

FLAME RETARDANTS IN ELECTRIC AND ELECTRONIC APPLICATIONS

pinfa

non-halogenated phosphorus, inorganic
and nitrogen (PIN) flame retardants



pinfa: sustainable fire safety via environmentally friendly flame retardants

pinfa, the Phosphorus, Inorganic and Nitrogen Flame Retardants Association 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).

Fire-safety is at the center of our activities. The main objective of the association is to co-operate with members of the value chain including industry organisations involved in the use of non-halogenated phosphorus, inorganic and nitrogen flame retardants in order to communicate the advantages of the flame retardants technology for the safe use of otherwise easily flammable materials. **pinfa** members also seek the dialogue with stakeholders along the supply chain in order to learn about the technical evolutions and regulatory requirements.

pinfa members believe that their products form an essential part of environmentally compatible fire safety solutions and share the common concept of an ideal flame retardant as one which:

- is not toxic to humans, animals and plants
- does not migrate out of finished products
- does not release additional toxic or corrosive gases in case of fire
- does not impede the recycling of finished articles
- is either degradable or remains neutral in the environment such as naturally occurring substances

For more information, please contact:

Philippe Salémis

pinfa Secretary General

Tel +32 2 676 72 86

GSM +32 476 76 30 28

Fax +32 2 676 73 92

psa@cefic.be

www.pinfa.org

Publisher & Editors

pinfa – Phosphorus, Inorganic and Nitrogen Flame Retardants Association
a sector group of Cefic
Avenue E. Van Nieuwenhuysse 4
B-1160 Brussels

pinfa Editorial Team for this brochure

Thomas Futterer – Budenheim
Reiner Sauerwein – Nabaltec
Maggie Baumann – FRX Polymers
Philippe Salémis – **pinfa**
Antonio Nerone – Dupont
Adrian Beard – Clariant
Yuejiang Liang – Nabaltec
Uli Wietschorke – Adeka

Layout

Edito3

Print

Van der Poorten

October 2017, 3rd edition

pinfa



FOREWORD

Dear reader,

Welcome to this third edition of the pinfa – Flame Retardants in Electronic and Electronic (E&E) applications – brochure. Our aim is to explore the evolution of the PIN Flame Retardants technologies and to report our best knowledge in this captivating and essential field of fire safety and flame retardants. From our perspective, flame retardants are comparable to a discrete fireman always present and close to you.

Members of pinfa share the common vision that sustainable fire safety must be achieved with environmentally friendly flame retardants. To that effect, members of pinfa are committed to continuously improving the environmental and health profile of their flame retardant products. This vision is coupled with a commitment to maintain high fire safety standards across the world, standards which minimize the risk of fire to the general public. The three pillars of pinfa are summarised as follows.



FIRE SAFETY

Phosphorus, Inorganic and Nitrogen (PIN) flame retardants can protect people from fatal or irreversible injury in fire. They are used to improve the fire safety of materials and to meet safety standards in consumer goods, buildings, transport and industry.

PIN flame retardants prevent fire from starting or delay its development, allowing more time for people to escape and fire fighters to intervene on site.

Smoke and toxic fire gases are often the biggest danger in fires because of toxicity, immobilisation of victims and visual inhibition of escape. PIN flame retardants reduce gas emissions by reducing burning intensity during the initial phase of a fire, and tend to ensure lower-smoke density and do not contribute to possible gas corrosivity and smoke toxicity.



ENVIRONMENT AND HUMAN HEALTH

PIN flame retardants are non-halogenated. Our goal is to limit risks to human health and the environment in the production, use and end-of-life of fire-safe products.

We work with environmental groups, regulators, scientists and many others to assess and improve these PIN flame retardant substances across environmental, health benchmarks and circular economy.



COMMITMENT TO COLLABORATION

pinfa works in partnership with stakeholders like regulators, fire safety experts, user industries, NGOs, environmental bodies, consumer associations, and scientists to ensure safe use of flame retardant products. pinfa commits to:

- Building on existing chemical assessment systems, addressing data gaps and improving assessment of exposure
- Accepting that FRs are in most cases persistent in order to be durably effective, and investigating the best ways to manage this while retaining their effectiveness and usefulness
- Accepting that FRs may have some hazardous properties as neat substances, therefore investigating ways to minimise exposure while ensuring they do their important job
- Taking into consideration the full life cycle including e.g. production, end of life, reuse, recycling, disposal and biodegradation
- Taking into account release risk
- Developing appropriate criteria for assessing the safety of inorganic flame retardant components (existing criteria are largely designed for organics)
- Defining how to treat areas where information is not available to get the best possible level of environmental and fire safety.

TABLE OF CONTENTS

1	INTRODUCTION – WHY FLAME RETARDANTS	5
2	WIRE & CABLE	9
2.1	Introduction	9
2.2	History and Standards Development in respect to developments in the area of Halogen free flame retardancy	9
2.3	Flame retardants used for HFFR compounds	10
2.3.1	The mechanism of metal hydroxides as flame retardant	10
2.3.2	How to achieve flame retardancy with metal hydroxides	11
2.4	Current developments in the area of metal hydroxides	12
2.4.1	Processability	12
2.4.2	Surface treatment	12
2.4.3	Nanocomposites / Flame Retardant Synergists	12
2.4.4	Improved morphology of the metal hydroxide	12
2.5	Flame retarded thermoplastic elastomers for cable applications	13
3	ELECTRIC ENCLOSURES	15
3.1	Introduction	15
3.2	PC/ABS blends	17
3.3	Recyclability of FR-PC/ABS composites using non-halogen flame retardants	18
3.4	PPO/HIPS	19
3.5	Battery enclosures cases	19
4	ELECTRIC INSTALLATIONS AND COMPONENTS	20
4.1	Scope and material requirements for electrical components	20
4.1.1	Mechanical properties	20
4.1.2	Electrical properties	21
4.1.3	Fire resistance	21
4.2	Overview of halogen-free FRs for electrical installations	21
4.3	Polymers used in electrical components and suitable FR systems	23
5	PRINTED WIRING BOARDS	24
5.1	Market environment and trends	24
5.2	Technical requirements of FR-4 printed wiring boards	24
5.3	Non-reactive fillers	25
5.3.1	Metal hydroxides	25
5.3.2	Metal phosphinates and polyphosphates	26
5.4	Reactive flame retardants	26
5.5	Amount of Flame Retardant necessary for UL 94 V0 classification	27
6	FUTURE TRENDS AND INNOVATION	28
7	ENVIRONMENTAL AND TOXICOLOGICAL PROPERTIES OF NON-HALOGENATED FLAME RETARDANTS	30
7.1	REACH	31
7.2	RoHS and WEEE	32
7.3	ENFIRO	33
7.4	US-EPA DfE	33
7.5	GreenScreen	34
7.6	Ecolabels	34
8	COMMON FIRE TESTS FOR E&E MATERIALS	35
	CONCLUSIONS	37
	LIST OF ABBREVIATIONS	38
	MEMBERS OF PINFA	back cover



INTRODUCTION – WHY FLAME RETARDANTS

WHAT ARE FLAME RETARDANTS?

HOW DO THEY CONTRIBUTE TO FIRE SAFETY?

This brochure describes the contribution to fire safety and the technical properties and advantages of a class of flame retardant substances designed as PIN flame retardants.

These PIN FRs are applied in key electrical and electronic 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 (non-halogenated) PIN flame retardants chemistries is now available. These chemistries are designed to respond to current expectations in terms of sustainable fire safety with environmentally friendly flame retardants.

Flame retardants have become a range of chemicals which receive more and more scientific and public attention. The discussions about flame retardants started, when some brominated flame retardants (BFRs) became a topic of environmental concern in the early 1990ies.,

when it was discovered that some BFRs could form halogenated dioxins and furans under severe thermal stress or when they were burnt in accidental fires or uncontrolled combustion¹. Findings in the environment and biota and the suspicion that some flame retardants bio accumulate in organisms have added to these concerns²⁻³⁻⁴⁻⁵. Meanwhile, the environmental and health properties of not only BFRs but also other types of flame retardants have been studied extensively such as to determine which FR's regardless of their chemistry could give a valid alternative in term of efficacy and environmental fates.

What are “PIN” flame retardants⁶? 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.

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 Ikonomou 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 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

- Nitrogen-based flame retardants are typically melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate, melem, melon). They are often used in combination with phosphorus based flame retardants.

Intumescent flame retardants are an example of a typical mechanism for non-halogenated 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, polyester- and epoxy resins.

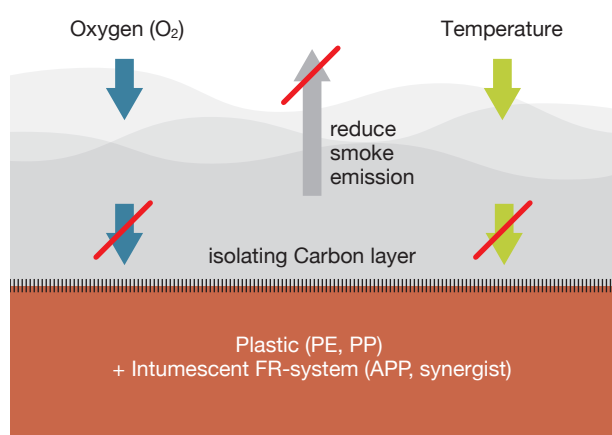


Figure 1-1
The mechanism of Intumescent flame retardant systems which are typically a combination of phosphorus and nitrogen compounds

There is not a universal flame retardant (as there is not a universal plastic, or a universal metal usable everywhere for every application). Each material has its own properties and compatibilities. This applies to flame retardants too.

