pin**f**a

Innovative and Sustainable Flame Retardants in Transportation



Non-halogenated phosphorus, inorganic and nitrogen flame retardants

.....

.....

...











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

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

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

For more information, please contact:

Brigitte Dero Sector Group Manager of **pinfa** Tel +32 2 676 72 86 Fax +32 2 676 73 92 bde@cefic.be www.pinfa.eu



Publisher

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

Editors

Prof. Dr. Manfred Döring Dr. Yana Bykov Dr. Ingmar E. Held Karlsruhe Institute of Technology Institut für Technical Chemistry Devision of Chemical-Physical Processing (ITC-CPV) Hermann-von-Helmholtz-Platz 1, Bldg. 725 D-76344-Eggenstein-Leopoldshafen, Germany phone +49 7247 82-0 www.katalyseundmaterialien.de

Layout

Stolz Grafisches Atelier · Karlsruhe

Print

Wilhelm Stober GmbH · Eggenstein

September 2010

Table of Contents

| 1 | Introduction1.1 What are halogen-free flame retardants?1.2 Why are FRs needed in transport applications?1.3 Why should one use halogen-free PIN FRs? | 5 | |
|----|---|----|--|
| 2 | Fire tests 2.1 Introduction 2.2 Car 2.3 Bus 2.4 Rail vehicles 2.5 Ship 2.6 Aviation | 10 | |
| 3 | Interior parts 3.1 Introduction 3.2 Plastics in interior parts 3.3 Some examples of HFFR in interior applications 3.4 Summary of HFFRs in interior applications | 13 | |
| 4 | Textiles 4.1 Introduction 4.2 Textiles and fire safety 4.3 Overview of textiles used in transportation 4.4 Wash resistance & application techniques of FR on textile products 4.5 PIN FR's used in transportation textiles | 18 | |
| 5 | Seats 5.1 Introduction 5.2 Automotive 5.3 Aeroplane 5.4 Rail vehicles (railway and subway) | 25 | |
| 6 | Cables 6.1 Introduction 6.2 Road transport (cars / trucks / buses) 6.3 Public mass transport (trains, ships, aeroplanes) | 29 | |
| 7 | Electric and electronic applications 7.1 Introduction 7.2 Electrical installations & components 7.3 Electronic devices & printed circuit boards 7.4 Comfort & infotainment: housing materials | 35 | |
| 8 | Innovation and future trends in transportation 8.1 Lightweight construction and electrically powered vehicles 8.2 Bioplastics and natural fibre-reinforced plastics 8.3 Flame retardancy requirements and new flame retardants (FR) | 42 | |
| 9 | Environmental and toxicological properties of halogen-free flame retardants 9.1 Europe: REACH and GHS (CLP) | 45 | |
| 10 | List of abbreviations | 50 | |
| 11 | Contributing companies | 52 | |

1 Introduction

As transport vehicles like aeroplanes, ships, trains, buses, and cars use a large number of flammable materials and are therefore subject to fire risks, pinfa has compiled this brochure to explain how its flame retardant technologies can contribute to the safety of materials and vehicles. After many years of research and development, a whole toolbox of halogen-free chemistries is now available for the materials engineer. Major application areas of flame retardants in transport vehicles are polymers for electrical or structural parts, cables, carpets, decorative and upholstery textiles, and polymer foams for insulation and upholstery.

In 2009, the non-halogenated phosphorus, inorganic and nitrogen flame retardants association (pinfa) was founded as a sector group of Cefic, the European Chemical Industry Council. Pinfa represents the manufacturers and users of the three major technologies of non-halogenated flame retardants. The members of pinfa share the common vision of continuously improving the environmental and health profile of their flame retardant products and offering innovative solutions for sustainable fire safety. Pinfa engages in the dialogue with the users of flame retardants on the development of environmentally friendly fire safety solutions. In addition to this brochure, our website www.pinfa.org offers valuable information as well as a "product selector" of pinfa flame retardants, where you can find data on the target polymers and materials for individual flame retardants as well as environmental and health information.

1.1 WHAT ARE HALOGEN-FREE FLAME RETARDANTS?

Halogen-free flame retardants¹ cover a variety 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 smaller extent.
- Phosphorus-based flame retardants include organic and inorganic phosphates, phosphonates, and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.

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

Intumescent flame retardants are an example of a typical mechanism of halogen-free flame retardants. The combustible material is separated from the fire or heat source by an insulating foam forming 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: The mechanism of intumescent flame retardant systems which typically represent a combination of phosphorus and nitrogen compounds

Figure 2 shows the regional split of global consumption of flame retardants by volume. The chart shows that halogenfree technologies already assume a major share of the market, with a strong dominance in North America and Europe. Asia is the leading consumer of brominated and chlorinated flame retardants, because they are mainly applied in electronic devices and manufacture of the latter moved from Europe and North America to Asia over the last decades. In addition, Asian producers focus on low-cost commodities rather than higher-value products. However, many original equipment manufacturers (OEMs) of electronic devices have announced roadmaps with deadlines for the transition to

¹ The proper designation is 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.



Figure 2: Global consumption of flame retardants by volume, split into regions, which total 1.8 million metric tons (for 2007, source: SRI Consulting, graphics courtesy of www.flameretardants-online.com)

non-halogenated flame retardants. Since these OEMs have their manufacturing base in Asia, a shift towards halogenfree technologies is also expected in this region.

Figure 3 shows the segmentation of the flame retardants (FR) market based on value by price and performance level and halogen / non-halogen technology. The diagram illustrates that halogen-free technologies already have a large share in the overall market, with a wide portfolio of products in all categories. Typical dosages of flame

retardants in polymers are in the range of 5% to 80%. Consequently, the flame retardant price has a significant impact on the cost of a flame-retarded polymer. There is no "one size fits all" flame retardant, because polymers and textiles have various requirements on their additives: temperature stability, being solid or liquid, viscosity, electrical properties, polarity, and miscibility are only a few properties which need to be matched between a suitable flame retardant and the polymer and its production process.



Figure 3: The area of a triangle represents the market share by value, indicated in billion USD. The total FR market size is 4.2 billion USD (2007). For abbreviations see the list of abbreviations.

1.2 WHY ARE FRS NEEDED IN TRANSPORT APPLICATIONS?

Polymers and textiles are increasingly applied in transport systems, because they provide comfort in the passenger compartment as well as many technical advantages for engineering applications. In the automotive area, for example, metal parts are more and more replaced by plastics, because these have less weight and provide for more freedom in design. According to PlasticsEurope, approximately 8% corresponding to 42 million tons of plastics are used for automotive applications in Europe. This is about 120 kg per car. Advanced polymer materials have adequate mechanical properties to even replace some structural parts and engineering thermoplastics are commonly used in high-temperature environments in the engine compartment. The increasing use of electronics in cars and other transport means results in more plastics being required for cables, electric and electronic parts, etc. It is also possible to integrate electronic functions in structural parts, e.g. using windows for display purposes. In the passenger compartment of cars, trains, ships, and aeroplanes, appealing

textile surfaces, carpets, and upholstered seats provide comfort and a feeling of luxury.

However, most polymer materials are inherently flammable and can be easily set on fire with a small ignition source, like a lighter, match, electric failure or mechanical overheating. It is interesting to note that the resistance of polymers to heat and ignition is somewhat correlated with their price and technical performance (with the exception of halogencontaining polymers like polyvinyl chloride (PVC)). Foamed materials used in insulation or upholstery have a tendency to ignite easily and burn vigorously, because they already represent a mixture of fuel with air. There are polymers which are inherently flame-resistant, but these high-performance polymers are very expensive and difficult to process. Manufacturers tend to substitute engineering thermoplastics by standard or commodity plastics for cost reasons, but also because the technical performance of commodity plastics has increased. In addition, reducing the number of different plastics used in a car facilitates recycling of the materials.



Figure 4: The pyramid or triangle of thermoplastics shows their ranking by capability, structure, and price (source: PlasticsEurope Market Research Group, PEMRG, 2010) There are many examples of catastrophic fires in cars, buses, trains, planes, etc. Over the last decades, these led to a number of fire safety requirements for materials used in these vehicles. Generally, the risk is defined as a function of ease of egress. Therefore, material requirements increase from car to bus, to train, to ship, to aeroplane. However, this approach does not take into account the fact that many fires occur after accidents or crashes which can severely limit the chances of getting out of a vehicle quickly. In a road accident, it may easily take 10 to 20 min before emergency services arrive, and if a car body is distorted, it may take up to 40 to 60 min to free the passengers. If a fire starts during this time, there is hardly any hope for the trapped people. However, there are also some positive examples of stringent safety regulations and fire-proof materials having prevented a disaster, e.g. the crash of an Air France Airbus A340 on August 2nd, 2005, while landing at Toronto's Pearson International Airport. Although a fire broke out, all 309 passengers and crew members escaped. Safety officials considered fire-resistant materials in the plane a key factor in preventing the loss of life.

1.3 WHY SHOULD ONE USE HALOGEN-FREE PIN FRS?

Flame retardants have become a class of chemicals which are increasingly attracting scientific and public attention due to their environmental and health effects. Discussions about flame retardants started, when first environmental concerns were expressed with respect to brominated flame retardants (BFRs) in the early 1990s. At that time, 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 combustion². Findings in the environment and biota and the suspicion that some flame retardants bioaccumulate in organisms have added to these concerns^{3 4 5 6}. Meanwhile, the environmental and health properties not only of BFRs, but also of other types of flame retardants have been studied extensively. The most widely used organic flame retardants became the subject of official risk assessments in Europe⁷ from the early 1990s until the transition to REACH. In 2008, the European Regulation on the Registration, Evaluation, and Authorization of Chemicals (REACH, 1907/2006/EC) entered into force, which requires that basic health and environmental data are submitted for all chemicals before commercialization ("no data no market") and that substances of concern will be evaluated further and their use will possibly be restricted.

Since electronics are a major application area for flame retardants, non-governmental organisations (NGOs), environmental scientists, and authorities have focussed their attention on this industry so far. Over the past decade, the fate of electronic waste and hazardous materials contained therein met with increasing political attention and led to the WEEE⁸ and RoHS⁹ Directives in Europe: The aim of these regulations is that electronic waste shall be recovered and recycled properly and that new equipment shall not contain any problematic substances. Flame retardants are affected, because according to the WEEE directive, plastics containing brominated flame retardants have to be separated before further treatment of the waste. Under RoHS, use of certain brominated flame retardants¹⁰ has no longer been permitted in new electronic equipment since July 2006. Other regions of the world have followed with similar legislation or are planning to do so. These legislative activities, together with pressure from environmental groups, have lead to an increasing demand for halogen-

- 2 Söderström G, Marklund S (2002): PBCDD and PBCDF from incineration of waste-containing brominated flame retardants. ES&T, Vol. 36. pp. 1959-1964
- 3 de Wit C (2002): An overview of brominated flame retardants in the environment. Chemosphere. pp. 583-624
- 4 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
- 5 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
- 6 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
- 7 http://ecb.jrc.it/existing-chemicals/
- 8 Directive 2002/96/EC on Waste of Electric and Electronic Equipment
- 9 Directive 2002/95/EC on Restriction of Certain Hazardous Substances in Electric and Electronic Equipment
- 10 Banned BFRs: Polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE); the exemption for Deca-BDE was repealed by the European Court of Justice, effective July 2008

free flame retardants. Many electronics OEMs have developed phase-out plans for brominated flame retardants, and some have even committed themselves with deadlines.

In the transport sector, it is mainly the automotive industry that has to deal with specific environmental legislation and concerns related to chemicals. In Europe, the End-of-life Vehicles Directive was published in 2000 (ELV, 2000/53/EC). The directive aims at making vehicle dismantling and recycling more environmentally friendly. It defines clear, quantified targets for reuse, recycling, and recovery of vehicles and components and encourages producers to manufacture new vehicles which are easy to recycle. However, there are no restrictions for flame retardants in the ELV, only the "usual" heavy metals are covered: lead, mercury, cadmium, and hexavalent chromium. To cope with the increasing complexity of supply chains and materials of concern, however, the automotive industry developed a web-based database for material declarations (IMDS = International Material Data System) and a harmonized list of critical chemicals called GADSL = the Global Automotive Declarable Substance List (www.gadsl.org) in which substances are classified as "declarable" or "prohibited". Other transport sectors have also established lists of substances of concern, often on a single company basis, e.g. Boeing in the airplane business¹¹.



