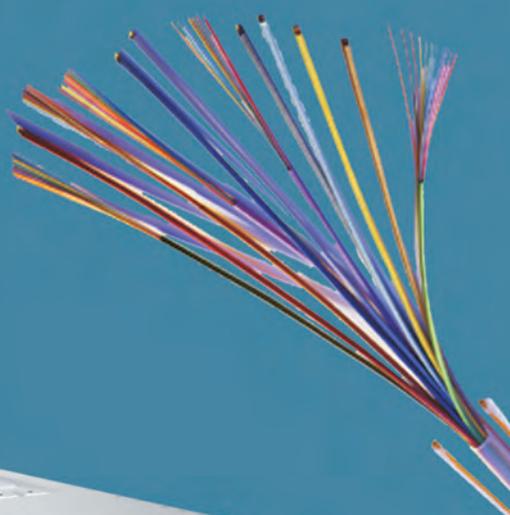




Innovative Flame Retardants in E&E Applications

Non-halogenated phosphorus, inorganic and nitrogen flame retardants



pinfa is the Phosphorus, Inorganic and Nitrogen Flame Retardants Association and is a Sector Group within Cefic, the European Chemical Industry Council. pinfa represents the manufacturers of non-halogenated phosphorus, inorganic and nitrogen flame retardants (PIN FRs).

Phosphorus (non-halogenated), inorganic and nitrogen flame retardants are additives that can be added to or applied as a treatment to organic materials such as plastics and textiles to impart fire protection to these materials.

The members of **pinfa** share the common vision of continuously improving the environmental and health profile of their flame retardant products. Therefore, pinfa members seek to dialogue with the users of PIN FRs in order to identify their needs and technologies they are looking for.

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Table of Contents

1	Introduction	4
2	Wire & Cable	8
2.1	Introduction	
2.2	History and standards development in respect to developments in the area of halogen-free flame retardancy	
2.3	Flame retardants used for HFFR compounds	
	2.3.1 <i>The mechanism of metal hydroxides as flame retardant</i>	
	2.3.2 <i>How to achieve flame retardancy with metal hydroxides</i>	
2.4	Current developments in the area of metal hydroxides	
	2.4.1 <i>Processability</i>	
	2.4.2 <i>Surface treatment</i>	
	2.4.3 <i>Nanocomposites</i>	
	2.4.4 <i>Improved morphology of the metal hydroxide</i>	
2.5	Flame retarded thermoplastic elastomers for cable applications	
3	Electric Enclosures	14
3.1	Introduction	
3.2	PC/ABS blends	
3.3	Recyclability of FR-PC/ABS composites using non-halogen flame retardants	
3.4	PPO/HIPS	
4	Electric Installations and Components	19
4.1	Scope and material requirements for electrical components	
	4.1.1 <i>Mechanical properties</i>	
	4.1.2 <i>Electrical properties</i>	
	4.1.3 <i>Fire resistance</i>	
4.2	Overview of halogen-free FRs for electrical installations	
4.3	Polymers used in electrical components and suitable FR systems	
5	Printed Wiring Boards	23
5.1	Market environment and trends	
5.2	Technical requirements of FR-4 printed wiring boards	
5.3	Non-reactive fillers	
	5.3.1 <i>Metal hydroxides</i>	
	5.3.2 <i>Metal phosphinates and polyphosphates</i>	
5.4	Reactive flame retardants	
6	Future Trends and Innovation	28
7	Halogen-free Flame Retardants and the Environment	30
8	Common Fire Tests for E&E Materials	32
9	List of Abbreviations	34
10	Contributing Companies	36

1 Introduction



PHOTO: CLARIANT

This brochure is meant to illustrate the technical properties and advantages of halogen-free flame retardants (FRs) for key application areas like housings, cables, connectors and switches as well as printed wiring boards. After many years of research and development a whole toolbox of halogen-free chemistries is now available for the materials engineer. In some areas, the development of commercial solutions is moving quickly.

Flame retardants have become a class of chemicals which receive more and more scientific and public attention. The discussions about flame retardants started, when brominated flame retardants (BFRs) became a topic of environmental concern in the early 1990s, when it was discovered that some BFRs could form halogenated dioxins and furans under severe thermal stress or when they were burnt in

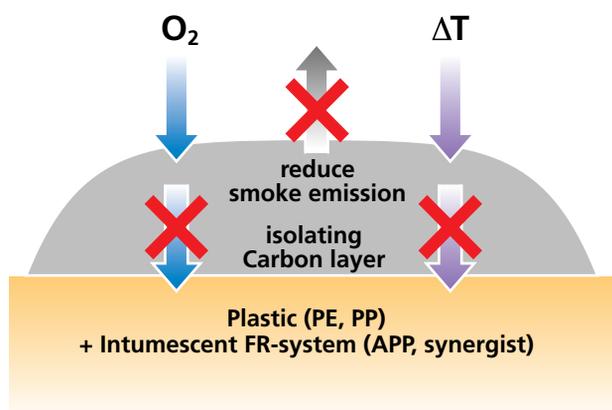


Figure 1: The mechanism of Intumescent flame retardant systems which are typically a combination of phosphorus and nitrogen compounds (Budenheim).

accidental fires or uncontrolled combustion¹. Findings in the environment and biota and the suspicion that some flame retardants bioaccumulate in organisms have added to these concerns^{2 3 4 5}. Meanwhile, the environmental and health properties of not only BFRs but also other types of flame retardants have been studied extensively. The most widely used organic flame retardants have become the subject of official risk assessments in Europe⁶.

What are halogen-free flame retardants⁷? This group covers a diverse range of chemicals which are commonly classified as:

- Inorganic: This category comprises mainly metal hydroxides like aluminium hydroxide and magnesium hydroxide. Other compounds like e. g. zinc borate are used to a much lesser extent.
- Phosphorus based flame retardants include organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.
- Nitrogen based flame retardants are typically melamine and melamine derivatives (e. g., melamine cyanurate, melamine polyphosphate, melam, melon). They are often used in combination with phosphorus based flame retardants.

1 Söderström G, Marklund S (2002): PBCDD and PBCDF from incineration of waste-containing brominated flame retardants. *ES&T*, Vol. 36. pp. 1959-1964

2 de Wit C (2002): An overview of brominated flame retardants in the environment. *Chemosphere*. pp. 583-624

3 Ikonomidou M, Rayne S, Addison R (2002): Exponential increases of the brominated flame retardants Polybrominated diphenyl ethers in the Canadian Arctic from 1981 to 2000. *ES&T*, Vol. 36, No. 9. pp. 1886-1892

4 Law R, Allchin C, Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit C. (2006): Levels and trends of brominated flame retardants in the European environment. *Chemosphere* Vol. 64, pp. 187-208

5 Sjödin A, Patterson D, Bergman A (2001): Brominated Flame Retardants in Serum from U.S. Blood Donors. *ES&T*, Vol. 35, No. 19. pp. 3830-3833

6 <http://ecb.jrc.it/existing-chemicals/>

7 The proper designation is actually non-halogenated flame retardants, meaning that no halogens are intentionally added and contained in the products. Trace amounts of halogens are found everywhere and also in commercial chemicals.

Intumescent flame retardants (mechanism see Figure 1) are an example of a typical mechanism for halogen-free flame retardants. The combustible material is separated from the fire or heat source by an insulating foam which forms at the surface. Intumescent flame retardant systems can be applied to decrease flammability of thermoplastic polymers such as polyethylene, polypropylene, polyurethane, polyesters and epoxy resins.

Figure 2 shows the current European consumption of different flame retardant types – halogen-free FRs do already present the major market share. In addition, Figure 3 illustrates the variety of polymer types used for E&E installations, which explains why so many different FR technologies are necessary, because FRs need to match polymer properties and specific processing requirements. The total European plastics demand for E&E applications was estimated at 2.1 million tons in 2007 (source: PlasticsEurope).

For cables the estimated total polymer consumption for 2007 was 1.3 mio. tons for Europe, dominated by PE (52 %) and PVC (40 %). Other materials make up the remaining 8 %. Low smoke, zero halogen cables have been growing strongly in Europe and reached a consumption of 93 000 tons of polymer compounds in 2005 (source: AMI Consulting, UK).

Over the past decade, the fate of electronic waste and the contained hazardous materials have gained increasing political attention and have led to the WEEE⁸ and RoHS⁹ Directives in Europe: The aim of these regulations is that electronic waste shall be properly recovered and recycled; new equipment shall not contain problematic substances. Flame retardants are affected, because according to the WEEE directive, plastics containing brominated flame retardants have to be separated before further treatment of the waste. Under RoHS, certain brominated flame retardants¹⁰ are no longer allowed in new electronic equipment since July 2006.

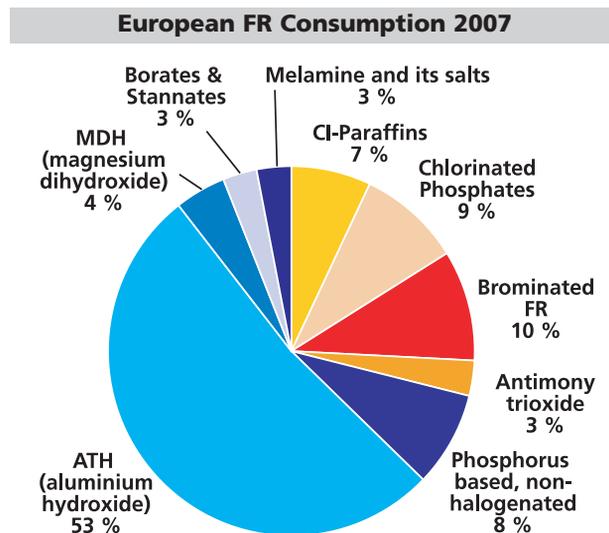


Figure 2: The current consumption of flame retardants in Europe, which amount to a total of 498 000 metric tons (source: EFRA). Halogen-free FRs are shown in different shades of blue.

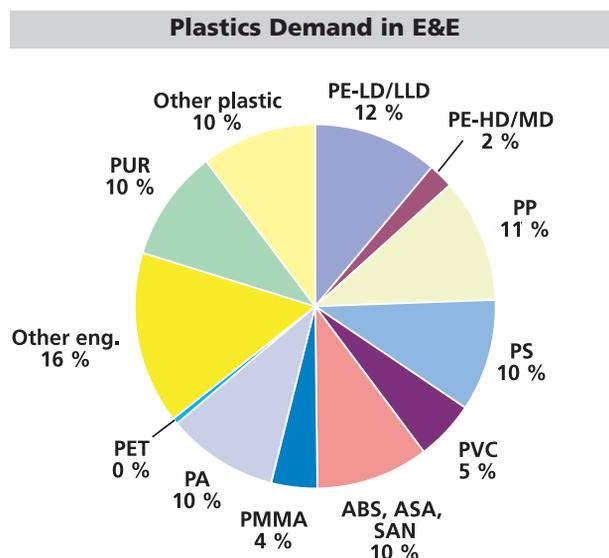


Figure 3: Plastics demand for electrical and electronics applications in Western Europe in 2007 (total of 2.1 million tons; source: PlasticsEurope)

⁸ Directive 2002/96/EC on Waste of Electric and Electronic Equipment

⁹ Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment

¹⁰ Banned BFRs: Polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE); the exemption for Deca-BDE was repealed by the European Court of Justice, effective July 2008

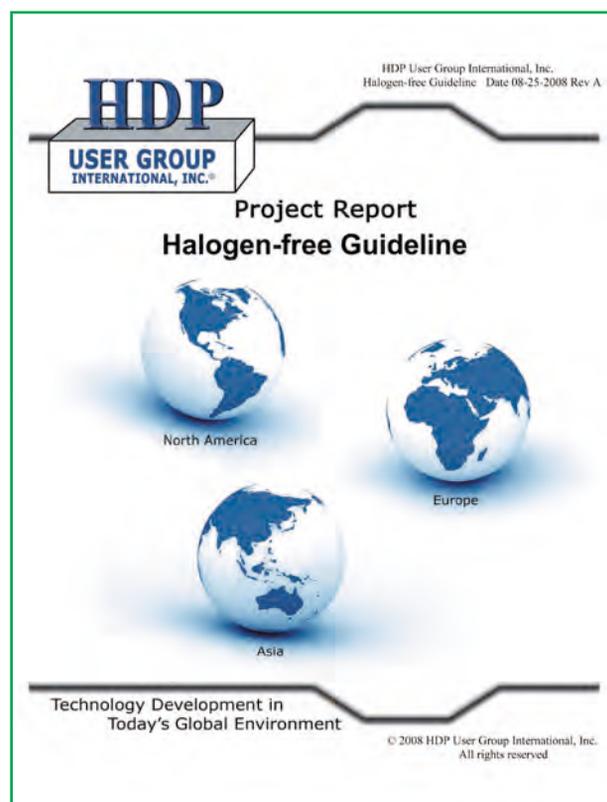


Other regions of the world are about to follow with similar legislation. These activities increased the interest in halogen-free flame retardants, not only in engineering plastics but also in thermoset resins and printed wiring boards. In addition to legal requirements, ecolabels have been introduced since the 1970s as voluntary measures in order to promote environmentally friendly products. The idea is that the consumer can make a conscientious decision for such products, if they are labelled according to an accepted and respected scheme. Worldwide, today, there are about 25 ecolabel organizations and schemes (see: <http://www.gen.gr.jp>). Even in Europe there are several national labels in addition to the EU flower. Ecolabels are specifically designed to go beyond legal requirements like RoHS, because they are meant to endorse the “best in class” and advance environmental benchmarks. Traditionally, many ecolabel systems have prohibited the use of halogenated flame retardants in their criteria for electronic products (e. g. EU label, Blue Angel in Germany, Nordic Swan in Scandinavia, TCO in Sweden). Often, the flame retardants which are used in products need to be declared to the ecolabelling organization. Ecolabels are also relevant for green public procurement, because e. g. in Europe ecolabel criteria can be included in public calls for tender. In Switzerland, a “consensus forum”¹¹ on endocrine effects from BFRs with participants from industry (including the BSEF, the lobby group of BFR manufacturers), academia and regulators came to the conclusion that “Efforts must be promoted to search for alternatives to brominated flame retardants that persist in the environment.”