Figures 1-2 and 1-3 show the current European and worldwide consumption of different flame retardant types. - One may notice the dramatic increase of more environmentally friendly flame retardants. In addition, Figure 1-5 illustrates the variety of polymer types (plastics) used in Europe. FRs need to match polymer properties and specific processing requirements. This variety explains why so many different FR technologies are necessary in E&E and other applications.

**Western + Central & Eastern Europe:
Flame Retardants Market Size, by type**

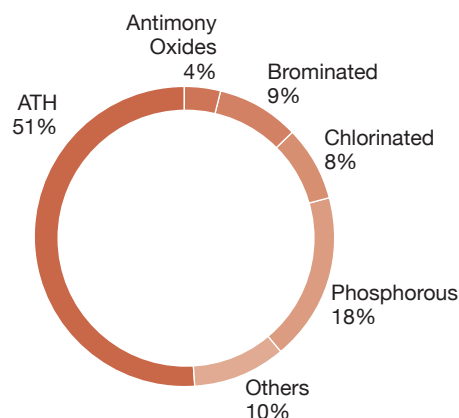


Figure 1-2
The current consumption of flame retardants in Europe, which amounted to a total of 498,000 metric tons (Market and Market). PIN FRs are shown in different green and blue shades (2015)
Source: Courtesy from MarketsandMarkets

Flame retardants market size, by type, 2014-2021 (kiloton)

Type	2014	2015	2016	2021	CAGR (2016-2021)
ATH	799.5	842.4	888.0	1.186.6	5.97%
Antimony Oxide	208.7	218.5	228.3	296.0	5.33%
Brominated	476.5	499.5	523.4	684.9	5.53%
Chlorinated	170.6	178.3	186.4	239.4	5.13%
Phosphorous	351.7	375.4	401.0	565.7	7.12%
Others	233.0	247.5	262.4	358.9	6.46%
Total	2,240.0	2,361.7	2,489.5	3,331.5	6.00%

Table 1-1
Estimated Market Size reflecting the evolution of FR uses to increase fire safety
Source: Courtesy MarketAndMarket

2015 global market share by volume

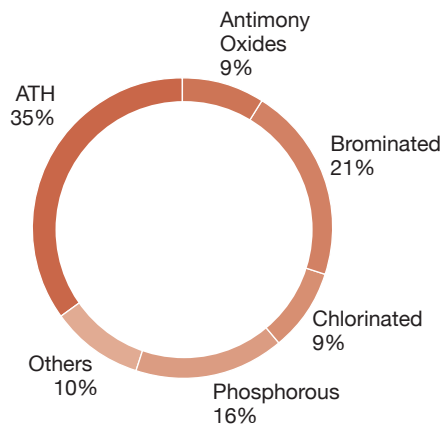


Figure 1-3

The current Global consumption of flame retardants, which amounted to a total of 498,000 metric tons (Market and Market) (2015)

Source: Courtesy from MarketsandMarkets

European Plastics Demand* by Resin Type (2011)

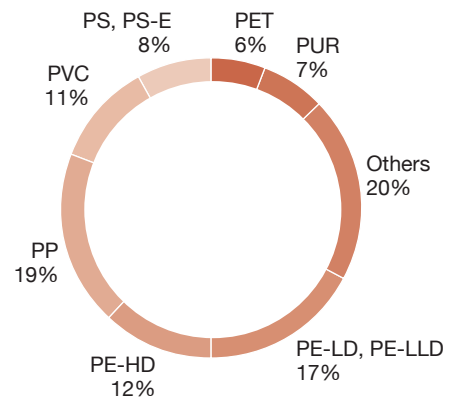


Figure 1-4

* EU-27 + N/CH incl. Other Plastics (- 5,7 Mtonne)

Source: PlasticsEurope Market Research Group (PEMRG)

Evolution of European plastics* demand by polymer type

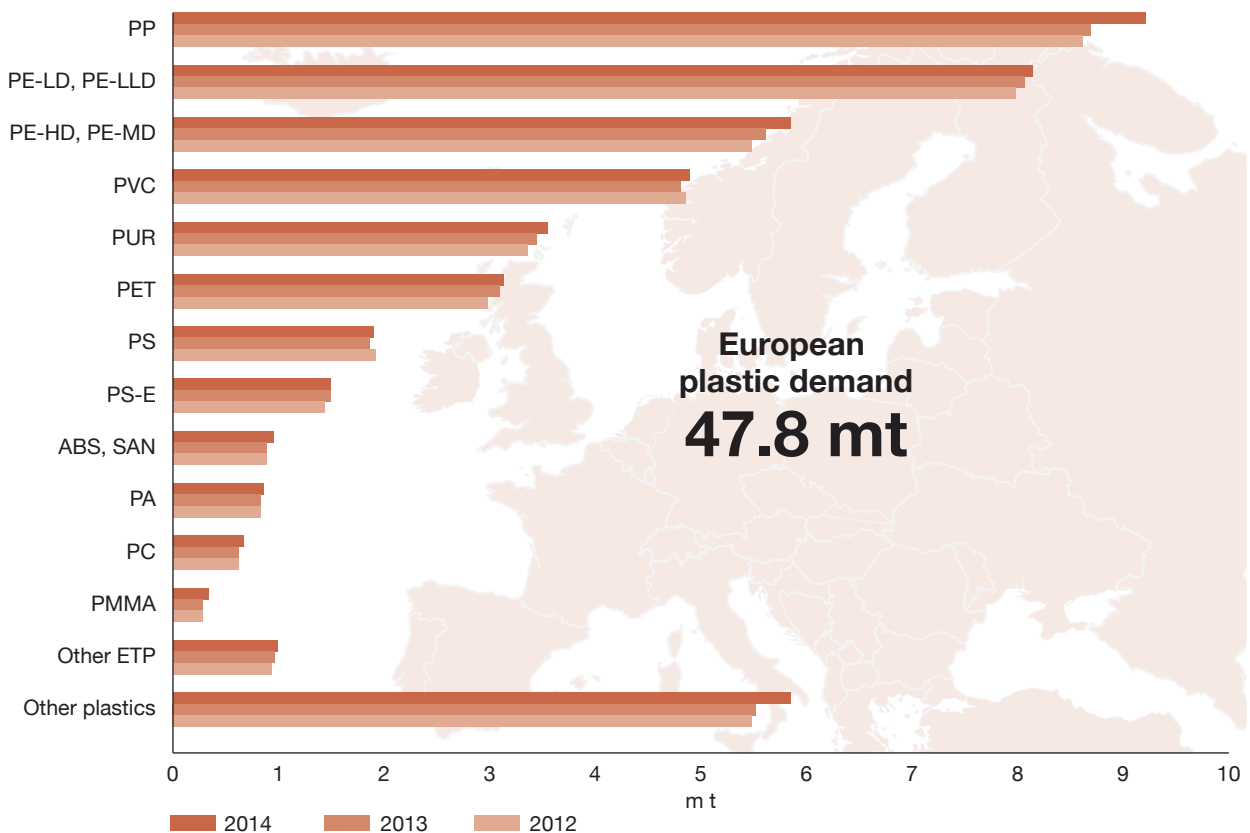


Figure 1-5

Plastics demand by polymer type in Western Europe in 2014

* Includes plastics materials (thermoplastics and polyurethanes) and other plastics (thermosets, adhesives, coatings and sealants).

Does not include the following fibers: PET-, PA-, PP- and polyacryl-fibers.

Source: PlasticsEurope

In 2014 about 12% of all used FRs in Europe were for electronic and appliances and another 20% for wires and cables. Largest use is in Building and construction (37%). Over the past decade, the fate of electronic waste and the contained hazardous materials have gained increasing political attention and have led to the WEEE⁷ and RoHS⁸ 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. The circular economy project will eventually call for even better profiled substances allowing easy recovery and reprocessing of the materials.

pinfa is fully committed and actively involved in the circular economy projects. For example, at the date of the publication of this brochure, pinfa is currently participating in projects aimed at defining recyclability in terms of amount and number of recycling cycles without properties' alteration of the final product. One of these projects is lead by the Fraunhofer LBF Institute with the support of the German Ministry for Industrial Development.

Several regions of the world have implemented regulations similar to RoHS legislation. This has increased the interest in PIN flame retardants, not only in engineering plastics for housing and components, but also in thermoset resins for example in printed wiring board substrates. In addition to legal requirements, ecolabels have been introduced since the 1970's as voluntary measures in order to promote environmentally conscious 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 there are about 25 ecolabel organizations and schemes.

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 most 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 Eco labelling 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"⁹ on endocrine effects from BFRs with participants from industry (including the BFR manufacturers association BSEF), academia and regulators came to the conclusion that "Efforts must be promoted to search for alternatives to the brominated flame retardants that persist in the environment."

Due to this regulatory and environmental pressure, a number of original equipment manufacturers (OEMs) have developed alternative fire safety solutions using PIN flame retardants.

⁷ Directive 2002/96/EC on Waste of Electric and Electronic Equipment

⁸ Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment

⁹ Trachsel M (2007): Consensus Platform "Brominated Flame Retardants", National Research Program "Endocrine Disruptors". Swiss National Science Foundation

2

WIRE & CABLE

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 corrosion ability.

The excellent performance of so called non-halogenated flame retardant or low-smoke, zero Halogen (LSFOH) cables versus traditional cable designs especially in regard to smoke density, and to smoke toxicity and acidity have addressed successfully 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 2-1*.

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 WEEE¹⁰ and RoHS¹¹ is a further requirement for flame retardant cable compounds.

