toxic metal and a 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.