The electronics organisation HDPUG (high density packaging user group, www.hdpug.org) has developed a guideline for halogen-free technologies in E&E applications¹². Their guideline complements this document in that it goes beyond the flame retardant chemistries into more detail for the specific applications and shows that commercially viable halogen free solutions already exist in many areas. In 2008, HDPUG started another project dedicated to halogen free cables and re-started a project to build up a database for halogen free components and material suppliers.

Due to this regulatory and environmental pressure, a number of original equipment manufacturers (OEMs) have developed phase out plans for BFRs, some have even made strong commitments with deadlines as shown in Table 1.



11 Trachsel M (2007): Consensus Platform "Brominated Flame Retardants", National Research Program "Endocrine Disruptors". Swiss National Science Foundation, http://www.nrp50.ch/uploads/media/finaldocumentenglish_06.pdf. pp. 1-13

12 O'Connell S (2008): Halogen Free Guideline - Project Report. HDPUG, www.hdpug.org. pp. 1-68

halogen specification	PVC		Br, Cl and their compounds	
	specification	timeline	specification	timeline
Nokia	not intentionally added		Br < 900 ppm, Cl < 900 ppm	all products by 2008
Sony-Ericsson	banned	exclusion by end of 2006	Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	all new products by end of 2006
Lenovo	banned (> 25 g part)	new product from 2009		all products from 2009
Dell	not intentionally added (> 25g part)		Br < 900 ppm, Cl < 900 ppm	all products from 2009
LG	< 100 ppm	begin phase out in 2008; exclusion from all products 2010	Br < 900 ppm, total halogen < 1500 ppm	all products from 2010
Sony	banned (FFC and package)			
Samsung	banned (package)			all mobile phone products from 2010
Toshiba	not intentionally added	begin phase out 2009		begin 2009
Wistron			Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	begin 2008 3Q
Apple	not intentionally added (> 25 g part)		Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	all products by the end of 2008
HP	Cl < 900 ppm	all new computing products from 2009	Br < 900 ppm	all new computing products from 2009
Intel	1000 ppm (reporting threshold only)		not intentionally added	

Table 1: Halogen-free commitments and timelines for various electronics OEMs based on the availability of suitable alternatives (source: Foxconn presentation and OEM announcements at Intel Halogen Free Symposium sponsored by IPC, 15+16 Jan 2008, Scottsdale, AZ, USA).

2 Wire & Cable

An overview of the most relevant technologies in HFFR cable compounding

2.1 INTRODUCTION



In the discussion of preventive fire safety, cables hold a position of high attention. The reason is that nowadays, cables can be found everywhere, in buildings, mass-transport and even within your cell phone. In addition to the concerns in regard to the

flammability of cables, the actual smoke generation during a fire scenario has gained more and more interest over the last 25 years within the wire and cable requirements, as well as topics such as smoke toxicity and corrosivity.

The excellent performance of so called Halogen-free, flame retardant (HFFR) or low-smoke, zero Halogen (LSFOH) cables versus traditional cable designs especially in regard

to smoke density, smoke toxicity and acidity have successfully addressed these concerns with safer and ecologically acceptable cable compounds.

2.2 HISTORY AND STANDARDS DEVELOPMENT IN RESPECT TO DEVELOPMENTS IN THE AREA OF HALOGEN-FREE FLAME RETARDANCY

In the last 30+ years the usage of so called HFFR compounds in Wire & Cable applications have been driven by several major incidents, in which mostly the smoke density and the smoke toxicity in case of a fire in a highly populated area has caused numerous casualties, see Figure 4.

In addition, the awareness of the impact of flame retardant polymers on our environment, especially in case of “end-of-life” scenarios has become an additional aspect of the design of flame retardant cables. Nowadays the conformity of cables and wires with WEEE¹³ and RoHS¹⁴ is a further requirement for flame retardant cable compounds.

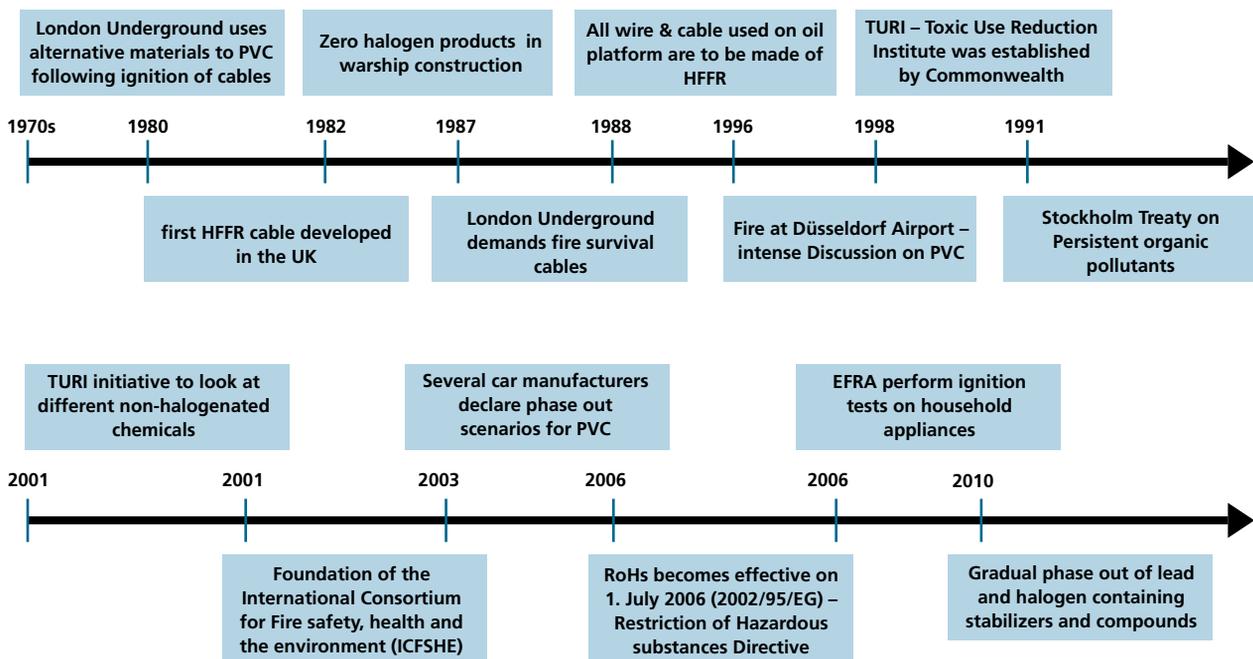


Figure 4: Key events which lead to the development of halogen-free cable development (Nabaltec)

¹³ Directive 2002/96/EC on Waste of Electric and Electronic Equipment

¹⁴ Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment

2.3 FLAME RETARDANTS USED FOR HFFR COMPOUNDS

The following table gives a general overview of the different flame retardants used in HFFR cable compounds.

Flame retardant	Polymers	Applications and effectiveness
Aluminium-tri-hydroxide (ATH) Magnesium-dihydroxide (MDH) Boehmite (AOH) (aluminium-oxide-hydroxide)	Low density polyethylene Ethyl vinyl acetate Polyolefins	In fire, these mineral FRs decompose, absorbing energy, releasing water (reducing fire intensity and diluting fire gases), and causing charring (fire barrier)
Phosphorus flame retardants	Used in fire resistant coatings for cables	The coatings form a charred foam layer on the cables
Zinc borate	Synergist with ATH	
Phosphate esters (e. g. Tricresyl Phosphate TCP)	Rubber	Flame inhibition and charring fire resistance properties of phosphorus
Melamine cyanurate, melamine phosphate,	Polyamides Polypropylene	A low dosing between 7–15 % results in polymer decomposing (PA) without flaming
Red phosphorus	Polyolefins	
Intumescent products based on Ammonium polyphosphate (APP), Aluminium phosphinates, Aryl phosphates	Polyolefins, Thermoplastic Elastomers	With loadings of 15–30 % newly developed products can achieve highest fire safety standards (UL 94 V0) by formation of an insulating fire barrier

Table 2: Overview of the different flame retardants used in HFFR cable compounds.

In the following sections, the mechanism and function of aluminium hydroxide (ATH), aluminium-oxide-hydroxide (AOH), magnesium hydroxide (MDH) and nanocomposites will be discussed, as these flame retardants are by far the most important ones in regard to HFFR cable compounds by volume and variety of application within the cable industry.

2.3.1 THE MECHANISM OF METAL HYDROXIDES AS FLAME RETARDANT

Metal hydroxides are

- Halogen-free
- Environmentally friendly
- Non-toxic
- Not volatile

- Substantial reduction of smoke
- No corrosive or toxic decomposition products
- Reduction of subsequent damages

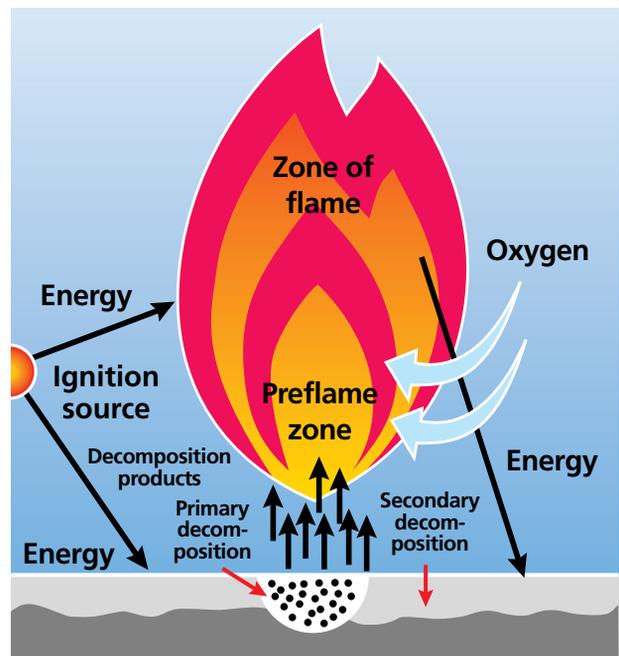


Figure 5: Flame retardancy mechanism of metal hydroxide (Nabaltec)

The function of metal hydrates as flame retardants is based on physical and chemical processes. The schematic drawing shows the involved processes of a metal hydroxide filled polymer in case of a fire. In the presence of an ignition source – a flame or a hot object – the thermal decomposition of the metal hydroxide into metal oxide and water according to the reactions A to C takes place:



During this process, energy is detracted from the ignition source, as the decomposition is an endothermic reaction. At the same time, the released water vapour cools the surface of the polymer and particularly dilutes the concentration of burnable gases in the surrounding area. The remaining metal oxide residue has a high internal surface where sooty particles, respectively polycyclic aromatic hydrocarbons are absorbed. Additionally, the oxide residue acts as a barrier, disabling the further release of low molecular weight decomposition products as well as a heat barrier protecting the polymer against further decomposition. Depending on the decomposition temperature of the metal hydroxide, the usage as flame retardant filler in cable compounds is restricted (see Figure 6). The maximum processing temperatures range from 200 °C (ATH) to 320 °C for MDH and 340 °C for AOH.