In fire sciences, the composition and toxicity of smoke became a dominant topic

over the last years, because in fires, most people die from the inhalation of toxic smoke rather than from the direct impact of heat or radiation. PIN FRs tend to release less smoke, because their function is based more on physical processes like the release of water and formation of a charred layer at the product surface than on inhibiting the reactions in the flame zone. In addition, PIN FRs do not release halogen acids (HBr, HCl) and have no potential for the formation of halogenated dioxins and furans. Therefore, PIN FRs are commonly used in aeroplanes, trains, and public buildings because of strict smoke and smoke toxicity requirements. The role of the combustion behaviour of materials in transport systems also is in the focus of a current European research project "TRANSFEU". The project started in May 2009 and will take 3.5 years. With a budget of \in 3.5 million, the project focuses on the toxicity of fire effluents in trains and ships. Coordinated by the French Laboratoire National de Métrologie et d'Essais (LNE), the consortium consists of 22 partners. The project pursues an alternative holistic approach by consideration of larger, complex vehicle structure designs, together with the presence of more complex phenomena due to combined effects of toxic emission, heat release, smoke distribution, and active / passive safety on vehicles. The main objective of TRANSFEU is to propose and develop a range of alternative and complementary fire safety strategies using innovative advanced materials meeting the design requirements of railways and other surface transportation means, such as marine craft. The project intends to directly contribute to the finalisation of the European standard EN 45545 Part 2 "Fire protection on railway vehicles - Part 2: Requirements on the fire behaviour of materials and components" by a dynamic measurement of toxicity and the use of fire safety engineering (FSE) and simulation as a possible alternative to current prescriptive fire safety regulations and standards. More details can be found under: http://www.transfeu.eu/.

Pinfa strives to enter a constructive dialogue with all stakeholders, including environmental NGOs. The need for (fire) safe products needs to be balanced with environmental concerns and flame retardants should be optimised to meet technical, economic, and environmental criteria.

11 http://www.boeingsuppliers.com/environmental/TechNotes/TechNotes2004-02.pdf

2 Fire tests



FMVSS 302

2.1 INTRODUCTION

The fire performance of materials is assessed mainly through the parameters of ignitability, ease of extinguishment, flame spread, heat release, and smoke formation. These criteria are measured by appropriate fire tests depending on the application of the material. The fire tests simulate more or less the main fire scenarios of the different applications. Consequently, numerous fire and smoke tests are known. These tests are performed either on representative samples or on a component part. Tests can be from the small scale up to the full scale.

For transportation, fire scenarios can differ widely. In some areas, the escape time can be short. In other areas, the escape time can be extremely long. These differences are reflected by the different fire standards. In areas with a long escape time, e.g. planes and subways, the requirements regarding ignition and smoke formation are very high, whereas in cars the requirements are much weaker.

In any case, all the fire tests can only simulate the fire risk scenario and not predict the performance in case of a real fire.

2.2 CAR

2.2.1 INTERNATIONAL REGULATION

FMVSS 302 (automotive vehicles: car, bus) Specimens taken from the passenger compartment are clamped horizontally and subjected to a Bunsen burner flame for 15 s. The rate of flame spread measured over a distance of 254 mm should not exceed 101.6 mm/min for any of the specimens. The specimen thickness must correspond to that of the component and should not exceed 12.7 mm. This test is also used for buses. The standard is in accordance with DIN 75200 and ISO 3795.

2.3 BUS

2.3.1 EU REGULATION: 95/28/EG

- Horizontal burning rate: FMVSS 302 (see car) with a maximum flame spread of 100 mm / min.
 The standard is in accordance with DIN 75200 and ISO 3795.
- Dripping test
- Vertical burning rate: DIN 50051 Testing of the vertical burning rate of specimens like curtains or blinds. The specimen is 560 mm high and 170 mm thick. The flame impingement time is 5 s. The burning rate has to be <100 mm/min.</p>

2.4 RAIL VEHICLES

2.4.1 EUROPEAN STANDARD: CEN/TS 45545-2

- ISO 5658-2 Spread of flame
 Determination of lateral flame spread of a specimen exposed to a heat radiator and an ignition flame.
 Specimen: 800 mm*155 mm.
 Measurement of the critical heat flux at extinguishment.
- ISO 5659-2 Smoke generation (railcar, ship) A specimen is exposed to a heat flux with or without an impinging pilot flame. Thus, smoke is generated both under smouldering and flaming conditions. The smoke

produced by the sample is accumulated in an airtight box. Optical density through the smoke is measured by using a lamp and a photo cell. IMO FP Part 2 (International Maritime Organisation) also uses this standard for measuring toxic gas species. Classification criteria exist for products to be used on ships.

 ISO 5660-1 Cone calorimeter (rate of heat release) Time-depending determination of the site-related heat release with the oxygen consumption method. Heat flux: 25 kW/m² or 50 kW/m² Duration of examination: 20 min Specimen dimensions: (100*100* <50) mm



ISO 5660-1 (Cone Calorimeter)

■ DIN 54837 Fire behaviour

Determination of fire behaviour and fire side effects of vertically arranged specimens exposed to a wide-trench Bunsen burner for 3 minutes.

■ ISO 9705 Seats

The flame length above the highest point of the seat surface should not exceed 100 cm.

The flame should extinguish after 15 min. The lateral edge of the seat should not be reached by the flame. Flame impingement through a paper cushion.



ISO 5658-2

EN 9239-1 Flooring

Determination of the fire behaviour and formation of smoke of horizontally arranged floor covering. It is exposed to radiation in a test chamber and ignited with a pilot flame.

Specimen dimensions: (1050*230*d) mm Duration of examination: max. 30 min Measurement of the critical heat flux

■ EN 60695-11-10 (UL94V) Electronic

2.5 SHIP

2.5.1 INTERNATIONAL STANDARD

- ISO 5658 / IMO A. 653 Spread of flame_ The lateral flame spread as a function of time is measured on a vertical 800 mm long sample that is exposed to a heat flux of 50 kW/m² and then decreased to 1.5 kW/m² along the length axis. The ISO spread of flame is similar to an IMO version test procedure used for the approval of marine products to be used on ships. At the same time, a system measures the heat release rate with a thermal method.
- ISO 5659 Smoke generation (see railcar)

2.6 AVIATION

5.1 INTERNATIONAL REGULATION: FAR

Vertical test FAR Part 25 (according to DIN EN 2310)

This test is demonstrates whether materials are "selfextinguishing" (Table 1).

| Test criteria | | |
|---------------------------------------|--------|--------|
| Duration of examination | 12 s | 60 s |
| Afterburning | 15 s | 15 s |
| Destroyed length | 150 mm | 200 mm |
| Afterburning of the dripping material | <3 s | <5 s |
| Category | В | А |

Table 1: Standards according to FAR Part 25

Kerosene burner test

The seat cushion fire blocking test limits the contribution of aeroplane seats to fire spread and smoke emission. The test is performed with a kerosene burner simulating post-crash fire burning through the fuselage. The contribution of the seat to heat development and smoke emission is restricted, as only 10% of the mass of the seat is allowed to be burned.

Specimens:

Bottom: 508 mm*457 mm*102 mm Back: 635 mm*457 mm*51 mm

Flame application: 2 min to the side of the seat bottom

Requirements:

The average percentage of weight loss must not exceed 10%



Kerosene burner test

Smoke density

NBS chamber for smoke density and toxicity. The ABD 0031 technical specification for Airbus allows materials with a low smoke density and low toxicity in the cabin area only (Table 2).

| Limit value for toxicity | [ppm] |
|-----------------------------------|-------|
| HF | 100 |
| HCI | 150 |
| HCN | 150 |
| SO ₂ /H ₂ S | 100 |
| NO/NO ₂ | 100 |
| CO | 1000 |

Table 2: Limit values for toxicity according to ABD 0031

Heat release

For large parts inside the aeroplane passenger cabin, a heat release test was developed at Ohio State University (OSU).

Specimens:

Three specimens, surface 150 mm*150 mm

Specimen position:

vertical ignition source: 35 kW/m² radiant heat attack, pilot flame on lower end of specimen

Test duration:

5 min

Requirements:

Maximum heat release rate (HRR) within 5 min: 65 kW/m² Total heat release (HR) during the first 2 min: 65 kW min/m²



Heat release test

3 Interior parts

3.1 INTRODUCTION

Interior parts for transport applications, i.e. automobiles, aeroplanes, ships, are complex systems that include visible items, such as flooring, textiles (chap. 4), seats (chap. 5), lavatories, ceilings, sidewalls, stowage bins, bag racks, closets, dash boards, and windows, and items that are not visible to passengers, such as ducting, wiring (chap. 6), electrical & electronic components (chap.7), insulation blankets, coatings, sealants, and adhesives.

The materials' properties must address the needs of users of the materials. These needs include the processing and production capabilities of the material suppliers and manufacturers; the ability to meet the design, performance, comfort, and aesthetic demands of interior applications; and compliance with environmental, health, and safety regulations.

3.2 PLASTICS IN INTERIOR PARTS

Plastics have revolutionised the interior design of means of transportation. They have proven to be ideal materials for creating comfortable, durable, and aesthetically pleasing interiors, while reducing noise, harshness, vibration, and weight. Plastics offer a design flexibility which helps manufacturers create innovative, integral, single-piece, lightweight components, while cutting costs, saving time, and helping lessen the problems associated with interior redesign.

| Typical values vs. material | Density [kg/m ²] | E-modulus [Gpa] | CLTE [*] mm/m / °Cx10 ⁻⁶ |
|--------------------------------|---------------------------------|--------------------|---|
| Steel | 7800 | 210 | 12 |
| Aluminium | 2800 | 72 | 24 |
| Polyamide 6 | 1130 | 2 | 95 |
| Polycarbonate | 1200 | 2.5 | 60 |
| ABS | 1070 | 3 | 85 |
| Polypropylene | 905 | 2 | 180 |

*Coefficient of Linear Thermal Expansion

Table 3: Comparison of materials used for interiors



As obvious from Table 3, the right choice of the most suitable material strongly depends on the requirements in the final application. For instance, instrument panels were traditionally made of several separate components that needed to be painted and that were all held together by a steel support beam that lay behind the panel. Today, thanks to modern plastics technology, instrument panels are made of acrylonitrile-butadiene-styrene (ABS), ABS/polycarbonate (PC) alloys, PC, polypropylene (PP), modified polyphenylene ether (m-PPE), and SMA (styrene maleic anhydride) resins. These plastics allow for complex designs of items, such as airbag housings, centre stacks for instrument panels, and large, integrated instrument panel pieces. They are also used in manufacturing the rest of the automobile's interior trim. These plastics are also capable of eliminating the need for a steel support beam, allowing manufacturers to dramatically save costs of the instrument panel while substantially reducing its weight.

Polymeric materials are predominant and appear in a wide range of product forms, including moulded sheet or shapes, composite-faced honeycomb sandwiches, textile fibres (fabrics or carpets), foams, sealants, and adhesives. Interiors currently contain materials having different flammabilities. They are selected according to their particular application and a variety of additional factors, such as availability, cost, and processability. Most of the polymers used need FRs to comply with the current fire standards (cf. chapter 2).

3.3 SOME EXAMPLES FOR HFFR IN INTERIOR APPLICATIONS

Intumescent systems, for instance, are very effective flame retardants, which can fulfil highest standards concerning flame retardancy, smoke density, and smoke toxicity as required e.g. in the Airbus standard ABD 0031 (Table 4). Hand lay-up, sheet moulding compounds (SMC), and pultrusion are widely used for the production of mainly glass fibre-reinforced liquid resin parts which are used in transport applications.

Typical products of hand lay-up are rotor wings for wind mills, boat hulls, and parts for train heads. SMC products are more used for the production of e.g. sidewall parts made of highly filled resins (320 phr mineral fillers are easy to be used) for highest flame retardancy. Pultrusion is mostly used for long, uniform parts like ducts. Here, the size of the ATH particles and the viscosity in the resin are decisive to achieve good wetting of the glass fibres and to prevent filtration and sedimentation of the minerals. The typical processes for hand lay-up and pultrusion are shown in Figure 5.

A good processability of the resin mixture is crucial. For railway applications, comparably high contents of flame retardants are necessary to comply with severe standards. Often, a mineral flame retardant, namely, ATH is used for such applications. If e.g. 200-400 phr of ATH are properly mixed into 100 phr of UP resins, hand lay-up, SMC or pultruded composites pass the test according to the French standard NF P 92-501 or the German railway standard DIN 5510 S4, with some of these composites being provided with a gel coating. Mainly viscosity-optimised ATH grades

| | Condition | 20% Intumescent system | 25% Intumescent system | Limit (ABD 0031) |
|---|------------------------|------------------------------|------------------------------|---------------------|
| Smoke density (DS after 4 min) | non flaming flaming | 160 122 | 134 161 | - |
| Hydrogen cyanide HCN [ppm] | non flaming | 1 | 1 | 150 |
| | flaming | 5 | 5 | 150 |
| Carbon monoxide CO [ppm] | non flaming | 20 | 10 | 1000 |
| | flaming | 200 | 200 | 1000 |
| Nitrous gases NOx [ppm] | non flaming | 0 | 0 | 100 |
| | flaming | 10 | 10 | 100 |
| Sulfur dioxide hydrogen sulfide | non flaming | 0 | 0 | 100 |
| SO2-H2S [ppm] | flaming | 0 | 0 | 100 |
| Hydrogen fluoride HF [ppm] | non flaming | 0 | 0 | 100 |
| | flaming | 0 | 0 | 100 |
| Hydrogen chloride HCI [ppm] | non flaming | 0 | 0 | 150 |
| | flaming | 0 | 0 | 150 |
| Pass ABD 0031 (commercial aircraft interiors" ABD 0031) | non flaming flaming | Yes Yes | Yes Yes | |

Table 4: Intumescent systems in ABD 0031



Figure 5: Hand lay-up and pultrusion processes

are recommended for this use, as they allow such high loading levels without making the resin too viscous.