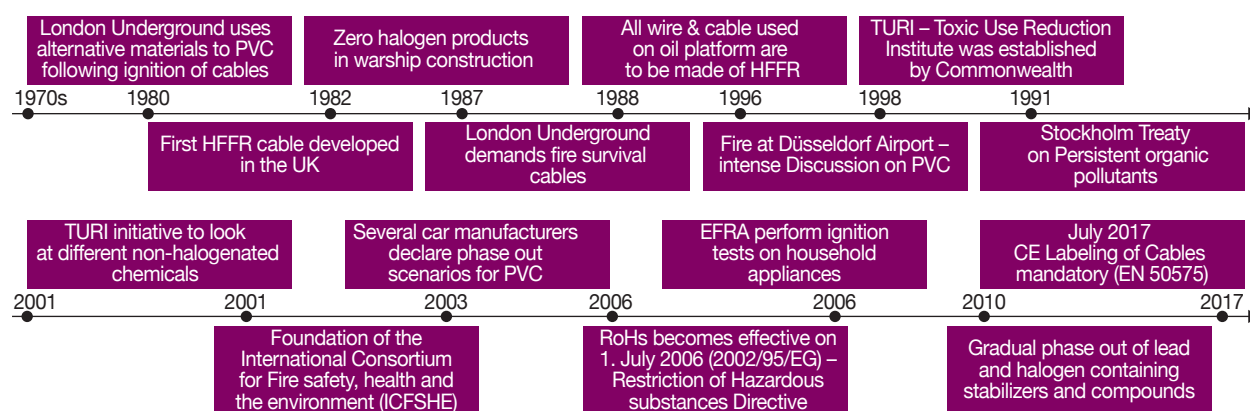


Figure 2-1

Key events which lead to the development of halogen free cable development (Nabaltec)

¹⁰ Directive 2002/96/EC on Waste of Electric and Electronic Equipment

¹¹ 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.

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.

Flame retardant	Polymers
Aluminium-tri-hydroxide (ATH) Magnesium-dihydroxide (MDH) Boehmite (AOH) (aluminium-oxide-hydroxide)	Low density polyethylene Poly-ethyl-co-vinyl acetate Polyolefin elastomers
Phosphorus flame retardants	Used in fire resistant coatings for cables
Zinc borate	Synergist with ATH
Red phosphorus	Polyolefins
Phosphate esters (eg. Tricresyl Phosphate TCP)	Rubber
Melamine cyanurate, melamine phosphate	Polyamides Polypropylene
Ammonium polyphosphates	Polyolefins

Table 2-1

Overview of the different flame retardants used in HFFR cable compounds

2.3.1 THE MECHANISM OF METAL HYDROXIDES AS FLAME RETARDANT

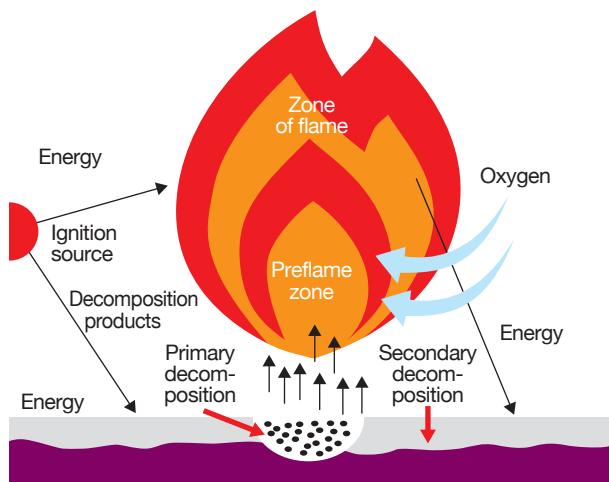


Figure 2-2

Flame retardancy mechanism of metal hydroxide (Nabaltec)

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

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 2-3). The maximum processing temperatures range from 200 °C (ATH) to 300 °C for MDH and 320 °C for AOH.

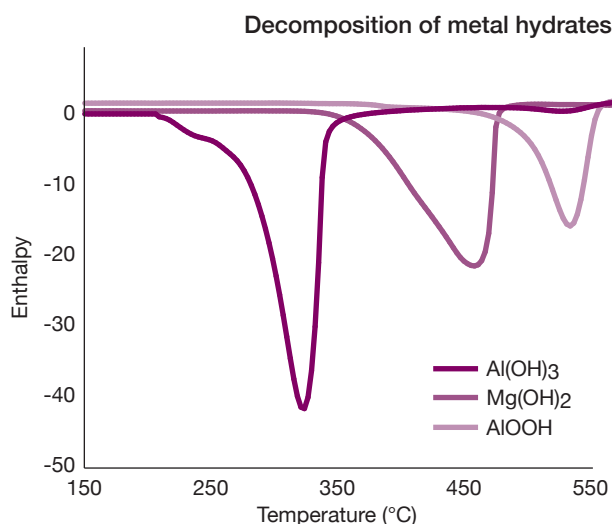


Figure 2-3
Decomposition of metal hydroxides versus temperature (Nabaltec)

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 2-4 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)

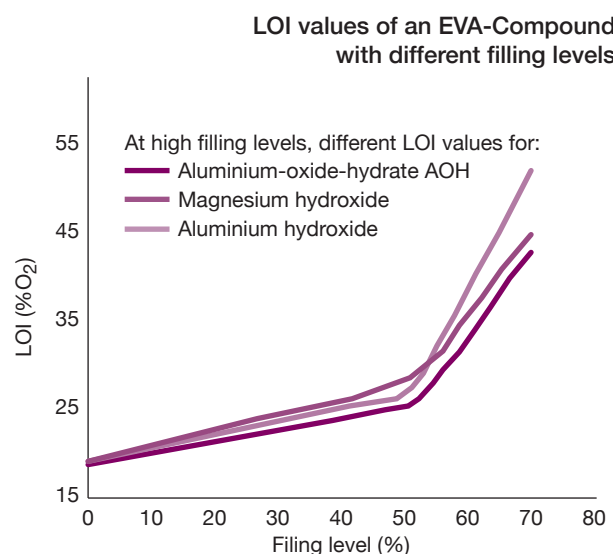


Figure 2-4
LOI values of an EVA compound with different filling levels

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 which directly influence chemical reactions in the flame or in the bulk polymer (radical generators and char forming phosphorus containing flame retardants respectively).

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 into 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 still today 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 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, 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 / FLAME RETARDANT SYNERGISTS

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, hectorite or sepiolite) has been modified with organic salts to improve polymer compatibility and promote delamination of filler stacks 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 3-5%. The content of the traditional flame retardant in these compounds can be reduced down to 50% versus 60-65% in absence of the organoclay for moderate and standard flame retardant requirements. To fulfil higher classifications of Reaction to Fire cables, the total loading including nanocomposite synergists are in the range of 65%.

The function of the organoclay and other nano fillers as flame retardant synergist 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.

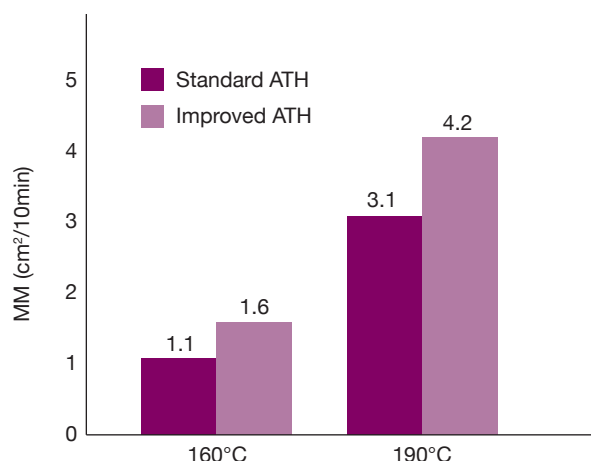


Figure 2-5

Melt volume rate for EVA (19% VA) compound filled with 60 wt.-% ATH, Aminosilane coupled

Figures 2-5 and 2-6 show important parameters for the extrusion of an insulated copper wire with a PE/EVA compound containing 60% ATH. Improved ATH is compared to its predecessor product (standard 4 m²/g ATH).

The significantly reduced values for diehead pressure and diehead melt temperature for the improved ATH enable an approximate 30% increase in extrusion speed.

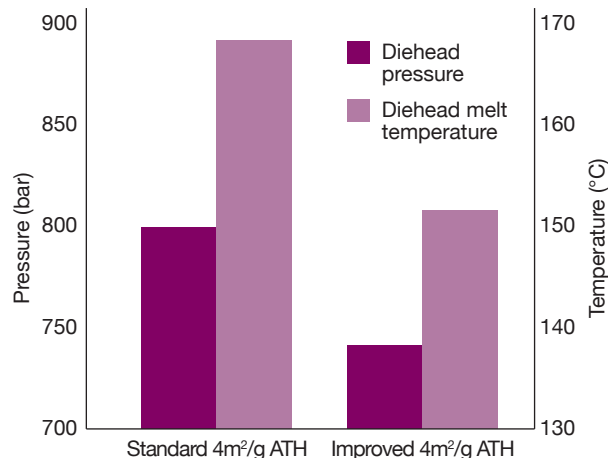


Figure 2-6

Diehead pressure and diehead melt temperature at:

- 0.5 mm² copper wire (single, round)
- die diameter 1.4 mm
- insulation thickness approx. 0.35 mm
- line speed 650 m/s

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) 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 can effectively balance mechanical properties and flame retardancy in TPEs. Polyphosphonates have also been found to perform well in TPE-E systems.

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 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 TPE-Es are used for cable extrusion, wire coating, connectors, conveyor belts or corrugated pipes. Polyphosphonates demonstrate good synergy with metal phosphinates for improved flame retardancy and mechanical properties and help improve the surface appearance of the elastomer cable.

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 2 ... 3 µm) with nitrogen synergists the classification UL 94 V-0 is achieved. The same is achieved with appropriate formulations containing melamine cyanurate. By the addition of a further anti-ripping agent like talc, dripping of test specimen can be prevented. Applications for flame retarded TPU are cable extrusion, injection moulding of artificial leather. Polyphosphonates are being used in TPU extrusion applications especially if transparency or translucency is desired. Polyphosphonates also work synergistically with melamine cyanurate and metal phosphinate for improved flame retardancy and mechanical properties.

