OVERVIEW OF PHOSPHORUS BASED HALOGEN FREE FLAME RETARDANTS FOR ELECTRIC AND ELECTRONIC APPLICATIONS

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Introduction

Brominated flame retardants have been widely studied with regard to their environmental distribution and effects. This brings up the question whether there are alternative flame retardant systems. Therefore, our paper will present an overview of halogen free flame retardants for electrical and electronic applications. The focus will be on commercially available phosphorus based products for engineering thermoplastics as well as thermosets like printed circuit boards, because Clariant is a prominent manufacturer of phosphorus based FRs and has first hand experience from the market introduction of a new phosphinate based FR system. Their chemical characteristics as well as commercial availability will be presented. Their environmental profile will be discussed as well. A general overview of halogen free flame retardants by polymer application has been published by Troitzsch (2006, [1]).

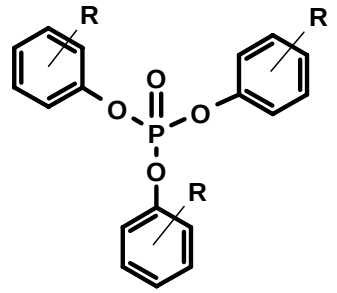
Engineering Thermoplastics

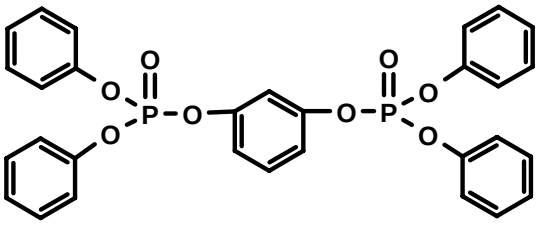
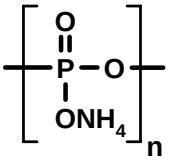
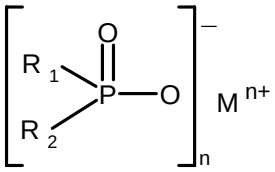
Commonly used flame retardants for thermoplastics are summarized in Table 1 and Table 2. Advantages of phosphorus based FRs are a high effectiveness in some polymers, the tendency to produce less smoke and products of incomplete combustion, and no negative impact on UV-stabilizers for plastics.

Table 1: Halogen free flame retardants for thermoplastics

metal hydroxides, -hydroxy carbonates	**PE, PP, PVC, PA**
organic phosphorus compounds	**PS-HI, PS/PPE, PC/ABS**
inorganic phosphorus compounds	**PA 6.6 - GF (red P), [PP, PE]**
phosphorus / nitrogen systems	**PP, PE**
nitrogen compounds	**PA 6 (melamine cyanurate)**
boron compounds	**PVC, PA (zinc borate)**

Table 2: Examples of halogen free flame retardants for thermoplastics

	Triaryl phosphates, e.g. triphenyl phosphate, used e.g. for styrenics

	RDP = resorcinol bis-diphenyl phosphate (e.g. for styrenics like PC-ABS)
	ammonium polyphosphate (together with nitrogen synergists for polyolefins)
	phosphinates (for polyamides and polyesters)

Printed Circuit Boards

Non halogenated products include three main chemical families:

- **Phosphorus** based chemicals: they have the particularity to work in the solid phase of polymers, by removing water and creating a carbon-rich char on the surface of the polymer. This FR mechanism is often of particular interest because there is no release of acid gases into the gas phase, which in turn results in very low smoke density and no side effect (e.g. gas phase corrosion through HCl or HBr). On a weight-% basis, phosphorus is also more effective than bromine (UL 94 V-0 achievable with a final P-content of 2,5 to 4%). Examples are shown in Fig. 1 and 2.
- **Nitrogen** based compounds work differently and have an effect both in the gas phase (by releasing non flammable nitrogen, which dilutes the oxygen content) and condensed phase, especially when combined with phosphorus compounds, helping the formation of a more stable, cross-linked char.
- **Mineral** flame retardants include mainly aluminium trihydrate (ATH) and magnesium hydroxide (MDH). Both share the same mechanisms: when exposed to the heat, they will decompose to release water vapor, which will cool down the system, dilute burnable gases in the flame and create an oxide layer at the surface. The difference between MDH and ATH is the price and temperature of decomposition (MDH>ATH). These FR are inexpensive and have a favorable FR mechanism, but have the drawback of requiring high loadings to achieve a certain performance. Other mineral FRs include Boehmite (alumina monohydrate, more temperature stable but less effective than ATH) and borates, which can only be used in synergy with more powerfull FRs, namely phosphorus and/or nitrogen based ones.

