White Paper

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Fire Retardancy What, Why and How

Abstract:
The paper takes a critical look at all aspects of fire retardancy, starting with the need for fire safety. The function of a flame retardant is examined and reactive and additive flame retardant classes are contrasted along with their chemical and physical effect mechanisms. Major flame retardant compounds, both halogen and halogen free, are examined in detail. Toxicology and environmental impact are examined, with particular emphasis on Tetrabromobisphenol-A, which is the most widely-used flame retardant in PCB materials. European legislative directives are also considered.

I. WHAT ARE FLAME RETARDANTS?

Flame retardants are compounds, which when added to materials during or after manufacture, inhibit or suppress the combustion process.

They interfere with combustion at various stages of the process, e.g. during heating, decomposition, ignition or flame spread. Their primary function is to suppress the spread of fires or delay the time of flashover so that people can escape.

Flame retardants used in plastic materials fall broadly into two categories, namely additive and reactive. Additive flame retardants are incorporated and dispersed into the plastic prior to, during, or most commonly following polymerization. If they are chemically compatible with the plastic, they act as plasticizers otherwise, they are considered as fillers. Reactive flame retardants are chemically bound to the polymer molecule by incorporating them into the polymer backbone or by grafting them onto the backbone as branches. As reactive flame retardants are chemically bound to the host polymer, they are prevented from bleeding out; and thus generally exert greater flame retardancy than additive compounds due to their greater availability throughout the life cycle of the polymer into which they are incorporated.

II. WHY DO WE NEED FLAME RETARDANTS?

On average, there are more than 4,500 fatalities annually in the EU-27 as a result of fires; this accounts for 2% of all fatal injuries [1]. Fires develop from inception through build-up, until a stage where the total thermal radiation from the fire-plume, hot gases and hot compartment boundaries cause the radiative ignition of all exposed combustible surfaces within the compartment. This sudden and sustained transition of a growing fire to a fully developed fire is called flashover [2]. At this point, the radiation of energy to the contents of the room raises all the contents to their ignition temperature, whereby the contents of the room suddenly and simultaneously ignite. It is estimated that in a domestic dwelling fitted with working fire alarms on all levels where the occupants are asleep upstairs and a fire starts on the main level of the residence, the occupants have about three minutes to escape if they are to have any chance of survival [3]. The presence of flame retardants in otherwise combustible materials has two possible effects;

- The flame retardant may prevent the fire from developing altogether or;
- The flame retardant may slow down the build-up phase of the fire by delaying the onset of flash over, thereby extending the escape time window.

In either case, the flame retardant serves its primary purpose of reducing the risk of fire-related fatalities.

The efficacy of the use of appropriate flame retardants can be seen by way of example from the introduction of "*The Furniture and Furnishings Fire Safety Regulations*" in the UK in 1988. These imposed a fire resistance requirement on all upholstered furniture supplied in the UK. Between 1988 and 2002 a government-commissioned report estimated that *the "Furniture and Furnishings Fire Safety Regulations*" played a direct role in saving 1,150 lives and preventing 13,442 injuries [4].

III. FLAME RETARDANT MECHANISMS

Flame retardants fulfil their purpose primarily by either physical or chemical action.

Physical action can be subdivided into three modes;

1. Cooling: An endothermic process is triggered by additives cooling the substrate to a temperature below that required for sustaining the combustion process.
2. Formation of protective layer: The combustible layer is shielded from the gaseous phase with a solid or gaseous protective layer. The oxygen required for the combustion process is excluded and heat transfer is impeded.
3. Dilution: Fillers are incorporated that evolve inert gases on decomposition diluting the fuel in the solid and gaseous phase so that the lower ignition limit of the gas mixture is not exceeded.

Chemical action can be subdivided into two modes;

1. Reaction in the solid phase: The flame retardant causes a layer of carbon to form on the polymer surface. This can occur through dehydration of the flame retardant forming a carbonaceous layer by cross linking. The carbonaceous layer acts as an insulation layer, preventing further decomposition of the material.
2. Reaction in the gas phase: The free radical mechanism of the combustion process that takes place in the gas phase is interrupted. The exothermic processes are thus stopped, the system cools down and the supply of flammable gases is suppressed.