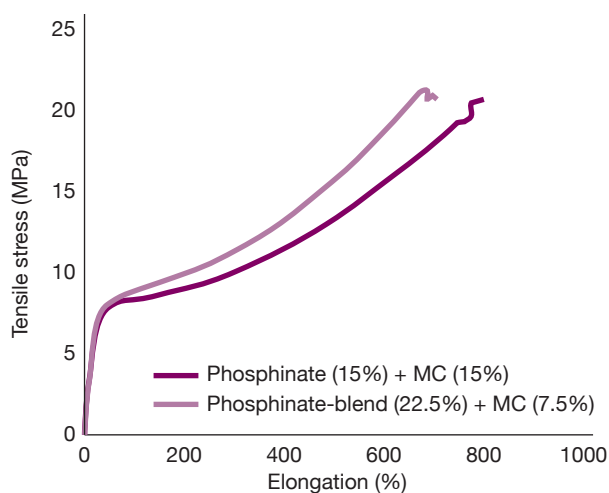


Figure 2-7
Stress-strain diagram (DIN 53504, S2,
200 mm/min) of flame retarded polyether-TPU
(Shore A 87)

MC = Melamine Cyanurate.

	TPE-E (Shore D 55)	TPE-E (Shore D 40)
Al-Phosphinate (20 - 22%)		
UL 94-test (1.6 mm)	V-0	V-1
GWIT 1 mm (°C)	775	650
GWFI 1 mm (°C)	960	900
Tensile strength (kJ/m2) (DIN 53504*)	20.5	16.9
Elongation at break (%) (DIN 53504*)	322	547
Notched impact str. (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 2-2
Fire performance and mechanical characteristics
of thermoplastic elastomers with phosphinate
flame retardants

* Specimen S2, 50 mm/min

Sample ID	Ester based TPU _{xw}	Formula 1	Formula 2	Formula 3	Ester based TPU	Formula 4	Formula 5
Ether based TPU	100	70	72.5	77			
Ester based TPU						72.5	77
DEPAL (wt%)		15	10	6		10	6
Phosphonate oligomer 5000 Mw (wt%)			2.5	2		2.5	2
MC (wt%)		15	15	15		15	15
Wt% P in blend		3.5	2.6	1.6		2.6	1.6
UL 94 at 1.6mm		V2	V0	V0		V0	V0
Shore A	85	94	93	92	85	93	93
Modulus, MPa		59	34	33		38	35
Tensile strength, MPa	45	> 12	> 15	> 16	49	> 22	> 22
Elongation@ break %	510	> 460	> 460	> 460	530	> 460	> 460
MVR (200°C/2.16kg)	7	7	6	7	7	6	5

Table 2-3
Fire performance and mechanical characteristics of thermoplastic elastomers
with phosphinate flame retardants according to polymer type.

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. Common polymer resins are high impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate / ABS blends (PC/ABS), polyphenylene ether / HIPS blends (PPE/HIPS) and polycarbonate. (PC).

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**
If a higher Heat Deflection Temperature (HDT) is required consider polyphosphonate
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 RoHS¹² and WEEE¹³ directives.

The combination of requirements can be fulfilled by using phosphorus based flame retardants, especially the aromatic phosphate esters presented in *Tables 3-1* and *3-2*.

¹² Directive 2002/96/EC on Waste of Electric and Electronic Equipment

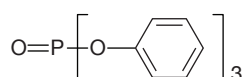
¹³ Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment

Properties	TPP	RDP	BDP	Resorcinolbis 2,6-dixylenyl phosphonate	Polyphosphonate co-carbonate
Chemical name	Triphenyl phosphate	Resorcinol bis (diphenyl phosphate)	Bisphenol A bis (diphenyl phosphate)	Resorcinol bis (2,6-dixylenyl phosphate)	Polyphosphonate co-carbonate
CAS number	115-86-6	57583-54-7	181028-79-5	139189-30-3	77226-90-5
Appearance	Solid	Liquid	Liquid	Solid	solid
Phosphorus content (%)	9,5	10,8	8,9	9,0	3,8-10,8
Density at 25°C (g/cm3)	-	1,31	1,26	-	1.21
Viscosity at 25°C (mPa.s)	Melting point 49°C	600	13000	Melting point 92°C	Tg 105 degrees C-130 degrees C

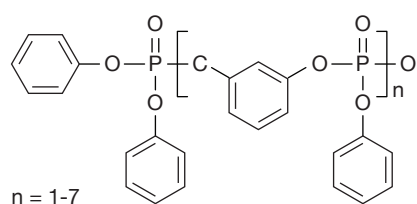
Table 3-1

PIN flame retardants for electronic enclosures

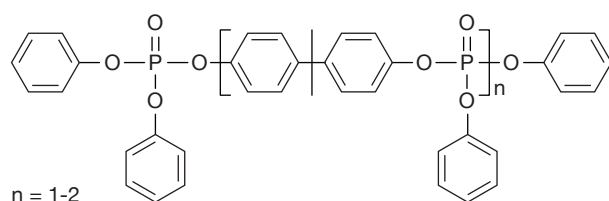
Triphenyl phosphate (TPP)



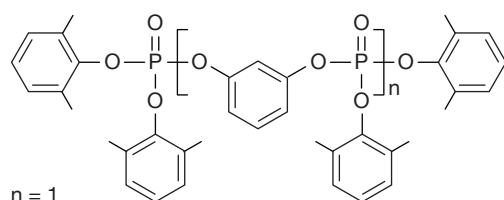
Resorcinol bis (diphenyl phosphate) (RDP)



Bisphenol A bis (diphenyl phosphate) (BDP)



Resorcinol bis (2,6-dixylenyl phosphate)



Wt. Loss	2%	5%	10%
TPP	202	220	235
RDP	288	325	360
BDP	273	327	393
2,6	295	340	395
Polyphosphonate co carbonate		430	

Table 3-2

TGA of phosphate esters

** 10°C/minute ramp rate in Nitrogen*

These four phosphorus compounds are non-halogenated 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. The fifth product, Polyphosphonate- Co-Carbonate is a polymeric form of Phosphorus therefore exhibits permanent FR and is non-migrating.

3.2 PC/ABS BLENDS

TPP, RDP, BDP, Resorcinol 2,6 and Polyphosphonate co-carbonate 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 V 0 rating with these products at 8 – 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%. Polyphosphonate co carbonate is added at levels of 15-20% with a co additive and enhance the performances to fire.

Various results about TPP, RDP, BDP Resorcinol 2.6 and Polyphosphonate co carbonate in PC/ABS blends are presented in *Tables 3-3, 3-4 and 3-5*.

PC/ABS 4/1	% FR Additive	UL94* (1.6mm)
RDP	9	V-0 (1.5)
BDP	12.3	V-0 (1.5)
PX-200	11.5	V-0 (1.5)
TPP	14	V-0 (1.7)
Polyphosphonate co carbonate	15-20	V-0 (1.5)

Table 3-3
UL-94 flammability in FR-PC/ABS (4/1)
* avg. flame time

PC/ABS (4/1)	FR Level	Tensile Strength	Flexural Modulus	Flexural Strength	HDT 1,80 MPa	Notched Izod Impact
Flame Retardant	%	N/mm2	MPa	N/mm2	°C	J/m
RDP	9	53,3	1586	81,4	83.3	651
BDP	12.3	55,6	1655	84,8	81.4	496
PX-200 (?)	11.5	54,0	1650	83.8	85.9	753
TPP	14	46,0	2620	82,7	67.8	123
Polyphosphonate Co-carbonate	20				120 degrees C	

Table 3-4
Physical Properties of UL94/V0 Rated FR-PC/ABS

FR-PC/ABS – V0	Additive	MFI
Composites	Level %	g/10 min. 260°/2.16kg
BDP	12.3	26.9
RDP	9	18.7
Resorcinol 2,6	11.5	25.9
Polyphosphonate co carbonate	20	

Table 3-5
Melt viscosities of V0 rated FR-PC/ABS composites

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 feedstream 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 sales¹⁴. 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, Resorcinol 2.6).

For current non-halogen options for FR-PC/ABS, to present properties which are relevant for performance in a realistic recycling program 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 stabilizers. Tables 3-6, 3-7 and 3-8 to present properties which are relevant for performance in a realistic recycling program 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 stabilizers.

Additive(s)	RDP	BDP
Cycle 1	V-0	V-0
Avg. flame time	1	1.1
Cycle 5	V-0	V-0
Avg. flame time	0.9	1.1

Table 3-6
Flammability of recycled FR-PC/ABS according to UL 94 Flammability

J/m		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
BDP	B1	491	491	512	512	532
RDP	R2	619	534	619	534	577

Table 3-7
Izod Impact (3.2 mm) of recycled FR- PC/ABS

ASTM-1238, 260°C/2kg		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 3-8
Recycling Influence on Melt Flow

¹⁴ "The End of the Computer as we Know it", Wall Street Secrets Plus Newsletter, Vol. 2, No. 58, July 22, 2005

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, stabilizers can be used.
- 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(PX-200) FRs are less susceptible to hydrolysis but will show PC polymer degradation eventually. Polyphosphonate Co- carbonates show good hydrolytic stability because they the phosphorus is bound in the backbone.
 - RDP analogs displayed instability earlier in the testing exposure regime but the addition of stabilizers, substantial improvements are seen.

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 V 0 rating are 30-70%; these blends also contain 10-20% of TPP, RDP , BDP and Resorciol 2,6.