Tables 5 and 6 present two formulation examples for hand lay-up and pultrusion. Here, it is obvious that with high loading levels of ATH good fire retardancy can be reached, strict fire standards can be fulfilled easily .Gel coatings are a way to protect composite materials by a top layer with a high concentration of flame retardants. Intumescent

| Component | Content (phr [*]) |
|---------------------------|-----------------------------|
| UP resin | 100 |
| ATH, viscosity-optimised | 200 |
| Property | |
| Viscosity | 2,7–3,4 Pa*s |
| LOI | 52–55 % O ₂ |
| * Parts per hundred resin | |

Table 5: Example of a hand lay-up FR formulation for UP resin

formulations can be used for epoxy or unsaturated polyester gel coatings at loadings of 75 -100 phr, depending on the resin system and the required fire test. Combinations with ATH are also possible. The advantages of gel coatings are the overall lower flame retardant loadings in the laminate, which result in a lower viscosity, better injection behaviour, and higher amounts of reinforcement materials. Overall, a lower density of the parts and better mechanical properties can be achieved.

| Component | Content (phr) |
|--------------------------|---------------|
| UP resin | 100 |
| ATH, viscosity-optimised | 300 |
| Additives | 5,6 |

Table 6: Example of an HFFR pultrusion formulation for UP resin to comply with DIN 5510 S4 and M1 according to NF P 92-501

Figure 6 shows an example of a complex sandwich system of epoxy laminates covering a PVC foam, with one side protected by a gel coating. Figure 7 shows the effect of the gel coating thermally insulating the layers underneath.



Figure 6: Example of an FR epoxy gel coating on a composite material consisting of a PVC foam core with laminate covers. The upper side was exposed to a flame for 10 min and nicely shows the intumescent effect (picture on the right).

3.4 SUMMARY OF HFFRS IN INTERIOR APPLICATIONS

The appropriate choice of the environmental friendly flame retardant strongly depends on the application and the required fire standard. Table 7 presents an overview of the main types of interior parts with their corresponding suitable polymers and flame retardants.



Figure 7: Demonstration of the effectiveness of gel coatings with different flame retardants. The temperature on the back of a sample board is recorded versus time while a flame impinges on the front side which is protected by the gel coating.

| Application | Polymer | HFFR |
|---|--|---|
| Flooring | PVC | ATH, isopropylated phosphate ester, CDP, zinc borate |
| | Polyolefins | MDH, ATH, intumescent systems, new phosphonates |
| | Ероху | ATH, APP, intumescents, ethylene diamine phosphate, melamine borate, DOPO |
| | Phenolic resins | Melamine borate, phosphate esters |
| | Urethane elastomers | Aluminium phosphinate, melamine cyanurate, TPP, CDP, APP, melamine phosphate, melamine polyphosphate |
| | Elastomers | ATH, MDH, P-based |
| Ceilings Sidewalls Panels Structural parts | UP resin VE resin Acrylate resin EP resin | ATH, APP, EDAP, intumescent systems, DMPP ATH, APP ATH, APP, intumescent systems ATH, APP, intumescent systems, DMPP, DOPO, cyclic phosphonate |
| | Phenolic resins | Melamine borate, phosphate esters |
| Dashboard Instruments Instrument panels Instrument cluster housing Speaker grilles Gear knobs Console parts Trunk tailgates Steering wheels Air ducts Tubing Door trim / handle Pillar claddings Door pockets Door panels Chairs Other interior devices | PC ABS PC/ABS TPU TPE Polyamide, nylon Polyolefin Reinforced PP RIM UPR | Sulphonates TPP, RDP, and BDP TPP, RDP, and BDP APP, metal phosphinate, melamine cyanurate, melamine polyphosphates, TPP, CDP, zinc borate Metal phosphinate +N-synergist, intumescent systems Melamine cyanurate metal phosphinate +N-synergist Intumescent systems Intumescent systems APP, ATH, melamine phosphate, melamine polyphosphate, intumescent systems ATH, APP, EDAP, melamine phosphate, DMPP, intumescent systems |
| Insulation materials | r-PUR PIR | P-polyols, DMPP, APP, TEP |
| Coatings | 2K-PU, epoxy, acrylates | ATH, phosphate esters, APP |
| Sealants (flame-retarded and/or fire-resistant) | PUR, acrylics, epoxy, elastomers, PVC | ATH, APP, RP, EDAP, melamine phosphate and -pyrophosphate, melamine polyphosphate, phosphate esters, melamine borate, zinc borate |

Table 7: Overview of HFFR solutions for different groups of applications

4 Textiles

4.1 INTRODUCTION

Textiles and fabrics can generally be described as flexible materials consisting of a network of fibres. Different techniques exist to produce woven (e.g. by weaving, knitting, crocheting, or knotting, etc) or non-woven articles (e.g. 'felt', produced by pressing fibres together).

Fibres can be of different origins:

- Animal, e.g. wool (cashmere, mohair, angora, etc.), silk, etc.
- Vegetal, e.g. cotton, flax, jute, hemp, sisal, etc.
- Mineral, e.g. glass fibres, basalt fibres, etc..
- Synthetic, e.g. acryl, polypropylene, polyester, polyamide, polyurethane ("spandex"), aramide, etc.

Textiles may be made of homogeneous fibres or blends (e.g. polyester/acryl, cotton/polyamide, etc.).

Textiles used for clothing and carpets have a long tradition, even dating back to prehistoric times. Modern uses are far more versatile and sophisticated, ranging from household (towels, curtains, upholstery, bedding, etc.) to strictly technical applications which have to meet stringent performance requirements, such as geotextiles, agro textiles, protective clothes (e.g. fire fighter clothing) and technical fabrics, e.g. as reinforcements for composite applications.

This section will deal with the more traditional uses of textiles in transportation, thus excluding e.g. natural fibres used in reinforced plastics or fabrics used in composites. Leather, although not a textile product per se, is an alternative material competing with textiles for the same functionality. It is therefore included in the scope of the document.

| | Fibre | Flammability and fire behaviour |
|--|--|---|
| + | Cotton Flax | Ignite easily Burn heavily with white smoke formation Do not melt away from the flame |
| | Viscose | Burn rapidly like cotton |
| | Acetates | Burn heavily May melt away from the flame without burning Form burning drops |
| Increasing fire hazard & need for FR treatment | Acrylics | Burn rapidlyForm burning dropsForm dense black smoke |
| | Polyamide Polyolefins Polyesters Other synthetics | Burn slower, while releasing a high amount of heat May melt away from the flame without burning Form burning drops May continue glowing after flame extinction |
| | Wool | Difficult to ignite Burn slowly May self-extinguish under certain conditions |
| | Modified acrylics ("Modacrylics") | Burn very slowly Tend to melt away from the flame without burning May self-extinguish under certain conditions |
| | Aramide | • Does not burn, strong char formation |

Table 8: Reaction to fire of various fibres (source: LNE¹²)

¹² Translated from Carine Chivas et al, Laboratoire National d'Essais (LNE, France), 2007. « Etude sur les effets de l'ignifugation de certains meubles rembourrés dans le cadre d'un projet de réglementation relative à la sécurité incendie. Partie 1 : Etat de l'Art ». Projet R&D 27EAF6707. ("Study about the effects of flame retardant treatments of certain upholstered furniture, in the frame of a draft legislation relative to fire safety. Part 1: State-of-the-Art")

4.2 TEXTILES AND FIRE SAFETY

Generally speaking, textile articles, due to their low mass, represent a relatively low quantity of fuel ('fire load') compared to other organic materials. However, most of them pose other fire risks due to their ignitability, their potential to propagate the flame, and in particular their ability to melt and produce burning droplets. Their "reaction-to-fire" is essentially determined by the chemical backbone of the raw materials, no matter whether these are of natural or synthetic origin. The behaviour of non-FR-treated textiles can therefore vary strongly when exposed to an ignition source.

| Fibre | LOI-value | Melting point [°C] | External ignition [°C] | Self ignition [°C] |
|---------------|-----------|-----------------------|---------------------------|-----------------------|
| Acrylic | 18 | 215–260 | 225 | 515 |
| Polypropylene | 19 | 160–175 | | 430–450 |
| Cotton | 19 | - | 350 | 400 |
| Viskose | 20 | - | 350 | 420 |
| Polyamide | 20 | 215–220 | 430 | 530 |
| Polyester | 21 | 255 | 390 | 510 |
| Wool | 25 | - | 325 | 590 |
| Modacrylic | 27 | 130–170 | | 650–700 |
| m-Aramide | 28 | - | | 675 |
| p-Aramide | 29 | - | | - |
| Carbon | > 60 | - | | - |

Table 9: Flammability properties of polymers according to Denkendorfer Fibre Tables © 1986 textil praxis international

4.3 OVERVIEW OF TEXTILES USED IN TRANSPORTATION

Textiles are used in a variety of ways in the different means of transportation. The most common ones are summarised below.

4.4 WASH RESISTANCE & APPLICATION TECHNIQUES OF FR ON TEXTILE PRODUCTS

Depending on their final use, textiles may be subjected to cleaning under various conditions. Different levels of wash resistance (relating to the permanency of the FR treatment) can be obtained:

| Transportation | Uses | Fabrics |
|----------------|---------------------------|---|
| cars / coaches | seat cover | polyester artificial leather (TPU-based) cellulosic/polyester blends leather |
| | insulating non-woven | polyester polypropylene viscose |
| | carpet/floor covering | polyester or polypropylene |
| | rubber band | polyester |
| | belt | polyester |
| | curtains (buses) | polyester |
| | airbags | polyamide |
| aeroplane | seat cover | wool or wool/polyamide leather |
| | floor covering backing | wool, polyamide or wool/polyamide cellulosic fibre |
| | wall covering | wool/aramid or aramid |
| | draperies | wool polyester |
| railways | seat cover | wool or wool/polyester leather |
| | | artificial leather (TPU-based) |
| | wall and ceiling | polyester |
| | curtain | polyester |
| | floor covering | wool, polyamide or wool/polyamide |
| | backing | cellulosic fibre |
| ship | seat cover | polyester |
| | curtain | polyester |
| | floor covering | wool or wool/polyamide |
| | backing | cellulosic fibre |

Table 10: Overview of textiles used in transportation



- Non-durable: not resistant at all to washing
- Semi-durable: FR treatment can survive a limited number of washing / soaking cycles
- Durable: FR treatment remains when subjected to a number of wash cycles

These different levels of permanency are achieved by applying FR by different methods.

- a) Non-durable treatment, as e.g. required in cars, results from depositing water-soluble salts onto and between the fibres by padding and drying. In a continuous process, the textile is immersed in a bath of a flameretardant solution and then squeezed between two rollers at a controlled pressure. By this process, a predetermined quantity of the flame retardant is added to the textile. The amount applied must be sufficient to reach the required performance. The textile is then dried, again in a continuous process, at temperatures in the range of 100–160°C depending on the material.
- b) Semi-durable treatment can be achieved in two ways: - Weak cross-linking of special FR salts with the fibre: this is normally limited to a few textile/FR combinations, such as cotton with specific FR substances. After the impregnation, the fabric will be dried and cured. - Application through back-coating: this technique is suited for all textiles in general and application is limited only when fabrics have a sensitive surface structure that could be damaged during processing. An FR coating is applied, as either a paste or foam, onto the back of the textile using a system of rollers or blades, to apply a level that ensures the required performance. The coating is then dried and the temperature raised, to crosslink the binder. The durability of these coatings is essentially determined by the nature and characteristics of the binder.

c) Durable treatment is achieved by the following five techniques and processes:

 Reactant cross-linking: chemically stable cross-linking between substrate and FR, e.g. FR treatment of cellulosic fibres.





The FR is applied as a solution, before drying and curing. Non-reacted molecules are then neutralised and washed off, before the fabrics can finally be dried.

– Self cross-linking: Polymerisation or polycondensation of the FR onto the substrate, e.g. for FR treatment of knitted or woven fabrics.

An FR pre-condensate is applied by padding in an aqueous medium. The treated fabrics are then forwarded into a closed chamber, where ammonia gas will react with the pre-condensate to create an insoluble FR polymer. The treated fabrics will then go through various oxidation, ventilation, neutralising and washing processes to remove nonreacted molecules and reaction by-products before drying.





Thermal fixation: deposition of the FR inside the fibre,
 e.g. post-treatment of polyester fibres.

