

# INNOVATIVE AND SUSTAINABLE FLAME RETARDANTS **IN TRANSPORTATION**

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pinfa

Non-halogenated Phosphorus, Inorganic  
and Nitrogen (PIN) flame retardants





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# INTRODUCTION

Transport vehicles - airplanes, ships, trains, buses, and cars – increasingly rely on flammable materials, for reasons of weight (energy savings), design and performance, and are therefore subject to fire risks. pinfa has compiled this brochure to explain how PIN flame retardant technologies can contribute to the safety of materials and vehicles. After many years of research and development, a whole toolbox of non-halogen chemistries is now available for the materials engineer. Major application areas of flame retardants in transport vehicles are polymers and composites 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 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](http://www.pinfa.org) offers updates and information and in particular a “product selector” of PIN flame retardants, where you can find data on the target polymers and materials for individual flame retardants as well as environmental and health information.

pinfa strives to enter a constructive dialogue with all stakeholders, including regulators, downstream users, OEMs, scientists and environmental NGOs. The need for fire safety should be balanced with environmental concerns and flame retardants should be optimised to meet technical, economic, health safety and environmental criteria.

## 1.1. WHAT ARE PIN FLAME RETARDANTS?

PIN<sup>1</sup> flame retardants<sup>2</sup> cover a variety of non-halogenated<sup>3</sup> chemicals which are commonly classified as:

- **Phosphorus**-based flame retardants include organic and inorganic phosphates, (poly) phosphonates, and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.
- **Inorganic**, including metal hydroxides, like aluminium hydroxide and magnesium hydroxide, specific minerals such as clays or graphite, and other inorganic compounds like e.g. zinc borate, which are used to a smaller extent or as synergists with other PIN FRs.
- **Nitrogen**-based flame retardants are typically melamine and melamine derivatives (e.g. melamine cyanurate, melamine polyphosphate). They are often used in combination with phosphorus-based flame retardants.

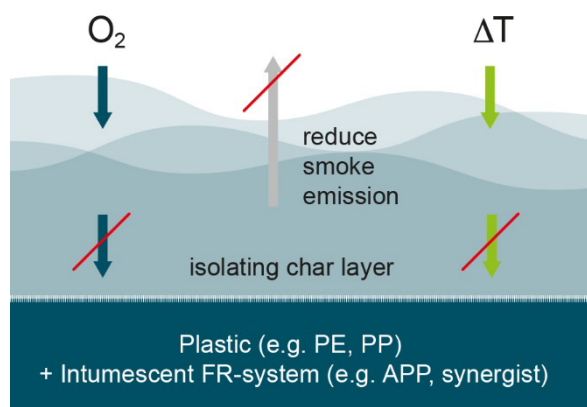
<sup>1</sup> PIN = Phosphorus, Inorganic, Nitrogen

<sup>2</sup> PIN flame retardants are often commercially indicated as HFFR = Halogen Free Flame Retardant, ZHFR = Zero Halogen Flame Retardant, LSZH or LZ0H = Low Smoke Zero Halogen, etc.

<sup>3</sup> Non-halogenated means that no halogens are intentionally added and contained in the products. Trace amounts of halogens are found everywhere and also in commercial chemicals.

Intumescent flame retardants are an example of a typical mechanism of non-halogen flame retardants. The combustible material is separated from the fire or heat source by an insulating foam forming at the surface.

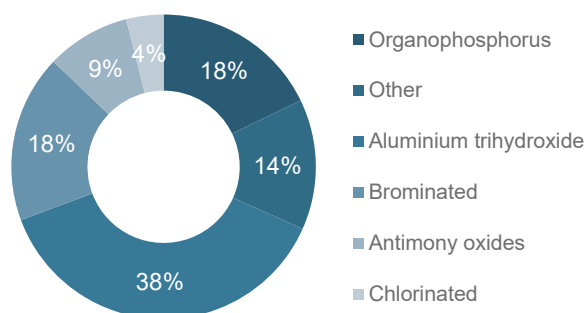
Intumescent flame-retardant systems can be applied to decrease flammability of thermoplastic polymers, such as polyethylene, polypropylene, polyurethane, polyester- and epoxy resins, polycarbonate.



**Figure 1 - How intumescent FR systems work.**  
The mechanism of intumescent flame retardant systems which typically represent a combination of phosphorus and nitrogen compounds.

## 1.2. GLOBAL CONSUMPTION OF DIFFERENT FRS

The figure shows the global consumption of different flame retardant types (by volume). The chart shows that halogen-free 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. However, many original equipment manufacturers (OEMs) of electronic devices have announced roadmaps with deadlines for the transition to non-halogenated flame retardants. Since these OEMs have their manufacturing base in Asia, a shift towards non-halogen technologies is also expected in this region.



**Figure 2 - Global consumption of flame retardants by % volume.**  
In this figure, "Organophosphorus" includes both non-halogenated and halogenated organophosphorus compounds; "Other" includes inorganic phosphates, nitrogen-based compounds, etc. Data is for 2019. Total = 2.39 million tonnes. Source: IHS Markit.

## 1.3. WHY ARE FRS NEEDED IN TRANSPORT APPLICATIONS?

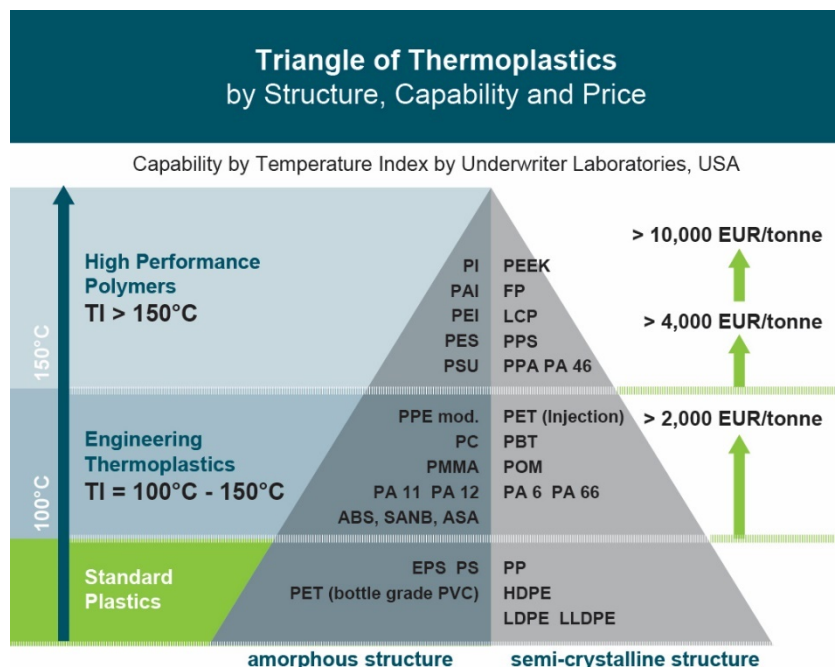
Polymers and textiles are increasingly used in transport systems, because they provide comfort in the passenger compartment as well as many technical advantages for engineering applications. In the automotive area, for example, metal parts are more and more replaced by plastics, because these have less weight and provide for more freedom in design. Plastics represent 10-12% of the weight of a medium size modern car, this is about 180-225 kg per car<sup>4</sup>. Advanced polymer materials have high-performance mechanical properties, especially when reinforced with fibres (glass, cellulose, carbon fibre) and can even replace some structural parts. Engineering thermoplastics are today commonly used in high-temperature environments in the engine compartment. The increasing use of electronics in cars and other transport results in more plastics being required for cables, electrical 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 airplanes, 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. The resistance of polymers to heat and ignition is somewhat correlated with their price and technical performance (with the exception of halogen-containing polymers such as polyvinyl chloride PVC). Foamed polymers used in insulation or upholstery can ignite easily and burn vigorously, because they represent a mixture of fuel with air.

<sup>4</sup> In Plastics Europe "Automotive The World moves with plastics" <https://www.plasticseurope.org/en/resources/publications/104-automotive-world-moves-plastics-brochure>

Polymers which are inherently flame-resistant are available, but these high-performance polymers are relatively 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 3 - The thermoplastics pyramid.**

The pyramid or triangle of thermoplastics shows their ranking by capability, structure, and price (source: PlasticsEurope Market Research Group, Business Data and Charts 2020)

Sadly, 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 airplane. 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 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.

## 1.4. WHY USE NON-HALOGENATED FRs?

Flame retardants are a class of chemicals which attract scientific and public attention because some of them have environmental and health effects, and because they are widely used in many consumers and professional articles. 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 combustion<sup>5</sup>.

Findings in the environment and biota and the suspicion that some flame retardants bioaccumulate in organisms have added to these concerns.<sup>6,7,8,9</sup> 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 Europe<sup>10</sup> from the early 1990s until the

<sup>5</sup> Söderström G, Marklund S (2002): PBCDD and PBCDF from incineration of waste-containing brominated flame retardants. *ES&T*, Vol. 36, pp. 1959-1964

<sup>6</sup> de Wit C (2002): An overview of brominated flame retardants in the environment. *Chemosphere*, pp. 583-624

<sup>7</sup> Ikononou 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

<sup>8</sup> 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

<sup>9</sup> 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

<sup>10</sup> <http://ecb.irc.it/existing-chemicals/>

transition to REACH (the European Regulation on the Registration, Evaluation, and Authorization of Chemicals EC 1907/2006). In 2008, REACH entered into force, which required that basic health and environmental data are submitted for all chemicals before commercialisation (“no data no market”) and that substances of concern are evaluated further and their use is possibly restricted.

Since electronics are a major application area for flame retardants, non-governmental organizations (NGOs), environmental scientists, and authorities have focused their attention on this industry so far. Over the past decades, the fate of electronic waste and hazardous materials contained therein met with increasing political attention and led to the WEEE<sup>11</sup> and RoHS<sup>12</sup> 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 specifically concerned, 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 retardants<sup>13</sup> is no longer 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 led to an increasing demand for non-halogen 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 (ELV) Directive was published in 2000 (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 (GADSL = the Global Automotive Declarable Substance List) ([www.gadsl.org](http://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 business<sup>14</sup>.



In fire sciences, the composition and toxicity of smoke has become an important topic over recent years, because in fires, most people die from the inhalation of toxic smoke rather than from the direct impact of heat or radiation. This is particularly critical in transport applications, where smoke will be released into a confined space (e.g. metro, train, airplane). 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 rather 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 airplanes, trains, and public buildings because of strict smoke and smoke toxicity requirements. The role of the combustion behaviour of materials in transport systems has been studied in the European research project “TRANSFEU”<sup>15</sup>.

<sup>11</sup> Directive 2002/96/EC on Waste of Electric and Electronic Equipment

<sup>12</sup> Directive 2002/95/EC on Restriction of Certain Hazardous Substances in Electric and Electronic Equipment

<sup>13</sup> Banned BFRs: Polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE); the exemption for Deca-BDE was repealed by the European Court of Justice, effective July 2008

<sup>14</sup> [www.boeing.com/suppliers/environmental/TechNotes/TechNotes2004-02.pdf](http://www.boeing.com/suppliers/environmental/TechNotes/TechNotes2004-02.pdf)

<sup>15</sup> TRANSFEU: <https://cordis.europa.eu/project/id/233786>

# 2

## FIRE TESTS

### 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. airplanes 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. FIRE TESTS RELEVANT FOR AUTOMOBILE

#### 2.2.1. FMVSS 302

FMVSS 302 (automotive vehicles: car, bus) is the main reference for flammability requirements. Test 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.



*Figure 4 - FMVSS 302 – Horizontal burning rate determination. Credits ©Currenta*

## 2.3. FIRE TESTS RELEVANT FOR BUS AND COACH

### 2.3.1. UNECE REGULATION NO. 118 <sup>16</sup>

This Regulation entered into force in 2005, and replaced EU Regulation 95/28/EC. The Regulation applies to the burning behaviour of interior materials used in vehicles, carrying more than 22 passengers.

The tests to be performed to obtain approval are listed in Annexes 6 through 8:

#### **Annex 6 – Test to determine the horizontal burning rate of materials**

Test method is equivalent to FMVSS 302 and ISO 3795.

Test specimen is held in horizontal position and exposed to a flame for 15 sec.

Horizontal burning rate shall be not more than 100 mm/min.

#### **Annex 7 – Test to determine the melting behaviour of materials**

Test specimen is placed in a horizontal position and exposed to heat radiation. Falling drops shall not ignite the cotton wool below the sample.

#### **Annex 8 – Test to determine the vertical burning rate of materials**

Typically applied to curtains or blinds. Test specimen is held in vertical position and exposed to a flame for 5 sec (or 15 sec if no ignition occurs). Vertical burning rate shall be not more than 100 mm/min.

## 2.4. FIRE TESTS RELEVANT FOR RAIL VEHICLES

### 2.4.1. EUROPEAN STANDARD: EN 45545-2 <sup>17</sup>

Each application inside and outside the railway carriage will have its own set of requirements: R1 until R28.

These sets of requirements typically consist of several different tests to be performed. The most important test methods applied are described below.

#### **ISO 5658-2 – Spread of flame**

Determination of lateral flame spread of a specimen exposed to a heat radiator and an ignition flame. Output parameter is the Critical Heat Flux at Extinguishment (CFE) in kW/m<sup>2</sup>.

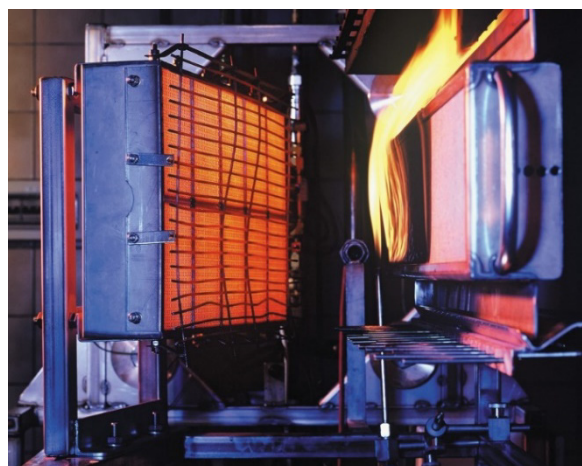


Figure 5 - ISO 5658-2 – Spread of flame test.  
Credits ©Currenta

#### **ISO 5659-2 – Smoke generation**

A specimen is exposed to a heat flux with or without an impinging pilot flame. Thus, smoke is generated both under smoldering 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.