Physical property	HIPS	HIPS + Deca + Sb ₂ O ₃	PPO/ RDP	PPO/ RDP
Loading, wt. %		20	40	35
UL-94, 3.2 mm		V-0	V-0	V-1
Tensile strength, N/mm ²	21.8	20.7	25.2	31.7
Izod, J/m	80.1	64.1	64.1	69.4
Tg, °C	88	86	64	84

Table 3-9

Combustion and physical properties of phosphorus-based flame retardants in HIPS

3.5 BATTERY ENCLOSURES CASES

e-mobility, smart phones, computers, etc.. have generated a continuously growing demand for high density energy storage and quick energy restitution, pushing forward the innovations in the batteries technologies.

Increasing energy density brings increased hazards of fire initiated by overheating or short circuits requesting better fire safety and fire protection of the battery enclosures. Intensive research and development is going on in this field to achieve fire safety of the typical enclosures with environmentally friendly flame retardants. For example if polyamides are used then phosphinates pin fr could be used to retard the fire.

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 dish washers, 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	
PCB 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:

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 wperform 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. UL94 V-0 for example, is probably the most commonly used flammability requirement anywhere in the world.

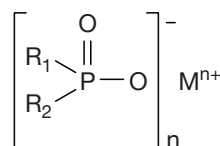
Depending on the end application, for IEC standards approval is based on either material testing or on testing the finished component, whereas under UL tests are always performed on the material only. Despite the differences between these test methods one common denominator in all tests is the specified 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 NON-HALOGENATED FRs FOR ELECTRICAL INSTALLATIONS

Metal phosphinates

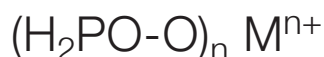
Metal phosphinates: These are well suited for glass fibre reinforced polyamides and polyesters and are added at levels of about 20% - often combined with N-synergists. Key aspects are a high phosphorus content (> 23%), no affinity to water and a good thermal stability (up to 320°C) which make them compatible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



General structure of Phosphinates

Inorganic Metal phosphinates

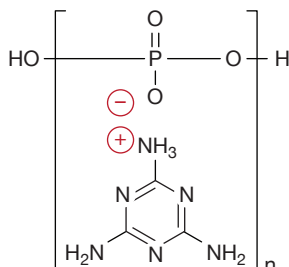
Inorganic Metal phosphinates are an old known chemical class recently introduced as active FR component in different proprietary synergistic blends under the Phoslite® trade name. Used in different polymers, especially Polypropylene homo and copolymer for UL-94 V2 applications at some percent loading,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



General structure of Inorganic phosphinates

Melamine Polyphosphate

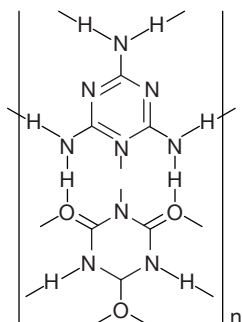
Melamine Polyphosphate (MPP) is especially suited for glass fibre reinforced polyamide 6,6, where it is added at ca. 25% for UL V0 performance. It has a good thermal stability (ca. 300 °C). MPP is often used as synergist in combination with other phosphorus based FRs.



Structure of melamine polyphosphate

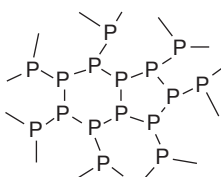
Melamine cyanurate

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



Red phosphorus

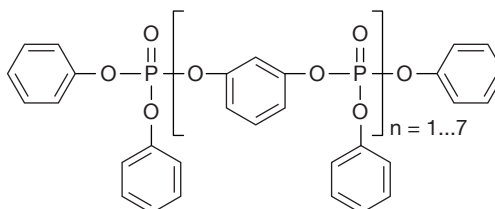
Red phosphorus is a polymeric form of elemental phosphorus. It is used mainly in glass fibre reinforced PA 6,6 at 5 to 8% addition level where its high efficiency at low loading guarantee to maintain the excellent mechanical and electrical properties of the polymer while obtaining the highest flame proofing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



Structure of red phosphorus

Aryl phosphates and phosphonates

Aryl phosphates and phosphonates: their main use is styrenic 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 plasticizing effect and a certain volatility at high processing temperatures. Blooming may have a negative influence on electrical properties.



e.g. RDP

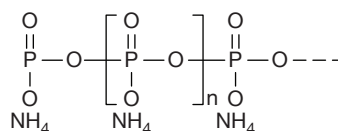
Magnesium hydroxide (MDH)

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

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 non-halogenated 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	notched impact	CTI	GWIT	UL 94
Polyamide 6	0	melamine cyanurate	~ 75	~ 4	600	> 775 °C	V-0
	30	metal phosphinate + melamine polyphosphate	~ 160	~ 15	600	775 °C	V-0
Polyamide 6,6	30	metal phosphinate + melamine polyphosphate	~ 150	~ 14	600	775 °C	V-0
	30	red phosphorus	~ 160	~ 18	600	775 °C	V-0
	30	melamine polyphosphate	~ 140	~ 12	400	675 °C	V-0
HTN	30	metal phosphinate	~ 140	~ 8	600	775 °C	V-0
PBT	0	metal phosphinate + melamine polyphosphate	~ 45	~ 3	600	775°C	V-0
	30	metal phosphinate + melamine polyphosphate	~ 110	~ 7	500	800 °C	V-0
	30	Metal phosphinate +melamine polyphosphonate co-carbonate					
PET	0	metal phosphinate (+melamine polyphosphate)	-	-	-	800 °C	V-0
	30	metal phosphinate (+melamine polyphosphate)	-	-	-	800 °C	V-0
Polyolefins	0	intumescent system	10 - 30	-	600	800 °C	V-0
	30	intumescent system	20 - 60	-	600	825 °C	V-0



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 and RoHS 2, 2011/65/EU) has stimulated a change in the base material market, particularly 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 ($T_g > 165^\circ\text{C}$) epoxy-novolac resins 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 PIN 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 non-halogenated 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 reinforcement. They are most commonly used in the electronics industry (about 80%) and 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 T_g
- No or little impact on electrical properties in particular D_k and 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.

In order to make the transition towards HFFR based PWB, the electronics organisation iNEMI carried out an extensive project to investigate, through testing, the technical performance and suitability of non-halogenated laminates compared to a benchmark brominated material¹⁵. 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 materials.

The leadership workgroup concluded that the electronic industry is ready for the transition and that the key electrical and thermo-mechanical properties of the HFFR laminates can meet the required criteria¹⁵.

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 with non halogenated flame retardants (NHFR) materials and the total loss for these materials is generally equivalent to or lower than the baseline.
- Interconnect stress testing: all HFFR based laminate showed acceptable via reliability performance (> 500 cycle average).
- Conductive anodic filament (CAF) testing: HFFR materials out performed their brominated FR-4 counterparts for both bias levels (80 vs. 100 volts)¹⁶.



Performances of PIN Flame retardants versus other chemistries

Thermal Properties

Thermal expansion	lower	+
Thermal conductivity	higher	+

Physical Properties

Flammability	equal	o
Moisture absorption	higher	+
Peel strength	lower	-
Modulus	equal	o

Electrical Properties

CAF resistance	higher	+
Dielectric constant	slightly higher	+
Dissipation factor	lower	+

Workability

Drill bit wear	higher	-
----------------	--------	---

Table 5-1

Qualitative properties of pin FR laminates vs. other chemistries (3)

+ means better, - worse, o indifferent.

Note: Phosphonate oligomers are currently being specified in an FR4 board where a higher Tg and improved peel strength, modulus and Df vs other non-halogen additives has been achieved.

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).

¹⁵ Published e.g. in Tisdale S, Long G, Krabbenhoft R, Papathomas K, Fisher T (2008): iNEMI BFR-free PCB Materials Evaluation Project Report. SMTAI Conference, Edina MN, USA

¹⁶ Published in Tisdale S, Davigon J, Hall S, Leddige M, Hinaga S, Senk D (2011): iNEMI HFR-Free Leadership Project Report. Electronic Goes Green EGG Konferenz 2012, Berlin

Aluminium Trihydroxide (ATH)



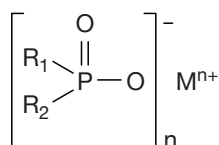
Although concerns can be raised due to the moderate thermal stability (regular ATH starts to decompose at approx. 200 °C), ATH is still used in halogen-free formulations. Rather high loadings are necessary to achieve the necessary fire performance. Therefore, the combination with other FR's is common.

Alumina monohydrate



The transition to lead-free solders with significantly higher temperatures is certainly a challenge for ATH. It may be replaced by alumina monohydrate (Boehmite), which excels in a high temperature stability up to 340 °C. Thus, absolutely no decomposition and water release (water can catalyse 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.

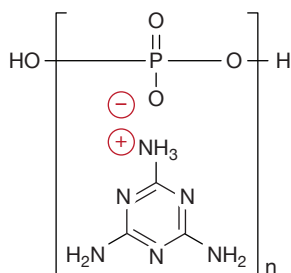
5.3.2 METAL PHOSPHINATES AND POLYPHOSPHATES



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 a 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 are 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 15-20 phr (parts per hundred resin) of metal phosphinate are recommended. Metal phosphinates are also suitable for flexible printed circuit boards (FPC).

Melamine Polyphosphates (MPP) are mainly used to reach UL 94 V0 (1,6 to 0,4 mm) classifications in highly glass fibre filled polyamides and polyesters. MPP is often combined with other FRs. Typical loadings are in the range of 7 to 10% plus the phosphorus containing synergist, such as metal phosphinates. MPP has a highthermal stability up to 330 °C (2% weight loss) and low influence on Tg. In the case of fire MPP provides a charring mechanism, which, in combination with metal phosphinates, leads to the flame retardancy effect.



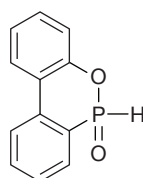
Structure of melamine polyphosphate

5.4 REACTIVE FLAME-RETARDANTS

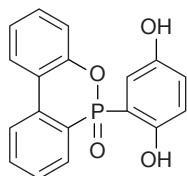
Reactive FRs are chemically bound to the polymer. This solves most of the migration problems, e. g. vaporisation.