The FR is added to an aqueous liquor which is applied at higher temperature (190-210°C), thus penetrating into the fibre. When the fibres cool down, the FR is trapped between the polymer chains and can no longer be removed by washing, although it is 100% water-soluble. It is also possible to apply an FR from the polyester dye bath. The high temperature dyeing opens the fibre structure, allowing penetration of the FR. After dyeing, the fibre cools down trapping the FR within the fibre.

- Ionic linkage: binding of negatively charged complexes to positively charged basic groups, e.g. FR treatment of wool.

Application by exhaustion from an acidified liquor. Ions are exchanged between the FR and the fibre. This results in the exhaustion of negatively charged complexes onto positively charged basic groups. The final result is an ionic linkage. – Inherently FR fibres can be produced. These technologies relate more to polymer chemistry than to textile treatment.

aa) by adding an FR co-monomer or FR pigment in the polymerisation step (e.g. polyester fibres, such as Trevira[®] CS, Trevira; HEIM[®] (Toyobo); Lenzing FR[®], Lenzing)

bb) by designing polymer backbones with very high heat and flame resistance, e.g. polyaramide fibres based on meta-polyphenylene isophtalimide (Nomex[®], DuPont; Conex[®], Teijin), polyamide-imide (Kermel[®], Kermel), parapolyphenylene terephtalimide (Kevlar[®], DuPont; Twaron[®], Teijin), polytetrafluoroethylene (PTFE, i.e. GORE-TEX®, W.L. Gore), and a few others.

4.5 PIN FR'S USED IN TRANSPORTATION TEXTILES

The following table lists the substances that are most commonly used in textiles. With a few exceptions, combinations of different substances must be used in order to meet the various requirements, including the necessary fire standard, but also other aspects, such as the functionality of the textile, wash resistance, handling (soft, hard), etc.

| Substance | Physical form | Use |
|--|----------------------------|---------------------------------------|
| Aluminium-tri-hydroxide (ATH) | Powder | Back-coating or added to polymer melt |
| Aluminium phosphinate | Powder | Back-coating or impregnation |
| Amino-Ether-HALS derivatives | Powder | Added to polymer melt |
| Ammonium phosphate | Powder or aqueous solution | Back-coating or impregnation |
| Ammonium polyphosphate | Powder | Back-coating |
| Ammonium sulphamate | Powder or aqueous solution | Back-coating or impregnation |
| Ammonium sulphate | Powder or aqueous solution | Back-coating or impregnation |
| Cyclic phosphonate | Liquid | Impregnation Added to polymer melt |
| Dicresyl phosphate | Liquid | Added to polymer melt |
| Diethyl phosphinic acid, aluminium salt | Powder | Back-coating or added to polymer melt |
| Guanidine phosphate | Powder or aqueous solution | Back-coating or impregnation |
| Isopropyl phosphate ester | Liquid | Added to polymer melt |
| Melamine | Powder | Back-coating |
| Melamine cyanurate | Powder | Back-coating or added to polymer melt |
| Melamine phosphate | Powder | Back-coating |
| Melamine polyphosphate | Powder | Back-coating or added to polymer melt |
| Methyl phosphonic acid, amidino-urea compound | Liquid | Back-coating or impregnation |
| Oxaphosphorinane oxy-bis-dimethyl sulphide | Powder | Back-coating or added to polymer melt |
| Potassium hexafluoro titanate | Powder | Reacted on fibre |
| Urea | Powder or aqueous solution | Impregnation |
| Zinc borate | Powder | Back-coating or added to polymer melt |
| Zirconium acetate | Liquid | Reacted on fibre |

Table 11: Halogen-free flame retardants for transportation textiles

5 Seats

5.1 INTRODUCTION

Seats are essential components of all transportation systems. They are integral parts of the safety concept and, at the same time, they offer comfort to the passengers. In general, most of the seats are built of three main components:

Framework:

The framework determines the general shape of the seat. It also provides for the main mechanical properties. It can be made of metal or plastics (mainly polypropylene or polyamide).

Foam:

Foams offer body support (load bearing) as well as comfort (vibration damping) to the passengers. They are mainly made of flexible polyurethane.

Covering:

Coverings protect the foam and framework against soiling. At the same time, the covering should also contribute to the comfort of the passengers and to the design of the vehicle. Usually textiles, leather, and artificial leather are used as coverings. All kinds of coverings are described in chapter 5 (Textiles) and, hence, not covered in this section.

5.2 AUTOMOTIVE

Seats in automotive applications, such as passenger cars and buses, offer comfort, ergonomics, and safety to passengers. These functions should be maintained over the many years of service life of the vehicles.

At the same time, seats should not contribute to any fire risk and, hence, have to comply with fire standards. The most common one is the Federal Motor Vehicle Safety Standard 302 (FMVSS 302) that has been adopted by several countries as ISO 3795 and is therefore used all over the world for automotive interiors, including seats. The standard was developed in the 1970s and no major updates have been made since then, although the types and amount of materials used in vehicles have increased and changed considerably over the last decades.



5.2.1 FRAMEWORK

The framework of automotive seats is made of metal or plastics. Frameworks made of metal are inherently flameresistant and can therefore be used without FR treatment.

Plastics are also used to reduce weight without compromising the mechanical function.

The most common framework materials are polyamide (PA) and polypropylene (PP). Both polymer families are organically based materials and, hence, relatively easy to ignite and can burn heavily. However, both PA and PP usually pass the required FMVSS 302 fire test (horizontal flame propagation) at a certain thickness without the addition of a flame retardant.

5.2.2 FOAM

Automotive foams are usually made of flexible polyurethane. They are produced either as slabstock or as moulded foam. The foam is that component of the seat that essentially contributes to the comfort of the passenger. The main functions of the seating cushions are body support and vibration damping. Both properties should be maintained over long periods of use. Flexible polyurethane (PUR) foams are inherently flammable like most organic materials. Foams in general tend to be easily ignitable, as they represent a pre-mixture of fuel and air in physical structure. The fire performance of PUR foams is influenced by several parameters, such as raw materials used (nature of the polyol, foam stabilisers, etc.), foam density, and air flow. High-density PUR foams in particular pass the FMVSS 302 fire standard without modification. At lower densities, flame retardants have to be added to meet the FMVSS 302 fire standard. In addition to the required level of fire safety, the flame retardants used have to meet the following criteria:

- No impact on the dynamic properties
- No impact on the properties after ageing (high-temperature and humidity)
- No contribution to fogging or emission

These requirements are fulfilled by several different halogen-free flame retardants. Phosphorus-based flame retardants, such as liquid and solid phosphates, are most commonly used. Generally speaking, three different groups of phosphorus-based flame retardants are used for automotive seats:

Additive liquid flame retardants: This group of products can be incorporated easily in the foam, because most of the raw materials are handled in the form of liquids. On the other hand, they can affect the mechanical proper-

| Flame retardants | Chemical name | Appearance | Phosphorus content [%] | Viscosity at 25°C [mPa.s] |
|-------------------------|--|------------|---------------------------|------------------------------|
| IPP | Isopropylated triphenyl phosphate | liquid | 7.4 | 100 |
| BPP | Butylated triphenyl phosphate | liquid | 8.1 | 92 |
| ITAP | Isopropylated triaryl phosphate | Liquid | 8.3 | 60 |
| CDP | Cresyl diphenyl phosphate | liquid | 9.1 | 45 |
| ТСР | Tricresyl phosphate | liquid | 8.4 | 75 |
| RDP | Resorcinol bis (diphenyl phosphate) | liquid | 10.8 | 600 |
| BDP | Bisphenol A bis-(diphenyl phosphate) | liquid | 8.9 | 13.000 |
| Oligomeric phosphate | Oligomeric alkyl phosphate | liquid | 19.0 | 2.250 |
| Reactive P/N polyol | N,N-dihydroxyethylamino-methan Phosphonic acid ester | liquid | 12.1 | 175 |
| P-Polyol 1 | Proprietary, functionality 2 | liquid | 11.5 | < 500 |
| APP | Ammonium polyphosphate | solid | 31.5 | - |
| MEL | Melamine | solid | 66.4% N | - |
| EDAP | Ethylene diamine Phosphate | solid | 19.5% P 17.5% N | - |
| MP | Melamine phosphate | solid | 14.5% P 37% N | _ |

Table 12: Overview of common halogen-free flame retardants for automotive PUR foams

No impact on the processing of the foams

| No impact on the mechanical properties (hard | ess) |
|--|------|
|--|------|

ties due to their plasticising properties. Furthermore, they can contribute to emissions from the foam, as they are not incorporated in the polymer matrix.

- Reactive liquid flame retardants: This group of products is incorporated in the polymer chain usually by a reaction with isocyanate. Thus, they are integral parts of the polymer and do not contribute to emissions from the foam, nor do they have a plasticising effect. The processing window of these products often is narrow and some of them may influence the ageing properties of the foam.
- Solid flame retardants act as fillers in the foam. Hence, they do not contribute to emissions and tend to increase the hardness of the foam. They may affect the dynamic properties of the foam. Usually, they are incorporated in the liquid raw materials as a dispersion.

An overview of common halogen-free flame retardants for automotive PUR foams is presented in Table 12.

These flame retardants are typically added in dosages between 2 and 15 php (parts per 100 parts polyol) to meet FMVSS 302 depending on the foam density and raw materials used.

In recent years, fogging and other emission sources gained increasing attention when studying the equipment of automotive interiors. Seats which are among the largest interior components and especially foams might contribute to the emissions in a car. Therefore, the contribution of flame retardants in foams to total emissions is an increasingly important criterion for the selection of a product. The fogging and emissions are measured by several test methods. In all these methods, the material is heated for a certain time at a fixed temperature. All emitted substances are collected and either weighed (e.g. DIN 75201) or detected by GC-MS (VDA 278).

Fogging data of various flame retardants of a typical automotive PUR foam are shown in Figure 8.



Figure 8: Fogging data of flame retardants of a typical automotive PUR foam: Polyether, density 28 kg/m³, 6 php (parts per 100 parts polyol) flame retardant; measured according to DIN 75201 (6 hours at 100°C)

5.3 AEROPLANE

5.3.1 FRAMEWORK

The framework of aeroplane seats is usually made of metal. These frameworks are inherently flame-resistant and can therefore be used without taking any further fire safety measure.

5.3.2 FOAM

Foams for aeroplane seats or seat cushions are usually made of flexible polyurethane. In order to meet the very stringent fire blocking requirements (i.e. FAR 25 or ABD 031) for aeroplane seats, the foam must be treated or has to be protected by a fire-proof layer. Usually, expandable graphite is added to the foam as flame retardant, often in combination with other liquid phosphates.

It is also possible to use melamine foam for the seat cushions. This material has an inherent fire resistance.

In addition, seats in aeroplanes have to fulfil smoke density and smoke toxicity requirements. This is another reason for the use of fire-blocking layers in seats. This layer protects the seat from the flame attack and therefore reduces the contribution of the seat to heat development and smoke density.

Since the toxicity tests strictly limit the release of hydrogen chloride (HCI), use of flame retardants containing chlorine is restricted.

5.4 RAIL VEHICLES (RAILWAY AND SUBWAY)

Rail vehicles may operate in different environments, e.g. above ground (with or without tunnels) or underground. These environments have a strong influence on the fire risk of a rail vehicle. The new harmonised European fire standard for railways CEN/TS 45545 takes this into consideration and distinguishes between several operation and design categories, with the material being classified according to different hazard levels.

Seats as integral parts of all rail vehicles are also affected by these different hazard levels. Several materials are used to build up a seat system. Many of the materials are poly-



mers and must be flame-retarded to pass the required fire standards.

According to CEN/TS 45545, complete seats have to be tested in their final configuration, but the single components also have to be tested individually. In some cases, parts have to be tested as composites when used as such, e.g. textiles laminated on PUR foam.

The relevant fire standard is based on calorimetric data (rate of heat release, peak heat release), smoke density as well as the toxicity of smoke.

5.4.1 FRAMEWORK

The framework of sub- and railway seats is usually made of metal. These frameworks are inherently flame-resistant and can therefore be used without taking any further fire safety measure.

5.4.2 FOAM

Foams for railway seats are usually made of flexible polyurethanes of higher density. In order to meet the very stringent fire safety requirements, the foam usually contains a combination of a liquid flame retardant with solid flame retardants, such as expandable graphite, ammonium polyphosphate or melamine (or its derivatives). It is also common to use less flammable polyols for the production of these types of foams. Such polyols usually contain nitrogen and/or phosphorus compounds dispersed in the liquid phase.

6 Cables

6.1 INTRODUCTION

Modern transportation is unthinkable without cables. Cables transmit energy and ever growing amounts of data. Large numbers of them are installed in vehicles like cars, trains, ships, or aeroplanes. They are installed in horizontal direction underneath floors or horizontally and vertically between walls and ceilings. Thus, fire tests for such cables also include different scenarios. Cables generally contain a substantial amount of inherently flammable polymer materials as insulation, sheathing, or bedding compounds. Due to their presence all over the vehicle and the nature of their installation, a burning cable may cause dramatic fires and the fire may spread over large distances. Typical causes of fires in vehicles are ignited waste containers or leaking fuels or oil¹³.