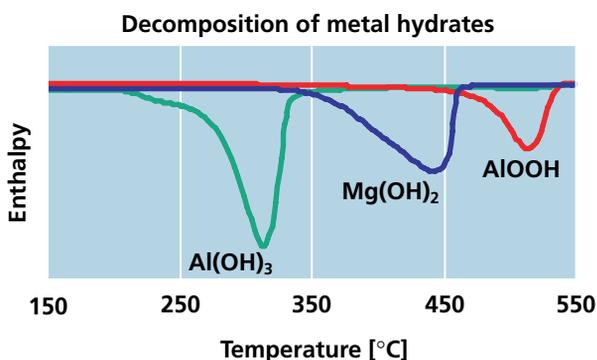
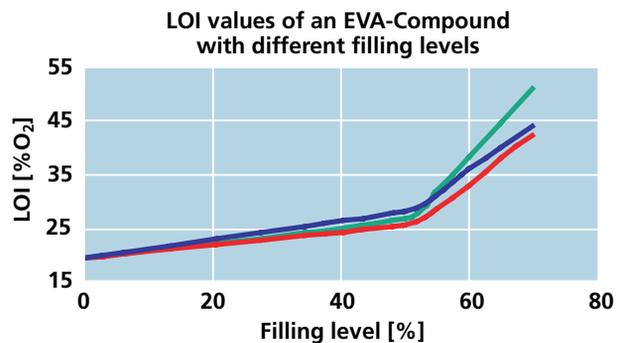


Figure 6: Decomposition of metal hydroxides versus temperature (Nabaltec).

2.3.2 HOW TO ACHIEVE FLAME RETARDANCY WITH METAL HYDROXIDES

The most commonly used test to describe the flammability of a cable compound is still the Limiting Oxygen Index (LOI) in accordance with ISO 4589. This test describes the minimum concentration of oxygen in an oxygen/nitrogen mixture which is just sufficient to support the combustion of a vertically oriented specimen. At a lower oxygen concentration, the flame is extinguished. High LOI values thus indicate high flame retardancy or low flammability. Figure 7 shows the LOI values for EVA (Poly-ethyl-co-vinyl acetate) with varying wt% concentrations of Aluminium hydroxide (ATH), Aluminium-oxide-hydrate (AOH) and Magnesium hydroxide (MDH)



At high filling levels, different LOI values for:

- Aluminium-oxide-hydroxide AOH
- Magnesium hydroxide
- Aluminium hydroxide

Figure 7: LOI values of an EVA compound with different filling levels (Nabaltec).

Experience shows that LOI values of at least 30 % oxygen are necessary to fulfil the basic flame retardancy requirements in a wide range of applications. In the example given here this corresponds to a filling level of around 55 % by weight in EVA. For more stringent standards far higher values are required. The initially very flat curves illustrate that the physical mechanism requires a minimum concentration of flame retardant agent which is higher than for products with specific chemical reactions such as phosphorus containing flame retardants.

2.4 CURRENT DEVELOPMENTS IN THE AREA OF METAL HYDROXIDES

2.4.1 PROCESSABILITY

One downside of the use of metal hydroxides is the high filling level which is required to achieve a basic flame retardancy for a cable compound. Therefore a lot of work has been spent on the improvement of either the efficiency of metal hydroxides as flame retardants and on the processability of such compounds by adjusting the metal hydroxide properties such as particle size distribution, bulk density or oil absorption. The major goal of these developments has been and still is to improve the extrusion behaviour of such metal hydroxide based compounds, thus manufacturing cost both in compounding and cable extrusion can be reduced. To achieve this goal, basically three different options are investigated:

2.4.2 SURFACE TREATMENT

Historically, the usage of surface treated fillers is a well known technology to improve the incorporation of a mineral filler into a polymer matrix. Due to the improved interaction between coated filler and polymer, not only the mechanical properties of the compound improved but also the compound viscosity can be reduced. This improves the processing behaviour during compounding and cable extrusion.

Whereas for magnesium hydroxide the usage of surface coated grades is essential for the mixing behaviour of the magnesium hydroxide and the achievable compound properties, the usage of surface treated aluminium hydroxide and boehmite is getting less and less common.

In addition to the extra cost of surface treating metal hydroxides, one has to be careful in regard to the selection of the proper surface treatment, e. g. vinyl silane versus amino silane, as the nature of the surface treatment may also have an impact on the long-term mechanical properties of the compound as well as the electrical properties, especially the water absorption can become problematic.

2.4.3 NANOCOMPOSITES

A good deal of research work is being carried out on nanoparticles and their contribution in the field of plastics. Polymers reinforced with as little as 2 % to 5 % of these particles via melt compounding or in-situ polymerization exhibit dramatic improvements in thermo-mechanical properties, barrier properties and flame retardancy. They also can outperform standard fillers and fibres in raising heat resistance, dimensional stability and electrical conductivity.

The two types of nano-fillers that have been most widely discussed and the first to break into commercial use are nanoclays and carbon nanotubes. Both must be chemically modified with surface treatments in order to achieve the fine dispersion and resin coupling required to derive maximum benefit. Both of these nano-fillers have demonstrated improvements in structural, thermal, barrier and flame retardant properties of plastics. Carbon nanotubes also enhance electrical conductivity.

For HFFR cable compounds, nanocomposites based on so called modified nanoclays (organoclays) are the most commonly used ones. In these organoclays the layered silica (montmorillonite or hectorite) has been modified with organic salts such as tetra-alkylammonium salts to improve the compatibility with polymers in order to generate polymer-layered silicate nanocomposites.

For wire and cable applications organoclays are normally used in combination with traditional flame retardants such as ATH and MDH because compounds containing only organoclays are not fulfilling the required flame retardancy. So far the usage of organoclays is nearly entirely within EVA based cable compounds, with filling levels in the range of 3 to 5 %. The content of the traditional flame retardant in these compounds can be reduced down to 50 % versus 60 to 65 % in absence of the organoclay.

The function of the organoclay as flame retardant is basically to form a stable and strong char (barrier) on the polymer surface in case of a fire. This barrier prevents the exposure of further low molecular decomposition products, thus stopping the "refueling" of the fire and works as a thermal insulation preventing further polymer degradation.

2.4.4 IMPROVED MORPHOLOGY OF THE METAL HYDROXIDE

Whereas the two previous technologies require the usage of an additional ingredient to improve the processability of the metal hydroxide as such and/or the HFFR compound, most recently a lot of work has been carried out to adjust the particle morphology of the metal hydroxide to obtain better performance. The basic principle behind this work has been to produce a metal hydroxide with much lower oil absorption and more consistent bulk density. The lower oil absorption reduces the compound viscosity, thus extrusion processes can be run substantially faster. Compound viscosities can be reduced by 30 to 50 %¹⁵.

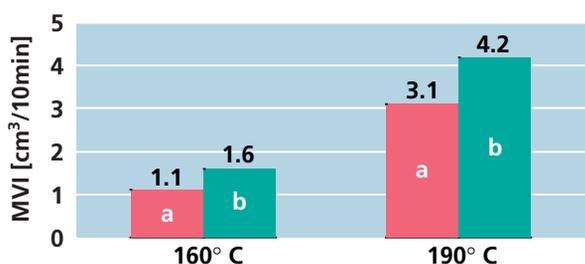


Figure 8: Melt volume rate for EVA (19 % VA) compound filled with 60 wt% ATH, Aminosilane coupled; a) standard ATH, b) improved ATH (Nabaltec)

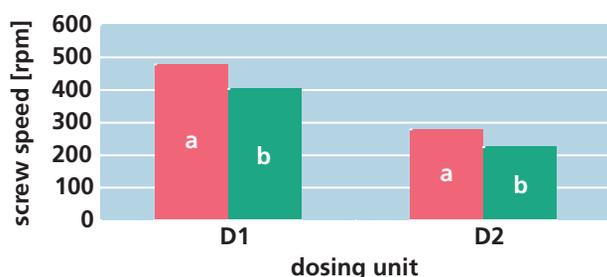


Figure 9: Screw speed of a gravimetric dosing unit with constant mass flow; a) regular ATH, b) improved ATH (Nabaltec)

Although the specific gravity of Metal hydroxides used in HFFR Cable compounds is in the area of $\sim 2.5 \text{ g/cm}^3$, bulk densities of the used hydroxides is much lower. These low bulk densities in combination with strong attractive forces between the fine inorganic filler particles lead to poor flow properties and bridge building in the feeding process which limits output rates of continuous compounding processes. Low bulk densities also slow down the filler uptake by the polymer melt and the air, which is entrapped by the melt, has to be removed by vacuum degassing¹⁶. As shown in Figure 9 a metal hydroxide with more consistent bulk density also gives up to 20 % lower screw speeds in a gravimetric dosing unit commonly used in continuous compounding lines. This difference in screw speed of up to 20 % clearly demonstrates the improved feeding characteristics which consequently enhance the space for further improvements in the entire production process.

2.5 FLAME RETARDED THERMOPLASTIC ELASTOMERS FOR CABLE APPLICATIONS

Thermoplastic Elastomers (TPE) are plastic materials which combine the processing advantages of thermoplastics with the flexible, low modulus properties of elastomers. Block copolymer TPEs are made up of segmented blocks formed by polymerizing a thermoplastic monomer with an elastomeric comonomer. Engineering TPEs include thermoplastic urethanes (TPU), copolyesters (TPE-E), styrene copolymers (TPE-S), polyolefinic/rubber blends (TPE-O), polyolefinic elastomer blends (TPE-V) and polyether block amide (PEBA). Due to the different desired properties, a huge amount of TPE types are on the market ranging from Shore A 10 to Shore D 75 hardness. Metal phosphinates as well as intumescent systems can effectively balance mechanical properties and flame retardancy in TPEs.

Copolyester elastomers combine toughness and resilience with excellent resistance to creep, impact, tearing and flexural fatigue. Their hard segments are based on polybutylene terephthalate and the soft segments based on polyether groups. The hardness of TPE-Es is in the range from Shore D

15 R. Sauerwein: New generation of aluminium hydroxide flame retardant filler for the wire and cable industry, *Cables 2003*, Cologne, Germany, March 2003

16 R. Sauerwein, M. Klimes: Process Optimized Fine Precipitated Aluminium hydroxide offering outstanding Compound Properties, *53rd IWCSI/Focus Philadelphia, PA, USA, 14-17 November 2004*

25 to Shore D 75. With finely grained metal phosphinates, flame retarded TPE-Es with excellent mechanical and electrical properties can be achieved. Addition of PTFE prevents burning dripping. According to the shore D hardness, a dosage of 20–30 % is recommended. In some cases, the addition of nitrogen synergists can improve the performance. The flame retarded TPEs are used for cable extrusion, wire coating, connectors, conveyor belts or corrugated pipes.

Thermoplastic urethanes are made of long chain polyols, chain extenders and polyisocyanates. The soft segments are either hydroxyl terminated polyesters or polyethers, the hard segment is normally diphenylmethane diisocyanate (MDI). Thermoplastic urethanes are easy to ignite and difficult to flame retard. By adding 12–15 % metal phosphinate with d50 of 20–40 µm or finer grades (d95 of max. 10 µm and d50 of 3 µm) with nitrogen synergists the classification UL 94 V0 is achieved. The same is achieved with appropriate formulations containing melamine cyanurate or intumescent systems. By the addition of a further antidripping agent like talc, dripping of test specimen can be prevented. Applications for flame retarded TPU are cable extrusion and injection moulding of artificial leather.

TPE-S, TPE-V, TPE-O

Intumescent systems can be used at moderate loading levels to pass e.g. UL 94, UL 62 (VW-1, US flexible cords and wires), vertical cable test (UL 1581) or 45° cable test (ISO 6722/1). This new family of halogen-free flame retardant TPEs provides an alternative to traditional flexible vinyl jack-

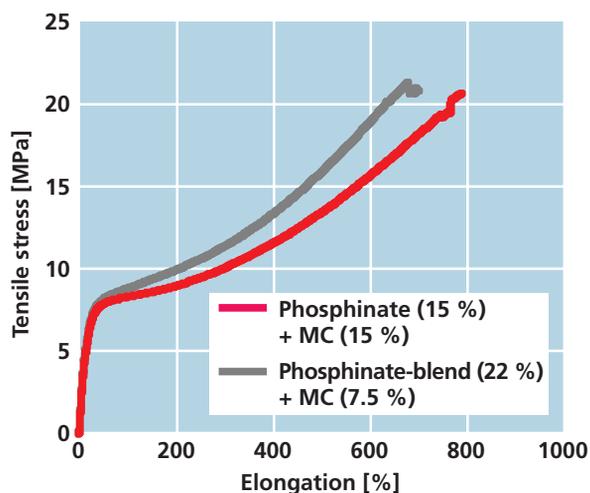


Fig. 10: Stress-strain diagram (DIN 53504, S2, 200 mm/min) of flame retarded polyether-TPU (Shore A 87). MC = Melamine Cyanurate.

eting and insulation for e.g. consumer electronics applications. They can be used e.g. for cable extrusion, corrugated pipes and cable conduits. The intumescent mechanism ensures high FR performance and very low smoke density/toxicity, passing for instance the ABD 0031 smoke toxicity test (Airbus standard). Modern intumescent systems based on surface treated particles can even pass demanding water storage tests required in the cable industry¹⁷. Due to a moderate FR loading the TPE HFFR technology offers a very good FR performance combined with excellent aesthetics and haptic properties.