In printed circuit board material, a number of these mechanisms are employed to achieve flame retardancy by appropriate choice of flame retardant compound. In some cases, more than one mechanism is used and synergists can also be added to improve the efficacy of a primary flame retardant.

Halogenated flame retardants form the largest group of flame retardants used in printed circuit board materials.

Halogens comprise five chemically-related, highly reactive non-metallic elements found in group 17 of the periodic table. They are namely Fluorine, Chlorine, Bromine, Iodine and Astatine. The artificially created element 117 falls into group 17 and may also be classed as a halogen.

Since Astatine is amongst the rarest elements and occurs on Earth only as the result of the radioactive decay of heavier elements and element 117 is entirely synthetic with a half-life of less than one second these will not be considered further.

The other four Halogens, however, find many uses in everyday life, Table 1.

Table 1

Fluorine	Chlorine	Bromine	Iodine
UF6: Used for Uranium Enrichment Fluoroplastics: PTFE (Teflon) Viton (synthetic rubber) SF6: Gaseous insulator in high voltage switchgear NaF, SnF2, Na2PO3F: Anti decay additive in toothpaste	NaCl: Table salt PVC: Pipes, building materials, electrical insulation, clothing SiCl4: Manufacture of Silicon for semiconductors HCl Medicine Pesticide	Flame retardants Fumigants and disinfectants Water purificants Medicine: Sedatives, anti-convulsants, anti-histamines Photographic paper Halogen lighting	Thyroid hormone production Dietary supplements X-ray contrast agents Chemical catalyst, for example in epoxy resin manufacture Water purification Antiseptic Halogen lighting

Fluorine and Iodine are not used as flame retardants as neither effectively interferes with the combustion process. Chlorine-containing flame retardants release HCl (hydrogen chloride) over a wide temperature range so the flame retardant concentration is reduced and is thus less effective.

Bromine is the most effective halogen flame retardant since its bonding to carbon enables it to interfere at a more favorable point in the combustion process. The effective agent, HBr (hydrogen bromide), is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone.

The mechanism used by brominated flame retardants (BFRs), is that bromine breaks down to form a bromine radical which then reacts with the hydrocarbon to form HBr. The HBr removes the high-energy H and OH radicals by reaction. The high-energy radicals are replaced with low-energy bromine radicals. The HBr consumed is then regenerated by reaction with the hydrocarbon. Figure 1.

In PCB substrates, the bromine source is usually 2,2 ,6,6 -Tetrabromo-4,4 -isopropylidenediphenol (Tetrabromobisphenol-A or TBBPA) and this is incorporated as an additive flame.

In the category of non-halogenated flame retardants phosphorous containing compounds are the most popular and of these 9,10-Dihydro-9-Oxa-10-Phosphaphenantrene-10-Oxide (DOPO) is the most widely used. The compound is reacted as an additive flame retardant. The flame retardant mechanism is that the phosphorus containing compound is converted by thermal decomposition to phosphoric acid. The phosphoric acid then dehydrates the oxygen containing polymer and causes charring. Figure 2.

Figure 1

The bromine breaks down to form a bromine radical which then reacts with the hydrocarbon to form HBr.

$$\text{R-Br} \longrightarrow \text{R}\bullet + \text{Br}\bullet$$

The HBr removes the high energy H and OH radicals by reaction.

The high energy radicals are replaced with low energy bromine radicals.

$$\text{HBr} + \text{OH}\bullet \longrightarrow \text{H}_2\text{O} + \text{Br}\bullet$$

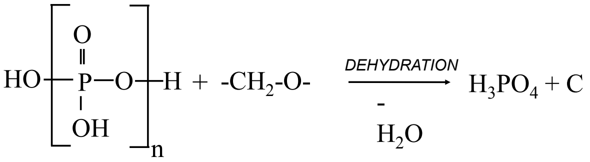
$$\text{HBr} + \text{H}\bullet \longrightarrow \text{H}_2 + \text{Br}\bullet$$

The HBr consumed is regenerated by reaction with the hydrocarbon.