Depending on the difficulties for people to escape from a burning vehicle, the fire resistance standards are more or

¹³ The FIPEC-report, Fire Performance of Electric Cables – new test methods and measurement techniques – Interscience Communications Ltd. 2000



less severe. As escape from aeroplanes, ships, or trains usually is more difficult than from a car, the materials used in the former must be more fire-resistant according to several national and international standards.

Halogen-free flame retardant (HFFR) or low-smoke free-ofhalogen (LSFOH) polymer compounds can be used in many ways to produce safe and functional cables. Selected polymers and the corresponding flame retardants, together with some general facts about the flame-retardant (FR) systems, are presented in Table 13.

| Flame retardant | Polymers | Applications and effectiveness |
|---|--|---|
| Aluminium tri-hydroxide (ATH) Magnesium di-hydroxide (MDH) Aluminium oxide-hydroxide (AOH, boehmite) Also coated grades are available. | Low-density polyethylene (LDPE) Ethylene vinyl acetate (EVA) Polyolefins Elastomers Silicone rubbers (SiR) | In case of a fire, these mineral flame retardants decompose absorbing energy. releasing water (thus reducing fire intensity and diluting fire gases). creating an oxide fire barrier against heat from the flame and to prevent burnable polymer decomposition products from reaching the flame. |
| Phosphorus flame retardants Phosphate esters (eg. tricresyl phos- phate TCP) Intumescent products based on: ammonium polyphosphates (APP), metal phosphinates, aryl phosphates Melamine phosphate Red phosphorus | Used in fire-resistant coatings for cables Polyolefins Elastomers Thermoplastic Elastomers (TPE) Polypropylene (PP) | Flame inhibition and charring prop- erties of phosphorus-based materials reduce the flammability of polymers. A char on the surface prevents heat transfer and protects polymer below. |
| Melamine Cyanurate (MC) | Polyamides (PA) | Results in polymer decomposition without flaming, especially in PA. |

Table 13: Selected flame retardants for use in HFFR cable compounds, selected polymers for which they are recommended, and information on their working mechanism

Depending on the use of a cable in a vehicle, different standards have to be complied with and the materials have to be chosen according to the mechanical and thermal stresses during installation and service life. Not only the cable, but the whole construction in the vehicle must be flame-retardant. Cable ducts which are often used to accommodate cables and to protect them from damage have to be mentioned in particular. These ducts must have a level of flame retardancy comparable to that of the cables, but they do not need to have the flexibility of a cable and are usually made of thermoplastic materials like PVC or polyolefins, mainly PE or PP, as polymer matrix.

A formulation for a cable duct based on Polyolefins could be more or less comparable to cable compound formulations with a relatively high amount of aluminium hydroxide or magnesium hydroxide as well as intumescent FR systems as mentioned below. High filling levels of >50 wt-% of a mineral flame retardant are necessary to guarantee relevant FR properties, e.g. good UL 94V ratings, as shown in Table 14 and in Figure 9.

The working mechanism of mineral FRs is based on physical phenomena. Hence, relatively high amounts of these materials are needed to reach a high flame resistance compared to FR systems that work via specific chemical routes.

For TPE-S, TPE-V, TPE-O, and polyolefins, intumescent systems can be used at moderate loading levels to pass the UL-94, UL-62 (VW-1, US flexible cords and wires) vertical cable (UL 1581), or 45° cable tests (ISO 6722/1). The new family of halogen-free flame-retardant TPEs, for instance, is

| Polymer system | Filling level [wt%] |
|---------------------------------|------------------------|
| Epoxy resins | 55 |
| Unsaturated polyester resins | 58 |
| EVA | 62 |
| PE | 65 |
| PP | 67 |

Table 14: Minimum ATH filling levels to reach UL 94 V0 (at 3.2 mm) for selected polymers

an alternative to traditional flexible vinyl jacketing and insulation for e.g. consumer electronics applications, cf. chapter 6 of this brochure. They can be used among others for cable extrusion, corrugated pipes, and cable conduits. The intumescent mechanism ensures high FR performance and very low smoke density/toxicity. TPEs, for instance, successfully pass the ABD 0031 smoke toxicity test (Airbus directives). Modern intumescent systems based on surface-treated particles even pass demanding water storage tests required in cable industry. Due to a moderate FR loading, the TPE HFFR technology reaches a very good FR performance combined with excellent aesthetics and haptic properties.

The following chapters will describe some cable compounds for use in vehicles in more detail.



Figure 9: LOI values of EVA compounds plotted against the filling content of metal hydrate in the compounds

6.2 ROAD TRANSPORT (CARS / TRUCKS / BUSES)

In road vehicles cables are used in large numbers, mainly under the hood. The constantly growing use of electronic devices in such vehicles led to a large demand for e.g. data bus cables for sensors and monitoring systems over the last decades. In 1955, a typical passenger car contained 45 m of cables. In the 1960s, roughly 200 m of cables were installed. Nowadays, up to 1500-5000 m of different cables are installed in a road vehicle depending on the type and equipment. Today's focus is on thinner cable insulation and sheathing and on less dense cable compounds of the same performance level to reduce the weight of this integral part of a car¹⁴.

Depending on their use, e.g. their distance to the engine, cables in automobiles have to withstand certain temperature ranges which are classified from class A to H (T1 to T8). According to these temperature classes, different polymers (halogenated and halogen-free products) can be used to produce cable insulation and sheathing compounds. Some examples are listed in Table 15, together with useful flame retardants for this application. Cables in automobiles do not only have to be resistant against a broad temperature range, but also against different media like oils, battery acid, or fuels to avoid large damage after a spill of a small amount of such aggressive fluids.

A compound for an automotive cable can be based on cross-linked PE, as mentioned in Table 16.

| Component | Content [phr] |
|-------------------------------------|---------------|
| PE | 100 |
| Maleic anhydride grafted polymer | 10 |
| Antioxidants | 0,5 |
| MDH | 130–150 |

Table 16: XLPE guiding formulation with MDH as flame retardant

| Class | Temperature range [°C] | Polymers | Flame retardants |
|--------|------------------------|---|---|
| A (T1) | -40 to +85 | PE, PP, PVC, TPE, XLPVC | ATH, MDH, phosphate esters |
| B (T2) | -40 to +100 | EVA, PA, PE, PP, PVC, TPE, XLPE, XLPVC | APP, ATH, MDH, phosphate esters |
| C (T3) | -40 to +125 | EVA, PP, PUR, PVC, TPE, TPU, XLPE, XLPVC | APP, ATH, MC, MDH |
| D (T4) | -40 to +150 | TPE, TPU, XLPE, fluoropolymers (ETFE, FEP, PVDF) | APP, MC, MDH or intrinsically fire-resistant polymers |
| E (T5) | -40 to +175 | ETFE, FEP, SIR | Intrinsically fire-resistant |
| F (T6) | -40 to +200 | ETFE, FEP, SiR | Intrinsically fire-resistant |
| G (T7) | -40 to +225 | Fluoropolymers (PTFE, PFA) | Intrinsically fire-resistant |
| H (T8) | -40 to +260 | PTFE, PFA | Intrinsically fire-resistant |

Table 15: Temperature ranges for the temperature resistance classification (3000 h) of cables in road vehicle use according to ISO 6722, useful polymers, and flame retardants¹⁵</sup>

 ¹⁴ a) Karl Brown (Equistar Chemicals LP, LyondellBasell) AMI Conference Cables, 9-11 March 2010, Cologne, Germany;
 b) White Paper Automotive, February 2007, Nexans

 ¹⁵ a) Kabelbuch 2003, Automobilleitungen Coroplast Fritz Müller GmbH & Co KG.
 b) Huber+Suhner AG, Pfäffikon, "Automotive Products", Edition 2009.
 c) Leoni Kabel GmbH, Roth, "We keep on moving" Business Unit Automotive Cables.
 d) White Boase Automotive, Entruore 2023, Navara

d) White Paper Automotive, February 2007, Nexans.

| Property | TPE-E (Shore D 55) | TPE-E (Shore D 40) | |
|-------------------------|--------------------|--------------------|--|
| | Al-phosphina | ate (20–22%) | |
| UL 94 rating [1.6 mm] | VO | V1 | |
| GWIT 1 mm [°C] | 775 | 650 | |
| GWFI 1 mm [°C] | 960 | 900 | |
| TS [kJ/m ²] | 20.5 | 16.9 | |
| E@B [%] | 322 | 547 | |
| Notched impact strength | 13.1 | No breaking | |
| Shore D | 56 | 38 | |
| MFI [g/10 min] | 42 | 20 | |
| Spiral flow [cm] | 47 | 42 | |

Table 17: Selected properties of TPE cable compounds containing phosphinate flame retardants

In Europe, the main mineral flame retardant for this application is magnesium hydroxide (MDH), whereas in the USA, the use of aluminium hydroxide (ATH) for automotive XLPE cables is more common¹⁶.

Sustainability has become a major issue and trend in individual transport, the focus being on alternative fuels and on (partly or completely) electric cars. In electric and hybrid cars, typical voltage is higher than in fuel-driven cars. Hence, cables in these cars must be specially designed for operation under more severe conditions and to resist sparkover voltage. TPE-, PVC-, or XLPE-based cable compounds can be recommended for use in such installations¹⁷.

In HFFR TPE cable compounds, intumescent FR systems and finely grained metal phosphinates can be used. Depending on the Shore hardness and the overall balance of required properties, dosage should range between 20 and 30% metal phosphinate. A combination with nitrogen synergists can further improve the FR system and small amounts of PTFE can prevent dripping of burning material during the fire.

Some properties of cable compounds based on TPE materials are presented in Table 17.

6.3 PUBLIC MASS TRANSPORT (TRAINS, SHIPS, AEROPLANES)

Trains

It is important to note that also in public mass transport systems like trains, ships, and aeroplanes, fires cannot be avoided completely. Hence, flame propagation must be slow and smoke development must be as low as possible to allow people to escape safely. This is reflected by more severe standards compared to road transport vehicles.

In recent years, efforts were made to develop common standards for materials to be used in trains in Europe – the CEN/TS 45545 describes them. Details will be given in the chapter on standards in this brochure. Among others, tests for vertical flame spread, smoke density or toxicity of the smoke are required.

Numerous cables are installed in trains for different purposes, as shown in Figure 10. In every single wagon, different cables are required, e.g. for lighting, control panels and for information and entertainment of the passengers. Motor cables, control panels, and different cables for communication to the train are installed in the locomotive. Between

¹⁶ Karl Brown (Equistar Chemicals LP, LyondellBasell) AMI Conference Cables, 9-11 March 2010, Cologne, Germany.

¹⁷ Leoni Kabel GmbH, Roth, "We keep on moving" Business Unit Automotive Cables.



Figure 10: Selected cables in a train, position and purpose. Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.

the single wagons, jumper cables guarantee the transmission of data and energy.

As mentioned above, cables for trains have to comply with severe standards for fire resistance and low smoke development. For this reason, usually higher amounts of mineral flame retardants are used here compared to cables for automobiles. This leads to an improved flame-retardancy and reduced smoke density at the same time. A typical content of ATH in such cables is around 60 wt.-%, but it may vary according to the detailed formulation.

According to their installation and use, the mechanical properties and resistance of cables against environmental impacts have to be adjusted, e.g. cables which are close to fluid-containing installations should be resistant to these media.

Two examples of cables in a train are shown in Figures 11 and 12, a cable for installation in a wagon or locomotive and a jumper cable.



Figure 11: Cable for installation in a wagon. Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.



Figure 12: Jumper cable. Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.

As shown in the figures above, cables for installation in trains usually consist of several layers. The insulation protects the single conductors and the sheathing protects the cable from environmental impacts. The composition of the polymer compounds is adjusted to the purpose, e.g. the sheathing often contains more flame retardant substances than the other layers of the cable.

Typical polymer compounds for insulation of the metal wire or glass fibre for cables in public transport are XLPE, PVC, or Ethylene propylene rubber (EPR), but also PA, TPE, SiR, or fluoropolymers can be used. For the sheathing compound, typical polymers are Polyolefins, PE, PP, EVA or PVC¹⁸.

Cross-linked materials have the advantage that they do not soften or melt when heated contrary to thermoplastic materials. Thus, they offer better protection against a spread of fire via burning droplets and can improve the functionality of the cable even during and after a fire. However, the additional step of cross-linking of the polymer may result in more demanding production processes for the cable.

Ships

On ships and especially on submarine vessels, it is even more focused on reduced smoke density, as will be described in the chapter 2 of this brochure. Moreover, cables on marine vessels are likely to get in contact with aggressive media like saltwater and the sheath must be able to resist these over the lifetime of the cable.