DOPO

DOPO (Dihydrooxaphosphaphenanthrene) is a cyclic hydrogenphosphinate 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.

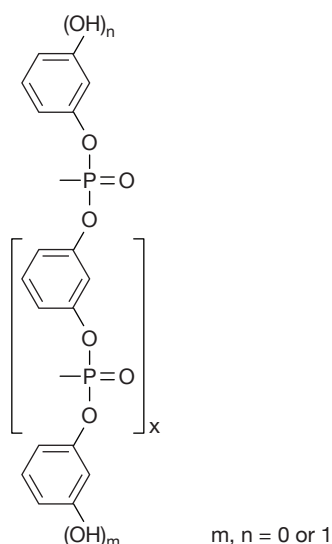


Today, DOPO can be regarded as the major building block used to make phosphorus containing epoxy resins (Tg up to 150°C). DOPO is commercially available from different suppliers and global capacities have consequently increased over the past 2 years to respond to the increasing market demand from PCB.



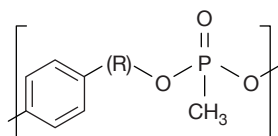
Poly(1,3-phenylene methylphosphonate)

Due to its hydroxyl groups and phosphonate sites it can react into the polymer and act as a curing agent for epoxies. It is recommended in combination with ATH. High temperature stability is reported (high Tg, pressure cooker test).



Phosphonate Oligomers

Phosphonate oligomers primarily react with epoxy resins via phosphonate sites in the backbone. With a high crosslink density, cured resins can achieve high Tg (185°C), excellent thermal properties, improved peel strength, increased modulus, and low loss (Df) properties.



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 cast resins without glass fibre reinforcement.

Resin hardened with DICY / Fenuron

Flame Retardant	Phosphorus-content (%)	FR-content (%)	UL 94 (4 mm)	Tg (DSC) (%)
Metal phosphinate	3.2	16.7	V0	169
Poly (1,3-phenylene Methyl-phosphonate)	3.2	23.5	V0	165
DOPO-HQ	1.4	17.0	V0	161
DOPO	1.60	11.2	V0	155
DOPO + 30% Boehmite	1.00	6.9+30	V0	168

Table 5-2

DOW DEN 438 resin hardened with DICY / Fenuron (no glass fibre): Amount of Flame Retardant necessary for UL94 V0 classification

Resin hardened with phenol novolak / NMI

Flame Retardant	Phosphorus-content (%)	FR-content (%)	UL 94 (4 mm)	Tg (DSC) (%)
Metal phosphinate	0.6	3.0	V0	Ca. 172
Poly (1,3-phenylene Methyl-phosphonate)	0.7	4.9	V0	174
DOPO-HQ	0.7	7.4	V0	169
DOPO	0.8	5.6	V0	164

Table 5-3

DOW DEN 438 resin hardened with phenol novolak / NMI (no glass fibre): Amount of FR necessary for UL94 V0 classification



6

FUTURE TRENDS AND INNOVATION

In recent years, new 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.

Novel, mainly phosphorus-organic flame retardants have been developed and introduced for various materials in E&E applications. As mentioned in the previous chapters, four 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, Flame retardants based on aluminium phosphinates, melamine salts and phosphonate oligomers have gained a wide acceptance. New oligomer phosphoric acid esters were developed and are presently applied for electric enclosures including enclosures for the fast growing Lithium ion battery market.

Furthermore, a noteworthy application of phosphorus-organic flame retardants belongs to its incorporation into the electrolytes of Lithium ion batteries. Their unique effectiveness as FR against high flammability of standard carbonate based electrolytes gives an important significance to them. 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, 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 phosphazenes, 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, polyphosphonate co-carbonate, 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 retardants for epoxy resins that can be processed easily and which are suitable for carbon fiber composites.

Phosphorus compounds that primarily act via the gas phase are preferred for this purpose. Innovations are regularly discussed at dedicated international conferences, e. g.:

- Interflam, biannual
www.intersciencecomms.co.uk
- European Meeting on Fire Retardant Polymeric Materials (FRPM)
www.frpm17.com/
- Fire and Materials Conference, biannual, USA
www.intersciencecomms.co.uk
- Annual BCC Conference on Flame Retardancy, Stamford, CT, USA
www.bccresearch.com/conferences.html

Further literature and the latest developments on pin flame retardants can be found in recent publications such as:

“Non-Halogenated Flame Retardant Handbook”, edited by Alexander B. Morgan and Charles A. Willie, ISBN 978-1-118-68624-9

“Polymer Green Flame retardants”, Edited by Constantine D. Papaspyrides and Pantelis Kiliaris, Elsevier – 2014, ISBN 978-0-444-53808-6

- EV is requiring unprecedented high current and voltages for Automotive market leading to need of materials with High CTI, High Dielectric Strength at high temperature and low contact corrosion
- TS (Phenolic, SMC, BMC, Epoxy) replacement is getting more traction because of concerns about toxic emissions during manufacturing, beside recyclability
- Appliance market is pushing for Non Hal materials able to pass GWIT at 775C according to IEC 60695-2-13
- In both above mentioned cases non Halogen solutions are preferred by market

Several conferences related to pin FR's, their uses and environmental fates are occurring regularly. Please visit pinfa website for related info.

www.pinfa.org

7

ENVIRONMENTAL AND TOXICOLOGICAL PROPERTIES OF NON-HALOGENATED FLAME RETARDANTS

Whereas the previous chapters focussed on the technical properties of pin flame retardants in various application areas, this chapter discusses their environmental and toxicological properties. From a molecular perspective, there is a big difference between additive and reactive flame retardants. As the name implies, reactive flame retardants react into the polymer or onto a material surface to form strong chemical bonds to the material to be protected (the matrix). Therefore, in their original form they must have some reactivity which can also be linked to toxic or environmental effects, whereas in the final reacted state they are inert and have the advantage that they cannot migrate or leach out of a finished material. However, for the recycling of materials this means that the chemical bonds must be broken to separate the flame retardant from the matrix again, unless the flame retarded matrix or polymer can be recycled as such.

Additive flame retardants are only physically mixed into the material they are meant to protect or brought onto the surface with a carrier or as part of a coating. These molecules must have a certain chemical stability to survive the processing of the target material which may occur at temperatures of up to and above 300 °C for thermoplastics. Furthermore, a degradation of the flame retardant during the use phase of the finished article is not desirable. Construction materials or electric installations have a service life time of many years to even decades.

This chemical stability relates to persistence of these materials in the environment. Therefore, there is some degree of conflict between desired functional properties and an ideal environmental behaviour. It is also important to note that the concept of degradation and persistence is appropriate only for synthetic organic materials, where the ideal environmental fate is the degradation to carbon dioxide and water (and further oxidation products depending on composition). For inorganic materials like aluminium hydroxide or zinc borate this concept does not make sense. Here the correct question to ask is whether they are neutral in the environment and whether these materials react to form more toxic species in the environment over time.

Most flame retardants have an environmentally friendly profile, which means that they pose no harm to the environment and do not bio-accumulate in biota. Generally speaking, PIN flame retardants have a low (eco)toxicity profile and will eventually mineralize or are inert in nature. Due to these characteristics, none of the commercial PIN flame retardants are considered to be PBT or vPvB. Please refer to **pinfa product selector guide** for a legislative status overview of pin FR's.

www.pinfa.org/index.php/en/product-selector

7.1 REACH

In Europe chemicals are controlled by REACH, the Regulation on Evaluation, Authorisation and Restriction of Chemicals (1907/2006/EC). The major changes from the previous chemical legislation was the mantra “no data, no market” and the “reversal of the burden of proof” principle. “No data, no market” means that the producer or importer of a chemical needs to provide sufficient information and test data on the product for a proper evaluation of its safety. All chemicals on the market need to be registered and information submitted to a central authority, the European Chemicals Agency (ECHA). Under REACH not only hazard data, but also data concerning emissions, uses and end of life are gathered. The burden of proof is now on the producer to prove that a chemical is safe, whereas before the authorities had to demonstrate that there was an issue with a substance before any legal measures could be taken. REACH entered into force in 2006, and in mid 2008 first chemical registrations started with products manufactured in high volume or having certain hazards. By mid 2018 all chemicals down to those with small production or import volumes of 1 ton need to be registered. This means that a wealth of information is available on all these chemicals including flame retardants.

Most of the data is publicly accessible here:



www.echa.europa.eu/web/guest/information-on-chemicals/registered-substances

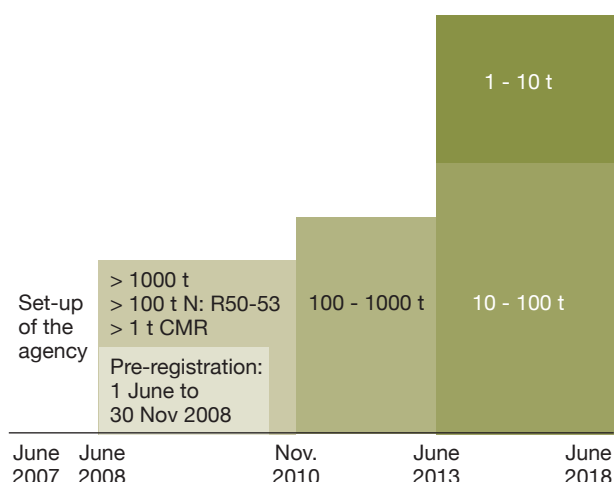


Figure 7-1

Timeline of REACH implementation showing when high hazard substances and each production tonnage band needs to be registered
www.echa.europa.eu

REACH restricts the marketing and use of chemicals in different ways. Some restrictions for legacy hazardous chemicals were grandfathered into REACH via Annex 17. Chemicals evaluated based on REACH dossiers as candidates for “Substances of Very High Concern” (SVHC) are governed by Annex 14. *Table 7-1* presents the currently covered flame retardants. Mostly legacy products are listed which have been debated for many years already, but there are also less prominent new entries like boric acid and trixylylphosphate (TXP).