$$\text{R-H} + \text{Br}\bullet \longrightarrow \text{R}\bullet + \text{HBr}$$

Figure 2

The phosphorus containing compound is converted by thermal decomposition to phosphoric acid. The phosphoric acid dehydrates the oxygen containing polymer and causes charring.



$$HO\left[\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O\right]_n H + -CH_2\text{-}O- \xrightarrow[-H_2O]{DEHYDRATION} H_3PO_4 + C$$

Figure 3

Aluminium Trihydrate (ATH) breaks down around 200ºC to aluminium oxide in an endothermic reaction with the release of water vapor.

$$2\,Al(OH)_3 \xrightarrow[-298\ kJ/mole]{\triangle} Al_2O_3 + 3H_2O$$

As a result of the endotherm, the polymer is cooled, therefore fewer pyrolysis products are formed.

The aluminium oxide, together with the charring products formed on the substrate, acts as an insulating protective layer.

The water vapor liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer.

The metal hydroxide alumina trihydrate (ATH, gibbsite) is a widely used synergist in non-halogen flame retardant systems.

The flame retardant mechanism of ATH is physical and combines cooling with the formation of a protective layer and gaseous phase dilution. The ATH breaks down around 200ºC to aluminium oxide in an endothermic reaction with the release of water vapor. The resulting endotherm cools the polymer so fewer pyrolysis products are formed. The aluminium oxide, together with the charring products formed on the substrate acts as an insulating protective layer and the water vapor liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer.

It is reported that undesired release of water due to thermal decomposition in multiple soldering operations in ATH systems may lead to a loss of the effectiveness of flame retardancy, reduced CAF (conductive anodic filamentation) performance and delamination. Aluminium monohydrate (AlOOH, boehmite) has been proposed as a thermally stable alternative [5].

IV. HALOGEN FREE?

In the context of printed circuit board materials, halogen free can be broadly interpreted as "free of halogenated flame retardant." Indeed the IEC defines halogen free as[6];

- 900 ppm maximum chlorine
- 900 ppm maximum bromine
- 1500 ppm maximum total halogens

It is necessary to have such a definition, as halogens are always present to some extent. Epoxy resins, for example, are produced by reacting bisphenol-A with epichlorohydrin, which contains chlorine. Therefore all epoxy resins contain measurable traces of chlorine; iodine is also widely used as a necessary constituent of the catalyst used in epoxy resin production.

It is an interesting diversion to consider PTFE materials that are used in some PCB applications. PTFE contains fluorine, which is highly toxic and the most reactive halogen, seems to have largely escaped attention in the context of halogen-free materials. However, in PTFE the fluorine is tightly bound to the carbon atoms and is therefore not available as free fluorine. It is useful here to underline the distinction between compounds and native elements and their respective physical and chemical properties. The best common example would be that of table salt, NaCl, which comprises the elements sodium and chlorine. Sodium is a highly reactive metal and is classified as being very hazardous in case of skin contact and chlorine is a highly corrosive toxic gas. However, the two elements combine to form sodium chloride which is benign and essential to human life.

The same distinction must be drawn when considering flame retardants incorporating phosphorous and bromine. These are toxic in elemental form, however when used reactively as flame retardants, have limited bioavailability and as such do not pose any significant threats to human life or the environment.

V. TOXICOLOGY STUDIES

There have been many studies into the toxicology of flame retardants and there is no sign of activity in this area abating. It is of great importance that people are protected from risk of death or serious injury by fire, but also that the systems used to provide that protection do so without adding risks to human health or the environment. The most widely used flame retardant in PCB materials is Tetrabromobisphenol-A or TBBPA, and is amongst the most studied flame retardants.

A study carried out in 1999 by the University of Surrey[7] assessed the risks posed by common flame retardants, including TBBPA and concluded for the smoke and gases released in case of fire: *"The major hazards of most fires arise from the existence of the fire and not the materials burned and there is no evidence that flame retardants contribute to the direct human health risks arising from toxic gas effects."*

The report also concluded: *"Examination of the toxicology of six of the more common flame retardants used in consumer products indicates that in general they do not pose any significant threats to human life and the environment. Moreover any indication of risk from the toxicology of flame retardants themselves in isolation will be exaggerated because of their limited bioavailability when they are incorporated into a polymer matrix."*

Under the framework of the European risk assessment (RA) a report into the human health risks of exposure to TBBPA published in 2006 concluded [7]:

"Human health

No health effects of concern have been identified for TBBPA.