A peroxide cross-linked elastomeric EVM cable compound containing ATH as a flame retardant and useable for offshore applications can be described by the formulation in Table 18.

| Component | Content [phr] |
|--|---------------|
| EVM (60% VA content) | 100 |
| Anti-ageing system | 5.4 |
| Processing aids, coupling and plasticizer | 11.5 |
| Curing system | 7.4 |
| ATH | 160 |
| Zinc borate | 10 |

Table 18: EVM formulation for an offshore cable compound with ATH as flame retardant The wide variety of aluminium hydroxide products on the market opens up several ways to adjust the compound. For example, it is possible to combine best mechanical performance and FR properties by using submicron-sized ATH particles.

The ageing resistance in different media is very important for marine cable compounds according to standards like the British Navy Def Stan 61-12 or the German "Deutsche Marine VG 95218-28/29". Physical dimensions and mechanical values of the compounds are usually influenced by ageing processes. These changes must not exceed certain limits according to the standards.

Here again, the broad range of HFFR compounds offers several possibilities to adjust the cable to meet specific requirements.

Aeroplanes

Materials for cables in aeroplanes have to meet stringent requirements not only in terms of ignitability and heat release during burning, but also in terms of smoke density and smoke toxicity, as will be mentioned in the chapter on standards in this brochure. Additionally, the weight of all materials must be considered. Often fluoropolymers are used for cable insulation and sheathing compounds in aeroplanes. These intrinsically fire-resistant polymers in general do not require any further addition of flame retardants.

HFFR TPE compounds which contain intumescent flame retardants also pass e.g. the ABD 0031 test for smoke toxicity. Due to the efficiency of intumescent flame retardants as regards flame properties and smoke emission, moderate loading levels result and good FR properties can be combined with optimised mechanical and surface properties for this kind of cable compounds.

¹⁸ The FIPEC-report, Fire Performance of Electric Cables – new test methods and measurement techniques – Interscience Communications Ltd.2000.

7 Electric and electronic applications

7.1 INTRODUCTION

Modern individual, public, and goods transport vehicles range from automobiles, coaches, buses, trucks, and mobile homes to trains, commuter trains, underground vehicles, trams, and guided transport vehicles. They provide for both short-distance and long-distance transport of people (individual, groups, and mass transport) and goods. Fuel-driven and electrically powered engines are used. Depending on the transport vehicle and the predominant motivation, such as

- mobility
- safety
- comfort
- energy efficiency

more or less visible and invisible electric and electronic applications are used.

7.2 ELECTRICAL INSTALLATIONS & COMPONENTS

7.2.1 SCOPE AND MATERIAL REQUIREMENTS OF ELECTRICAL COMPONENTS

Connectors and switches play an essential role in every electrical component, from the point where electricity enters the vehicle, the electric generator or the battery (accumulator) to the electrical motor, appliance, sensor or device. They are found everywhere where electricity is used.

| Types of connectors | Switches and switchgear |
|--|-------------------------|
| Terminal blocks | Low-voltage switchgear |
| Crimp-on terminals | Light switches |
| Insulation displacement connectors | Rotary switches |
| Plug and socket connectors | |
| Component and device connectors | |
| Printed circuit board (PCB) connectors | |



Over the years, plastics have gained importance 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. Due to the wide variety of application areas and the increasing number of different international requirements each of these applications needs to meet, it is no surprise that many different plastics used today are tailored to meet these very different national and international al standards. The plastic ultimately chosen to design a specific part or component depends very much on its performance in terms of mechanical, electrical, and fire properties.

7.2.1.1 Mechanical properties

Polyamides, for example, are often chosen because of their good toughness and rigidity. In connectors, so-called "living hinges" can be designed, which can be opened and closed easily without breaking. Toughness is particularly important in snap fits for terminal blocks to allow easy assembly. Polyamides typically also perform well as regards heat ageing, which is important because of the increasing temperatures due to miniaturisation of electrical components. PBT, on the other hand, offers the benefit of good dimensional and hydrolytic stability.

7.2.1.2 Electrical properties

An important electrical requirement is the insulation efficiency which is expressed as the dielectric constant for alternating currents and signals. The closer this value is to one, the better is 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 carbonised track. The higher the CTI value, the better does the material performs. With some halogen-free FRs, the CTI of polymers remains the same as for the neat polymer.

7.2.1.3 Fire resistance

Plastics tend to easily ignite when exposed to heat or a flame. Hence, 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, fire safety requirements for connectors and switches are determined by technical standards by 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. In addition to IEC standards, many requirements from the American Underwriters Laboratories (UL) have been adopted in Europe and Asia as well. UL 94 VO, for example, probably is the most commonly used flammability requirement anywhere in the world. Depending on the end application, approval according to IEC standards is based on either material testing or testing of the finished component, whereas UL tests are always performed on the material only. Despite the differences between these test methods, the common feature of all tests is the specified ignition source and the way a sample is exposed to the ignition source.

Choosing the right polymer for an electrical connector or switch means finding the right balance between fire safety and mechanical and electrical properties. A variety of halogen-free flame retardants are available today, which allow compounders to optimise their formulations.

7.2.2 OVERVIEW OF HALOGEN-FREE FR'S FOR ELECTRICAL INSTALLATIONS

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

Melamine polyphosphate (MPP) is especially suited for glass fibre-reinforced polyamide 6,6. For UL 94 V0 performance, about 25% are added. It has a good thermal stability (approx. 370°C). MPP is often used as synergist in combination with phosphorus FRs.

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

Red phosphorus is a polymeric form of elemental phosphorus. It is used mainly in glass fibre-reinforced PA 6,6, the addition level being 5 to 8%. Due to its inherent colour, compounds are limited to red or black colours. In addition, precautions against degradation have to be taken.

Aryl phosphates and phosphonates (e.g. RDP) are mainly added (10 to 20%) to styrenic blends for UL 94 V0. They are often used as co-components in FR formulations. Their limitations are possible plasticising effects and a certain volatility at high processing temperatures. Blooming can have a negative influence on electrical properties.

Magnesium dihydroxide (MDH): high filler levels of about 45 to 50% are necessary to reach UL 94 VO. Because of its



limited temperature stability, it is mainly used in low glass fibre PA 6.

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

For details and chemical formulas, see Pinfa E&E brochure June 2009, 2nd edition.

7.2.3 POLYMERS USED IN ELECTRICAL COMPONENTS AND SUITABLE FR SYSTEMS

Table 19 presents an overview of typical technical properties which can be achieved with halogen-free flame retardants in different polymers and with different glass fibre contents. The values are meant for orientation only, because the exact properties depend on the specific polymer used, additive packages, and processing conditions.

| | Glass fibre [%] | Halogen- free FR | Tensile strength [N/mm ²] | Notched impact [kJ/m ²] | СТІ [V] | GWIT [°C] | UL 94 |
|---------------|-----------------------|---|---|---|------------|--------------|-------|
| Polyamide 6 | 0 | Melamine cyanurate | ~ 75 | ~4 | 600 | > 775 | V0 |
| | 30 | Metal phosphinate + N-synergist e.g. MPP | ~160 | ~15 | 600 | 775 | VO |
| Polyamide 6,6 | 30 | Metal phosphinate + N-synergist e.g. MPP | ~150 | ~14 | 600 | 775 | VO |
| | 30 | Red phosphorus | ~160 | ~18 | 600 | 775 | VO |
| | 30 | Melamine polyphosphate | ~140 | ~12 | 400 | 675 | VO |
| HTN | 30 | Metal phosphinate | ~140 | ~8 | 600 | 775 | V0 |
| РВТ | 0 | Metal phosphinate + N-synergist e.g. MPP | ~45 | ~3 | 600 | 775 | VO |
| | 30 | Metal phosphinate + N-synergist e.g. MPP | ~110 | ~7 | 500 | 800 | VO |
| PET | 0 | Metal phosphinate + N-synergist e.g. MPP | - | ~2 | - | 800 | VO |
| | 30 | Metal phosphinate + N-synergist e.g. MPP | - | ~8 | - | 800 | VO |
| Polyolefins | 0 | Intumescent system | 10 - 30 | ~3 | 600 | 800 | VO |
| | 20 | Intumescent system | 70 | ~6 | 600 | 825 | VO |
| HIPS/PPO | 0 | RDP | 25.2 | | | | VO |
| PC/ABS (4:1) | 0 | RDP | 53.3 | ~1 | | | VO |
| | 0 | BDP | 55.6 | ~0.5 | | | VO |
| | 0 | TPP | 46.0 | ~0.1 | | | V0 |

Table 19: Examples of halogen-free flame retardant systems to achieve UL 94 VO

7.3 ELECTRONIC DEVICES & PRINTED CIRCUIT BOARDS

7.3.1 OVERVIEW

Today, electronic devices play an increasingly important role e.g. in cars to improve safety, comfort, convenience, and performance. The average new car contains about 100 to 200 active electronic components (= mini computers). Complex interactions of sensors and response elements as described below have been developed already and this trend will continue.

| Safety | Passenger Restraint System |
|-------------|------------------------------------|
| | (Airbags, Active Seatbelts) |
| | Tracking Control System (TCS/ABS) |
| | Collusion Avoidance System |
| | (Night Vision, Obstacle Detection) |
| Comfort | Climate Control System |
| | Noise Control System |
| | Suspension Control System |
| Convenience | Steering Enhancement System |
| | Navigation System (GPS) |
| | Information & Communication System |
| | (Phone, Network) |
| Performance | Environment: |
| | Engine/Emission Control System |
| | Energy: |
| | Hybrid Engine System |
| | (electric drive, fuel cells) |

Virtually all electronic items contain a printed circuit board (PCB). For safety reasons, requirements are made on the fire resistance of PCBs, the UL 94 V0 classification being the most widely used specification. Many common PCB materials need a flame-retarding system to achieve this classification.

The backbone of a PCB is a copper clad laminate, where thin copper foil is laminated on typically epoxy resin prepregs. There are several National Electrical Manufacturers Association (NEMA) classes of fire-retardant laminate materials used for PCBs. Well-known prepreg materials used in PCB industry are FR-2 (phenolic cotton paper), FR-3 (cotton paper and epoxy), FR-4 (woven glass and epoxy), FR-5 (woven glass and epoxy), and FR-6 (ground glass and polyester).



The European Directive on the Restriction of Certain Hazardous Substances in E&E (RoHS, 2002/95/EC) has caused a change in the base material market, because it has been banning products that contain lead (Pb) since July 2006, unless use is expressly exempted. Lead has been used so far as solder in fusible metal alloys. Due to the higher process temperatures for lead-free soldering materials, it is necessary to reformulate base material recipes. Many manufacturers have taken this opportunity to investigate halogen-free FRs when developing new materials.

7.3.2 TECHNICAL REQUIREMENTS ON FR-4 PRINTED CIRCUIT BOARDS

PCBs of the FR-4 classification are made of 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 glass transition temperature (Tg)
- No or little impact on electrical properties, in particular Dk and Df
- 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

7.3.3 REACTIVE FLAME RETARDANTS AND RESIN MODIFICATION

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

DOPO (dihydro-oxa-phosphaphenantrene-oxide)

DOPO (dihydro-oxa-phosphaphenantrene-oxide) is a cyclic hydrogen phosphinate containing a P-H bond. It is monofunctional, but several modifications are possible, which, when properly catalysed, can be grafted to C=C linkage or reacted with epoxy groups. Today, DOPO may be considered the major building block used to make phosphoruscontaining 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 meet the increasing PCB market demand. Poly(1,3-phenylene methylphosphonate): Due to its hydroxyl groups, it can react to the polymer and act as a curing agent for epoxies. It is recommended in combination with ATH or AOH. High temperature stability is reported (high Tg, pressure cooker test).

7.3.4 NON-REACTIVE FILLERS

7.3.4.1 Metal Hydroxides

These minerals are useful flame retardants, no matter whether used alone or in combination with other flame retardants. They act by consuming energy during thermal decomposition, releasing water, and forming an oxide layer. Thus, they cool the polymer, dilute the combustion gases, 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 of reducing the CTE down to very low values (< 40 ppm are possible).

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, combination with other FRs is common.



Alumina monohydrate

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

7.3.4.2 Metal phosphinates and Melamine polyphosphates

Metal phosphinates are a new class of non-halogenated flame retardants which can be used for rigid as well as flexible PCBs or similar applications. Unlike most other phosphorus-containing compounds, metal phosphinate is not hygroscopic, has an extremely low solubility in water and common solvents, and does not hydrolyse in the presence of water. The latter point is especially crucial, since the release of phosphoric acid is not tolerable in E&E applications. Further key aspects are the high phosphorus content (> 23%) and its good thermal stability (> 300 °C) which makes it compatible with lead-free soldering operations. Electrical properties show virtually no impact on Dk / Df even at frequencies well above one GHz. However, the metal phosphinate cannot be used alone to achieve a UL 94 V0 classification. It is usually combined with an 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 VO rating for laminate thicknesses between 1.6 mm to 0.05 mm, the addition of 15 to 20 wt-% metal phosphinate in a varnish formulation is a good starting point. In any case, however, the dosage of the metal phosphinate depends on the chemical nature of the varnish backbone. For example, in combination with a phosphorus-modified epoxy resin, 15 to 20 phr (parts per hundred resin) of metal phosphinate are recommended. Metal phosphinates are also suitable for adhesives in flexible printed circuit boards (FPC).