	TPE-E (Shore D 55)	TPE-E (Shore D 40)
	Al-Phosphinate (20 - 22%)	
UL 94-test (1.6 mm)	V0	V1
GWIT 1 mm [°C]	775	650
GWFI 1 mm [°C]	960	900
Tensile strength [kJ/m ²] (DIN 53504*)	20.5	16.9
Elongation at break [%] (DIN 53504*)	322	547
Notched impact strength (Charpy, ISO 179/1eA)	13.1	no break
Shore D (ISO 868)	56	38
Melt flow rate [g/10 min]	42	20
Spiral flow [cm]	47	42

Table 3: Fire performance and mechanical characteristics of thermoplastic elastomers with phosphinate flame retardants.

17 Wermter, T. Futterer: Environmental friendly flame retardants and light active pigments for cable applications, *Polymers in Cables 2009*, Phoenix, USA, March 2009

3 Electric Enclosures

3.1 INTRODUCTION

Electronic enclosures are a market segment which includes primarily the enclosures of consumer and information technology equipment such as televisions, desktop or notebook computers, monitors, printers, copiers, household appliances, etc. These housings are made of different types of polymer resins such as high impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate / ABS blends (PC/ABS) and polyphenylene ether / HIPS blends (PPE/HIPS).

International standards provide that the plastic materials used for these housings usually should meet high fire safety standards such as UL 94 V or similar flame retardant specification. In general, it is not possible to meet these requirements with the pure polymer resins. Therefore, flame retardants are added to the polymer compound. Halogen-free phosphates based flame retardants are of growing importance in this electronic enclosures segment, because the electronics industry tends to move to more sustainable flame retardants. In addition to the required level of fire safety, the used polymer resins have to meet additional criteria such as:

1. Processability

Important for a good processability is a high melt flow, which allows a high throughput.

2. Thermal stability

Especially a high Heat Deflection Temperature (HDT) is required.

3. Mechanical properties

In particular a high impact strength is requested.

4. Hydrolytic stability

A high resistance against degradation caused by moisture is stipulated.

5. Recyclability

The used polymer resins must be suitable for easy separation and they should be recyclable with standard processes.

6. RoHS and WEEE directives

The polymer resins have to comply with the RoHS¹⁸ and WEEE¹⁹ directives.

The combination of requirements can be fulfilled by using phosphorus based flame retardants, especially the aromatic phosphate esters presented in Table 4.

Properties	TPP RDP		BDP	RDX
Chemical name	Triphenyl Phosphate	Resorcinol Bis-(Diphenyl Phosphate)	Bisphenol A Bis-(Diphenyl Phosphate)	Resorcinol bis(2,6-dixylenyl phosphate)
CAS number	115-86-6	57583-54-7	5945-33-5	139189-30-3
Appearance	Solid	Liquid	Liquid	Solid
Phosphorus content [%]	9.5	10.8	8.9	9.0
Density at 25 °C [g/cm³]	–	1.31	1.26	–
Viscosity at 25 °C [mPa·s]	Melting point 49 °C	600	13000	Melting point 92 °C

Table 4: Halogen-free flame retardants for electronic enclosures

¹⁸ Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment

¹⁹ Directive 2002/96/EC on Waste of Electric and Electronic Equipment

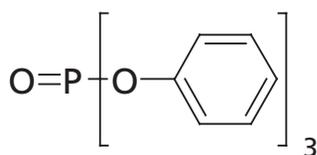
These four phosphorus compounds are halogen-free and are based on aromatic phosphate esters. All four phosphorus compounds can be used in PC/ABS blends as well as in PPE/HIPS blends.

Wt. Loss	2 %	5 %	10 %
TPP	202	220	235
RDP	288	325	360
BDP	273	327	393
RDX	295	340	395

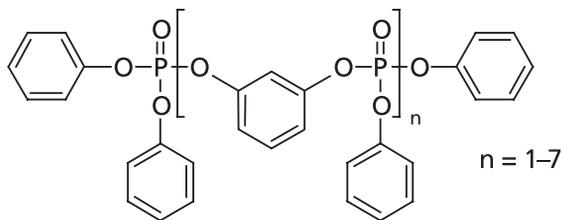
*10 °C/minute ramp rate in Nitrogen

Table 5: Thermogravimetric analysis (TGA) of phosphate esters: The values in the table indicate the temperatures at which a certain weight loss is reached.

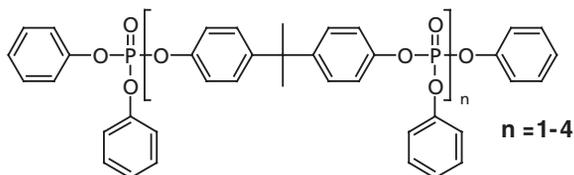
Tri-phenyl phosphate (TPP)



Resorcinol bis (diphenyl phosphate) (RDP)



Bis-phenol A bis (diphenyl phosphate) (BDP)



Resorcinol bis (2,6-dixylyl phenyl phosphate) (RDX)

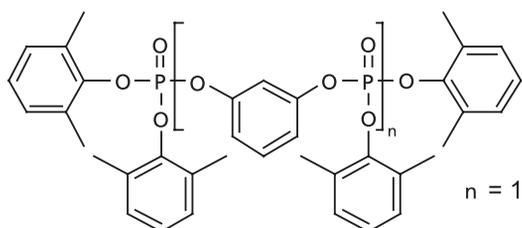


PHOTO: LANXESS

3.2 PC/ABS BLENDS

TPP, RDP, BDP, and RDX are suitable halogen-free flame retardants for PC/ABS blends. The required loadings depend on the ratio of PC and ABS in the blend. In commercial PC/ABS blends where the ABS content normally does not exceed 25 % it is possible to achieve a UL 94 V0 rating with these products at 8 to 15 wt% loading in combination with a co-additive. The co-additive usually retards the dripping. A common anti-dripping agent is PTFE with loadings up to 0.5 wt%.

Various results about TPP, RDP, BDP, and RDX in PC/ABS blends are presented in Table 6 to Table 8.

PC/ABS 4/1	% FR Additive	UL 94* (1.6 mm)
RDP	9.0	V0 (1.5)
BDP	12.3	V0 (1.5)
RDX	11.5	V0 (1.5)
TPP	14.0	V0 (1.7)

* avg. flame time

Table 6: UL 94 flammability in FR-PC/ABS (4/1)

FR-PC/ABS – V0	Additive	MFI
Composites	Level [%]	g/10 min. 260°/2.16 kg
BDP	12.3	26.9
RDP	9.0	18.7
RDX	11.5	25.9

Table 7: Melt viscosities of V0 rated FR-PC/ABS composites

PC/ABS (4/1)	FR Level	Tensile Strength	Flexural		HDT	Notched Izod Impact
			Modulus	Strength	1.80 MPa	
Flame Retardant	[%]	[N/mm ²]	[MPa]	[N/mm ²]	[°C]	[kJ/m ²]
RDP	9.0	53.3	1586	81.4	83.3	651
BDP	12.3	55.6	1655	84.8	81.4	496
RDX	11.5	54.0	1650	83.8	85.9	753
TPP	14.0	46.0	2620	82.7	67.8	123

Table 8: Physical properties of UL 94 V0 rated FR-PC/ABS

3.3 RECYCLABILITY OF FR-PC/ABS COMPOSITES USING NON-HALOGEN FLAME RETARDANTS

The European WEEE (Waste Electrical and Electronic Equipment, 2002/96/EC) Directive is an example of regulations which force producers to consider the full life-cycle of manufactured goods. Plastic components not recycled directly are stripped of hardware, washed, granulated and recycled back into the market for use in a similar or completely different application. The WEEE directive bans recycling of composites containing hazardous heavy metals and brominated flame retardants back into the feed stream. Current waste technology prefers not to have halogenated additives in this feed stream as it may limit or “poison” the subsequent generation of products. Although the U.S. and other regional markets do not have similar regulations, many manufacturers/fabricators are global producers and prefer to standardize their products using similarly sourced materials. By de facto, these companies force these regulations and the practice of recycling components becomes a design consideration in the life-cycle of products.

With a new public consciousness over the life cycle of plastics, manufacturers are designing products with the intent to recycle. This is especially true with computer and office equipment manufacturers where both industry and consumers rely on a desktop, laptop and/or a PDA to organize their day to day lives. Because of the fast pace of innovation in this market, hardware becomes outdated very quickly and is replaced with products that are faster, cheaper and smaller but with greater capability than its predecessor. And more mobile: in May 2005, for the first

time laptop computers outsold desktop units claiming 53 % of all computer sales²⁰. It is these units that are particularly vulnerable to flammability because they carry their own power (and ignition) source. PC/ABS composites are used extensively for housing components in these applications and as a result, are becoming more significant in the plastic waste stream. For many of these systems, some form of flame retardancy either through system design or component materials is used. Due to environmental concerns, many of these systems use non-halogen flame retardants such as triaryl phosphate flame retardants (TPP, RDP, BDP or RDX). For current non-halogen options for FR-PC/ABS, Table 9 to Table 11 present properties which are relevant for performance in a realistic recycling programme using techniques common to the industry. Because phosphate esters are known to be susceptible to hydrolysis, this study also considers composites utilizing additives found useful as stabilisers.

Additive(s)	RDP	BDP
Recycle 1	V0	V0
Avg. flame time	1.0	1.1
Recycle 5	V0	V0
Avg. flame time	0.9	1.1

Table 9: Flammability of recycled FR-PC/ABS according to UL 94 flammability (1.6 mm)

20 “The End of the Computer as we Know it”, Wall Street Secrets Plus Newsletter, Vol. 2, No. 58, July 22, 2005

Izod [kJ/m ²]	Recycle 1	Recycle 2	Recycle 3	Recycle 4	Recycle 5
BDP	491	491	512	512	532
RDP	619	534	619	534	577

Table 10: Izod impact (3.2 mm) of recycled FR-PC/ABS

ASTM-1238, 260 °C/2 kg.	BDP
	g/10 minutes
Initial BDP	19.0
Recycle 1	20.5
Recycle 3	22.1
Recycle 5	20.9
	RDP
Initial RDP	14.5
Recycle 1	16.3
Recycle 3	17.2
Recycle 5	16.8

Table 11: Recycling influence on melt flow

Hydrolytic Stability: FR-PC/ABS

- Polycarbonate is sensitive to acidic conditions.
- Different phosphate esters have different hydrolytic stabilities.
 - All phosphate esters decompose to acid species especially after exposure to high heat and humidity.
 - Bis-phenol A bridged phosphate (BDP) and 2.6-xylenol reacted phosphate (RDX) FRs are less susceptible to hydrolysis.
 - RDP analogs displayed instability earlier in the testing exposure regime but with the addition of stabilisers, substantial improvements are seen.

Summary recyclability:

- Used at typical recycling rates (20 % recycle), all bis-phosphate FRs used in this study meet industry standards.
 - Retention of flammability
 - Retention of impact properties
 - Stable melt viscosity
- Where hydrolytic stability is an issue, stabilisers can be used.

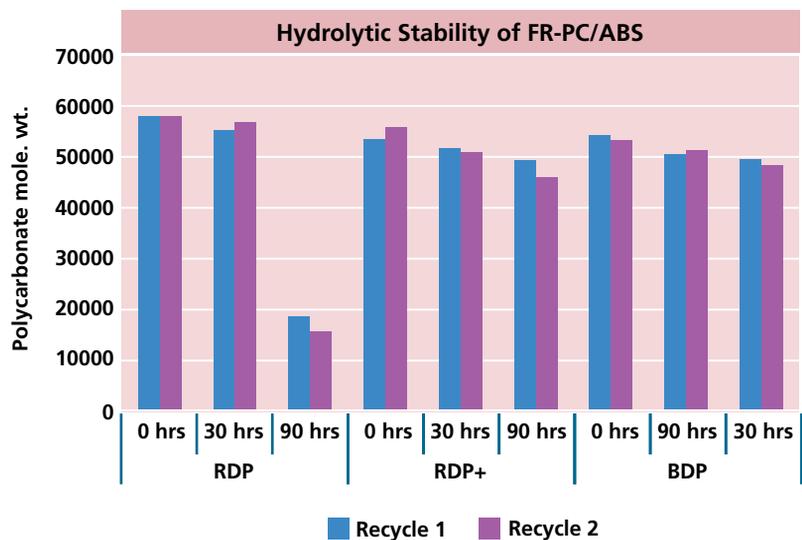


Figure 10: Hydrolytic stability of FR-PC/ABS

3.4 PPO/HIPS

PPO/HIPS blends can be flame retarded with the aromatic phosphates TPP, RDP and BDP. Typical levels of PPE used to achieve a UL 94 V0 rating are 30 to 70 %; these blends also contain 10 to 20 % of TPP, RDP or BDP and RDX.