Workers

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

No health effects of concern to adults have been identified.

Therefore conclusion (ii) is reached in relation to all endpoints and for all exposure scenarios.

Consumer

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Given that consumer exposure is negligible conclusion (ii) is reached in relation to all endpoints."

Underlining the use of TBBPA as an additive flame retardant BSEF states[8]: *"TBBPA is classified in the EU as an H410 substance, which means that it is toxic to aquatic organisms and it has to be labeled to reflect this classification. However, TBBPA loses this classification when it is reacted into the printed circuit board resin, which represents more than 80% of its uses. TBBPA is employed as a starting material that fully reacts to form the epoxy resins of laminates for printed circuit boards. This full integration into the epoxy resin ensures that the final product, flame retarded printed circuit boards, no longer contains TBBPA, leaving the user free from any possible exposure."*

VI. REACH AND ROHS

REACH is a European Union regulation concerning the registration, evaluation, authorization and restriction of chemicals. It came into force on June 1, 2007 and replaced a number of European directives and regulations with a single system. The aim of REACH is to improve the protection of human health and the environment through early identification of hazardous properties in chemical substances while maintaining the competitiveness and enhancing the innovative capability of the EU chemicals industry. REACH requires registration of substances manufactured or imported into the EU in quantities of 1 tonne or more per year. TBBPA was registered under REACH in October 2010.

Under the REACH regulations, substances that may have serious and often irreversible effects on human health and the environment can be identified as substances of very high concern (SVHCs). If a substance is identified as an SVHC, it will be added to the Candidate List for eventual inclusion in the Authorization List. As of December 13, 2013 the Candidate List of Substances of Very High Concern numbered 151 substances [9]. TBBPA is not included as a SVHC.

The Restriction of Hazardous Substances Directive 2002/95/EC, RoHS, was adopted in the European Union in February 2003 and restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment. Polybrominated biphenyls (PBB) and Polybrominated diphenyl ether were among the restricted materials. No restrictions were placed on the use or manufacture of TBBPA.

RoHS was revised in 2011 (RoHS II): no new substance restrictions were added, *but* provision was made for future substance review by the Commission.

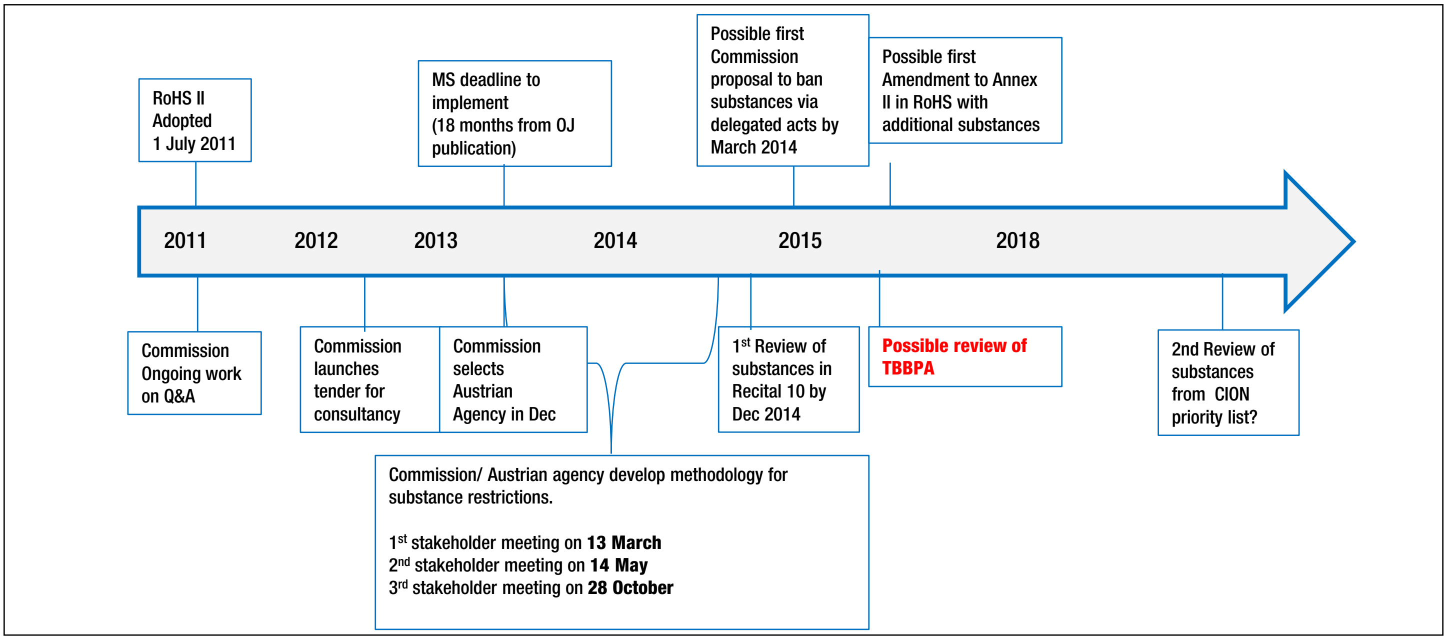
Currently, the Commission is working on developing the methodology for future substance restrictions. The final methodology will be published in July 2014.