Output parameters are the Smoke Density ( $D_{s,4}$  and  $D_{s,max}$ ) and the accumulated Smoke Density  $VOF_4$ .

#### **ISO 5660-1 – Heat release rate (cone calorimeter)**

Test method for assessing the heat release rate and dynamic smoke production rate of specimens exposed in the horizontal orientation to controlled levels of irradiance with an external igniter. Heat flux can be either 50 kW/m<sup>2</sup> or 25 kW/m<sup>2</sup>; test duration is 20 min. Results are expressed as Maximum Average Rate of Heat Emission (MARHE) in kW/m<sup>2</sup>.



Figure 6 - ISO 5660-1 – Cone Calorimeter.  
Credits ©Currenta

<sup>16</sup> UNECE Regulation No. 118 – Uniform technical prescriptions concerning the burning behaviour and/or the capability to repel fuel or lubricant of materials used in the construction of certain categories of motor vehicles

<sup>17</sup> EN 45545-2 – Railway applications - Fire protection on railway vehicles – Part 2: Requirements for fire behaviour of materials and components

### EN 17084 – Toxicity

New test method to replace Annex C from previous version of EN 45545-2. During testing in the smoke box according to ISO 5659-2, samples of the smoke are taken after 4 and 8 min and analysed using Fourier-transform infrared spectroscopy (FTIR). The Conventional Index of Toxicity (CIT<sub>G</sub>) is calculated from the concentrations of eight specific components.

### EN 16989 – Fire behaviour test for a complete seat

New test method replacing Annexes A & B from previous version of EN 45545-2, building upon ISO 9705 test method. A complete (vandalised) passenger seat is subjected to a specific flaming ignition source. Fire test responses are heat release (MARHE), total smoke production (TSP), and the flame height above the seat base.

### ISO 9239-1 – Horizontal flame spread of floorings

Method for assessing the burning behaviour and spread of flame of horizontally mounted floorings. Test specimen is placed in a horizontal position and exposed to a defined heat flux. A pilot flame is applied to the hotter end of the specimen. Fire test response is the Critical Heat Flux at Extinguishment (CHF) in kW/m<sup>2</sup>.

## 2.5. FIRE TESTS RELEVANT FOR SHIPPING

### 2.5.1. INTERNATIONAL MARITIME ORGANIZATION

In 2012 the International Maritime Organization (IMO) implemented the new FTP Code -"International Code for Application of Fire Test Procedures, 2010" (2010 FTP Code) according to IMO-Resolution MSC.307(88). This Code covers fire tests of materials and components for use on ships and yachts. The different parts and corresponding standards are given in the table. As it would exceed the scope of this brochure, the additional fire tests are not explained in detail.

#### FTP Parts

| Test                                                                        | Testing Procedure                            |
|-----------------------------------------------------------------------------|----------------------------------------------|
| <b>Part 1</b>                                                               |                                              |
| Testing of non-combustibility                                               | ISO 1187                                     |
| <b>Part 2</b>                                                               |                                              |
| Testing of smoke density and toxicity                                       | ISO 5659-2<br>(see rail vehicles)            |
| <b>Part 3</b>                                                               |                                              |
| Fire testing of vertical and horizontal divisions                           | ISO 834-1                                    |
| <b>Part 4</b>                                                               |                                              |
| Testing of fire door control system                                         | -                                            |
| <b>Part 5</b>                                                               |                                              |
| Fire testing of surface flammability for linings, coatings and floor covers | ISO 5658-2<br>(see rail vehicles)            |
| <b>Part 7</b>                                                               |                                              |
| Fire testing of vertically supported textiles and films                     | ISO 6940/41,<br>EN 1101/02                   |
| <b>Part 8</b>                                                               |                                              |
| Fire testing of upholstered furniture                                       | BS 5852-1,<br>ISO 8191-1 / 2,<br>EN 1021-1/2 |
| <b>Part 9</b>                                                               |                                              |
| Fire testing of bedding components                                          | EN 597-1 / 2                                 |
| <b>Part 10, appendix 2</b>                                                  |                                              |
| Testing of heat release, smoke production, mass loss rate                   | ISO 5660<br>(see rail vehicles)              |

Figure 7 - IMO FTP testing procedures.

## 2.6. AIRCRAFT

### 2.6.1. FAR 25.853

Most countries have adopted the Federal Aviation Regulations (FAR) prepared by the U.S. Federal Aviation Administration (FAA), as the basis for ensuring airworthiness. Particularly relevant for plastics manufacturers is Part 25, section 853 for passenger compartment interiors ("FAR 25.853").

Tests most often performed for interior applications are the Vertical Bunsen Burner test, the OSU Heat Release test, and Smoke Density and Toxicity tests. For seat testing the Oil Burner test is applied.

#### Vertical Bunsen burner test

This test is used to demonstrate that materials are "self-extinguishing" and can be performed using either a 12 s or 60 s flame application time.

| FAR Part 25, App. F, Part 1 |                |
|-----------------------------|----------------|
| (a)(1)(i)                   | (a)(1)(i)      |
| Flame application           |                |
| 60 s                        | 12 s           |
| Burn length                 |                |
| ≤152 mm (6 in)              | ≤203 mm (8 in) |
| Flame time                  |                |
| ≤15 s                       | ≤15 s          |
| Flame time drippings        |                |
| ≤3 s                        | ≤5 s           |

Figure 8 - Requirements for vertical Bunsen burner test.

#### OSU Heat Release Test

For large parts inside the passenger cabin of aircraft, a heat release test was developed at Ohio State University (OSU). The intent of the test is to model a post-crash, fuel-fed fire. Test specimen is placed in a vertical position and exposed to a radiant heat flux of 35 kW/m<sup>2</sup> for 5 min. Output variables are the maximum heat release rate at 5 min, and the total heat released in the first 2 min.

| FAR Part 25, App. F, Part IV (g)  | (a)(1)(ii)                |
|-----------------------------------|---------------------------|
| Maximum heat release rate (5 min) | ≤65 kW/m <sup>2</sup>     |
| Total heat released (first 2 min) | ≤65 kW min/m <sup>2</sup> |

Figure 9 - Requirements for heat release testing with OSU calorimeter.

#### Smoke density & toxicity test

For the determination of the Smoke density performance, the material is tested in an NBS smoke box (same as used in ASTM E662). The test specimen is measured in vertical position for 4 minutes, in flaming mode with pilot burners on. The maximum specific optical density shall be not more than 200.

For toxicity testing the same NBS smoke box is applied. Gas samples are taken right after the 4-minute smoke density test, and analysed for six different components. Maximum allowed concentrations are different for Airbus and Boeing qualifications (see table).

| Gas component                       |        |
|-------------------------------------|--------|
| Concentration limits [ppm]          |        |
| Airbus                              | Boeing |
| Hydrogen fluoride (HF)              |        |
| 100                                 | 200    |
| Hydrogen chloride (HCl)             |        |
| 150                                 | 500    |
| Hydrogen cyanide (HCN)              |        |
| 150                                 | 150    |
| Sulphur dioxide (SO <sub>2</sub> )  |        |
| 100                                 | 100    |
| Nitrous gases (NO/NO <sub>2</sub> ) |        |
| 100                                 | 100    |
| Carbon monoxide (CO)                |        |
| —                                   | 3500   |

Figure 10 - Maximum allowed concentrations in smoke density & toxicity test.

#### Seat cushion flammability test

This test simulates a post-crash fire burning through the fuselage. The intent is to limit the contribution of aircraft seats to fire spread and smoke emission. The test is performed with a kerosene burner. Only 10% of the mass of the seat is allowed to be burnt.



Figure 11 - Oil burner for seat cushion flammability test. Credits ©Currenta

## 2.7. ADDITIONAL TESTING OF COMPONENTS

### 2.7.1. UL 94

The UL 94 test is the most commonly referenced test in the E&E sector. It is a good measurement to evaluate the flammability of materials and so the effectiveness of flame retardants used. Traditional testing is performed on injected molded specimens or on samples cut from finished parts. The pilot flame has an energy output of 50 W. The sample can be oriented horizontally (HB, HBF) or vertically (5VA, 5VB, V-0, V-1, V-2), where the vertical test is the more challenging one. The classification result depends on how long the specimen continues to burn after removal of the pilot flame and whether a cotton piece below is ignited by flaming droplets. Results depend on the sample thickness (a thin sample will burn more readily) and test classification results should always specify the thickness of the sample tested (in mm). The test is defined in the following standards: Underwriters Laboratories (UL) 94, ASTM D 3801, ASTM D 635, IEC 60695-11-10/20, ISO 1210, ISO 10351.

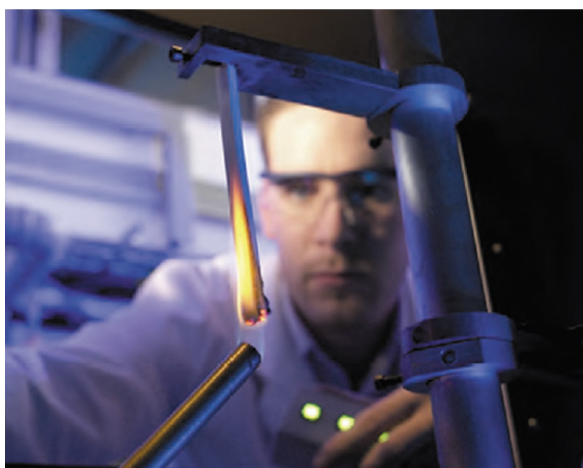


Figure 12 - Test setup during an UL 94 V (vertical) test.

### 2.7.2. GLOW WIRE TEST

The glow wire test (GWT) according to IEC 60695-2-11 - 13 is used to simulate malfunction, misuse or failure of an end product. The test is performed with a heated resistance wire which is pressed against a specimen for 30 sec and then removed. For a given glow wire temperature, the test criterion is whether the specimen ignites during contact to the hot wire (or within the 30 sec after withdrawal) and whether droplets can ignite a filter paper below the specimen. The test temperature is increased by 50 K steps. The glow wire ignition temperature (GWIT) relates to the ignition of the sample where only a flame of very short duration is permitted ( $\leq 5$  sec). The glow wire flammability index (GWFI) indicates the temperature where the occurrence of flames is less than 30 sec.

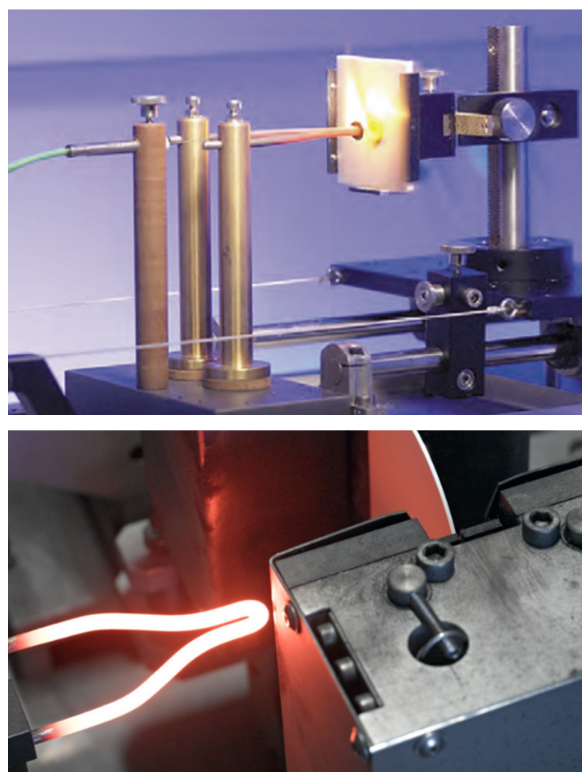


Figure 13 - Experimental setup of a glow wire test.  
Credits ©UL International

### 2.7.3. COMPARATIVE TRACKING INDEX (CTI)

The CTI test according to IEC 60112 is used to provide an accelerated simulation of electrolytical corrosion on the surface of a specimen which would possibly result in tracking and failure of insulating materials. Two electrodes are applied with adjustable test voltage usually between 100 and 600 Volt. 50 drops of an electrolyte are applied between the electrodes and the voltage is successively increased by 25 V steps. Failure criteria are a burning material or a cut-off current  $\geq 0,5$  A during a time of  $>2s$ . The higher the CTI of a material, the better the insulation performance.