Annex 17 Restrictions

- Pentabromodiphenyl ether* (PentaBDE, 0,1% w/w) – UN Stockholm Convention (2011)
- Octabromodiphenyl ether* (OctaBDE, 0,1% w/w)
- Deca-BDE: proposal to add the commercial mixture (c-decaBDE) to the Stockholm Convention on Persistent Organic Pollutants; ECHA to prepare Annex XV dossier
- Inorganic ammonium salts in cellulose insulation materials**
- Not allowed in articles for skin contact (e.g. textiles):
 - Tris(aziridinyl)phosphin oxide
 - Tris (2,3 dibromopropyl) phosphate (TRIS)
 - Polybromobiphenyls (PBB)

* as commercial formulations, i.e. including other congeners

** after 2018-07-14, only if emission of NH₃ exceeds limit value of 3 ppm

Annex 14 (Candidate) List of Substances of Very High Concern for Authorisation

- Hexabromocyclododecane (HBCD) – PBT substance
- Tris(chloroethyl)phosphate (TCEP) – Reprotox Cat. 1b
- Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins) – PBT and vPvB
- Boric Acid – Reprotox
- Trixylylphosphate (TXP) – Reprotox Cat. 1b

Table 7-1

Restrictions for Flame Retardants under REACH and reasoning for concerns (status 2017-03)

With inorganic ammonium salts and trixylylphosphate (TXP) the first PIN FRs are listed in annex 14 and 17 of REACH. The restriction of inorganic ammonium salts relates to the regrettable use of inappropriate materials in cellulosic building insulation material which caused the emission of ammonia in the past, mainly in France. Therefore, the restriction is very specific for this application. TXP is an aryl phosphate which can be used in E&E applications. However, PIN alternatives to this substance exist, should it become an SHVC.

In order to evaluate additional substances, the European Chemicals Agency (ECHA) runs a so-called Community Rolling Action Plan, the CoRAP working list, which contains substances suspected of posing a risk to human health or the environment. Its update for 2017-2019 contains 117 chemicals (22 are newly added), of which 8 are flame retardants or synergists (2). After a member state submits a dossier on each of these chemicals which indicates a high level of concern, the review process for inclusion on the SVHC candidate list can start.

So whilst REACH has dealt with flame retardants one could argue that even after ten years of implementation it has only taken out some already well known “bad actors” by legal restriction. However, it has pushed the industry to evaluate their whole product portfolio. Some smaller volume products may be discontinued even before the final registration deadline, because the cost of testing and data gathering is not justified by the small revenue generated (this can of course also affect environmentally preferable products). REACH was also not able to become the one and only regulation to govern the use of chemicals, e.g. RoHS restricts certain brominated flame retardants and heavy metals in electronics.

7.2 ROHS AND WEEE

The increasing amount of waste electronics over the last decades together with widespread findings of heavy metals and problematic brominated flame retardants in the environment lead to two legislative initiatives in Europe: one to properly collect and recycle electronic waste, the Directive on Waste Electric and Electronic Equipment (WEEE, 2002/96/EC), the other Directive on the Restriction of certain Hazardous Substances in Electric and Electronic equipment (RoHS, 2002/95/EC).

It bans polybrominated biphenyls (PBBs) and polybrominated diphenylethers (PBDEs) in E&E equipment since July 2006. Certain exemptions can be granted under the directive. The WEEE Directive also contains a requirement to separate materials containing problematic brominated flame retardants before further recycling to prevent the “contamination” of new products with these materials via recycle streams. Both directives were reviewed and so-called “re-casts” published (WEEE 2012/19/EU; RoHS 2011/65/EU). The WEEE re-cast increased the recycling quotas, whereas the RoHS re-cast widened the scope of products covered and installed a new system to regularly update the list of restricted substances. In a first approach the Austrian Ministry for Environmental Protection (Umweltbundesamt) worked out a methodology and a list of priority substances.

www.umweltbundesamt.at/rohs2

Meanwhile, other countries have adopted the approach to restrict critical substances in E&E equipment, most notably China (regulation SJ/T 11363-2006 “China RoHS 1”). China’s Ministry of Industry and Information Technology (“MIIT”) published a revision which entered into force in mid 2016 as “Management Methods for the Restriction of the Use of Hazardous Substances in Electrical and Electronic Products”. The debate around RoHS and WEEE in Europe created a strong demand for non-halogenated flame retardants, because original equipment manufacturers (OEMs) were looking for sustainable alternatives to legacy brominated flame retardants. Since many E&E products participate in a global market, this trend was not limited to Europe but was supported globally by international OEMs.

Electronic waste ready for recycling



7.3 ENFIRO

During the revision of RoHS the European Commission saw the necessity to generate more information on alternatives to legacy brominated flame retardants which were considered for further restrictions. Therefore an international research project called ENFIRO was funded to study the environmental and health properties of these alternative flame retardants in a holistic way, not only looking at chemical hazards but also potential exposure, application properties in the use phase and end of life aspects. A number of suitable alternatives were identified in the project, backed up by a wealth of experimental and theoretical data.

The results of the project are not only summarized in a report

www.cordis.europa.eu/publication/rcn/15697_en.html

but also in a video on

www.enfiro.eu



Figure 7-2
The ENFIRO project approach for holistically assessing alternative flame retardants

Category	Flame Retardants	Comments
Generally safe, few issues of low concern identified	Aluminium diethylphosphinate (Alpi) Aluminium hydroxide (ATH) Ammonium polyphosphate (APP) Melamine polyphosphate (MPP) Dihydrooxaphosphaphenanthrene (DOPO) Zinc stannate (ZS) Zinc hydroxstannate (ZHS)	<ul style="list-style-type: none"> Inorganic and organic substances with low acute (eco-)toxicity and no bioaccumulation potential Chemical stability required for application results in limited degradation (persistence) Stannates: in vitro (neuro-)tox effects were not confirmed in-vivo, probably due to low bioavailability

Table 7-2
Flame Retardants of low concern identified in the ENFIRO project.

7.4 US-EPA DFE

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 so-called FR4 laminates for printed circuit boards. 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. The combustion products of brominated and halogen free laminates were also studied. The formation of brominated dioxins from TBBPA in uncontrolled burning is a key element, because it relates to still practised crude recycling operations in countries like China or India.

A report is available on the EPA website.

www.epa.gov/saferchoice/design-environment-alternatives-assessments

Meanwhile also reports on other major brominated FRs have been published with a wealth of data on alternatives to these:

- hexabromo cyclododecane (HBCD)
- decabromo diphenylether (DecaBDE)
- pentabromo diphenylether (PentaBDE) and others for polyurethane foams in furniture.

7.5 GREENSCREEN

Whereas REACH and RoHS define the legal basis for producing and marketing of chemicals in Europe, they do not create a strong pull to substitute low performing products on the environmental and health side with better and safer alternatives. Therefore, other schemes and initiatives like eco-declarations, ecolabels and alternatives assessment schemes come into play.

The environmental organisation “Clean Production Action” has developed a methodology for evaluating chemicals based on their hazard profile. As a result a chemical will be assigned to one of four benchmarks, from benchmark 1 being “Avoid – Chemical of High Concern” to benchmark 4 “Prefer – Safer Chemical”. It is related to existing schemes used by the US-EPA in their Design for Environment projects and REACH legislation in Europe in that it uses criteria related to their PBT (persistent, bioaccumulative, toxic) and CMR (carcinogenic, mutagenic, 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. pinfa engaged early on with Clean Production and started a pilot project in 2010 to evaluate some PIN FRs. Meanwhile more assessments have become publicly available in online sources like GreenScreen Store, Clariant and IC2-Database with many PIN FRs in benchmark 2 and 3 which is generally accepted as a good environmental and health profile. A few PIN FRs were also categorized as benchmark 1. These need further attention and proper evaluation of risk. pinfa member companies are also considering other alternatives and chemical assessment methodologies.

www.cleanproduction.org

Examples of ecolabels and alternatives assessments' labels



Der Blaue Engel



EPEAT



EU Ecolabel



Eco Mark



TCO Development



GreenScreen

7.6 ECOLABELS

There are many ecolabel schemes throughout the world. Like the Blue Angel in Germany, many criteria schemes have made requirements on flame retardants. Either halogenated FRs are not allowed in general, or specific problematic substances like PBDEs are restricted. However, ecolabel criteria for chemicals are often not defined in a consistent and balanced way. The Swedish organization TCO took a radically new approach in moving away from a “black list” approach to the definition of a “positive” list: FRs used in their certified product have to be non-halogenated, but also included on a positive list based on the GreenScreen approach (with a minimum requirement of benchmark 2).

www.tcodevelopment.com/news/flame-retardants-accepted-under-tco-certified-is-growing/

with the TCO Certified Accepted Substance List.

As a consequence of all these initiatives and studies, the benefits in terms of better environmental profile as well as similar or equal workability of PIN FR's became more obvious and allowed their wider acceptance and growing usage.

REFERENCES

1. Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
2. ECHA Draft Community Rolling Action Plan (CoRAP) update for years 2017-2019, 27th October 2016, <https://echa.europa.eu/fr/information-on-chemicals/evaluation/community-rolling-action-plan/draft-corap>
3. Directive 2011/65/EU of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (Recast of 2002/95/EC)

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 an 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.