The Austrian Environment Agency (Umweltbundesamt) on behalf of the Commission developed the first draft of the methodology and identified substances used in E&E for future evaluations. The Commission is now organizing a working group of stakeholders to finalize the last stage of the methodology. Each substance will be evaluated on an individual basis, taking into account all existing science. Both Member States and the Commission can nominate substances.

TBBPA has been identified as a substance for future reviews under the RoHS, as it is used in electronic and electrical equipment.

The timeline of RoHS II discussions and possible review of TBBPA are shown in Figure 4 [10].

Figure 4



VII. FLAME RETARDANTS AND THE FUTURE

Neils Bohr famously said *"Prediction is very difficult, especially if it's about the future."* Fire safety will surely remain a primary requirement for electronic and electrical equipment. In order to ensure fire safety, there will be a need to incorporate flame retardants into plastic systems forming part of such electronic and electrical equipment that would otherwise pose a significant fire safety risk.

Halogenated materials form by far the largest group of flame retardants used in PCB materials with a global estimated market share of greater than 80%. In Europe, the figure is estimated to be closer to 95%.

UL has recognized that traditional FR-4 [11] materials have evolved in recent years and now represent a diverse family of materials. In recognizing this, for testing purposes UL has now divided the FR-4 category into two sub-categories, FR4.0 and FR4.1[12], Figure 5.

Figure 5: New UL/ANSI Types Replacing FR-4 from IPC proposal

UL/ANSI Type	Primary Resin	Secondary Resin(s)	Filler[1]	Flame Retardant	Reinforcement
FR-4.0 (Brominated FR-4)	Epoxy[2]	Any	Inorganic Max 45%	Bromine	Woven Glass
FR-4.1 (Non-Halogen FR-4)	Epoxy[2]	Any	Inorganic Max 45%	Bromine	Woven Glass

[1] Examples of inorganic fillers include, but are not limited to: Silica, Clay, Talc, Ceramic, Calcium Carbonate, Aluminum Hydroxide, Fumed Silica and Titanium Oxide.

[2] Epoxy functionality, minimum 50% by weight of organic resin.

The new UL classifications of FR4.0 and FR4.1 divide the materials into "brominated" and "non-halogen" respectively.

There is no clear scientific evidence based driver to restrict the use of halogenated flame retardants. Legislation under REACH and RohS II should be expected to apply rigorous scientific methodology in assessing risks to human health; such studies to date have not raised concerns about the continued use of halogenated flame retardants.

Performance requirements are driving PCB materials suppliers to develop materials for high-speed applications, while improving electrical and thermal reliability. However, ultimately consumer choice is also a driver and may well play into the market vector of high-speed and high-reliability requirements.

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