Physical property	HIPS	HIPS + Deca + Sb ₂ O ₃	PPO/ RDP	PPO/ RDP
Loading [wt%]		20	40	35
UL 94 (3.2 mm)		V0	V0	V1
Tensile strength [N/mm ²]	21.8	20.7	25.2	31.7
Izod [kJ/m ²]	80.1	64.1	64.1	69.4
Tg [°C]	88	86	64	84

Table 12: Combustion and physical properties of phosphorus based flame retardants in HIPS



PHOTO: LANXESS

4 Electric Installations and Components

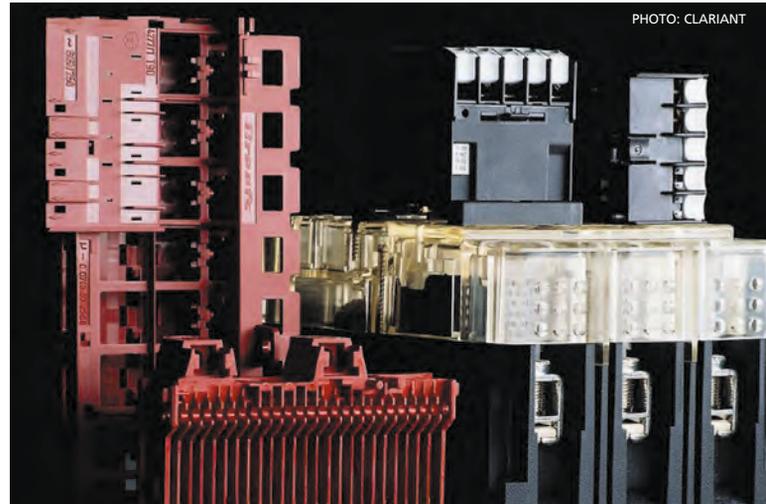
4.1 SCOPE AND MATERIAL REQUIREMENTS FOR ELECTRICAL COMPONENTS

Connectors and switches play an essential role in every electrical component, from the point where electricity enters the home or office to the actual electrical appliance or (industrial) equipment. Whether it is in dishwashers, laptop computers, coffee makers, TV sets or in car electrical systems, trains, planes, you find them everywhere where electricity is used.

Types of connectors	Switches and switchgear
Terminal blocks	Low Voltage Switchgear
Crimp-on terminals	Light switches
Insulation displacement connectors	Rotary switches
Plug and socket connectors	
Component and device connectors	
Printed wiring board connectors	

Over the years plastics have become ever more important in the development and innovation of electrical equipment. Besides the obvious benefit of offering electrical and thermal insulation, plastics allow designers to develop smaller and lighter parts.

Because of the very broad array of application areas, and the increasing number of different international requirements each of these applications need to meet, it does not come as a surprise that there are many different plastics in use today that are tailored to meet these very different national and international standards. Which plastic is ultimately chosen to design a specific part or component depends very much on the performance of a plastic with respect to mechanical, electrical and fire properties.



4.1.1 MECHANICAL PROPERTIES

Polyamides for example are often chosen because of their good toughness and rigidity. In connectors this enables the design of so called “living hinges” that need to be opened and closed easily without breaking, whereas toughness is particularly important in snap fits for terminal blocks to allow easy assembly. Polyamides typically also perform well regarding heat ageing, which is important because of the increasing temperatures due to miniaturization of electrical components. PBT on the other hand offers the benefit of good dimensional and hydrolytic stability

4.1.2 ELECTRICAL PROPERTIES

An important electric requirement relates to the insulation efficiency which is expressed as the dielectric constant for alternating currents and signals. The closer this value is to one the better the insulating effect. The other important parameter is the Comparative Tracking Index or CTI (expressed in Volts) which specifies the electrical breakdown (tracking) properties of an insulating material. Tracking is an electrical breakdown on the surface of an insulating material. A large voltage difference gradually creates a conductive leakage path across the surface of the material by forming a carbonized track. The higher the value, the better performing the material is. With some halogen-free FRs the CTI of polymers remains as for the neat polymer.

4.1.3 FIRE RESISTANCE

Most plastics are derived from fossil fuels. As a result plastics have a tendency to easily ignite when exposed to heat or a flame. Therefore fire safety is particularly important for plastics used in components that (potentially) generate heat due to the use of electricity, or in case of malfunctions.



In Europe the fire safety requirements for connectors and switches are determined by technical standards from the International Electrotechnical Commission (IEC). Some of the most important standards include IEC 60898 for circuit breakers, IEC 60947 for industrial control equipment and IEC 60335 for the area of domestic appliances. Besides the

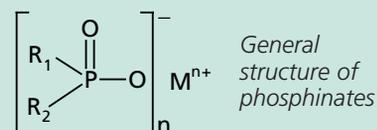
IEC standards many of the requirements from the American Underwriters Laboratories (UL) have been adopted in Europe and Asia as well. UL 94 V0 for example, is probably the most commonly used flammability requirement anywhere in the world.

Depending on the end application, for IEC standards approval is based on either material testing or on testing the finished component, whereas under UL tests are always performed on the material only. Despite the differences between these test methods one common denominator in all tests is the specified ignition source and the way a sample is exposed to the ignition source.

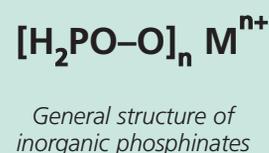
Ultimately choosing the right polymer for an electrical connector or switch evolves around finding the right balance between fire safety on one hand and mechanical and electrical properties on the other hand. A variety of halogen-free flame retardants are available today, that allow compounders to optimize their formulations.

4.2 OVERVIEW OF HALOGEN-FREE FRS FOR ELECTRICAL INSTALLATIONS

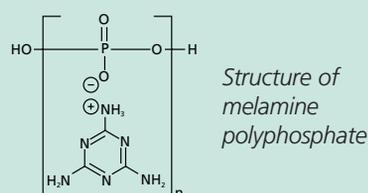
Metal phosphinates: These are well suited for glass fibre reinforced polyamides and polyesters and are added at levels of about 20 % – often combined with N-synergists. Key aspects are a high phosphorus content (> 23 %), no affinity to water and a good thermal stability (up to 320 °C) which make them compatible with lead-free soldering operations.



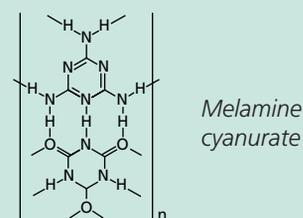
Inorganic Metal phosphinates are an old known chemical class recently introduced as active FR component in different proprietary synergistic blends. Used in different polymers, especially Polypropylene homo and copolymer for UL 94 V2 applications at some percent loading, gives very high GWIT on thin items. They can be used in PC, PC/ABS, PS, TPU and some engineering polymers like PBT and PA6 thanks to his very high phosphorus content in the range 20 to 40 %, thermal stability, and non blooming characteristics.



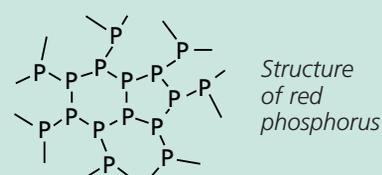
Melamine Polyphosphate (MPP) is especially suited for glass fibre reinforced polyamide 6,6, where it is added at ca. 25 % for UL 94 V0 performance. It has a good thermal stability (ca. 300 °C). MPP is often used as synergist in combination with phosphorus FRs.



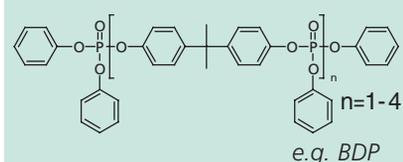
Melamine cyanurate (MC) is especially suited for unfilled and mineral filled polyamides. UL 94 V0 can be achieved with 10 to 15 % in unfilled PA and up to 20 % for UL 94 V2 in low glass filled PA 6. MC is often used as synergist in combination with phosphorus FRs.



Red phosphorus is a polymeric form of elemental phosphorus. It is used mainly in glass fibre reinforced PA 6,6 at 5 to 8 % addition level, where its high efficiency at low loading guarantee to maintain the excellent mechanical and electrical properties of the polymer while obtaining the highest flame proofing characteristics. Due to its inherent colour, compounds are limited to red or black colours. In addition, precautions against degradation have to be taken.



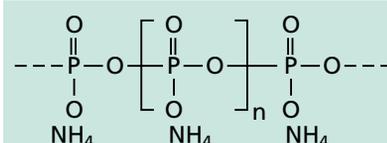
Aryl phosphates and phosphonates: their main use is PC/ABS blends at 10 to 20 % addition level for UL 94 V0. They are often used as co-components in FR-formulation. Their limitations are possible plastisicing effects and a certain volatility at high processing temperatures. Blooming can have a negative influence on electrical properties.



Magnesium hydroxide (MDH): high filler levels of about 45 to 50 % are necessary to reach UL 94 V0. Because of its limited temperature stability, it is mainly used in low glass fibre PA 6.



Ammonium polyphosphate in combination with nitrogen synergists can be used in polyolefins at addition levels of ca. 20 to 30 %.



4.3 POLYMERS USED IN ELECTRICAL COMPONENTS AND SUITABLE FR SYSTEMS

The following table presents an overview of typical technical properties which can be achieved with halogen-free flame retardants in different polymers and with different glass fibre contents. The values are meant for orientation only, because the exact properties depend on the specific polymer used, additive packages and processing conditions.

	glass fiber [%]	halogen-free FR	tensile strength [N/mm ²]	notched impact [kJ/m ²]	CTI [M]	GWIT [°C]	UL 94
Polyamide 6	0	melamine cyanurate	~ 75	~ 4	600	> 775	V0
	30	metal phosphinate + N-synergist	~ 160	~ 15	600	775	V0
Polyamide 6,6	30	metal phosphinate + N-synergist	~ 150	~ 14	600	775	V0
	30	red phosphorus	~ 160	~ 18	600	775	V0
	30	melamine polyphosphate	~ 140	~ 12	400	675	V0
HTN	30	metal phosphinate	~ 140	~ 8	600	775	V0
PBT	0	metal phosphinate + N-synergist e. g. melamine polyphosphate	~ 45	~ 3	600	775	V0
	30	metal phosphinate + N-synergist e. g. melamine polyphosphate	~ 110	~ 7	500	800	V0
PET	0	metal phosphinate + N-synergist e. g. melamine polyphosphate	–	~ 2	–	800	V0
	30	metal phosphinate + N-synergist e. g. melamine polyphosphate	–	~ 8	–	800	V0
Polyolefines	0	intumescent system	10–30	~ 3	600	800	V0
Polyolefines	20	intumescent system	70	~ 6	600	825	V0

5 Printed Wiring Boards

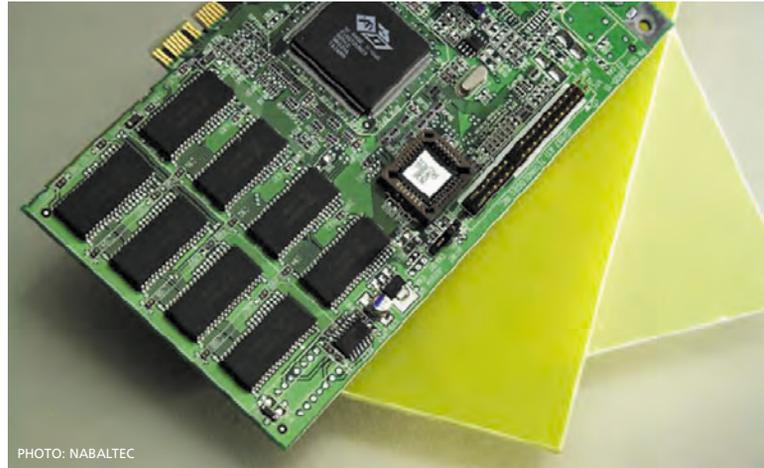
5.1 MARKET ENVIRONMENT AND TRENDS

Electronic devices play an increasing role in our daily life and virtually all electronic items contain a printed wiring board (PWB). For safety reasons, there are requirements for the fire resistance of PWBs, the UL 94 V0 classification being the most widely used specification. Many common PWB materials need a flame retarding system to achieve this classification.