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

7.4 COMFORT & INFOTAINMENT: HOUSING MATERIALS

7.4.1 INTRODUCTION

Especially when it comes to long-distance transport of groups of people, entertainment and infotainment are often expected and provided. Electronic housing is a market segment which includes housing of consumer and information technology equipment, such as audio, video, DVD, and game devices. These housings are made of different types of polymer resins, such as high-impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate / ABS blends (PC/ABS), and polyphenylene oxide (PPO) / HIPS blends (HIPS/PPO). According to international standards, the plastic materials used for these housings usually should meet high fire safe-ty standards, such as UL 94 V or similar flame-retardant specifications. 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 housing 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

Good processability is ensured by a high melt flow which allows for a high throughput

2. Thermal stability

In particular, a high heat deflection temperature (HDT) is required

3. Mechanical properties

In particular, 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 RoHS and WEEE directives

7.4.2 HIPS AND BLENDS

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

7.4.3 PC/ABS BLENDS

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



8 Innovation and future trends in transportation

8.1 LIGHTWEIGHT CONSTRUCTION AND ELECTRICALLY POWERED VEHICLES

One of the most important tasks of engineering and industry in the near future is the lightweight construction of transport systems, because light aeroplanes, ships, and vehicles require far less energy. This means that more and more plastics and polymer composites will be employed in the construction of aeroplanes and vehicles. An example is the fabrication of new passenger aeroplanes. The Airbus A 380 contains about 22% carbon fibre-reinforced plastics (CRP), whereas the new Boeing B787 Dreamliner (first delivery in 2010) and Airbus A350 XWB (first delivery in 2012) have a CRP content greater than 50%. Aeroplane fuselage and wings are largely made of these composites.

Also automotive manufacturers are increasingly applying these materials in order to reduce the weight. Nowadays, many vehicle parts, such as coverings, carpeting, car wings, are made of plastics. In the foreseeable future, supporting parts will be made of lightweight composite materials as well. While the weight of cars increased constantly in the past years (VW Golf I 1974: ~775 kg; VW Golf VI 2008: ~1275 kg), lightweight constructions are supposed to reverse this trend. Application of CRP can reduce the weight of industrial products in comparison to aluminium and steel by 30 and 50 percent, respectively. Lightweight construction will be especially important for the development of the e-car. However, the increasing use of plastics and their composites significantly increases the fire load of vehicles. It is therefore required to define new flame protection standards for the transportation sector. Such stricter regulations have already been introduced for the European railways. New standards are necessary for the e-car in particular due to the high energy flows and densities.

8.2 BIOPLASTICS AND NATURAL FIBRE-REINFORCED PLASTICS

The use of materials, such as natural fibres or bioplastics, could greatly contribute to building environmentally friendlier vehicles. More and more renewable raw materials, especially natural fibre-reinforced plastics (FRP), are applied in vehicle construction. In current automobile models, their share already amounts to several tens of kilograms (10-50 kg). According to the German Association of Automobile Industry, such construction parts have even more advantages. As a rule, they are CO₂ neutral and exhibit good material properties. They are usually lighter than conventional building materials and, consequently, contribute to weight reduction and fuel saving. Ford reports that the use of biomaterials has already cut fuel consumption by 9 metric tonnes/year and carbon dioxide emissions by around 15 metric tonnes/year¹⁹. These materials probably will help to reduce carbon dioxide emissions of their vehicles by 30 percent from 2006 to 2020. At the moment, the focus lies on natural fibre-reinforced polypropylene containing 25-60% flax, sisal, kenaf, hemp, wheat straw, and others.

Figure 13: An example of natural fibre (Jute) used in FRP to lighten the weight of modern cars



¹⁹ David Vink "Ford focuses on sustainable materials" (27 July 2010): http://www.plasticsnews.com/china/english/headlines2.html?id=1279812407&storycat=100&q=ford Additionally, natural fibre-reinforced engineering plastics, such as polyamide 6 with 25% Curauá fibres (Curauá - Ananas lucidus – is a plant species of the Bromeliaceae family), are commercially available and produced for automobile parts using the injection moulding technique. The other already established materials in vehicle design are natural fibre-reinforced polyurethane: polyurethane composites with both natural fibre mats and natural fibre-reinforced for automotive interior applications. Biopolymers, for example polylactide (PLA), are employed increasingly in technical applications due to growing production capacity. Even if they currently represent only a niche in vehicle application, the use of biopolymers will gradually increase in fibre/tissue industry. Additionally, they can be employed as bulk and reinforced polymers.

Although numerous halogen-free flame-retarded thermoplastics and thermosets were developed in the last 20 years, there have only been scarce reports on the flame behaviour and flame retardancy of newly developed natural fibre-reinforced plastics. Here, there is considerable need for R&D. Halogen-free solutions for PLA-based reinforced and non-reinforced materials exist already. Moreover, last year a halogen-free flame-protected biodegradable kenaf-reinforced PLA is commercially established for personal computer case applications by NEC Corporation²⁰.

8.3 FLAME RETARDANCY REQUIREMENTS AND NEW FLAME RETARDANTS (FR)

On the fire safety side, a number of serious recent fires of busses and coaches – like the bus fire with 20 fatalities on the motorway near Hannover, Germany, in November of 2008 – has revived the discussion around the fire safety requirements of road vehicles. In comparison to trams, trains and ships, the current requirements for these means of public road transport are very low. A reinforcement of flammability criteria for busses could also eventually lead to a revision and upgrade of the FMVSS (see chapter 2.2) requirements for automobiles which date back to the 1970ies and allow highly flammable materials in the passenger compartment^{21 22}.



Figure 14: Deployment of carbon fibre-reinforced composites in aeroplane manufacturing from 1970 until today

²⁰ Don Rosato "Biobased compounded an filled products form electronics" (12 January 2009): http://www.omnexus.com/resources/print.aspx?id=21749

²¹ Hirschler M, Digges K.H, Gann R, Grayson, M, Lyon R, Purser D, Quintiere J, Stephenson R, Tewarson A. (2007): Improving survivability in motor vehicle fires. Interflam 2007, 3-5 September: Fire Science and Engineering, University of London. pp. 1-10

²² Hofmann A, Krüger S, Klippel A (2010): Experimental and numerical investigations of the burning behavior of vehicle materials - Small, intermediate and large scale investigations. Interflam 2010, Nottingham UK, ISBN 978-0-9556548-7-9, pp. 1139 - 1150

On the side of flame retardant chemistries, as a result of increasing legislative, but also market-driven pressure on halogen-containing FR, new FR additives, synergists, and new polymer formulations are being developed. In recent years, metal phosphinates were introduced as a new class of flame retardants and used in technical polymers, such as glass fibre-reinforced polyesters and polyamides. More recently, polyphosphonates were scaled up commercially and will be available in larger quantities soon. They are expected to set a new standard in flame-retarded polycarbonate compositions and to provide for a high FR performance even in thin-walled applications. Based on the worldwide increasing DOPO production for application in halogen-free printed circuits boards, DOPO-based polymers are also available for flame protection equipment of polyethylene terephthalate (PET) fibres, glass fibre-reinforced polybutylene terephthalate (PBT), hot-melt adhesives, and other applications. In the development of new flame retardants, the trend goes towards polymeric additives. Use of such additives has a marginal effect on the original plastic properties. Moreover, the production process of the parts does not require any changes.

Other applications, such as thin polyolefin-based articles (films, tapes, fibres, etc.), can also now be treated with non-halogen FR based on new phosphonates (new substances under registration) closing the gap between traditional halogenated FR (i.e. chloroparaffins, hexabromocyclododecanes (HBCD), polybrominated diphenyl ethers (PBDE) or tris(bromoneopentyl) phosphate (TBNPP)) and the available amino-ether-based hindered-amine light stabiliser (HALS) compounds which were limited in both performance and possible material thickness.

It is worthwhile noting that these innovative PIN (phosphorus, inorganic and nitrogen) FR often surpass classical halogenated FR in terms of performance, which means that the dosage can be lowered compared to the traditional formulations. This typically results in better material properties, which sometimes allows for new applications that were not technically accessible before. In many cases, these new systems are also cost-competitive so that their use is supported by both technical and economic reasons. Interestingly, this goes far beyond purely environmentally driven considerations, which often were a strong motivation for developing new FR.

Apart from the synthesis of new substances, innovation activities in the field of PIN FR focus on the development of new synergists and/or the discovery of synergies between relatively well-known components. However, there are still many areas that are not accessible to PIN FR today, essentially for performance reasons. Such areas include mainly styrenic polymers, such as pure high-impact polystyrene (HIPS) and acrylonitrile/butadiene/styrene (ABS), as well as expanded polystyrene (EPS) and extruded polystyrene (XPS). Due to the anticipated restrictions of HBCD use, one of the major FR for such resins, R&D activities have increased and new FR solutions (both halogenated and non-halogenated) are expected to be introduced in the next months or years.

In many other areas, alternative PIN FR already exist, but their commercial development is often limited by higher costs. R&D activities are aimed at either improving the effectiveness of these solutions (a lower dosage or better processing behaviour often means lower costs) or at developing more cost-effective alternatives, but such developments are often limited to niche applications due to the fact that technical requirements (beyond FR specifications) are often as varied as the applications of plastics, as a result of which it is difficult or impossible to produce a universal solution. Where successful, such niche solutions often suffer from limited volumes which, in turn, adversely affect their costs. This is unlikely to change without legislation or pro-active decisions by the original equipment manufacturers (OEM).

9 Environmental and toxicological properties of halogen-free flame retardants

Whereas the previous chapters focussed on the technical properties of halogen-free flame retardants in various application areas, this chapter discusses their environmental and toxicological properties. It has often been claimed that not enough toxicological and environmental data exist to justify a switch from currently used flame retardants to halogenfree materials. It is true that a wealth of information and studies exists on halogenated high-volume products, but this is mainly a consequence of the concerns regarding health and environment and of risk assessment activities. For halogen-free flame retardants, no official European risk assessments (according to Council Regulation (EEC) 793/93 on Existing Substances, now replaced by REACH) have been carried out, because they did not make it onto the priority lists for high-volume chemicals, which were the basis for carrying out risk assessments in Europe.

Generally, the first level of an assessment of chemicals is an evaluation of their inherent hazards, like acute toxicity or bioaccumulation potential. This will tell you whether a chemical can be hazardous, if you are directly exposed to it. The next step is to assess the likelihood and occurrence of exposure for workers and consumers. Only if you have both hazard and exposure, you will have a risk. Hazard is a necessary, but not sufficient precondition for risk. However, carrying out a full exposure and risk assessment is a lengthy and complicated task, so that some NGOs have suggested using hazard data only when comparing substances in the same applications (thereby assuming the same exposure potential) or as a screening tool to filter out problematic substances. An example of such an approach is the "Greenscreen" developed by the group CleanProductionAction (see below).

Most halogen-free flame retardants have an environmentally friendly profile, which means that they pose no harm to humans or the environment and do not bio-accumulate in biota. In addition, they have a low (eco)toxicity profile and will eventually mineralise in nature. Due to these characteristics, none of the halogen-free flame retardants are considered to be PBT or vPvB. Pinfa has compiled an overview table of PIN flame retardants, which shows their target applications together with essential environmental and toxicity information. You find the current version of this table, the "pinfa product selector" at www.pinfa.eu/productselector.

In addition, pinfa has summarised the environmental and toxicological properties for a number of flame retardants in fact sheets. The data in the sheets are typical hazard-oriented data and should not be used as such to deduce risks. The sheets are divided into a Health and Environmental chapter and also include an overall PBT / vPvB analysis to indicate the regulatory status. The fact sheets can be downloaded from www.pinfa.eu/library/factsheets.



Figure 15: On the pinfa website you find fact sheets with environmental and health information on PIN FRs, as well as a "product selector", a table which lists flame retardants and their applications and regulatory information.

9.1 EUROPE: REACH AND GHS (CLP)

In Europe, a new regulation on the registration, evaluation, and authorisation of chemicals (= REACH, 1907/2006/EC) came into force in June 2007. The basic idea of REACH is that a manufacturer or importer of a chemical has to supply basic physical-chemical, environmental, and toxicity data on any substance before it can be placed onto the market ("no data, no market"). The amount of data which need to be supplied depends on the tonnage produced or imported (per legal entity) and certain hazard criteria. Furthermore, information on the intended uses of chemicals needs to be supplied, and registration is granted for certain uses only. Under the previous legislation, existing chemicals were grandfathered into the system and could be marketed with hardly any information on toxicity or environmental effects. Under REACH, the manufacturer or importer has to prove that a substance is safe to use and he is liable for product safety, whereas previously the authorities had to prove that a substance posed a risk before any restrictions could be implemented. Although REACH is a European regulation, it had global repercussions, not only because of international trade relations, but also because other regions are now also considering updating their chemical legislation. For example, the United States Environmental Protection Agency is considering a revision of the Toxic Substances and Control Act (TSCA) which dates back to the 1970s and has limitations which are similar to the previous European chemical regulation.