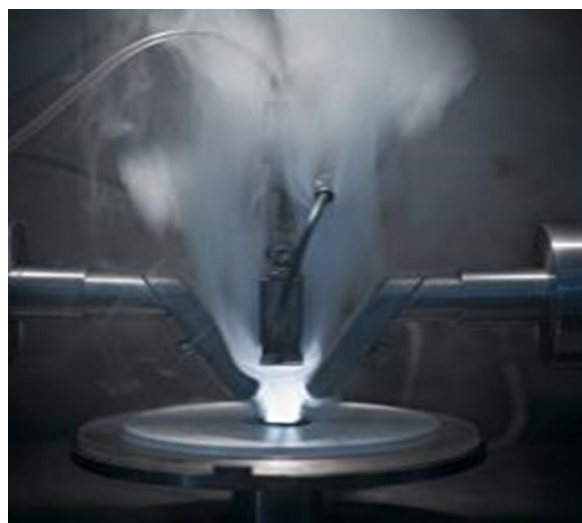


Figure 14 - Failing material after applying the test procedure for CTI. Credits ©UL International

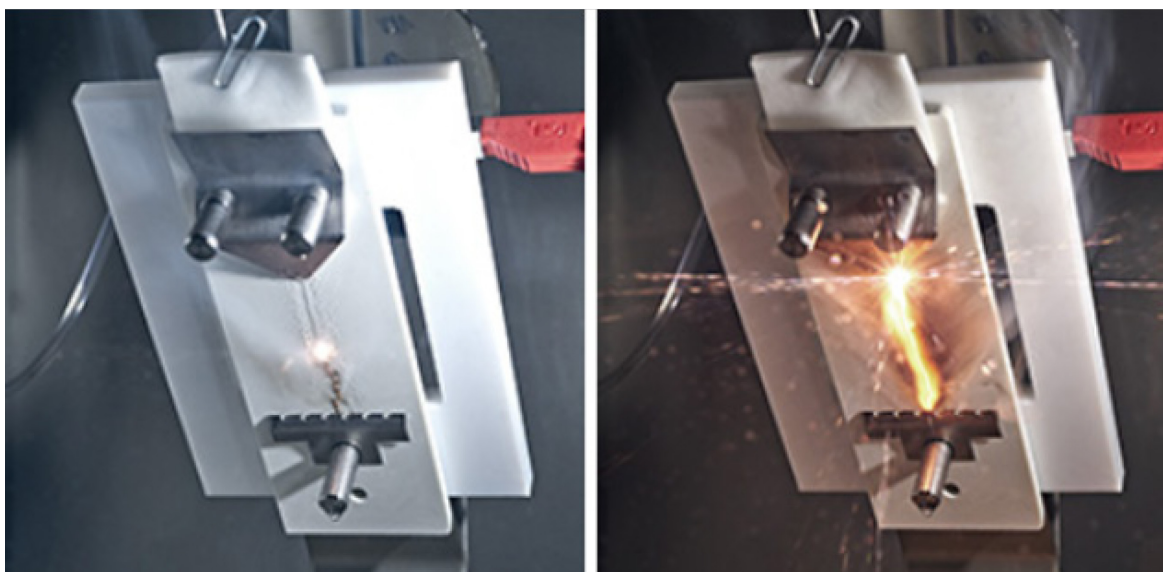


Figure 15 - Experimental setup for inclined plane tracking. Credits ©UL International

#### 2.7.4. INCLINED PLANE TRACKING (IPT)

IPT according to IEC 60587 and ASTM D2303 is a test to simulate the insulation behaviour of a material to be used under severe outdoor conditions, that is exposed to contamination and humidity. Samples are inclined at an angle of 45 degrees, electrodes are installed at the top and bottom of the sample, on the downward facing side. The applied test voltages are between 1 kV and 35 kV, increased in 500 V steps. Failure criteria are the formation of holes, a burning sample or a tracking path that reaches 25 mm as well as a current that exceeds 60 mA.

#### 2.7.5. BALL PRESSURE TEST

The ball pressure test in accordance with IEC 60695-10-2 is used to simulate thermal stress under pressure. The test material is placed horizontally, and a steel ball is pressed on its surface with a force of 20N. The test is carried out for 60 min at 23 - 300°C. After the test, the steel ball is removed, and the specimen is cooled down to room temperature. The material passes the test at a certain temperature when the indentation caused by the ball does not exceed 2 mm in diameter.

# 3

## INTERIOR PARTS

### 3.1. INTRODUCTION

Interior parts for transport applications (automobiles, airplanes, 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, 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.



Figure 16 - Credits ©Budenheim

### 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, light-weight components, while cutting costs, saving time, and helping lessen the problems associated with interior redesign.

#### Typical values for each material

| Density [kg/m <sup>3</sup> ] | E-modulus [Gpa] | CLTE* [mm/m/°C x 10 <sup>-6</sup> ] |
|------------------------------|-----------------|-------------------------------------|
| <b>Steel</b>                 |                 |                                     |
| 7800                         | 210             | 12                                  |
| <b>Aluminum</b>              |                 |                                     |
| 2800                         | 72              | 24                                  |
| <b>Polyamide 6</b>           |                 |                                     |
| 1130                         | 2               | 95                                  |
| <b>Polycarbonate</b>         |                 |                                     |
| 1200                         | 2.5             | 60                                  |
| <b>Epoxy</b>                 |                 |                                     |
| 1200                         | 5               | 50                                  |
| <b>ABS</b>                   |                 |                                     |
| 1070                         | 3               | 85                                  |
| <b>Polypropylene</b>         |                 |                                     |
| 905                          | 2               | 180                                 |

Figure 17 - Comparison of materials used for interiors.

\* Coefficient of Linear Thermal Expansion

As obvious from the table, the 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).

Further flexibility is now availability with 3D-printing, which allows innovative forms and structures, and economic production of customised components. However, 3D-printed components may have different fire performance from items produced using the same plastic compound, because of different internal structure (e.g. polymer linking, air pockets).

### 3.3. SOME EXAMPLES FOR PIN FR 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). 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 windmills, 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 like ATH or much less APP-based products are easy to be used) for highest flame retardancy. Pultrusion is mostly used for long, uniform parts like ducts. Here, the size of the flame retardant 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 the figure.

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. In the past each European country had its own protection regulations. The country specific, local regulations for the fire protection of railway vehicles were finally harmonized under the highly demanding EN 45545-2 standard. The different components of train interiors are now grouped in R-classes and in each R-class three different hazard levels (HL1, 2 and 3) are defined. The measured values for smoke density, smoke toxicity, spread of flame and heat release (cone calorimeter) define the hazard level where the product can be used.

|                                                                              | 20%<br>Intumescent<br>system | 25%<br>Intumescent<br>system | Limit<br>(ABD 0031) |
|------------------------------------------------------------------------------|------------------------------|------------------------------|---------------------|
| <b>Smoke density (DS after 4 min)</b>                                        |                              |                              |                     |
| ■                                                                            | 160                          | 134                          | -                   |
| ■                                                                            | 122                          | 161                          | -                   |
| <b>Hydrogen cyanide HCN [ppm]</b>                                            |                              |                              |                     |
| ■                                                                            | 1                            | 1                            | 150                 |
| ■                                                                            | 5                            | 5                            | 150                 |
| <b>Carbon monoxide CO [ppm]</b>                                              |                              |                              |                     |
| ■                                                                            | 20                           | 10                           | 1000                |
| ■                                                                            | 200                          | 200                          | 1000                |
| <b>Nitrous gases NOx [ppm]</b>                                               |                              |                              |                     |
| ■                                                                            | 0                            | 0                            | 100                 |
| ■                                                                            | 10                           | 10                           | 100                 |
| <b>Sulphur dioxide hydrogen sulphide SO<sub>2</sub>-H<sub>2</sub>S [ppm]</b> |                              |                              |                     |
| ■                                                                            | 0                            | 0                            | 100                 |
| ■                                                                            | 0                            | 0                            | 100                 |
| <b>Hydrogen fluoride HF [ppm]</b>                                            |                              |                              |                     |
| ■                                                                            | 0                            | 0                            | 100                 |
| ■                                                                            | 0                            | 0                            | 100                 |
| <b>Hydrogen chloride HCl [ppm]</b>                                           |                              |                              |                     |
| ■                                                                            | 0                            | 0                            | 150                 |
| ■                                                                            | 0                            | 0                            | 150                 |
| <b>Pass ABD 0031<br/>(commercial aircraft interiors ABD 0031)</b>            |                              |                              |                     |
| ■                                                                            | Yes                          | Yes                          |                     |
| ■                                                                            | Yes                          | Yes                          |                     |

Figure 18 - Intumescent systems in ABD 0031.  
■ non flaming condition ■ flaming condition

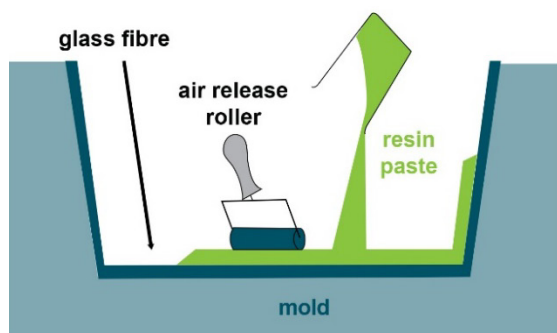
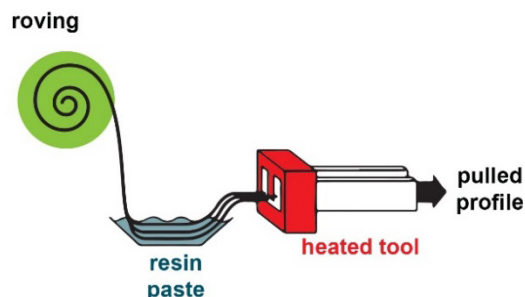


Figure 19 - Hand lay-up and pultrusion processes.



Before, mainly high amounts of ATH were used, but due to the more stringent test, optimized flame retardant systems based on ammonium polyphosphate (APP) were successfully introduced for parts based on epoxy or UP (unsaturated polyester) composites. They can either be added directly to the resin or are added to a gelcoat, in which case even larger loadings also of ATH can be used in the composite.

Traditionally UP based composites are used. However, when better performance is required for components subjected to higher loads, epoxy composites are used more frequently.

The lightweight composites help to reduce weight, and thereby the energy consumption of the train, plus they make train travel more comfortable. They show the advantage of low smoke and low smoke toxicity at still acceptable loadings.

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 or APP 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 like APP. Intumescent 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 | 150            |

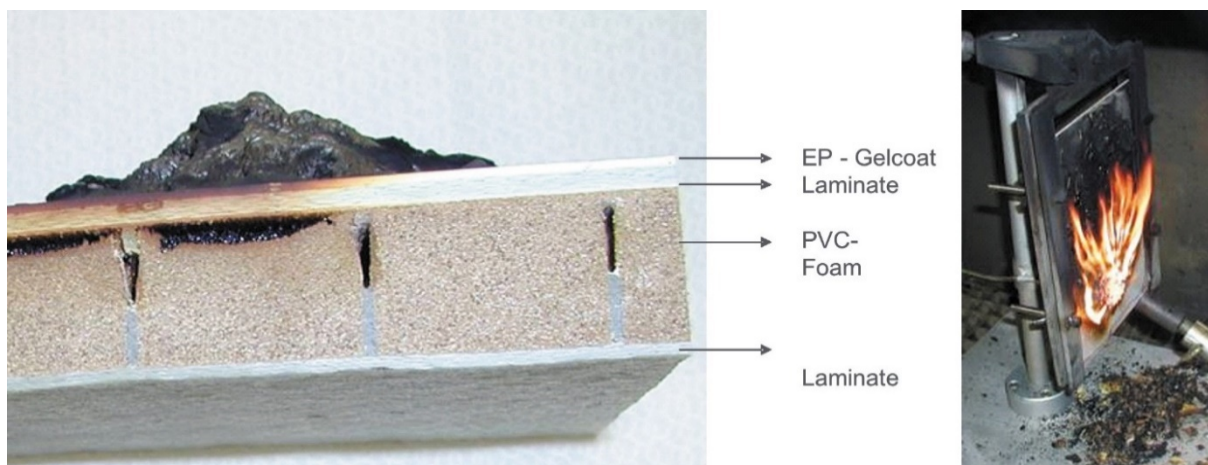
\* Parts per hundred resins

Figure 20 - Example of a hand lay-up FR formulation for UP resin to comply with UL 94 V-0.

| Component                                                                        | Content (phr*)       |
|----------------------------------------------------------------------------------|----------------------|
| UP resin                                                                         | 100                  |
| APP in composite, optimized formulation; or ATH in composite and APP in gel coat | 100; or<br>100 + 100 |
| ATH in composite                                                                 | 300                  |

\* Parts per hundred resins

Figure 21 - Example of a PIN FR pultrusion formulation for UP resin to comply with EN 45545-2 R1-HL3.

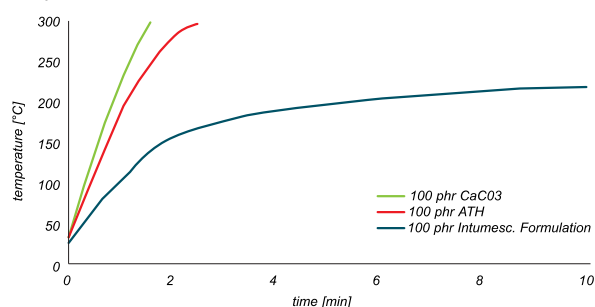


**Figure 22 - PIN FR coating for composite.**  
Credits ©Clariant

Example of an FR epoxy gel coating containing optimized APP-based flame retardants on a composite material consisting of a foam core with laminate covers. The upper side was exposed to a flame for ten minutes and nicely shows the intumescent effect (picture on the right).

### 3.4. SUMMARY OF PIN FRs IN INTERIOR APPLICATIONS

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



**Figure 23 - Effectiveness of gel coatings.**

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

Figure 24 - Overview of PIN FR solutions for different materials in transport 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, agrotextiles, protective clothes (e.g. fire fighter clothing) and technical fabrics, e.g. as reinforcements for composite applications.

Textiles are used in a variety of different transportation applications. In almost all uses, textiles must pass relevant fire performance standards. The most common uses and standards are summarised here.