Epoxy resins are widely used as resin backbone for PWB base materials. The European Directive on Restriction of certain Hazardous Substances in E&E (RoHS, 2002/95/EC) has stimulated a change in the base material market, because it bans products that contain lead (Pb) since July 2006, unless the use is specifically exempted. Due to the higher process temperatures for lead-free soldering materials, base materials with higher thermal stability have to be used. For halogen-free base materials with higher glass transition temperature ($T_g > 165\text{ }^\circ\text{C}$) epoxy-novolac resins are often employed. These epoxy-novolac resins need less flame retardants in comparison to the normally used diglycidyl ether of bisphenol-A (DGEBA) resins, which makes it easier to achieve the technical requirements with halogen-free flame retardants. The transition to base materials with higher thermal resistance makes it necessary to reformulate base material recipes. Many manufacturers have taken this opportunity to investigate halogen-free FRs when developing new materials.

5.2 TECHNICAL REQUIREMENTS TO FR-4 PRINTED WIRING BOARDS

There are several National Electrical Manufacturers Association (NEMA) classes of fire retardant laminate materials used for PWBs. For example FR-2 is made from a phenolic resin with paper reinforcement. These PWBs traditionally contain triphenyl phosphate as a halogen-free flame retardant. FR-3 boards (paper-epoxy system) are still in use for simple applications. Flexible Printed Circuits (FPC) are used for computer peripherals and mobile devices like cell phones. They are made from epoxy, polyurethane, polyimide, polyester or acrylic resins and usually contain brominated epoxy or phenoxy resins. PWBs of the FR-4 classification are made from epoxy resins with glass fibre reinforce-



ment. They are most commonly used in the electronics industry (about 80 %). Fire resistant formulations have to fulfil a number of requirements:

- No blisters or delamination after pressure cooker test (PCT)
- No decomposition or delamination during lead free soldering
- Chemical resistance against acid, alkaline and oxidative substances
- No or low water uptake
- Resistance against inner laminate electro migration (CAF)
- Small coefficient of thermal expansion (CTE)
- No or little impact on glass transition temperature (T_g)
- No or little impact on electrical properties in particular the dielectric constant (D_k) and dissipation factor (D_f)
- No or little impact on copper peel strength and inner laminate adhesion
- No impact on resin flow of prepregs for press process
- Optical aspect, no agglomerate for quality inspection



From 2007 to 2008 the electronics organisation iNEMI (www.inemi.org) carried out an extensive project to investigate, through testing, the technical performance and suitability of halogen-free laminates compared to a benchmark brominated material²¹. Working with the materials supplier base and printed wiring board manufacturers, the project team used known designs from IBM and Intel to judge the electrical, mechanical and reliability attributes of various HFR-free materials.

The project's investigation showed that not all HFR-free materials are equivalent, nor were any of the materials tested equivalent to the FR-4 baseline. Compared to the baseline, there were generally higher dielectric constant (Dk) values and lower dissipation factor (Df) values for the halogen-free materials. Findings include:

- *Material testing: Pre-preg and laminate properties evaluation showed good thermal stability, comparable moisture absorption, slightly lower CTE in the Z direction and no impact of filler on adhesion.*
- *Electrical testing (Dk/Df): In testing, bake/reflow did not significantly change the laminate dielectric constant – the Dk for HFR-free materials and the total loss for these materials is generally equivalent to or lower than the baseline.*
- *Adhesion testing: Through Pb-free solder compatibility testing, most HFR-free laminates did not show functional degradation; however, laminate cracking was observed in one of the materials tested during reflow²².*

A follow-on project – the “HFR-free High-Reliability PCB Project” – was launched in 2008. This new project will identify technology readiness, supply capability and reliability characteristics for halogen-free alternatives to conventional printed wiring board materials and printed wiring board assemblies, based on the requirements of the high-reliability market segment.

Performance of halogen free vs. brominated laminates		
Thermal Properties		
Thermal expansion	lower	+
Thermal conductivity	higher	+
Physical Properties		
Flammability	equal	o
Moisture absorption	comparable	+ / o
Peel strength	lower	- / o
Modulus	equal	o
Electrical Properties		
CAF resistance	higher	+
Dielectric constant	slightly higher	+
Dissipation factor	lower	+
Workability		
Drill bit wear	higher	-
+ means better, - worse, o indifferent		

Table 13: Qualitative properties of halogen free laminates vs. standard brominated materials.

21 published e.g. in Tisdale S, Long G, Krabbenhoft R, Papatthomas K, Fisher T (2008): iNEMI BFR-free PCB Materials Evaluation Project Report. SMTAI Conference, Edina MN, USA

22 iNEMI Annual Report 2008, thor.inemi.org/webdownload/annual_report/2008_AR.pdf

5.3 NON-REACTIVE FILLERS

5.3.1 METAL HYDROXIDES

These minerals are useful flame retardants, whether used on their own or in synergy with other flame retardants. They act by consuming energy during thermal decomposition, releasing water and forming an oxide layer. Thereby they cool the polymer, dilute the combustion gasses, and shield the resin substrate by the formed oxide layer. Furthermore, this oxide layer adsorbs soot particles leading to low smoke levels. A big advantage of these mineral flame retardants is their effect to reduce the CTE down to very low values (< 40 ppm are possible).

Aluminium Trihydroxide (ATH)

$Al(OH)_3$

Although concerns can be raised due to the moderate thermal stability (regular ATH starts to decompose at approx. 200 °C), ATH is still used in halogen-free formulations. Rather high loadings are necessary to achieve the necessary fire performance. Therefore, the combination with other FRs is common.

Aluminium monohydrate

$AlOOH$

The transition to lead-free solders with significantly higher temperatures is certainly a challenge for ATH. It may be replaced by aluminium monohydrate (Boehmite), which excels in a high temperature stability up to 340 °C. Thus, absolutely no decomposition and water release (water can catalyse conductive anodic filaments, CAF) appears during lead free soldering. Consequently, laminates produced with boehmites feature very high temperature stabilities resulting in very reliable products which are suitable for long term usage as well as usage under elevated temperatures, e. g. in automotive applications (“under the hood”). Due to the lower flame retarding efficiency in comparison to ATH a combination with other halogen-free FR or novolac based epoxy systems is recommended.



PHOTO: NABALTEC

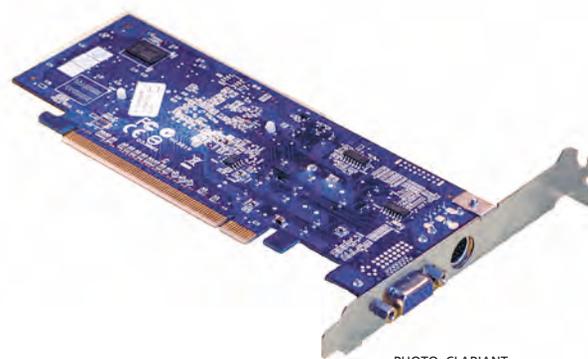
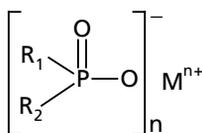


PHOTO: CLARIANT

5.3.2 METAL PHOSPHINATES AND POLYPHOSPHATES

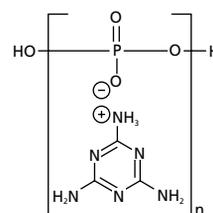
Metal phosphinates are a new class of non-halogenated flame retardants which can be used for rigid as well as flexible PWB or other applications around this area. Unlike



most other phosphorus containing compounds, the metal phosphinate is not hygroscopic, not toxic, has an extremely low solubility in water and common solvents and does not hydrolyse in the presence of water. The latter point is especially crucial, since the release of phosphoric acid is not tolerable in E&E applications. Further key aspects are the high phosphorus content (> 23 %) and its good thermal stability (> 300 °C) which makes it compatible with lead-free soldering operations. Electrical properties show virtually no impact on Dk / Df even at frequencies well above one GHz. However, the metal phosphinate can not be used alone to achieve a UL 94 V0 classification, therefore it is usually combined with N- synergist such as Melamine polyphosphate, with modified (phosphorus or nitrogen containing) epoxy resins or blends with other polymers (cyanate esters, benzoxazines, PPE or others).

To obtain a UL 94 V0 rating for laminate thicknesses between 1.6 mm to 0.05 mm, the addition of 15 to 20 wt% metal phosphinate in a varnish formulation is a good starting point. But in every case the dosage of the metal phosphinate depends on the chemical nature of the varnish backbone. For example, in a combination with a phosphorus modified epoxy resin 15 to 20 phr (parts per hundred resin) of metal phosphinate are recommended. Metal phosphinates are also suitable for flexible printed circuit boards (FPC).

Melamine polyphosphate is used in combination with other FRs (e. g. phosphinates, minerals). It has a good thermal stability and low influence on Tg.

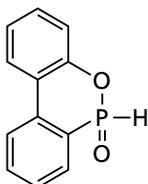


Structure of melamine polyphosphate

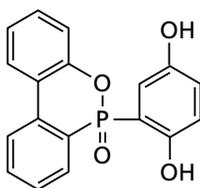
5.4 REACTIVE FLAME RETARDANTS

Reactive FRs are chemically bound to the polymer. This solves most of the migration problems, e. g. vapourisation.

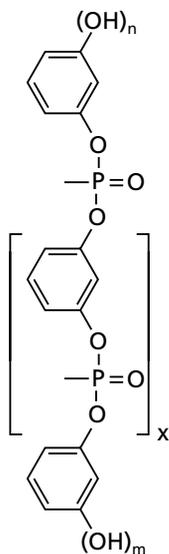
DOPO (Dihydrooxaphosphaphen-antrene) is a cyclic hydrogen-phosphinate containing a P-H bond. It is mono-functional, but several modifications are possible, which, when properly catalyzed, can be grafted to C=C linkage or reacted with epoxy groups.



Today, DOPO can be regarded as the major building block used to make phosphorus containing epoxy resins (Tg up to 150 °C). DOPO is commercially available from different suppliers and global capacities have consequently increased over the past 2 years to respond to the increasing market demand from PCB.



Poly(1,3-phenylene methylphosphonate): Due to its hydroxyl groups it can react into the polymer and act as a curing agent for epoxies. It is recommended in combination with ATH or AOH. High temperature stability is reported (high Tg, pressure cooker test).



$m, n = 0 \text{ or } 1$

5.5 AMOUNT OF FLAME RETARDANT NECESSARY FOR UL 94 V0 CLASSIFICATION

The following tables show the necessary flame retardant levels in order to achieve a UL 94 V0 classification. The experiments were performed with resins without glass fiber reinforcement by the Karlsruhe Institute of Technology.