For flame retardants, in particular high-volume products, a large amount of toxicological and environmental data have been compiled over the last years (e.g. for the European Risk Assessment procedure). These high-production-volume chemicals are due for registration by the end of 2010 (see Table 20) and flame retardants manufacturers are currently preparing the registrations. So-called substances of very high concern (SVHC) have to undergo authorisation in REACH, i.e. the authorities have to grant permission for defined uses which are limited in time. As of June 2010, the following halogenated flame retardants were on the candidate list for SVHCs: hexabromocyclododecane

(HBCD), short-chain chlorinated paraffins (SCCP), and tris(chloroethyl)phosphate (TCEP).

At the end of 2008, another European regulation on the Classification, Labelling, and Packaging of Substances and Mixtures was published (CLP 1272/2008/EC). This is the European implementation of the globally harmonised system (GHS) for classification and labelling of chemicals developed by the United Nations. The CLP regulation defines how chemicals need to be labelled according to their hazardous properties. In addition, a central database will be established by the end of 2010, where this information will be made publicly available for all chemicals on the market (there is no cut-off tonnage foreseen as in REACH).

By the end of 2010, manufacturers of flame retardants will submit the first registration dossiers for high-productionvolume products (> 1000 to annual production) required by the new European chemicals legislation, REACH (1907/2006/EC). Under REACH, not only hazard data, but also data concerning emissions, uses, and end of life will be gathered. Most of these data will eventually become public. Even before REACH, companies have started to gather additional environmental data, e.g. one company has commissioned a life cycle emission study²³.

In order to study the environmental and toxicological profile of alternatives to brominated flame retardants in detail, the European Commission funds the project "ENFIRO" from 2009 to 2012 with a budget of EUR 3.4 million²⁴. The project will deliver a comprehensive dataset on the viability of production and application, environmental safety, and a life cycle assessment of alternative flame retardants. Three FR/product combinations (e.g. metal-based FRs, phosphorus-based and nanoclay-based FRs in printed circuit boards, paints and foam) are studied for:

- Environmental and toxicological risks
- Viability of industrial implementation, i.e. production of the FR
- Fire safety
- Application of the FR in products (electronic equipment, specific plastics, paints, and textiles)

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

²⁴ The project is funded by the EC 7th Framework programme in "Environment (including climate change" (Contract-No. 226563), see www.enfiro.eu



Figure 16: Timeline for implementation of REACH, the European regulation on registration, evaluation, authorisation, and restriction of chemicals (1907/2006/EC). The graph indicates when substances have to be registered depending on their production volume and I or hazard properties.

The information is used for a risk assessment of the alternative FRs. The outcome of that assessment, together with socio-economic information, is used in a life cycle assessment. The project follows a pragmatic approach, striving for recommendations on environmentally compatible substitution options that will be viable for implementation by industry. The ENFIRO approach and the results will be useful for similar substitution studies, e.g. in REACH. Under their Design for Environment programme, the US Environmental Protection Agency (US-EPA) started a project on alternatives to TBBPA in 2006, which compared and evaluated alternative flame retardants which can be used in FR4 laminates. Reactive phosphorus-based flame retardants as well as additive FRs of different halogen-free chemistries were scrutinised. Their in-depth analysis of existing toxicity and environmental data, together with expert judgement



Figure 17: The ENFIRO logo

and computer modelling, showed that there are no "bad hidden surprises" for the alternatives. Although some chemical hazards were identified, these do not pose risks when taking into account potential exposures of consumers. At the workplace, during laminate production, and processing or recycling, proper industrial hygiene has to be followed. In an experimental part of the project, the combustion products of brominated and halogen-free laminates will be studied. The formation of brominated dioxins from TBBPA in uncontrolled burning is a key element, because it relates to recycling operations in countries like China or India. A draft report is available on the EPA website (www.epa.gov/dfe), the final results will also be published there, probably in early 2011.

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

In addition, there have been various independent, thirdparty evaluations of halogen-free flame retardants as part of environmental programmes initiated by authorities, agencies, or NGOs. The majority of these studies specifically assess alternatives to major brominated flame retardants. These reports sometimes come to different conclusions on the same products because of different criteria used and because not all authors had the same information available. An overview can be found at http://www.chemsec.org/images/stories/publications/ ChemSec_publications/Studies_alternatives.pdf.



INNOVATIVE FLAME RETARDANTS IN TRANSPORTATION

10 List of abbreviations

| ABS | Acrylonitrile butadiene styrene copolymers |
|----------------|---|
| AOH | Aluminium-oxide-hydroxide |
| APP | Ammonium polyphosphate |
| ATH | Aluminium-tri-hydroxide |
| BDE | Diphenyl ether |
| BDP | Bis-phenol A bis (diphenyl phosphate) |
| BET surface | Specific surface area according to Brunauer, Emmet, Teller |
| BFR | Brominated flame retardant |
| CAF | Conductive anodic filament |
| CDP | Cresyl diphenyl phosphate |
| CRP | Carbon fibre-reinforced plastics |
| CLP | Classification, labelling and packaging |
| CLTE | Coefficient of linear thermal expansion |
| CTE | Coefficient of thermal expansion |
| СТІ | Comparative tracking index |
| Df | Dissipation factor |
| Dk | Dielectric constant |
| DOPO | Dihydro-oxa-phosphaphenantrene-oxide |
| DMPP | Dimethyl propane phosphonate |
| E@B | Elongation at break |
| EDAP | Ethylene diamine phosphate |
| E&E | Electric and electronic |
| ELV | End-of-life Vehicles |
| EP | Ероху |
| EPA | Environmental protection agency |
| EPR | Ethylene propylene rubber |
| EPS | Expanded polystyrene |
| ETFE | Poly(ethylene-co-tetrafluoroethylene) |
| EVA | Poly-ethyl-co-vinyl acetate |
| EVM | Ethylene vinyl acetate elastomer |

| FEP | Fluorinated ethylene propylene |
|-------|---|
| FPC | Flexible printed circuit |
| FR | Flame retardant |
| FSE | Fire safety engineering |
| FRP | Fibre-reinforced plastics |
| GADSL | Global automotive declarable substance list |
| GHS | Globally harmonized system |
| GWFI | Glow wire flammability index |
| GWIT | Glow wire ignition temperature |
| HALS | Hindered-amine light stabiliser |
| HBCD | Hexabromocyclododecane |
| HDT | Heat deflection temperature |
| HFFR | Halogen-free flame retardant |
| HIPS | High impact polystyrene |
| HTN | High temperature nylon |
| IEC | International electrotechnical commission |
| IMDS | International material data system |
| LDPE | Low-density polyethylene |
| LNE | Laboratoire National d'Essais |
| LOI | Limiting oxygen index |
| LSFOH | Low smoke free of halogen |
| МС | Melamine cyanurate |
| MDH | Magnesium-di-hydroxide |
| MFI | Melt flow index |
| MPP | Melamine polyphosphate |
| NEMA | National electrical manufacturers association |
| NGO | Non-governmental organization |
| OEM | Original equipment manufacturer |
| PA | Polyamide |
| PBDE | Polybrominated diphenyl ether |

| PBT | Persistent, bioaccumulative, and toxic or (differ- ent meaning) Polybutylene terephthalate |
|-------|---|
| РС | Polycarbonate |
| РСВ | Printed circuit board |
| РСТ | Pressure cooker test |
| PE | Polyethylene |
| PET | Polyethylene terephthalate |
| PFA | Perfluoroalkoxy |
| PIN | Phosphorus, inorganic and nitrogen |
| PLA | Polylactide |
| PP | Polypropylene |
| PPE | Polypropylene ether |
| PPO | Polyphenylene oxide |
| PTFE | Polytetrafluoroethylene |
| PUR | Polyurethane |
| PVDF | Polyvinylidene fluoride |
| PVC | Polyvinyl chloride |
| PWB | Printed wiring board (synonymous to printed cir- cuit board) |
| RDP | Resorcinol bis (diphenyl phosphate) |
| RDX | Resorcinol bis (dixylenyl phosphate) |
| REACH | Registration, evaluation and authorisation of chemicals |
| RoHS | Restriction of certain hazardous substances |
| SCCP | Short-chain chlorinated paraffins |
| SiR | Silicone rubber |
| SMA | Styrene maleic anhydride |
| SMC | Sheet moulding compounds |
| SVHC | Substances of very high concern |
| TBBPA | Tetrabromobisphenol A |
| TBNPP | Tris(bromoneopentyl) phosphate |
| TCEP | Tris(chloroethyl)phosphate |

| ТСР | Tricresyl phosphate |
|-------|--|
| TEP | Triethyl phosphate |
| Тд | Glass transition temperature |
| TGA | Thermogravimetric analysis |
| TPE | Thermoplastic elastomer |
| TPE-O | Thermoplastic elastomer olefine based |
| TPE-S | Thermoplastic elastomer styrene based |
| TPE-V | Thermoplastic elastomer cross-linked |
| ТРР | Triphenyl phosphate |
| TPU | Thermoplastic polyurethane |
| TS | Tensile strength |
| TSCA | Toxic substances and control act |
| UL | Underwriters Laboratories |
| UL 94 | Flame retardancy test for polymer compounds according to Underwriters Laboratories |
| UP | Unsaturated polyester |
| VA | Vinyl acetate |
| VE | Vinyl ester |
| vPvB | Very persistent, very bioaccumulative |
| WEEE | Waste of electric and electronic equipment |
| XLPE | Cross-linked polyethylene |
| XLPVC | Cross-linked polyvinyl chloride |
| XPS | Extruded polystyrene |

11 Contributing companies

CONTACT DETAILS

Adeka Palmarole

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

BASF

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

Budenheim

Budenheim Iberica Extramuros S/N 50784 La Zaida / Zaragoza – Spain Phone: +34 976 1784 12 E-mail: budenheim@budenheim.es www.budenheim.es

Catena Additives

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

Clariant

Clariant International Ltd. Business Line Flame Retardants Rothausstrasse 61 4132 Muttenz – Switzerland Phone: +41 61 469 7912 E-mail: adrian.beard@clariant.com www.exolit.com

Dartex Coatings

Dartex Coatings Ltd. Acton Close Long Eaton Nottingham NG10 1FZ – United Kingdom Phone: +44 115 983 7697 E-mail: richard.haxby@dartexcoatings.com www.dartexcoatings.com

Delamin

Delamin Ltd. 4 Royal Scot Road Pride Park DE24 8AJ Derby – United Kingdom Phone: +44 1332 349384 E-mail: coates@delamin.com www.delamin.com

PRODUCTS

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

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

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

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

metal phosphinates (Exolit[®] OP) phosphorus polyols (Exolit[®] OP 5xx) ammonium polyphosphate (Exolit[®] AP) red phosphorus (Exolit[®] RP) FR formulations for textiles (Pekoflam[®])

PU coated textiles MelaphosFR[™] halogen free flame retardants

melem (Delacal 420)

CONTACT DETAILS

PRODUCTS

DSM Engineering Plastics

DSM Engineering Plastics P.O. Box 43 6130 AA Sittard – The Netherlands Phone: 00800-74663376 E-mail: info-europe.DEP@dsm.com www.dsm.com/en_US/html/dep/home_dep.htm

FRX Polymers

FRX Polymers, Inc. 200 Turnpike Road Chelmsford, MA. 01824 – USA Phone: +1 978 244 9500 E-mail: info@frxpolymers.com www.frxpolymers.com

Italmatch

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

KIT

Karlsruhe Institute of Technology Institute of Technical Chemistry (ITC-CPV) Hermann-von-Helmholtz-Platz 1, Bldg. 725 D-76344-Eggenstein-Leopoldshafen, Germany Phone: +49 7247 82 4385 E-mail: manfred.doering@kit.edu www.katalyseundmaterialien.de

Krems Chemie

Krems Chemie Chemical Services AG Hafenstrasse 77 3500 Krems – Austria Phone: +43 2732 81 500 0 E-mail: office@kccs.at www.krems.at

LANXESS

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

Nabaltec

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

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

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

Research and Developement halogen-free flame retardants

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

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

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

CONTACT DETAILS

Rhodia

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

Rockwood Clay Additives

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

Thor

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

William Blythe

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

PRODUCTS

polyamide (TECHNYL®)

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

non-permanent FR for textiles (Flammentin[®]) semi-permanent FR for textiles (Aflamman) permanent FR for textiles and range for plastics (Aflammit[®])

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