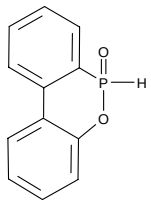


Fig 1: chemical structure of DOPO (Dihydro oxaphosphaphenantrene)

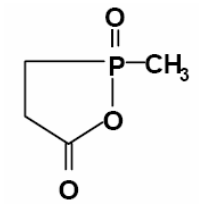


Fig. 2: chemical structure of oxaphospholane

Halogen free FR initiatives

In 2006 several initiatives developed which look at halogen free alternatives to established BFRs. The US-based industry consortium **iNEMI** launched a halogen-free initiative with the aim to promote standards and test guidelines for halogen-free materials, based on the requirements of the different market segments, and their technical, commercial and functional viability.

Interestingly, the introduction speech at the kick-off meeting in February in California, made by a representative of a major PC manufacturer, confirmed that their motivation is business driven, as this OEM estimated that in 2005 they missed business valued in double-digit million of dollars, because they could not participate in tenders where halogen-free materials were prescribed.

The US EPA (Environment Protection Agency) started a **Design for Environment (DfE) Electronics Partnership**. Its purpose is to identify and characterize commercially available flame retardants and their environmental, health and safety fate aspects in FR-4 printed circuit boards. This will include "commercially available FRs" but will not eliminate alternatives based on current costs, and will focus on areas of the life-cycle with greatest exposure such as chemical hazard during manufacturing, and end-of-life issues (combustion products in case of accidental fires, disposal, landfill, recycling).

The **High Density Packaging User Group** (HDPUG) will update its report on the environmental assessment of halogen-free PCBs (phase II report dated January 2004).

Among the motivations beyond these activities, two key aspects should be highlighted:

- The multiplication of available halogen-free materials, having presumably different characteristics (mechanical & electrical properties, chemical composition), makes it necessary to review and update past knowledge (certain halogen-free materials being today of 2nd or 3rd generation).

- These activities are not linked to scientific findings but motivated by business: certain OEM not having halogen-free materials in their portfolio noticed that they are missing opportunities (Green procurement, ecolabels).

Conclusion

Halogen-free materials are a growing niche. Its further development is no longer linked to the discussions like risk assessments on BFRs, but driven by market demand for alternative materials. The increasing number of both resin and additive chemistries make the development of formulations with distinguished properties possible and more attractive.

We expect that the growing use of halogen-free materials will help to reduce costs by economies of scale for a certain number of polymers and associated additives. Ongoing developments suggest that cost optimizations will also be realized by using new components. For printed circuit boards however, based on current knowledge, we do not anticipate that halogen-free material can match the price performance of TBBP-A based products. Halogen-free material tend to show certain technical advantages (thermal stability, CTE, higher TCI values, better electrical values than brominated products) but these are usually off-set by the cost penalty. For thermoplastics, price competitive systems are already available for some applications.

References and further reading [2, 3, 4]

Related websites:

http://www.flameretardants.eu
http://www.flameretardants-online.com/
http://www.exolit.com

[1] Troitzsch (2006): http://www.flameretardants-online.com/news/downloads/over_english/overview_non-hal_2006.pdf
[2] Trotizsch J (2004): Plastics Flammability Handbook. Hanser Publishers, Munich.
[3] Price A; Horrocks D (2000): Fire Retardant Materials; Woodhead Publishing; ISBN: 1855734192
[4] Durack D; Grand A F; Wilkie C A (2000): Fire Retardancy of Polymeric Materials. Marcel Dekker; ISBN: 0824788796