For environmental reasons, there is an increasing demand for biobased synthetic fibres (e. g. PLA) and fibres made of recycled raw materials (e.g. R-PET). Especially in the field of transportation, a reduction of weight is desirable to reduce CO<sub>2</sub> emissions. This will influence the processing and burning behaviour of future textiles. 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 and artificial leather, although these are not textile products per se, are alternative materials competing with textiles for the same functionality. They are therefore included in the scope of this document.

| ▲<br>INCREASING FIRE HAZARD & NEED FOR FR TREATMENT<br>▼ | Fibre             | Flammability and fire behaviour                                                                                                                              | LOI % |
|----------------------------------------------------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
|                                                          | Polyacrylonitrile | <ul style="list-style-type: none"> <li>• Burn rapidly</li> <li>• Form burning drops</li> <li>• Form black smoke</li> </ul>                                   | 17-18 |
|                                                          | Acetate           | <ul style="list-style-type: none"> <li>• Burn heavily</li> <li>• Melts</li> <li>• Form burning drops</li> </ul>                                              | 18    |
|                                                          | Polypropylene     | <ul style="list-style-type: none"> <li>• Burn rapidly</li> <li>• Form burning drops</li> </ul>                                                               | 18-19 |
|                                                          | Viscose           | <ul style="list-style-type: none"> <li>• Burn rapidly like cotton</li> </ul>                                                                                 | 18-19 |
|                                                          | Cotton            | <ul style="list-style-type: none"> <li>• Ignite easily</li> <li>• Burn heavily</li> <li>• Do not melt</li> <li>• May continue glowing after flame</li> </ul> | 18-19 |
|                                                          | Polyamide         | <ul style="list-style-type: none"> <li>• Burn while releasing a high amount of heat</li> <li>• Form burning drops</li> <li>• Forms smoke</li> </ul>          | 20-21 |
|                                                          | Polyester         | <ul style="list-style-type: none"> <li>• Burn while releasing a high amount of heat</li> <li>• Form black smoke</li> <li>• Form burning drops</li> </ul>     | 22    |
|                                                          | Wool              | <ul style="list-style-type: none"> <li>• Difficult to ignite</li> <li>• Burn slowly</li> <li>• Self-extinguish under certain conditions</li> </ul>           | 25    |
|                                                          | Modacrylic        | <ul style="list-style-type: none"> <li>• Burn very slowly</li> <li>• Tend to melt away from the flame without burning</li> </ul>                             | 27    |
|                                                          | Aramide           | <ul style="list-style-type: none"> <li>• Does not burn</li> <li>• Strong char formation</li> </ul>                                                           | 28-29 |
|                                                          | Melamin fibre     | <ul style="list-style-type: none"> <li>• Does not burn</li> </ul>                                                                                            | 32    |
|                                                          | Carbon fibre      | <ul style="list-style-type: none"> <li>• Does not burn</li> </ul>                                                                                            | > 60  |
|                                                          | Glass fibre       | <ul style="list-style-type: none"> <li>• Does not burn</li> </ul>                                                                                            | -     |

Figure 25 - Reaction to fire of various fibres (source LNE).

The column “Flammability and fire behaviour” is adapted from LNE<sup>18</sup>, the column “LOI” (Loss on Ignition) indicates typical values derived from several publications<sup>19</sup>

<sup>18</sup> Adapted 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. 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”).

<sup>19</sup> Materials Science and Engineering 254 (2017). Journal of Polymer and Biopolymer Physics Chemistry. 2014, 2(4), 78-83. Chemical Fibres International 62(4):183-186.

## 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 (true for almost all synthetic fibres) 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 fire behaviour of non-FR-treated textiles can therefore vary strongly when exposed to an ignition source and can be described by the LOI (limiting oxygen index). A lower LOI means that the material is easier to ignite compared with those having a higher LOI. Beside the LOI measurement the fire safety of textiles can be described by different FR standards. In the field of transportation, some of the most relevant standards are summarized in the table. If a textile doesn't pass the relevant FR standard, it is necessary to apply a flame retardant or to use an inherent FR textile material.

Additionally, as described below, wash resistant fire safety treatment is often required for textiles in transportation applications, that is durable or semi-durable FR.



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Figure 28 - Credits ©Freevideophotoagency – Shutterstock



Figure 26 - Credits ©Tratong – Shutterstock



Figure 29 - Credits ©Edvard Nalbantjan - Shutterstock

| Transportation       | Uses                                                   | Fabrics                                                                                                                                                             | FR Standards                                             |
|----------------------|--------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|
| <b>Car / coaches</b> | Seat cover                                             | <ul style="list-style-type: none"> <li>• Polyester</li> <li>• Artificial leather (TPU-based)</li> <li>• Cellulosic / polyester blends</li> <li>• Leather</li> </ul> | DIN 75200<br>FMVSS 302 (cars)<br>ECE 118 Annex 8 (buses) |
|                      | Insulating non-woven                                   | <ul style="list-style-type: none"> <li>• Polyester</li> <li>• Polypropylene</li> <li>• Viscose</li> </ul>                                                           |                                                          |
|                      | Carpet / Floor covering                                | <ul style="list-style-type: none"> <li>• Polyester or polypropylene</li> </ul>                                                                                      |                                                          |
|                      | Rubber band / Belt / Curtains (buses)                  | <ul style="list-style-type: none"> <li>• Polyester</li> </ul>                                                                                                       |                                                          |
|                      | Airbags                                                | <ul style="list-style-type: none"> <li>• Polyamide</li> </ul>                                                                                                       |                                                          |
| <b>Airplane</b>      | Seat cover                                             | <ul style="list-style-type: none"> <li>• Wool or wool / polyamide</li> <li>• Leather</li> <li>• Artificial leather</li> </ul>                                       | FAR 25853<br>Part a (1)(i)/(ii)<br>ABD 0031              |
|                      | Floor covering / Backing                               | <ul style="list-style-type: none"> <li>• Wool, polyamide or wool / polyamide</li> <li>• Cellulosic fibre</li> </ul>                                                 |                                                          |
|                      | Wall covering                                          | <ul style="list-style-type: none"> <li>• Wool / aramid or aramid</li> </ul>                                                                                         |                                                          |
|                      | Draperies / Blankets / Pillowcases / Duvet covers      | <ul style="list-style-type: none"> <li>• Wool / polyester</li> <li>• Polyester / cotton</li> </ul>                                                                  |                                                          |
|                      |                                                        |                                                                                                                                                                     |                                                          |
| <b>Railways</b>      | Seat cover                                             | <ul style="list-style-type: none"> <li>• Wool or wool / polyester</li> <li>• Leather</li> <li>• Artificial leather (TPU-based)</li> </ul>                           | EN 45545 H2                                              |
|                      | Wall and ceiling / Curtain                             | <ul style="list-style-type: none"> <li>• Polyester</li> </ul>                                                                                                       |                                                          |
|                      | Floor covering / Backing / Duvet covers (sleeping car) | <ul style="list-style-type: none"> <li>• Wool, polyamide or wool / polyamide</li> <li>• Cellulosic fibre</li> <li>• Cotton / polyester</li> </ul>                   |                                                          |
| <b>Ship</b>          | Seat cover / Curtain                                   | <ul style="list-style-type: none"> <li>• Polyester</li> </ul>                                                                                                       | IMO part 1-9                                             |
|                      | Floor covering / Backing / Bed covering                | <ul style="list-style-type: none"> <li>• Wool or wool / polyamide</li> <li>• Cellulosic fibre</li> <li>• Cotton / polyester</li> </ul>                              |                                                          |

Figure 30 - Overview of textiles used in transportation.

### 4.3. WASH RESISTANCE & APPLICATION TECHNIQUES OF FR ON TEXTILES

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 = durable or semi-durable FR) can be obtained:

- 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

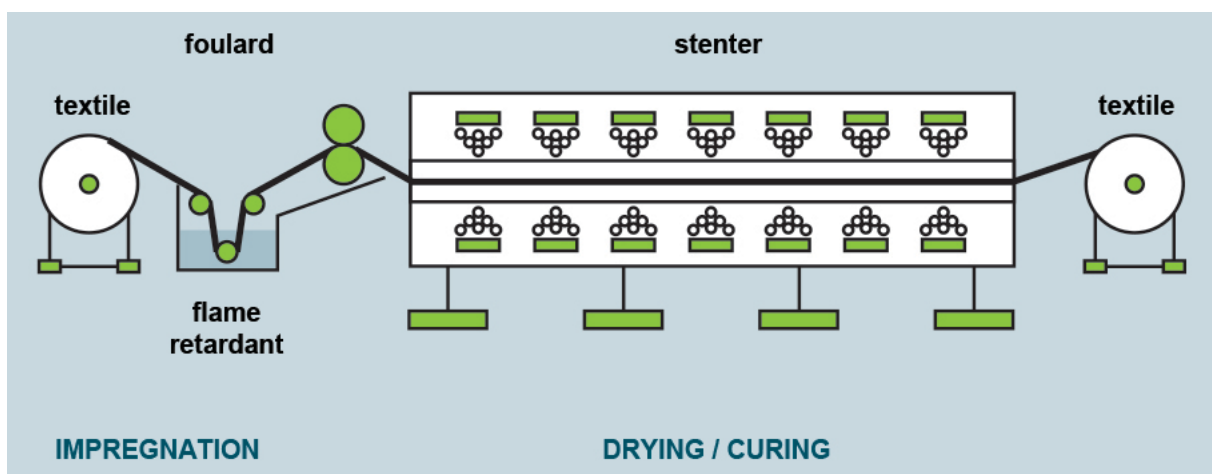


Figure 31 - Typical process for treating textiles with FR.

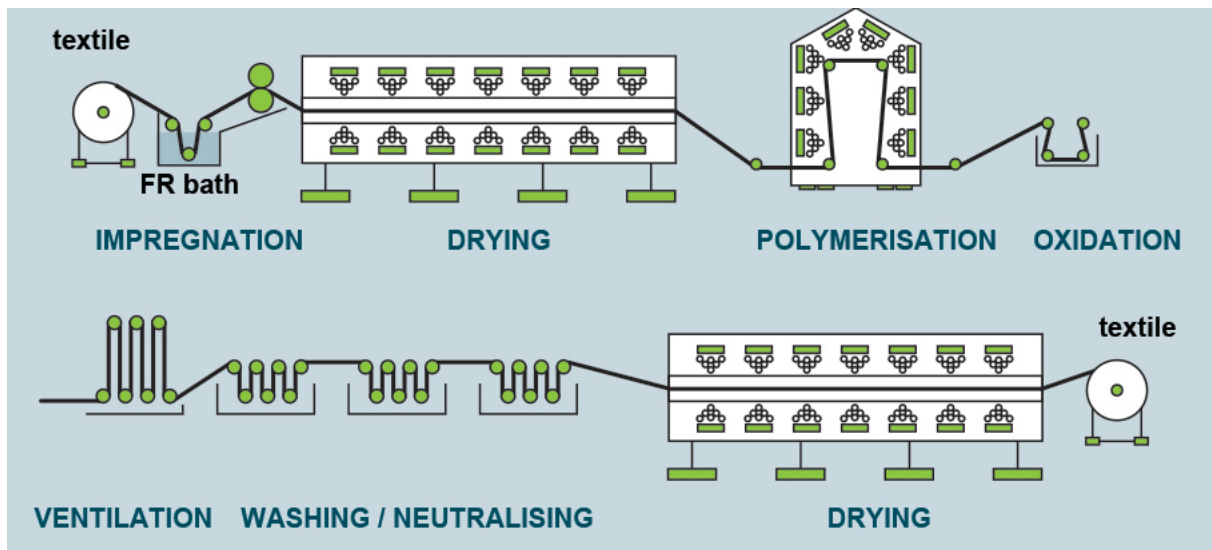


Figure 32 - Typical process for treating textiles with a durable FR.

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 flame-retardant solution and then squeezed between two rollers at a controlled pressure. By this process, a pre-determined 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 2 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 neutralized 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 non-reacted 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.
  - by adding an FR co-monomer or FR pigment (e.g. (poly)phosphonates, thiophosphate) in the polymerisation step or melt spinning (e.g. polyester fibres, such as Trevira® CS, Trevira; HEIM® (Toyobo); Lenzing FR®, Lenzing)
  - by designing polymer backbones with very high heat and flame resistance, e.g. polyaramide fibres based on meta-polyphenylene isophthalamide (Nomex®, DuPont; Conex®, Teijin), polyamide-imide (Kermel®, Kermel), para-polyphenylene terephthalamide (Kevlar®, DuPont; Twaron®, Teijin), polytetrafluoroethylene (PTFE, i.e. GORE-TEX®, W.L. Gore), and a few others.