Resin hardened with DICY / Fenuron				
Flame Retardant	Phosphorus-content [%]	FR-content [%]	UL 94 (4 mm)	Tg (DSC) [°C]
Metal phosphinate	2.0	10.0	V0	169
MPP + Metal phosphinate	1.6	8.0	V0	179
Poly(1,3-phenylene Methylphosphonate)	3.2	23.5	V0	165
DOPO-HQ	1.4	17.0	V0	161
DOPO	1.6	11.2	V0	155
DOPO + 30 % Boehmite	0.4	2.9	V0	168

Table 14: DOW DEN 438 resin hardened with DICY / Fenuron (no glass fibre): Amount of Flame Retardant necessary for UL 94 V0 classification

Resin hardened with phenol novolak / NMI				
Flame Retardant	Phosphorus-content [%]	FR-content [%]	UL 94 (4 mm)	Tg (DSC) [°C]
Metal phosphinate	0.6	3.0	V0	172
Poly(1,3-phenylene Methylphosphonate)	0.7	4.9	V0	174
DOPO-HQ	0.7	7.4	V0	169
DOPO	0.8	5.6	V0	164

Table 15: DOW DEN 438 resin hardened with phenol novolak / NMI (no glass fibre): Amount of FR necessary for UL 94 V0 classification

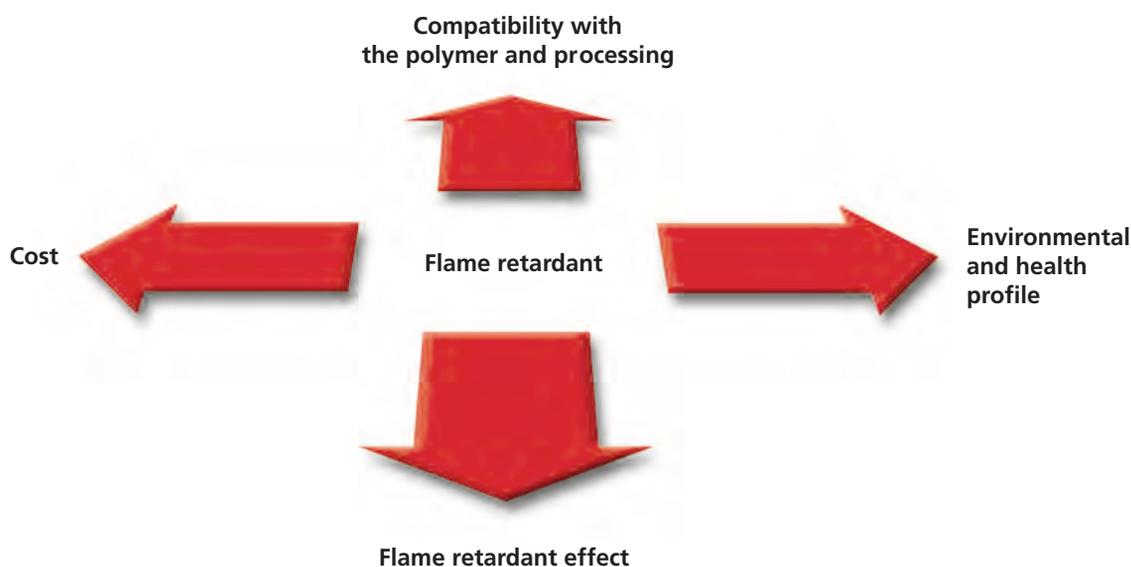
6 Future Trends and Innovation

In recent years, halogen-free flame retardants increasingly replaced conventional halogenated flame retardants in plastics used in the E&E sector. This was due to a growing environmental awareness of the population, legal regulations, and an equal ranking of both types of flame retardants in terms of cost and technology.

Costs of brominated flame retardants have increased drastically, novel phosphorus-organic flame retardants and particularly mixtures of HFFR have been developed and introduced for various materials in E&E applications. As mentioned in the previous chapters, three types of phosphorus-organic compounds were conceived for epoxy resins to be used in printed-circuit boards. Additionally, electric cast resins and coatings were developed to replace the traditional tetrabromobisphenol A, also when using existing technologies. In glass fibre reinforced polyamides and polyesters of electric components on the market, decabromodiphenylether was replaced by halogen-free alternatives based on aluminium phosphinates and melamine salts. New oligomer phosphoric acid esters were developed and are presently applied for electric enclosures. Phosphorus-organic flame retardants have been introduced, as the mode of action of these phosphorus-organic derivatives in both the condensed and the gas phase is increasingly understood. All these halogen-free

flame retardants are reactive systems that become part of the polymer network or represent salts or polymer species in the form of additive flame retardants. By reaction or by these low-volatile additives, migration of the flame retardants and, hence, loss of flame retardancy are prevented. At the same time, these additives have a sufficient thermal stability for them to be incorporated easily in the polymers mentioned.

Based on these findings, further development work is being pursued. It is aimed at creating synergistic systems with these substances and other additives like aluminium and magnesium hydroxides, nitrogen compounds, silicon or sulfur compounds. Next to the further improvement of the processability of mineral flame retardants by means of morphology alteration or surface treatments, the synergistic use of classical mineral FRs in sub-micron to nano size is examined and commercialized. Such synergistic systems should require smaller amounts of flame retardants, while the remaining material properties are hardly affected. Furthermore, major efforts are dedicated to developing halogen-free flame retardants for polystyrene based plastics. Examples are HIPS, ABS, SAN, PS-foams, and others. First work relating to HIPS is presented in this brochure (chapter 3).



In principle, all newly developed flame retardants must have a sufficient thermal stability and chemical neutrality for an easy incorporation in polymers and, at the same time, exhibit no tendency to migrate out of the polymer. By adding small amounts of the additive, a high flame-retarding effect should be achieved, while other material properties should not be affected. Two trends can be observed in the development of novel phosphorus-containing flame retardants: More sterically complex groups are incorporated mainly in arylphosphates to enhance the hydrolysis stability of the flame retardants. Another focus lies on the development of nitrogen-containing phosphorus compounds, e. g. phosphamides and phosphacenes, which require less flame retardants due to potential synergistic effects. This trend applies to both polymer enclosures and glass fiber-reinforced materials. For pure polycarbonates, alkali sulfonates and siloxanes are being developed. Already small amounts of these substances result in an excellent flame-retarding effect. In the area of epoxy resins, solutions are being developed for the transport sector based on the halogen-free flame retardants for printed-circuit boards referred to above. The aim is to find efficient flame retardant mixtures for epoxy resins that can be processed easily and which are

suitable for different fiber-reinforced composites. Depending on the application, the use of either gas-phase or condensed-phase acting phosphorus compounds is necessary. Those particular effects might be increased by synergistic addition of further HFFR. Innovations are regularly discussed at dedicated international conferences, e. g.:

- Interscience Conference on Flame Retardants, in 2010 together with InterFlam (www.intersciencecomms.co.uk/index.htm), held in UK
- European Meeting on Fire Retardant Polymeric Materials (FRPM), biannual, next in 2009 (<http://www.frpm09.com>)
- Fire and Materials Conference, biannual, next in 2011, USA, (<http://www.intercomm.dial.pipex.com>)
- Annual BCC Conference on Flame Retardancy, Stamford, CT, USA (<http://www.bccresearch.com/conferences.htm>)
- AMI "Fire Resistance in Plastics" conference, annual, held so far in Germany (www2.amiplastics.com/events/)
- SKZ conference "Trends in Fire Safety and Innovative Flame Retardants", Würzburg, Germany (www.skz.de)



PHOTO: FORSCHUNGSZENTRUM KARLSRUHE GMBH

REBEKA facility for the synthesis of flame-retarding, halogen-free polymer additives

7 Environmental and Toxicological Properties of Halogen-free Flame Retardants

Whereas the previous chapters focussed on the technical properties of halogen-free flame retardants in various application areas, this chapter discusses their environmental and toxicological properties. It has often been claimed that not enough toxicological and environmental data exist to justify a switch from currently used flame retardants to halogen-free materials. It is true that a wealth of information and studies exists on halogenated high volume products, but this is mainly a consequence of the concerns regarding health and environment and of risk assessment activities. For halogen-free flame retardants, no official European risk assessments have been carried out, because they did not make it onto the so called priority lists for high volume chemicals, which were the basis for carrying out risk assessments in Europe.

Most halogen-free flame retardants have an environmentally friendly profile, which means that they pose no harm to the environment and do not bio-accumulate in biota. In addition they have a low (eco)toxicity profile and will eventually mineralize in nature. Due to these characteristics, none of the halogen-free flame retardants are considered to be PBT or vPvB. For the purpose of this brochure the environmental and toxicological properties for a number of flame retardants have been summarized in fact sheets. The data in the sheets are typical hazard oriented data and should not be used as such to deduce risks. The sheets are divided into a Health and Environmental chapter, and also include an overall PBT / vPvB analysis to indicate the regulatory status. The fact sheets can be downloaded from <http://www.halogenfree-flameretardants.com>.

Manufacturers of flame retardants have started to identify data gaps and commission the necessary tests and studies, because these will also be required by the new European chemicals legislation, REACH (1907/2006/EC). Under REACH not only hazard data, but also data concerning emissions, uses and end of life will be gathered. One company has already commissioned a life cycle emission study²³.



Under their Design for Environment programme, the US Environmental Protection Agency started a project on alternatives to TBBPA in 2006 which compares and evaluates alternative flame retardants which can be used in FR-4 laminates. Reactive phosphorus based flame retardants as well as additive FRs of different halogen free chemistries were scrutinized. Their in-depth analysis of existing toxicity and environmental data together with expert judgement and computer modelling showed that there are no “hidden surprises” for the alternatives. Although some chemical hazards were identified, these do not pose risks when taking into account potential exposures of consumers. In the workplace, during laminate production and processing or recycling, proper industrial hygiene has to be followed. In an experimental part of the project, the combustion products of brominated and halogen free laminates will be studied. The formation of brominated dioxins from TBBPA in uncontrolled burning is a key element, because it relates to recycling operations in countries like China or India. A draft report is available on the EPA website (www.epa.gov/dfe), the final results will also be published there, probably in early 2010.



The environmental organisation “Clean Production Action” (www.cleanproduction.org) has developed a methodology for evaluating chemicals based on their hazard profile. It is related to existing schemes used by the US-EPA and REACH legislation in Europe in that it uses criteria related to their PBT (persistent, bioaccumulative and toxic) and CMR (carcinogenic, mutagenic or toxic to reproduction) categories. They rank chemicals by their inherent degree of being hazardous. However, an assessment of risk is omitted, i.e. the question of whether or not there is or can be any relevant exposure at all. One study they have done on Deca-BDE versus RDP and BDP as potential alternatives comes to the conclusion that RDP is indeed a preferable flame retardant (www.cleanproduction.org/library/Green_Screen_Report.pdf).

23 Marzi T, Beard A (2006): *The ecological footprint of flame retardants over their life cycle- A case study on the environmental profile of new phosphorus based flame retardants. Flame Retardants 2006 Conference. Interscience. ISBN 0954121678. pp. 21-30*



A case study from Japan:

HCA (DOPO, see chapter 5) does neither generate phosphine gases in combustion, a cause of concern for phosphorus-type flame retardants, nor dioxins and furans. Furthermore, after burning HCA (DOPO), the phosphorus component in the ashes is concentrated in the form of phosphoric acid, so that there are good prospects that this can be recycled into an industrial raw material or into fertilizer. When HCA (DOPO) is used as the flame retardant for printed circuit boards, recycling of this phosphorus should be realizable with a processing step before or after recycling the gold and copper. Further, when halogen compounds are turned into gases by burning, this can cause destruction of the ozone layer in the stratosphere, but there is no such worry with HCA (DOPO). Phosphorus is an indispensable element for humans, animals and plants, being a main component of bones and DNA. Japan agricultural policy is promoting a program for recycling into phosphorus fertilizers. In Japan, the government, private industry, and universities have launched a PHOSPHORUS RESOURCE RECYCLING ASSOCIATION. Sanko has joined this association as a HCA (DOPO) manufacturer. This association and also farmers have great expectations for a phosphorus recycling system that is to be completed in the near future. (Source: Sanko Corporation)

In addition, there have also been various independent, third party evaluations of halogen-free flame retardants as part of environmental programmes initiated by authorities, agencies or NGOs. The majority of these studies specifically assess alternatives to major brominated flame retardants. These reports sometimes come to different conclusions on the same products, because of different criteria used and because not all authors had the same information available. In various studies the data generated by the manufacturers have not been included. Examples are:

- An overview by ChemSec can be found at www.chemsec.org/rohs/alternative-flame-retardants and a market overview of products with non-halogenated flame retardants is here <http://www.chemsec.org/rohs/market-overview>
- Washington State Department of Health (2008): Alternatives to Deca-BDE in Televisions and Computers and Residential Upholstered Furniture. Department of Ecology State Washington. <http://www.ecy.wa.gov/biblio/0907041.html>
- German UBA 2001: Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals Volume I: Results and summary overview <http://www.umweltbundesamt.de/uba-info-medien/dateien/1988.htm>
- Danish EPA: Environmental Project no. 1141, 2007, Deca-BDE and Alternatives in Electrical and Electronic Equipment <http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf>
- An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD). March, 2006 Prepared for: The Jennifer Altman Foundation, By Gregory Morose <http://sustainableproduction.org/downloads/AlternativestoTBBPAandHBCD.pdf>
- Illinois Report: "Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues", Illinois Environmental Protection Agency, March 2007 <http://www.epa.state.il.us/reports/decabde-study/index.html>
- European Chemicals Bureau (2007): Review on production processes of decabromodiphenyl ether (Deca-BDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to Deca-BDE. http://ecb.jrc.it/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf

8 Common Fire Tests for E&E Materials

Limiting Oxygen Index (LOI)

In this vertical burn test the specimen is mounted in a cylinder which is supplied with an oxygen and nitrogen mixture from the bottom. The LOI value is the lowest oxygen concentration which will sustain burning of the specimen. A pilot flame from the top is used for ignition. In contrast to other vertical tests, the specimen burns downwards. The LOI value gives a approximate indication how well a material burns, e. g. LOI of around 20 (the natural concentration of oxygen in air is 21 %) and below indicate easily ignitable materials. These standards define the LOI method:

ASTM D 2863,
BS ISO 4589-2,
NES 714.