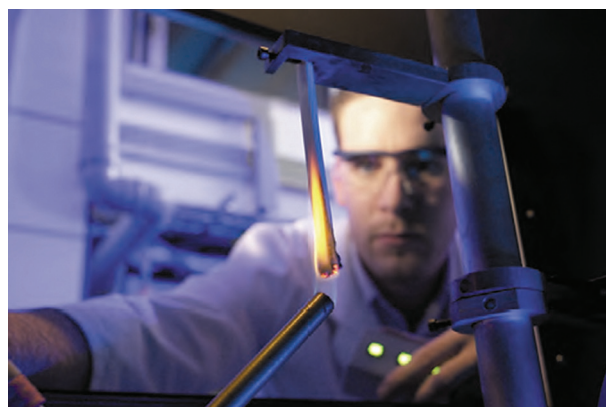
These standards define the LOI method: ASTM D 2863, BS ISO 4589-2, NES 714.



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.

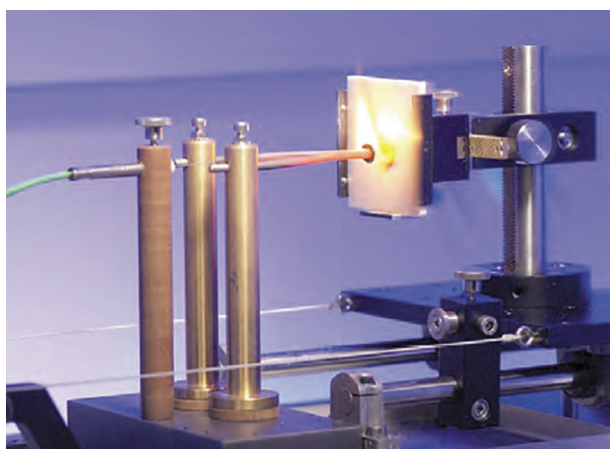
The test is defined in these standards: Underwriters' Laboratories (UL) 94, ASTM D 3801, IEC 60695-11-10, IEC 60707, ISO 1210.



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.

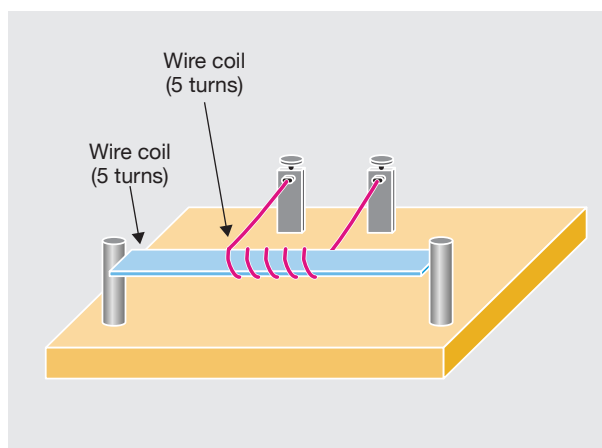
The test is specified in these standards:
IEC 60695-2-10 to 13.



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).

www.ul.com/plastics/746C.html



CONCLUSIONS

PIN Flame retardants (non-halogenated) are continuing to grow in electrical and electronic applications. Due to their good technical and environmental properties they are becoming the preferred technology in most consumer electronics applications.

pinfa, in line with its three pillars and commitments to society for a sustainable fire safety offers a vehicle for collaboration and information regarding innovative, environmentally friendly FRs and synergists.

Would you have any question or request or suggestion for improvement, please do not hesitate to contact us via our website : www.pinfa.org

pinfa. Committed
to sustainable fire safety
via environmentally
flame retardants used in:

ELECTRIC AND ELECTRONIC APPLIANCES



BUILDING AND CONSTRUCTION



TRANSPORT



FURNITURES AND BEDDING



pinfa warmly thanks all contributors to this brochure.
The material contained on this brochure is for information only. Cefic / pinfa has compiled the pages of this brochure very carefully, and the information is offered in utmost good faith. This information is believed to be correct. Cefic / pinfa makes no representations or warranties as to the completeness or accuracy of any of this information. Cefic / pinfa will in no event be responsible for damages of any nature whatsoever resulting from the use or reliance to the information contained in this brochure.

LIST OF ABBREVIATIONS

The flame retardants' world uses many abbreviations which are often confusing for people who are new to the field. Here we have put together a list of commonly used abbreviations. For chemical substances the CAS registry number is also given.

For a systematic list of flame retardant abbreviations, see "A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals", A. Bergman et al., Environmental International 49, 2012

ABS	Acrylonitrile butadiene styrene copolymers	DSC	Differential scanning calorimetry
AOH	Aluminium-oxide-hydroxide (Boehmite)	E&E	Electric and electronic
AP	Ammonium phosphates	EFRA	European Flame Retardants Association
APP	Ammonium polyphosphate 68333-79-9	EPA	Environmental Protection Agency
ATH	Aluminium trihydroxide 21645-51-2	EPEAT	Electronic Product Environmental Assessment Tool
ATO	Antimonytrioxide 1309-64-4	EPS	Expanded Polystyrene
BADP (or BPA-DPP)	Bisphenol-A diphenyl phosphate, EINECS 425-220-8	EVA	Poly-ethyl-co-vinyl acetate
BDP (or BPA-BDPP)	Bisphenol-A- bis- diphenylphosphate 5945-33-5, 181028-79-5	FPC	Flexible printed circuit
BFR	Brominated flame retardant	FR	Flame retardant
CAF	Conductive anodic filament	GWFI	Glow wire flammability index
CAS	Chemical Abstracts Service (run by the American Chemical Society)	GWIT	Glow wire ignition temperature
CPSC	US Consumer Product Safety Commission	GWT	Glow wire test
CTE	Coefficient of thermal expansion	HBCD	Hexabromocyclododecane 25637-99-4
CTI	Comparative tracking index	HBCDD	HBCD
Deca-DBDE	Decabromodiphenyl ether 1163-19-5	HDT	Heat deflection temperature
Df	Dissipation factor	HFFR	Halogen-free flame retardant
DfE	Design for the Environment (US EPA)	HIPS	High impact polystyrene
DGEBA	Diglycidyl ether of bisphenol-A	HTN	High temperature nylon
DICY	Dicyandiamide	IEC	International electrotechnical commission
Dk	Dielectric constant	IEEE	Institute of Electrical and Electronic Engineers
DOPO	Dihydro-oxa-phosphaphenanthrene-oxide	LOI	Limiting oxygen index
DOPO-HQ	Dihydro-oxa-phosphaphenanthrene-oxidehydrochinon	LSF0H	Low smoke – flame retardant – zero halogen
		MC	Melamine cyanurate
		MCPP	Medium-chain chlorinated paraffins 85535-85-8
		MDH	Magnesium hydroxide 1309-42-8
		MPP	Melamine polyphosphate
		NEMA	National electrical manufacturers association

NGO	Non-governmental organization	TBB (or EH-TBB)	2-Ethylhexyl ester 2,3,4,5-tetrabromobenzoate
NMI	N-methylimidazole	TBBPA	Tetrabromobisphenol-A 79-94-7
OBDE	Octabromodiphenyl ether 32536-52-0	TBEP (or TBOEP)	Tris (2-butoxyethyl) phosphate
OEM	Original equipment manufacturer	TBP (ot TNBP)	Tri-n-butyl phosphate 126-73-8
PA	Polyamide	TBPH (or BEH-TEBP)	1,2-Ethylhexyl 3,4,5,6-tetrabromo-benzenedicarboxylate or (2-ethylhexyl)-3,4,5,6 tetrabromophthalate
PBDE	Polybrominated diphenyl ethers in general	TCEP	Tris (2-chloroethyl) phosphate 115-96-8
PBT	Persistent, bioaccumulative, and toxic or (different meaning) Polybutyleneterephthalat	TCP (or TMPP)	Tricresyl phosphate 1330-78-5
PC	Polycarbonate	TCPP (or TCIPP)	Tris (chloroiso-propyl) phosphate 13674-84-5
PCT	Pressure cooker test	TDCP (or TDCIPP)	Tris(1,3-dichloro-2-propyl)phosphate 13674-87-8
PET	Polyethyleneterephthalat	Tg	Glass transition temperature
PIN	Phosphorus Inorganic Nitrogen	TGA	Thermogravimetric analysis
PINFA	Phosphorus Nitrogen and Inorganic Flame Retardants Association	THPC	tetrakis(hydroxymethyl)phosphonium chloride [P(CH ₂ OH) ₄ Cl], an organophosphorus compound combined with a mineral (non-organohalogen) chloride ion (Cl-) which is washed out in the finishing process
PPO	Polyphenylene oxide	TPP (or TPHP)	Triphenyl phosphate 115-86-6
PWB	Printed wiring board (synonymous to printed circuit board)	TSCA	US Toxic Substances Control Act
RDP (or PBDPP)	Resorcinol bis-diphenylphosphate 57583-54-7, 125997-21-9	UL	Underwriters Laboratories
RDX	Reorcinol bis (dixylenyl phosphate)	vPvB	Very persistent, very bioaccumulative
REACH	Registration, evaluation and authorisation of chemicals	WEEE	Waste of electric and electronic equipment
RoHS	Restriction of certain hazardous substances in electric and electronic equipment	XPS	Expanded Polystyrene
RP	Red Phosphorus 7723-14-0		
SAN	Poly-styrene-acrylonitrile copolymer		
SCPP	Short-chain chlorinated paraffins 85535-84-8		
SNUR	Significant New Use Rules		



pinfa Secretariat

Avenue E. van Nieuwenhuyse, 4
B-1160 Brussels - Belgium

Tel. : +32 2 676 74 36

Fax : +32 2 676 72 16

E-mail: pinfa@cefic.be

www.pinfa.org

MEMBERS OF PINFA AS PER OCTOBER 2017



NON-HALOGEN
FIRE RETARDANT ADDITIVES