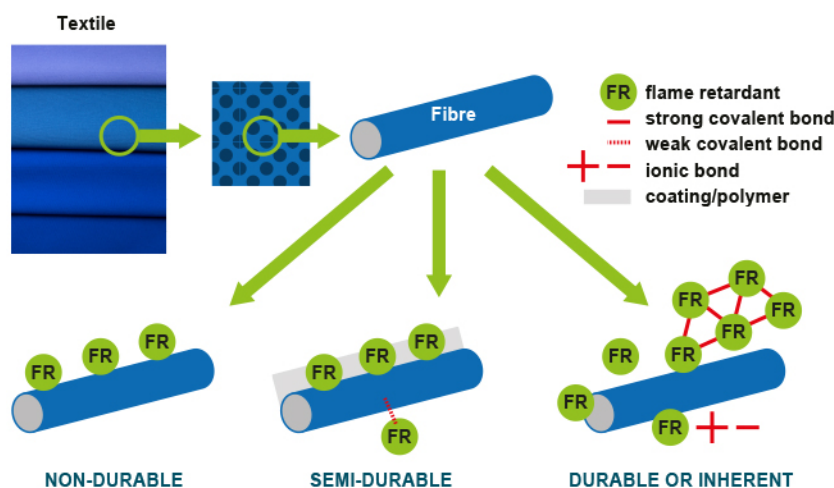


Figure 33 - Different ways of treating textiles with FRs. Credits ©Thor ©wedphotoline - Shutterstock

## 4.4. PIN FR'S USED IN TRANSPORTATION TEXTILES

The 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 demanding transport fire performance requirements, e.g. airplanes, trains.

| Substance                                                         | Physical form              | Use                                                               |
|-------------------------------------------------------------------|----------------------------|-------------------------------------------------------------------|
| <b>Aluminium-tri-hydroxide (ATH)</b>                              | Powder                     | Back-coating or added to polymer melt                             |
| <b>Aluminium phosphinate</b>                                      | Powder                     | Back-coating or impregnation                                      |
| <b>Amino-ether-HALS derivatives</b>                               | Powder                     | Added to polymer melt                                             |
| <b>Ammonium phosphate</b>                                         | Powder or aqueous solution | Back-coating or impregnation                                      |
| <b>Ammonium polyphosphate</b>                                     | Powder                     | Back-coating                                                      |
| <b>Ammonium sulphamate</b>                                        | Powder or aqueous solution | Back-coating or impregnation                                      |
| <b>Ammonium sulphate</b>                                          | Powder or aqueous solution | Back-coating or impregnation                                      |
| <b>Cyclic phosphonate</b>                                         | Liquid                     | Impregnation                                                      |
| <b>Spiro phosphonate</b>                                          | Solid                      | Impregnation,<br>Back-coating or added to polymer melt            |
| <b>Polyphosphonates</b>                                           | Solid                      | Added to polymer melt                                             |
| <b>Dicresyl- / arylphosphate</b>                                  | Liquid                     | Added to polymer melt / back-coating                              |
| <b>Diethyl phosphinic acid, aluminium salt</b>                    | Powder                     | Back-coating or added to polymer melt                             |
| <b>Diethyl [3-[(hydroxymethyl)amino]-3-oxopropyl] phosphonate</b> | Liquid                     | Reacted on fibre (cotton and blends)                              |
| <b>Guanidine phosphate</b>                                        | Powder or aqueous solution | Back-coating or impregnation                                      |
| <b>Isopropyl / alkylphosphate ester</b>                           | Liquid                     | Added to polymer melt / back-coating                              |
| <b>Melamine</b>                                                   | Powder                     | Back-coating                                                      |
| <b>Melamine cyanurate</b>                                         | Powder                     | Back-coating or added to polymer melt                             |
| <b>Melamine phosphate</b>                                         | Powder                     | Back-coating                                                      |
| <b>Melamine polyphosphate</b>                                     | Powder                     | Back-coating or added to polymer melt                             |
| <b>Methyl phosphonic acid, amidino-urea compound</b>              | Liquid                     | Back-coating or impregnation                                      |
| <b>Oxaphosphorinane oxy-bis-dimethyl sulphide</b>                 | Powder                     | Back-coating or added to polymer melt                             |
| <b>Potassium hexafluoro zirconate</b>                             | Powder                     | Reacted on fibre (wool)                                           |
| <b>THPC-urea-precondensate</b>                                    | Liquid                     | Polymerization on fibre (cotton, cotton/PA and cotton/PES blends) |
| <b>Zinc borate</b>                                                | Powder                     | Back-coating or added to polymer melt                             |
| <b>Zirconium acetate</b>                                          | Liquid                     | Reacted on fibre                                                  |

Figure 34 - Non-halogen 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 and wear. 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 (PVC or PU based) are used as coverings. All kinds of coverings are described in chapter 4 (Textiles) and, hence, not covered in this section.

### 5.2. AUTOMOTIVE



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#### 5.2.1. FRAMEWORK

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

Plastic frames are increasingly used to reduce weight, improve design flexibility, 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 strongly. However, both PA and PP usually pass the required FMVSS 302 fire tests (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 the 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 processing of the foams
- No impact on the mechanical properties (hardness)
- No impact on the dynamic properties
- No impact on the properties after ageing (high-temperature and humidity)
- No contribution to fogging or emission

| Flame retardants              | Chemical name                                        | Appearance | Phosphorus content [%] | Viscosity at 25°C [mPa.s] |
|-------------------------------|------------------------------------------------------|------------|------------------------|---------------------------|
| <b>BPP</b>                    | Butylated triphenyl phosphate                        | liquid     | 8.1% P                 | 92                        |
| <b>RDP</b>                    | Resorcinol bis (diphenyl phosphate)                  | liquid     | 10.8% P                | 600                       |
| <b>BDP</b>                    | Bisphenol A bis-(diphenyl phosphate)                 | liquid     | 8.9% P                 | 13.000                    |
| <b>DOPO derivative</b>        | Phosphorus compound based on DOPO                    | liquid     | 9.0% P                 | 6.500                     |
| <b>Oligomeric phosphate 1</b> | Oligomeric alkyl phosphate                           | liquid     | 19.0% P                | 2.250                     |
| <b>Oligomeric phosphate 2</b> | Reactive phosphonate oligomer                        | solid      | 10.5% P                | -                         |
| <b>Reactive P/N polyol</b>    | N,N-dihydroxyethylamino-methan Phosphonic acid ester | liquid     | 12.1% P                | 175                       |
| <b>P-Polyol 1</b>             | Proprietary, functionality 2                         | liquid     | 11.5% P                | < 500                     |
| <b>APP</b>                    | Ammonium polyphosphate                               | solid      | 31.5% P                | -                         |
| <b>MEL</b>                    | Melamine                                             | solid      | 66.4% N                | -                         |
| <b>EDAP</b>                   | Ethylene diamine Phosphate                           | solid      | 19.5% P<br>17.5% N     |                           |
| <b>MP</b>                     | Melamine phosphate                                   | solid      | 14.5% P<br>37% N       |                           |

Figure 36 - Overview of common PIN FRs for automotive PUR foams.

These requirements are fulfilled by various different non-halogen flame retardants. Phosphorus-based flame retardants, such as liquid and solid phosphates, are most commonly used. Generally speaking, four 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 properties due to their plasticising properties. Furthermore, they can contribute to emissions from the foam, as they are not incorporated in the polymer matrix.

**Polymeric flame retardants** are usually viscous liquids that can be incorporated in the foam together with the other raw materials. They usually have a lower impact on the mechanical properties due to their lower plasticising effect. In addition, polymeric flame retardants, e.g. phosphonate oligomers, show a lower contribution to fogging or emissions due to their higher molecular weight.

**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 non-halogen flame retardants for automotive PUR foams is presented in the table.

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 emissions have gained increasing attention when studying the equipment of automotive interiors. Seats which are among the largest interior components and especially foams can 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).

## 5.3. AIRCRAFT

### 5.3.1. FRAMEWORK

The framework of aircraft 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



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Foams for aircraft 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 0031) for aircraft 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 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 aircraft 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 (HCl), use of flame retardants containing chlorine is restricted.

## 5.4. RAILWAY AND SUBWAY ROLLING STOCK

Rolling stock 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 series for railways EN 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 polymer-based and must be flame-retarded to pass the required fire standards.

According to EN 45545-2, 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.

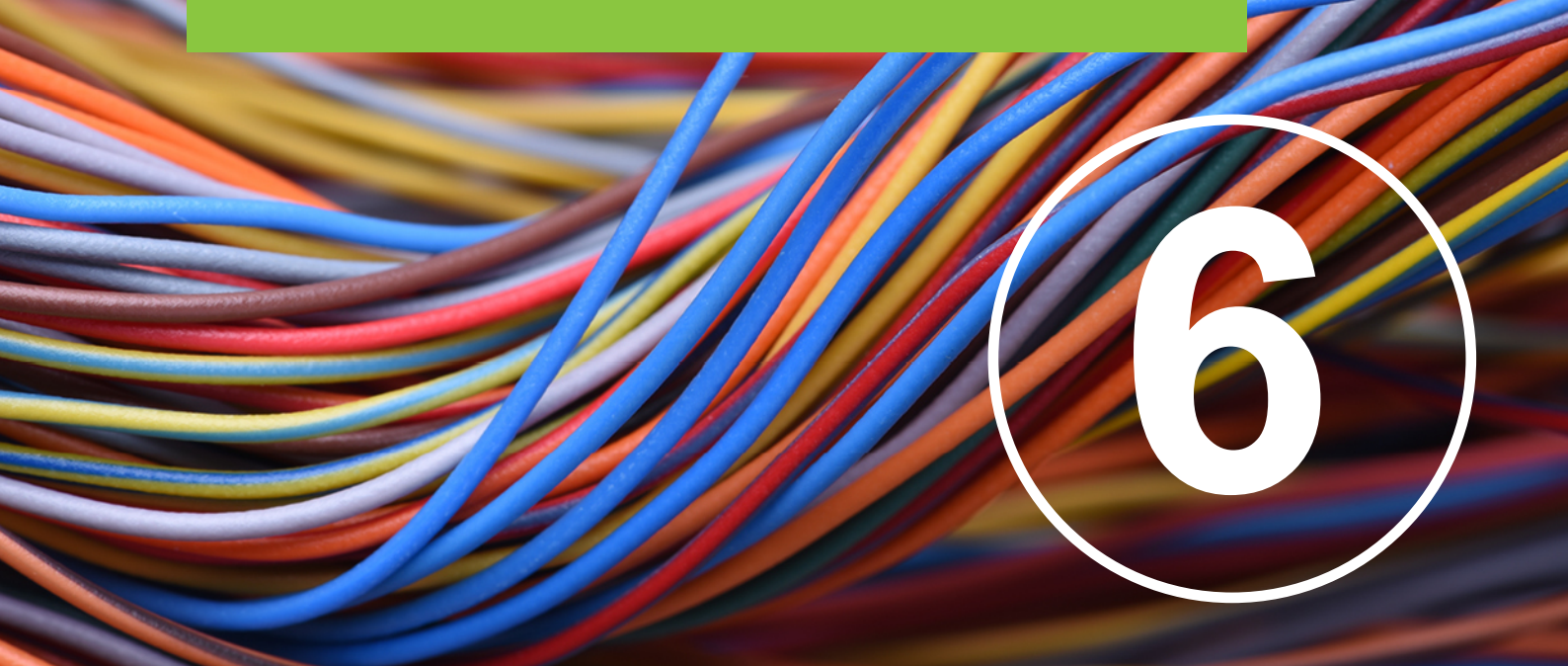
The relevant fire standard is based on calorimetric data (rate of heat release, peak heat release), smoke density as well as the toxicity of smoke.

### 5.4.1. FRAMEWORK

The framework of subway 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, phosphonate oligomers 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 electrical and optic cables. Cables transmit energy and ever growing amounts of data. Large numbers are installed in vehicles like cars, trains, ships, or airplanes. 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 flammable polymer materials as insulation, sheathing, or bedding compounds. Due to their presence all over the vehicle and the nature of their installation, burning cables may cause dramatic fires and transmit fire between compartments (e.g. from the motor to the passenger area) or over large distances<sup>20</sup>. Causes of fires in vehicles include electrical faults, mechanical faults / overheating, arson, ignited waste containers or leaking fuels or oil.

Depending on the difficulties for people to escape from a burning vehicle, the fire resistance standards are more or less severe. As escape from airplanes, 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.

Non-halogen flame retardant (PIN FR) or low-smoke free-of- halogen (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 the table.

<sup>20</sup> The FIPEC-report, *Fire Performance of Electric Cables – new test methods and measurement techniques* – Interscience Communications Ltd. 2000

| Flame retardant                                                                                                                                                                                                                 | Polymers                                                                                                                  | Applications and effectiveness                                                                                                                                                                                                                                                                                                                                             |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Inorganic flame retardants:</b><br><b>Aluminium tri-hydroxide (ATH)</b><br><b>Magnesium di-hydroxide (MDH)</b><br><b>Aluminium oxide-hydroxide (AOH, Boehmite)</b><br>Also coated grades are available.                      | Low-density polyethylene (LDPE) Ethylene vinyl acetate (EVA) Polyolefins<br>Elastomers<br>Silicone rubbers (SiR)          | In case of a fire, these mineral flame retardants decompose <ul style="list-style-type: none"> <li>• absorbing energy.</li> <li>• releasing water (thus reducing fire intensity and diluting fire gases).</li> <li>• creating an oxide fire barrier against heat from the flame and to prevent burnable polymer decomposition products from reaching the flame.</li> </ul> |
| <b>Phosphorus flame retardants</b><br><b>Phosphate esters</b><br><b>Intumescent products based on: ammonium polyphosphates (APP), metal phosphinates, aryl phosphates</b><br><b>Melamine phosphate</b><br><b>Red phosphorus</b> | Used in fire-resistant coatings for cables<br>Polyolefins Elastomers<br>Thermoplastic Elastomers (TPE) Polypropylene (PP) | Flame inhibition and charring properties of phosphorus-based materials reduce the flammability of polymers. A char on the surface prevents heat transfer and protects polymer below.                                                                                                                                                                                       |
| <b>Melamine Cyanurate (MC)</b>                                                                                                                                                                                                  | Polyamides (PA)                                                                                                           | Results in polymer decomposition without flaming, especially in PA.                                                                                                                                                                                                                                                                                                        |

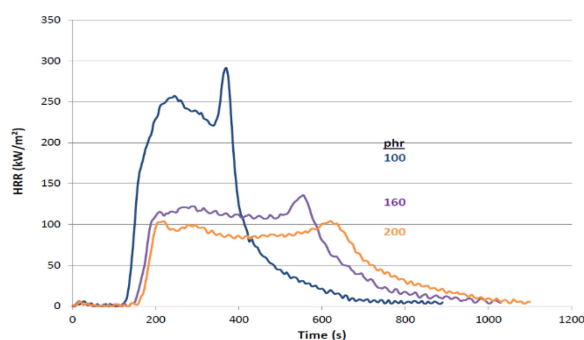
**Figure 38 - Typical PIN FR cable formulations.**

Selected flame retardants for use in PIN FR cable compounds, selected polymers for which they are recommended, and information on their flame retardancy mechanism

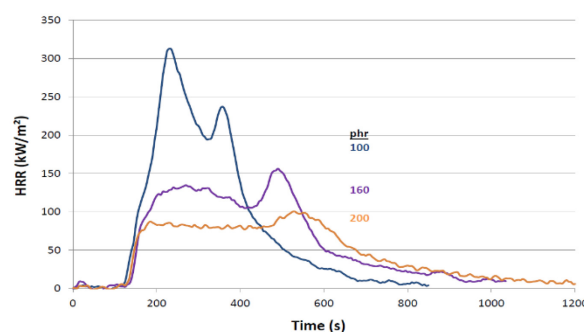
Depending on the use of a cable in a vehicle, different standards have to be complied with and the materials have to be chosen according to the mechanical and thermal stresses during installation and service life. Not only the cable, but the whole cable construction in the vehicle must be flame-retardant. 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. low heat release rates, as shown in the figures (results from cone calorimeter measurements @ 35 kW/m<sup>2</sup>).