UL 94

The UL 94 test is the most commonly referenced test in the E&E sector. It is a good measure of flammability of materials by a small ignition source like a match, a candle or similar – the pilot flame has an energy output of 50 W. The sample can be oriented horizontally or vertically, the latter being the more challenging test. The classification result depends on how long the specimen continues to burn after removal of the pilot flame and whether a cotton piece below is ignited by flaming droplets. The test is defined in these standards:

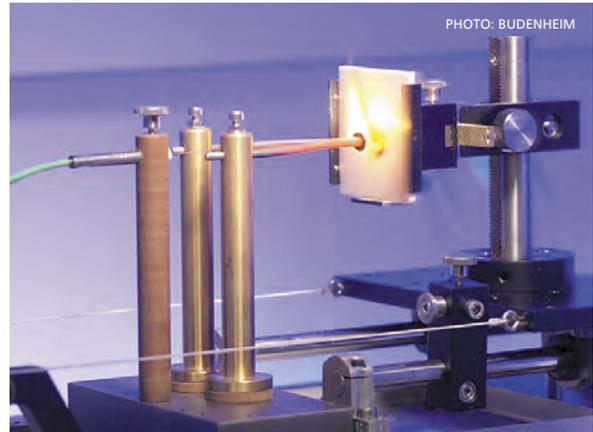
Underwriters' Laboratories (UL) 94,
ASTM D 3801,
IEC 60695-11-10,
IEC 60707,
ISO 1210.



GWT

The glow wire test (GWT) uses a heated resistance wire which is pressed against the specimen for 30 sec, then withdrawn. For a given glow wire temperature, the test criterion is whether the specimen ignites on contact (or in the 30 sec after withdrawal) and whether droplets can ignite a filter paper below the specimen. The glow wire ignition temperature (GWIT) relates to the ignition of the sample where only a flame of very short duration is permitted (< 5 sec). The glow wire flammability index (GWFI) indicates the temperature where the occurrence of flames is less than 30 sec. The test is specified in these standards:

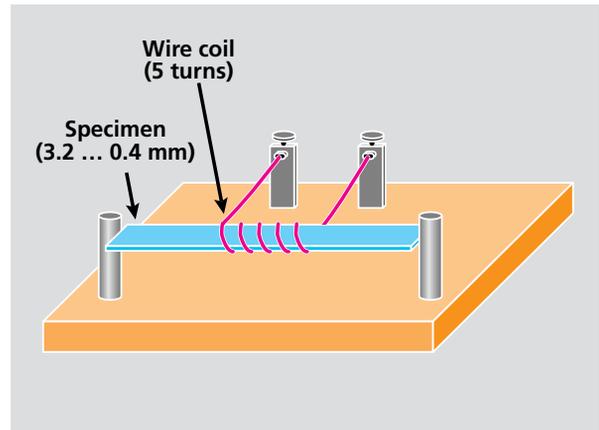
IEC 60695-2-10 ... 13.



Hot wire index (UL 746C)

The hot-wire ignition performance is expressed as the mean number of seconds needed to either ignite standard specimens or burn through the specimens without ignition. The specimens are wrapped with resistance wire that dissipates a specified level of electrical energy. Performance level categories (PLC) from 0 to 5 are defined depending on the time to ignition (> 120 sec to < 7 sec).

<http://www.ul.com/plastics/746C.html>



Definition of UL 94 Vertical test categories:

Class V0		V1	V2	n.r.
Afterflame time	< 10 s	< 30 s	< 30 s	> 30 s
Afterflame time, sum for 10 applications of flame	< 50 s	< 250 s	< 250 s	> 250 s
Ignition of cotton	No	No	Yes	Yes

9 List of Abbreviations

ABS	Acrylonitrile butadiene styrene copolymers	MC	Melamine cyanurate
AOH	Aluminium-oxide-hydroxide	MDH	Magnesium-dihydroxide
ATH	Aluminium-tri-hydroxide	MPP	Melamine polyphosphate
BDP	Bis-phenol A bis (diphenyl phosphate)	NEMA	National electrical manufacturers association
BFR	Brominated flame retardant	NGO	Non-governmental organization
CAF	Conductive anodic filament	NMI	N-methylimidazole
CTE	Coefficient of thermal expansion	OEM	Original equipment manufacturer
CTI	Comparative tracking index	PBT	Persistent, bioaccumulative, and toxic or (different meaning) Polybutyleneterephthalat
Df	Dissipation factor	PA	Polyamide
DGEBA	Diglycidyl ether of bisphenol-A	PC	Polycarbonate
DICY	Dicyandiamide	PCT	Pressure cooker test
Dk	Dielectric constant	PET	Polyethyleneterephthalat
DOPO	Dihydro-oxa-phosphaphenantrene-oxide	PPO	Polyphenylene oxide
DOPO-HQ	Dihydro-oxa-phosphaphenantrene-oxide-hydrochinon	PWB	Printed wiring board (synonymous to printed circuit board)
DSC	Differential scanning calorimetry	RDP	Resorcinol bis (diphenyl phosphate)
E&E	Electric and electronic	RDX	Reorcinol bis (dixylenyl phosphate)
EFRA	European Flame Retardants Association	REACH	Registration, evaluation and authorisation of chemicals
EVA	Poly-ethyl-co-vinyl acetate	RoHS	Restriction of certain hazardous substances in electric and electronic equipment
FPC	Flexible printed circuit	SAN	Poly-styrene-acrylonitrile copolymer
FR	Flame retardant	Tg	Glass transition temperature
GWFI	Glow wire flammability index	TGA	Thermogravimetric analysis
GWIT	Glow wire ignition temperature	TPP	Tri-phenyl phosphate
GWT	Glow wire test	UL	Underwriters Laboratories
HDT	Heat deflection temperature	vPvB	Very persistent, very bioaccumulative
HFFR	Halogen-free flame retardant	WEEE	Waste of electric and electronic equipment
HIPS	High impact polystyrene		
HTN	High temperature nylon		
IEC	International electrotechnical commission		
LOI	Limiting oxygen index		
LSFOH	Low smoke – flame retardant – zero halogen		



10 Contributing Companies

CONTACT DETAILS

PRODUCTS

Adeka Palmarole

Adeka Palmarole
103 Rue de Strasbourg
68300 Saint Louis – France
Phone: +33 3 89897350
www.adeka-palmarole.com

bisphenol A bis (diphenyl phosphate) (ADK STAB)
diphenyldiol bis (diphenyl phosphate) (ADK STAB)
P/N intumescent systems (ADK STAB)

BASF

BASF Schweiz AG
Klybeckstrasse 141
4057 Basel – Switzerland
Phone: +41 61 636 11 11
www.plastic-additives@basf.com

melamine cyanurate (Melapur[®] MC)
melamine polyphosphate (Melapur[®] 200)
melamine phosphate (Melapur[®] MP)
NOR HALS (Flamestab[®] NOR[™] 116)

Budenheim

Chemische Fabrik Budenheim KG
Rheinstraße 27
55257 Budenheim - Germany
Phone: +49 6139 89 0
E-mail: material-ingredients@budenheim.com
www.budenheim.com

ammonium polyphosphates (FR CROS[™])
melamine phosphates (Budit[™])
melamine polyphosphates (Budit[™])
melamine cyanurates (Budit[™])
melamine borate (Budit[™])
intumescent systems (Budit[™])

Catena Additives

Catena Additives GmbH & Co. KG
Neue Bergstrasse 13
64665 Alsbach-Haehnlein – Germany
Phone: +49 6257 5079 164
E-mail: t.dave@catena-additives.com

melamine-poly(aluminum phosphate) (Safire[®] 200)
melamine-poly(zinc phosphate) (Safire[®] 400)

Clariant

Clariant International Ltd.
Business Line Flame Retardants
Rothausstrasse 61
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Phone: +41 61 469 7912
E-mail: adrian.beard@clariant.com
www.exolit.com

metal phosphinates (Exolit[®] OP)
ammonium polyphosphate and
intumescent formulations (Exolit[®] AP)
red phosphorus, also in formulations (Exolit[®] RP)

Dartex Coatings

Dartex Coatings Ltd.
Acton Close Long Eaton
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E-mail: richard.haxby@dartexcoatings.com
www.dartexcoatings.com

PU coated textiles
halogen free flame retardants (MelaphosFR[™])

Delamin

Delamin Ltd.
4 Royal Scot Road Pride Park
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www.delamin.com

melem (Delacal 420)

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Phone: 00800-74663376
E-mail: info-europe.DEP@dsm.com
www.dsm.com/en_US/html/dep/home_dep.htm

PRODUCTS

flame retarded polymer compounds

FRX Polymers

FRX Polymers, Inc.
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Phone: +1 978 244 9500
E-mail: info@frxpolymers.com
www.frxpolymers.com

polyphosphonate homopolymer (FRX100™)
copolymer (FRX CO 35™)
oligomer (FRX OI 3101)
oligomer (FRX OI 5000)

Italmatch

Italmatch Chemicals S.p.A.
Via P. Chiesa 7/13
I-16149 Genova – Italy
Phone: +39 010 642081
E-mail: n.gatti@italmatch.it
www.italmatch.it

metal phosphinates (Phoslite™)
melamine cyanurate (Melagard™)
melamine phosphate (Melagard™)
melamine borate (Melagard™)
red phosphorus (Masteret™)

KIT

Karlsruhe Institute of Technology
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E-mail: manfred.doering@kit.edu
www.katalyseundmaterialien.de

Research and Development
halogen-free flame retardants

Krems Chemie

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3500 Krems – Austria
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E-mail: office@kccs.at
www.kccs.at

DOPO Dihydro-oxa-phosphaphenanthren-oxide
phosphatester FSMP
melaminphosphate T

LANXESS

LANXESS Deutschland GmbH
BU Functional Chemicals
51369 Leverkusen – Germany
Phone: +49 214 30 37201
E-mail: heiko.tebbe@lanxess.com
www.phosphorous-chemicals.com

triphenyl phosphate (Disflamoll® TP)
cresyl diphenyl phosphate (Disflamoll® DPK)
tricresyl phosphate (Disflamoll® TKP)
reactive P/N polyol (Levagard® 4090 N)
dimethyl propane phosphonate (Levagard® DMPP)

Nabaltec

Nabaltec AG
Alustrasse 50 – 52
D-92421 Schwandorf
Phone: +49 9431 53-458/-462/-467
E-mail: fillers@nabaltec.de

aluminium hydroxide (Apyral®)
boehmite (Apyral® AOH)
magnesium hydroxide (Apymag®)

CONTACT DETAILS**PRODUCTS**

Perstorp

Perstorp AB
Industripark
284 80 Perstorp – Sweden
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E-mail: david.james@perstorp.com
www.perstorp.com

carbon source for intumescent systems (Charmor™)

Rhodia

Rhodia Polyamide
Avenue Ramboz
69192 Saint Fons – France
Phone: +33 4 72 89 28 62
E-mail: florence.schutz@eu.rhodia.com
www.rhodia.com

flame retarded polymers (TECHNYL®)

Rockwood Clay Additives

Rockwood Clay Additives GmbH
Stadtwaldstrasse 44
85368 Moosburg – Germany
Phone: +49 8761 72 150-0
E-mail: rheoinfo@rockwoodadditives.com
www.rockwoodadditives.com

organoclay synergists for HFFR and
FR systems (Nanofil® / Cloisite®)

Thor

Thor GmbH
Landwehrstrasse 1
67346 Speyer – Germany
Phone: +49 6232 636-0
E-mail: jerome.deboysere@thor.com
www.thor.com

organic phosphorus compounds (AFLAMMIT® PCO)
inorganic compounds (AFLAMMIT® PCI)
melamine and nitrogen derivatives (AFLAMMIT® PMN)
intumescent blends (AFLAMMIT® PPN)
liquid flame retardants (AFLAMMIT® PLF)

William Blythe

William Blythe Limited
Bridge Street Church / Accrington
Lancashire BB5 4PD – United Kingdom
Phone: +44 1254 320 000
E-mail: john.williams@williamblythe.com
www.williamblythe.com

zinc hydroxystannate (Flamtard H)
zinc stannate (Flamtard S)



ADEKA
PALMAROLE

delamin

LANXESS
Energizing Chemistry

BASF
The Chemical Company

Unlimited. **DSM**

Nabaltec

Budenheim

FRX
polymers

Rhodia
Chemistry is our world, Responsibility is our way

KIT
Karlsruhe Institute of Technology

CATENA
Additives

ROCKWOOD
ADDITIVES

Italmatch Chemicals

Clariant

HREMS
CHEMIE
Chemical Services

THOR

dartex
coatings

Perstorp
WINNING FORMULAS

williamblythe
quality, chemistry, performance