The flame retardant mechanism of mineral FRs is based on endothermic decomposition into water vapor and metal oxide. The main difference between aluminium hydroxide and magnesium hydroxide is the thermal stability. ATH starts to decompose at 200° C while MDH is stable up to 320° C. Relatively high amounts of these materials are needed to reach a high flame resistance compared to FR systems that work via specific chemical routes.



**Figure 39 - Heat release values of PIN EVA compounds I.** Plotted as a function of MDH loading.



**Figure 40 - Heat release values of PIN EVA compounds II.** Plotted as a function of ATH loading.

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 non-halogen flame-retardant TPEs, for instance, is 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 PIN FR 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.

## 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, several km 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 car<sup>21</sup>.

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 non-halogen products) can be used to produce cable insulation and sheathing compounds.

Some examples are listed below, together with useful flame retardants for this application.

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

**Figure 41 - Temperature resistance classifications.**

Temperature ranges for the temperature resistance classification (3000 h) of cables in road vehicle use according to ISO 6722, useful polymers, and flame retardants.<sup>22</sup>

<sup>21</sup> a) Karl Brown (Equistar Chemicals LP, LyondellBasell) AMI Conference Cables, 9-11 March 2010, Cologne (Germany);  
b) White Paper Automotive, February 2007, Nexans

<sup>22</sup> a) Kabelbuch 2003, Automobilleitungen Coroplast Fritz Müller GmbH & Co KG, Huber+Suhner AG, Pfäffikon, "Automotive Products", Edition 2009. Leoni Kabel GmbH, Roth, "We keep on moving" Business Unit Automotive Cables. White Paper Automotive, February 2007, Nexans

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 below.

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

*Figure 42 – XLPE (cross linked PE) guiding formulation with MDH as flame retardant.*

In Europe, due to stringent requirements for resistance to abrasion 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 common<sup>23</sup>.

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 installations<sup>24</sup>.

In PIN FR 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 below.

| Property                | TPE-E (Shore D 55)      | TPE-E (Shore D40) |
|-------------------------|-------------------------|-------------------|
|                         | Al-phosphinate (20–22%) |                   |
| UL 94 rating [1.6 mm]   | V0                      | V1                |
| GWIT 1 mm [°C]          | 775                     | 650               |
| GWFI 1 mm [°C]          | 960                     | 900               |
| TS [kJ/m <sup>2</sup> ] | 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                |

*Figure 43 - Some PIN FR TPE cable compounds.  
Selected properties of TPE cable compounds containing phosphinate flame retardants*

<sup>23</sup> Karl Brown (Equistar Chemicals LP, LyondellBasell) AMI Conference Cables, 9-11 March 2010, Cologne, Germany.

<sup>24</sup> Leoni Kabel GmbH, Roth, "We keep on moving" Business Unit Automotive Cables

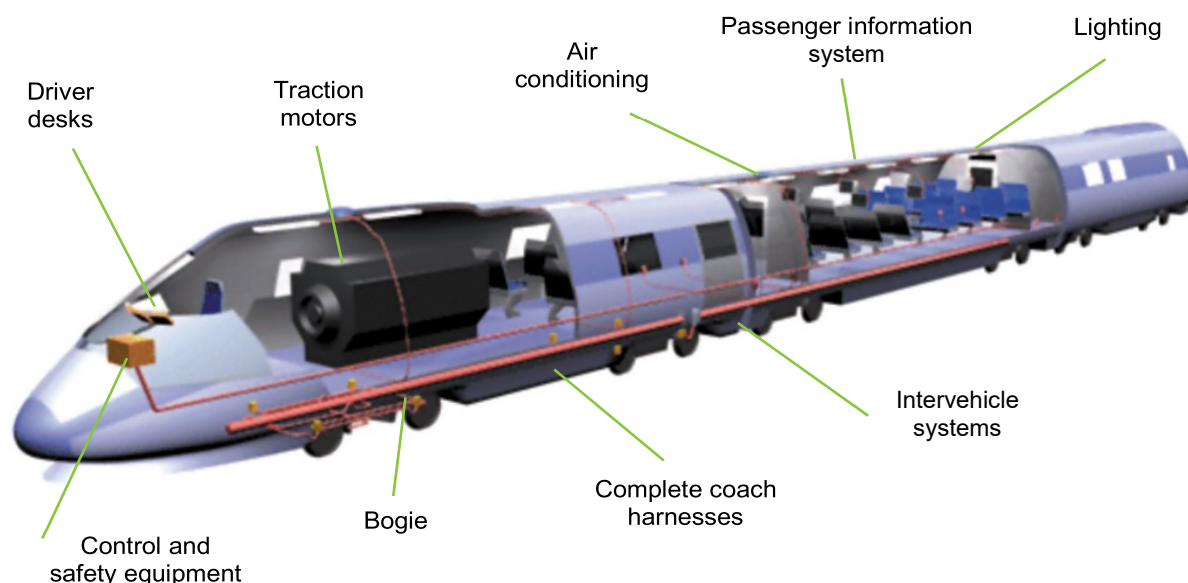
### 6.3. ROLLING STOCK (RAILWAY, METRO)

It is important to note that also in public mass transport systems like trains, ships, and airplanes, 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 EN 45545-2 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 below. 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 wagons, jumper cables guarantee the transmission of data and energy.

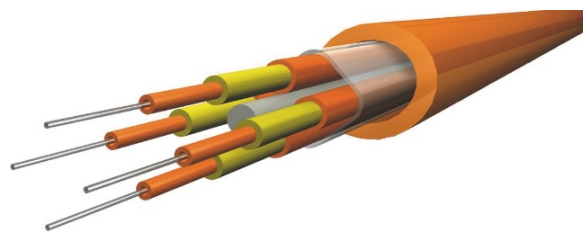


*Figure 44 - Selected cables in a train, position and purpose.  
(Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.)*

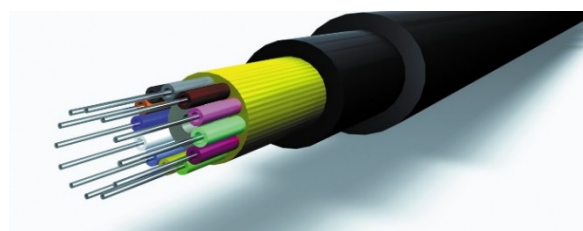
As mentioned above, cables for trains have to comply with severe standards for fire resistance and low smoke development. For this reason, usually higher amounts of mineral flame retardants are used here compared to cables for automobiles. This leads to an improved flame-retardancy and reduced smoke 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 the figures, a cable for installation in a wagon or locomotive and a jumper cable.



*Figure 45 - Cable for installation in a wagon.  
(Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.)*



*Figure 46 - Jumper Cable.  
(Courtesy of Huber+Suhner AG, Pfäffikon, Switzerland.)*

As shown in the figures, 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 PVC.

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 a more demanding production processes for the cable.

## 6.4. MARINE

On ships and especially on submarine vessels, it is even more focused on reduced smoke density, as described in 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 below.

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

*Figure 47 - 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 surface treated ATH particles.

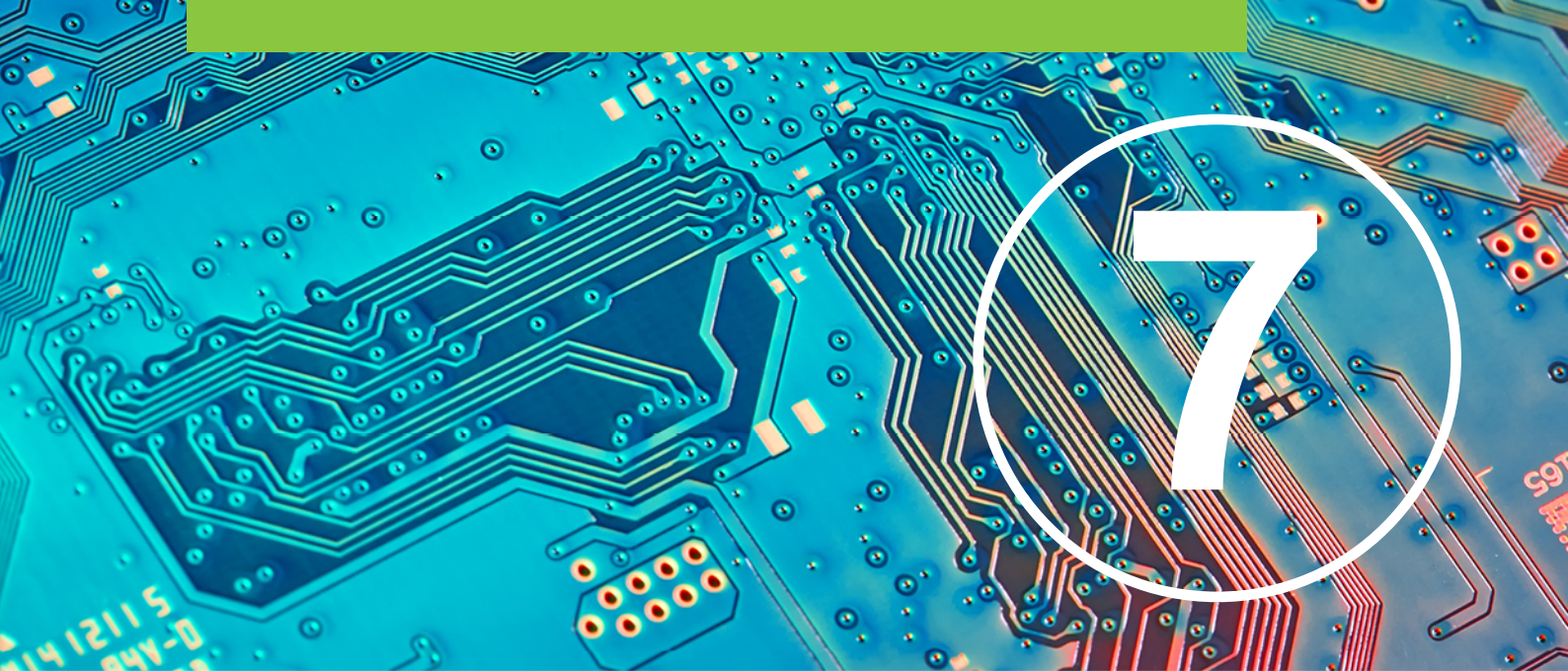
The ageing resistance in different media is very important for marine cable compounds according to standards like the British Navy Def Stan 61-12 or the German "Deutsche Marine VG 95218-28/29". Physical dimensions and mechanical values of the compounds are usually influenced by ageing processes. These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

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

## 6.5. AVIATION

Materials for cables in airplanes 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 airplanes. These intrinsically fire-resistant polymers in general do not require any further addition of flame retardants.

PIN FR 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.



# ELECTRICAL 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.

Very many more or less visible and invisible electrical and electronic applications are essential to modern transport vehicles, depending on the type of vehicle and the predominant motivation, such as

- mobility
- safety
- comfort
- energy efficiency

## 7.2. ELECTRICAL INSTALLATIONS & COMPONENTS

### 7.2.1. SCOPE AND MATERIAL REQUIREMENTS OF ELECTRICAL COMPONENTS

| Types of connectors                    | Switches, switchgear and Control Units                        |
|----------------------------------------|---------------------------------------------------------------|
| Terminal blocks                        | Low-voltage switchgear and circuit breakers                   |
| Crimp-on terminals                     | Light switches                                                |
| Insulation displacement connectors     | Rotary switches<br>Contactors<br>Relays<br>Fuse and ECU boxes |
| Plug and socket connectors             |                                                               |
| Component and device connectors        |                                                               |
| Printed circuit board (PCB) connectors |                                                               |

**Figure 48 - Connectors and switches.**  
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.

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 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.

### **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. Polybutyleneterephthalate (PBT), on the other hand, offers the benefit of good dimensional and hydrolytic stability.

### **Electrical properties**

Besides Volume and Surface resistivity, an important electrical requirement is the insulation efficiency which is expressed by dielectric strength which is measured in kV/mm particularly in electric and hybrid vehicles (xEV) where dielectric properties retention at temperatures as high as 150°C and above are a must. The introduction of 5G and Autonomous Driving (ADAS) have raised importance of Dielectric constant (Dk) for alternating currents and signals together with dissipation factor (Df). The closer dielectric constant value is to one, the better is signal transmission. The other key parameter is the comparative tracking index or CTI (expressed in volts) which specifies the electrical break-down (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 perform. With some non-halogen FRs, the CTI of polymer blends remains the same as for the neat polymer.

### **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 V-0, 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 NON-HALOGENATED 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. By combining these metal phosphinates with phosphorus synergists, the processability can be further improved.

Melamine polyphosphate (MPP) is especially suited for glass fibre-reinforced polyamide 6,6. For UL 94 V-0 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 V-0 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 (e.g. RDP) and polyphosphonates are mainly added (10 to 20%) to styrenic blends for UL 94 V-0. 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 V-0. Because of its limited temperature stability, it is mainly used in low glass fibre PA 6.



Figure 49 - Credits ©BASF

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.

### 7.2.3. POLYMERS USED IN ELECTRICAL COMPONENTS AND SUITABLE FR SYSTEMS

The table below presents an overview of typical technical properties which can be achieved with non-halogen 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 <sup>2</sup> ] | Notched impact [kJ/ m <sup>2</sup> ] | CTI [V] | GWIT [°C] | UL 94 |
|----------------------|-----------------|--------------------------------------------------------------|----------------------------------------|--------------------------------------|---------|-----------|-------|
| <b>Polyamide 6</b>   | 0               | Melamine cyanurate                                           | ~ 75                                   | ~4                                   | 600     | > 775     | V0    |
|                      | 30              | Metal phosphinate + P-synergist (or N-synergist e.g. MPP)    | ~160                                   | ~15                                  | 600     | 775       | V0    |
| <b>Polyamide 6,6</b> | 30              | Metal phosphinate + P-synergist (or N-synergist e.g. MPP)    | ~150                                   | ~14                                  | 600     | 725 (775) | V0    |
|                      | 30              | Red phosphorus                                               | ~160                                   | ~18                                  | 600     | 775       | V0    |
|                      | 30              | Melamine polyphosphate                                       | ~140                                   | ~12                                  | 400     | 675       | V0    |
| <b>HTN</b>           | 30              | Metal phosphinate                                            | ~140                                   | ~8                                   | 600     | 775       | V0    |
| <b>PBT</b>           | 0               | Metal phosphinate + N-synergist e.g. MPP                     | ~45                                    | ~3                                   | 600     | 775       | V0    |
|                      | 30              | Metal phosphinate, or polyphosphonate + N-synergist e.g. MPP | ~110                                   | ~7                                   | 500     | 800       | V0    |
| <b>PET</b>           | 0               | Metal phosphinate + N-synergist e.g. MPP<br>Polyphosphonate  | –                                      | ~2                                   | –       | 800       | V0    |
|                      | 30              | Metal phosphinate + N-synergist e.g. MPP<br>Polyphosphonate  | –                                      | ~8                                   | –       | 800       | V0    |
| <b>Polyolefins</b>   | 0               | Intumescent system                                           | 10 - 30                                | ~3                                   | 600     | 800       | V0    |
|                      | 20              | Intumescent system                                           | 70                                     | ~6                                   | 600     | 825       | V0    |
| <b>HIPS/PPE</b>      | 0               | RDP                                                          | 25.2                                   |                                      |         |           | V0    |
| <b>PC/ABS (4:1)</b>  | 0               | RDP                                                          | 53.3                                   | ~1                                   |         |           | V0    |
|                      | 0               | BDP                                                          | 55.6                                   | ~0.5                                 |         |           | V0    |
|                      | 0               | TPP                                                          | 46.0                                   | ~0.1                                 |         |           | V0    |
|                      |                 | Polyphosphonate co-carbonate                                 | 53.0                                   | ~0.5                                 |         |           | V0    |

Figure 50 - Examples of PIN flame retardant systems to achieve UL 94 V-0.

## 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 500+ active electronic components (= mini computers) and several m<sup>2</sup> of printed circuit board (PCB). Complex interactions of sensors and response elements as described below have been developed already and this trend will continue.

#### Examples of electronics in today's vehicles

##### Safety

- Passenger Restraint System (Airbags, Active Seatbelts)
- Tracking Control System (TCS/ABS)
- Collision Avoidance System (Night Vision, Obstacle Detection)

##### Comfort

- Climate Control System
- Noise Control System
- Suspension Control System

##### Convenience

- Steering Enhancement Systems
- Navigation System (GPS)
- Information & Communication System (Phone, Network)

##### Performance & Environment

- Engine and Emission Control Systems

##### Energy and Drive Transmission

- Hybrid Engine System
- Electric drive
- Battery Monitoring, Control, Safety
- Fuel Cell Control Systems

Figure 51 - Electronics in vehicles.

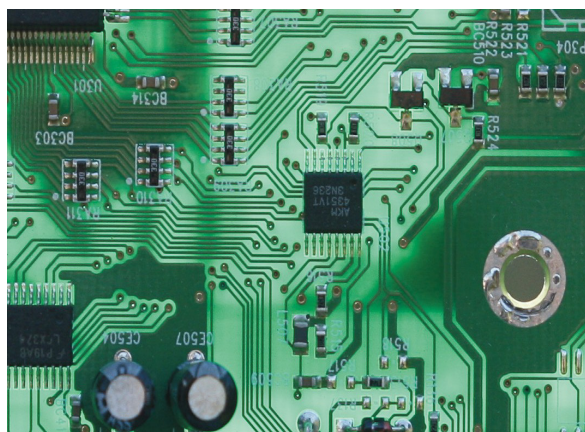


Figure 52 - Credits ©A. BEARD

Virtually all electronic items contain a PCB. For safety reasons, requirements are made on the fire resistance of PCBs, the UL 94 V-0 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 (CCL), 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 (2011/65/EU (RoHS 2) + (EU) 2015/863 (RoHS 3)) has caused a change in the base material market, because it bans products that contain lead (Pb) since July 2006, unless use is expressly exempted. Lead had previously been used 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 move to non-halogen FRs when developing new materials.

### 7.3.2. TECHNICAL REQUIREMENTS FOR 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 (T<sub>g</sub>)
- No or little impact on electrical properties, in particular D<sub>k</sub> and D<sub>f</sub>
- 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-phosphaphenanthrene-oxide) is a cyclic hydrogen phosphinate containing a P-H bond. It is mono-functional, 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 phosphorus-containing epoxy resins (T<sub>g</sub> up to 150°C). DOPO is commercially available from different suppliers and global capacities have consequently increased over the past 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 T<sub>g</sub>, pressure cooker test).

Other P-based reactive flame retardants with epoxy and hydroxyl groups (e.g. phosphonate oligomers) have recently been introduced to the market.

### 7.3.4. NON-REACTIVE FILLERS

#### *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

#### *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 non-halogen formulations. If used alone, rather high loadings are necessary to achieve the necessary fire performance. Therefore, combination with other FRs is common.

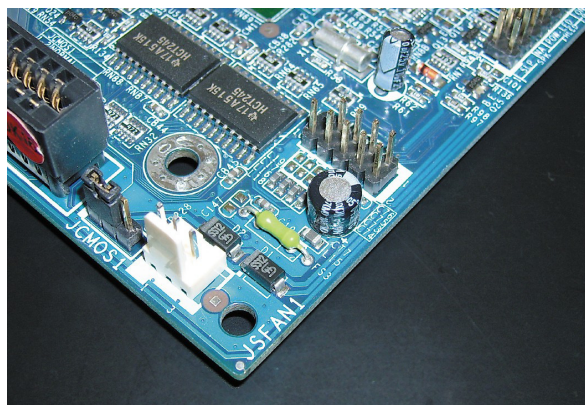


Figure 53 - Printed Circuit Board with Electronic Components.  
Credits ©NABALTEC

#### *Alumina monohydrate (Boehmite)*

The transition to lead-free solders with significantly higher temperatures 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 Boehmite 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 non-halogen FR or novolac-based epoxy systems is recommended.

#### *Metal phosphinates and Melamine polyphosphates*

Metal phosphinates are 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 high phosphorus content (> 23%) and 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, metal phosphinate cannot be used alone to achieve a UL 94 V-0 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, or others). To obtain a UL 94 V-0 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 T<sub>g</sub>.

## 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 ether (PPE) / HIPS blends (PPE/HIPS).

According to international standards, the plastic materials used for these housings usually should meet high fire safety standards, such as UL 94 V-0 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. Non-halogen phosphorus-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 polymer resin – FR compounds have to meet additional criteria, such as:

- **Processability**

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

- **Thermal stability**

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

- **Mechanical properties**

In particular, high impact strength is requested

- **Hydrolytic stability**

A high resistance against degradation caused by moisture is stipulated

- **Recyclability**

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

- **RoHS and WEEE directives**

The polymer resins have to comply with the RoHS and WEEE directives

### 7.4.2. PIN FRS FOR HOUSING / INFOTAINMENT APPLICATIONS

#### PPE/HIPS BLENDS

PPE/HIPS blends can be flame-retarded with the aromatic phosphates TPP, RDP, BDP and polyphosphonate. Typical levels of PPE used to achieve a UL 94 V-0 rating are 30 to 70%; these blends also contain 10 to 20% of TPP, RDP, BDP or polyphosphonate.

#### PC/ABS BLENDS

TPP, RDP, BDP and polyphosphonate co-carbonate are suitable non-halogen flame retardants for PC/ABS blends. The required loadings depend on the ratio of PC and ABS in the blend. In commercial PC/ABS blends, where the ABS content normally does not exceed 25%, it is possible to achieve a UL 94 V-0 rating with these products at 8 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-%.



Figure 54 - Credits ©LANXESS



# ELECTROMOBILITY

## 8.1. INTRODUCTION

The need to reduce global warming and the recent EU roadmap to become CO<sub>2</sub> neutral by 2050 have boosted the sales of electric and hybrid vehicles (xEV), this trend will continue and xEV sales are estimated at 70 million units worldwide in 2040. However massive introduction of xEV brings new safety challenges particularly concerning fire.

In the last 10 years more than 100,000 xEV have been recalled or caught fire mainly because of battery failures<sup>25</sup>. Therefore OEMs needed not only to adopt more efficient battery cooling systems (liquid vs. air), but also to introduce new flame resistance requirements such as UL 94 V-0 and/or IEC 60695-2-11 Glow Wire Flammability Index of 960°C to reduce fire risks. However, flammability alone is not enough and discussions are ongoing to reduce electrical risks by introduction of new standards to increase Comparative Tracking Index (CTI) from 600V currently in IEC 60112 to 1000V and to introduce Inclined Plane Tracking test at 1.5kV according to IEC 60587 or ASTM D2303. Beyond the vehicle itself critical components for safety are high power connecting systems and charging stations both wired and wireless. Connecting systems must not only ensure functionality in harsh outdoor conditions but must also be easily recognized in case of emergency. This is why the specific, bright orange colour is required. The need for fast charging is increasing the concerns about fire and electric hazards causing constant evolution of standards and regulations.

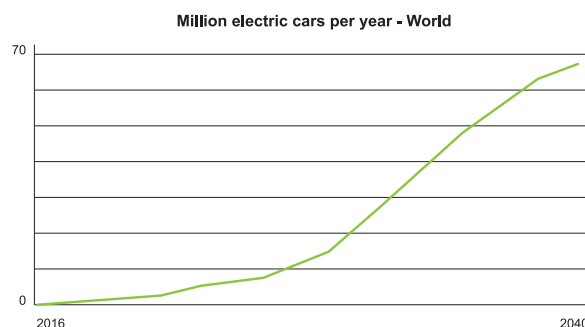


Figure 55 - Expected growth in electric cars

## 8.2. BATTERIES

The heart of every electric vehicle is a powerful battery which is built of individual battery modules which in turn consist of a number of cells. Most of the currently installed batteries are lithium-ion-batteries (LIB). Due to the high energy density located in the battery, this component brings increased hazards of fire initiated by overheating or short circuits resulting in Thermal Runaway (TR). Thermal runaway is a failure of a battery cell that results in an uncontrolled increase of temperature, leading to failure of adjacent cells and then propagation throughout the whole battery. Thus, TR is the main cause for large fires and explosions in xEVs.

<sup>25</sup> <https://edition.cnn.com/2020/11/10/success/electric-car-vehicle-battery-fires/index.html> and <https://www.bloomberg.com/news/articles/2020-11-13/gm-latest-automaker-to-recall-electric-car-for-battery-fire-risk>

Smaller lithium-ion batteries also pose fire hazards, as has been repeatedly illustrated by fires and explosions in smart phone and computer batteries, leading to bans in air travel and massive OEM recalls, in some cases involving hundreds of thousands of consumer items. Until 2021 xEV safety regulations have been only voluntary. This has led to a wide variety of battery designs and thermal management strategies. However, tests required on the complete battery pack are specified in the Chinese standard GB/T 31467.3-2015 including mechanical shock tests, vibration and immersion tests, salt spray tests and tests for external fire resistance. In January 2021 China further issued the standard GB 38031-2020. This new standard includes tests especially at the cell level, including short-circuit, crush tests, overcharge and over-discharge. A new and very important test in this standard is the “thermal propagation test”. This test is conceived to verify that thermal runaway of a single cell will not cause a fire or explosion of the battery module for at least five minutes. This allows for passengers to leave the vehicle in time in case of such destructive battery failure.

China is the first country to make this requirement for traction batteries mandatory, but it can be assumed that the requirement will also be imposed in this or a similar way for other countries.

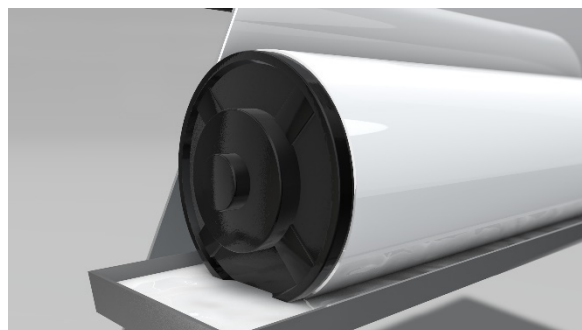
While final standardisation regarding flame retardancy is still in progress, materials used in batteries are commonly requested to fulfil flame retardancy classification according to UL 94 V-0 (similar to many E&E applications).

### 8.2.1. BATTERY CELLS

A typical battery cell consists of four main components: anode, cathode, separator and electrolyte. The separator is a porous membrane made from polymer (PP or PE) and acts as a separating layer between the positively charged cathode and its negative counterpart, the anode. Through the pores of the separator, lithium-ions move in the electrolyte to carry electrical energy from cathode to anode during charging and vice versa during discharging. Most battery failures are due directly or indirectly to separator damage. Separators can be damaged by mechanical stress, or if an overload or an external short circuit happens, the polymer based separator can shrink due to the sudden heat development. This allows a direct electrode contact between the cathode and the anode which results in an internal short circuit and thermal runaway, fire or explosion. With the continuing trend to increased battery energy density, batteries with simple polymeric separators can no longer meet safety requirements.

One approach is to coat the separator on one or both sides with a dispersion that contains mineral based PIN materials (e.g. aluminium oxide or Boehmite) to enhance the heat-resistance of the polymer. The ceramic layer will maintain the integrity and prevent shrinking of the separator foil in case of higher temperatures. The main characteristics of the separator, good permeability for ions and high porosity, must be maintained.

The standard UL 2591 – Outline of Investigation for Battery Cell Separators – covers test procedures on battery cell separators such as analytical tests, dimensional stability test, pore measurements etc. Final requirements are so far not specified in the latest issue from October 2018.



**Figure 56 - Battery separator FR treatment.**  
*Gravure roller coating system in which the mineral containing dispersion is applied to the separator. Credits ©Nabaltec*

Another strategy to improve the safety of lithium-ion batteries at the cell level is to incorporate PIN flame retardants into the electrolyte. The electrolyte acts as a medium allowing lithium ions to move between the two electrodes. Electrolytes are today based on organic liquid solvents, which are inherently highly flammable and contain dissolved lithium ions and additives. The addition of PIN flame retardants can reduce the flammability of the electrolyte. Both inorganic additives (e.g. silica compounds) and organic phosphorus compounds can be effective flame retardants in battery electrolytes. Gao 2020 states “Organic phosphorous compounds, with various types, low toxicity, suitable physical characteristics, good compatibility and low cost [58], are the most effective flame-retardant materials.” (Int. J. Electrochem. Sci., 15 (2020) 1391 – 1411, doi: 10.20964/2020.02.24). A future strategy to address this problem may be solid-state or gel electrolytes, but these are also organic based and will require flame retardancy.

Stability of cathodes of lithium ion batteries is also important for battery fire safety, and this can also be improved by integration of or coating with PIN materials, such as aluminium or phosphate minerals.

### 8.2.2. BATTERY PACKS

Thermal management is a key word when speaking of a lithium-ion battery. To keep the battery cells from overheating during fast charging, to maintain the overall electrical performance and to ensure longevity, the heat has to be conducted out of the battery packs to the battery enclosure where an external (active) cooling system is installed. Several solutions for such thermal interface materials (TIM) exist to dissipate the heat out of the battery during the charging and discharging processes.

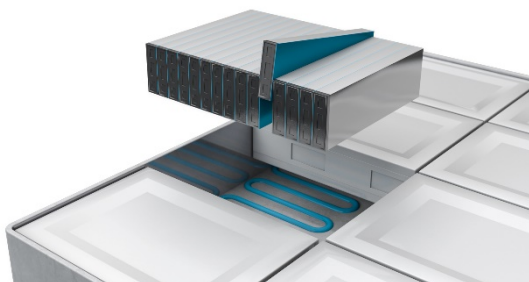


Figure 57 - Battery pack and components.  
Credits ©Nabaltec

Thermal conductive adhesives attach the packs to the enclosure. Tapes or pads can be installed between the single modules of the battery pack. Gap fillers or pastes enclose all battery cells in the pack and may also be used instead of tapes or pads in module assembly. Usually, TIM is a combination of a polymer matrix (often epoxy, polyurethane, silicone or silane modified polymer) with high loadings of a thermally conductive filler. By using ATH, boehmite (AOH) or MDH products from the PIN flame retardants portfolio, a high thermal conductivity and a definite UL 94 V-0 rating can be achieved in one step. Besides the active prevention of a thermal runaway due to the heat dissipation, the battery packs are also highly flame protected.

### 8.2.3. BATTERY HOUSINGS

The individual cells are placed in a battery housing, which allows the battery to be installed as one large component in the vehicle. Due to its considerable weight, it is usually located in the underbody. Currently there are different approaches and concepts how these housings are made and which materials are used, and there is not a standard type of housing in the market yet.

Often, housings are made of metal such as steel or aluminium, but they are also increasingly being replaced by solutions based on polymers. The total overall weight is thus reduced, so increasing the range of the vehicle, which is a key criterium in the acceptance of this new technology.

As the polymer matrix, reinforced thermoplastics like polyamides or thermoset resins like epoxy resins or unsaturated polyesters can be used.

Due to the severe test conditions flame retardant systems based on metal phosphinates or ammonium polyphosphate or phosphonate oligomers must be added to the polymer matrix.

## 8.3. CONNECTING SYSTEMS

Safety and reliability of connecting systems are essential to prevent fire and electric hazards. For this purpose, the automotive industry is adopting well established standards from the electric Industry and adapting them to the harsh environments which can be encountered during operation of cars. Therefore flammability, CTI of 1000V and IPT, as well as requirements for retention of insulation properties over time are becoming a must. New needs are for high Resistivity (Volume and Surface) and Dielectric Strength (DS) up to 150°C, CTI and PTI (Proof Tracking Index) after ageing at 150°C and in hot and humid environments (85%RH/85°C) for 1000hrs. Another key safety criteria is the bright orange colour, to enable easy identification of high voltage cables in case of accident, according to RAL 2003/2008 which must be retained after 1000 hrs at 140°C. Reliability is another important factor in xEV and PIN flame retardants are fulfilling this need because they help to limit corrosion of metal contacts and grant retention of insulation and flammability properties over time.

## 8.4. CHARGING STATIONS

The charging stations (charging infrastructure) take care of the supply of electric energy to electric road vehicles, either through cables and connectors, or wireless. Since these stations are very much like other regular E&E devices, also here the typical standards related to fire safety are being applied. However, EV charging requires higher current demand than standard electric installations, and must be safe in outdoor weather situations. Consequently, EV specific standards are being developed by various countries and/or organisations, unfortunately with a current lack of harmonisation.

### 8.4.1. WIRED CHARGING

One important EV specific standard is IEC 61851-1, "Electric vehicle conductive charging system – Part 1: General requirements", where the different modes of charging are defined:

- **Mode 1:** method for the connection of an EV to a standard socket-outlet of an AC supply network, utilizing a cable and plug, both of which are not fitted with any supplementary pilot or auxiliary contacts
- **Mode 2:** method for the connection of an EV to a standard socket-outlet of an AC supply network utilizing an AC EV supply equipment with a cable and plug, with a control pilot function and system for personal protection against electric shock placed between the standard plug and the EV
- **Mode 3:** method for the connection of an EV to an AC EV supply equipment permanently connected to an AC supply network, with a control pilot function that extends from the AC EV supply equipment to the EV
- **Mode 4:** method for the connection of an EV to an AC or DC supply network utilizing a DC EV supply equipment, with a control pilot function that extends from the DC EV supply equipment to the EV

This standard further defines most general requirements, with major focus on electrical protection.

According to IEC 61851-1 in combination with IEC 61439-1, a Glow Wire Flammability Index (GWFI) according to IEC 60695-2-12 of 650°C is required for enclosures.

UL 2594 “Electric Vehicle Supply Equipment” defines the flammability requirements for enclosures as follows:

- Portable equipment: V-1 (UL 94)
- Fixed in place equipment: 5V (UL 94)
- Large permanent enclosures (surface area > 0.93 m<sup>2</sup>): flame spread index  $Is \leq 200$  (ASTM E162)

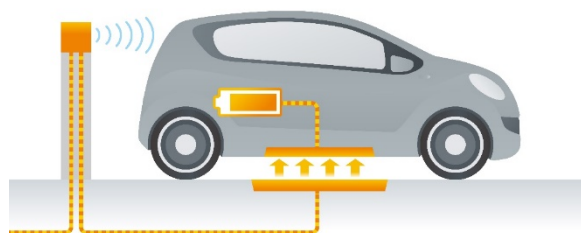
Although not specifically mentioned as a requirement in the standards, companies increasingly request polymeric materials based on halogen-free flame retardant systems. This is where PIN flame retardants come into play.

For plugs and sockets, the IEC standard IEC 62196-1 is most relevant. In this Part 1, requirements for insulating materials are given:

- Parts supporting live parts of rewirable accessories:
- Ball Pressure Test (IEC 60695-10-2) @ 125°C
- Parts of insulating material not necessary to retain current-carrying parts:
- Glow Wire Test (IEC 60695-2-11) @ 650°C
- Parts of insulating material necessary to retain current-carrying parts:
- Glow Wire Test (IEC 60695-2-11) @ 850°C
- Insulating parts supporting live parts: Proof Tracking Index (IEC 60112) @ 175V.

Also in this field of application, companies are increasingly looking for halogen-free solutions.

## 8.4.2. WIRELESS CHARGING



### Wireless Charging

Figure 58 - Wireless Charging scheme. Credits ©Shutterstock

The sharp rise in penetration of xEV has increased the need for easy and fast charging systems. Therefore, although still at very early stage, wireless charging is gaining consensus among users leading to the release of GB/T 38755, IEC 61980-1 and update of SAE J2954 standards in 2020. Besides fire safety and insulation properties, these standards pay particular attention to Wireless Power Transfer for AC up to 1000V and for DC up to 1500 V according to IEC 60038 to ensure safe operations during charging by controlling Electromagnetic Field to avoid impact on Cardiac Implantable Electronic Devices (CIED). To control Electromagnetic Field, SAE J2954 and IEC 61980-1-2-3 define three WPT levels: WPT1 up to 3.7kW, WPT2 up to 7kW and WP3 up to 11kW and, to prevent system overheating, sets rules for foreign metallic object detection and alignment tolerances. On top of fire and EMF (Electromagnetic Field) requirements, mechanical properties and part flatness are key criteria involving very accurate material selection and part design. In fact, a charging plate must withstand a load of 1350kg with temperatures ranging from -40°C up to 125°C and must grant sealing to avoid electrical failure because of moisture.

# INNOVATION AND FUTURE TRENDS IN TRANSPORTATION

The European “Green Deal”, the new European Roadmap, has the objective to make Europe the first climate neutral continent by 2050. The Green Deal will bring a wide and far reaching range of new policy and regulation, and is supported by considerable Covid recovery funding

Several sectors of the economy will be impacted, notably transport but also agriculture, buildings, and industries, including textiles, chemicals, and plastics.<sup>26</sup>



Achieving sustainable and smart mobility is a key objective of the Green Deal roadmap. How to reach this goal <sup>27</sup>?

- by increasing the capacity of railways and inland waterways
- by reducing CO<sub>2</sub> emissions from car and vans.
- by reducing the emission of air pollutants
- by using alternative power generation like lithium-ion batteries or fuel cells.

To expand fuel cell as power source and to achieve climate neutrality, a specific Roadmap for Clean Hydrogen has been proposed in July 2020<sup>28</sup>.

For the chemical and plastic industries, the focus is on control of greenhouse gas emission, the reduction of water and energy consumption and the minimization of raw material use. A list of critical raw materials for Europe has been established for which there will be a push to increase recycling level.

Furthermore, chemical and plastic industries are responsible for the toxicity and the end-of-life of their products.

<sup>26</sup> [https://ec.europa.eu/info/sites/info/files/european-green-deal-communication\\_en.pdf](https://ec.europa.eu/info/sites/info/files/european-green-deal-communication_en.pdf)

<sup>27</sup> [www.eumonitor.eu/9353000/1/j9vvik7m1c3gyxp/vl4d8dfd2dye](http://www.eumonitor.eu/9353000/1/j9vvik7m1c3gyxp/vl4d8dfd2dye)

<sup>28</sup> <https://cor.europa.eu/en/events/Pages/ENVE-Stakeholders-consultation-Towards-a-Roadmap-for-Clean-Hydrogen.aspx>

## 9.1. TRENDS IN THE TRANSPORT SECTOR

### 9.1.1. AUTOMOTIVE

One of the consequences of EU Green Deal will be the reduction of automotive CO<sub>2</sub> emissions by 47% in the period 2013- 2025. This will not only imply massive introduction of xEV (BEV, HEV, PHEV), estimated to represent more than 40% of global car sales in 2030, but will also accentuate the need for weight reduction and use of materials with lower environmental impact.

This poses a serious challenge for the industry because finding reliable sources of Post-Consumer or Post-Industrial plastic materials is extremely difficult both in terms of quality and availability. One way to overcome this problem is the move for chemical recycling, however this is actually a controversial matter because there are studies challenging the LCA analyses of the environmental impact of this technology. Bio-based polymers are also under evaluation even if there are still a lot of NGOs sceptical about this solution because of potential source conflicts with food production or water consumption.

xEV penetration is also introducing unprecedented technical challenges for very critical components such as batteries, high power connecting systems, chargers, inverters, and motors.

These challenges result in increasing demand for plastics in components, electronics, cables and batteries, to reduce weight and to respond to design flexibility. PIN flame retardants will be essential to ensure fire safety, whilst meeting demanding new standards for tests such as CTI and long-term heat ageing, just to mention two of the most critical ones. These topics are explained more deeply in the chapter Electromobility.

### 9.1.2. RAILWAY

Increasing capacity and better management of rail systems is one of the key actions of European Green Deal . Improving the EU railway network and connections involves higher digitisation. Increasing the speed of trains (i.e. more high-speed trains) encourages people to take trains instead of air travel, so reducing CO<sub>2</sub> emissions.

- With a higher offer in railway solutions, more modern trains will be in service with higher flame-retardant standards.
- The research is continuously looking for faster solutions, from high-speed trains to hyper-speed trains in the future.
- Old diesel trains will be removed everywhere and replaced by liquid natural gas (LNG) or electricity powered, less polluting units

Increasing use of plastics materials, to replace metals, will enable weight reduction, and so improved acceleration, braking and reduced energy consumption.

Alternative power generations will be implemented like hydrogen-based fuel cell or Li-ion batteries. Some pioneers are already working on alternative sources of energy:

- Coradia iLint from Alstom is the first train powered by hydrogen. The fuel cell powers an electric motor<sup>29</sup>. The excess of energy is stored in Li-ion batteries. This train is claiming to be the 1st 100% emission free.
- In collaboration with the German Ministry of Transport, Bombardier has developed the next generation Talent rolling stock i.e. Talent 3, a battery-powered electric multiple unit<sup>30</sup>.

### 9.1.3. AIRCRAFT

The fire threat in aeronautics has been decreasing over the last 3 decades, because of demanding fire safety requirements, but, the intensive use of polymer composites in new generation aircraft (A350 or B-787 families), for weight reduction and energy saving purposes, causes the fire scenarios to evolve in terms of threats.

Most of the plastic components in the passenger cabin, as well as in the cargo compartment are required to be self-extinguishing (i.e., stop burning after the flame source has been removed) or better. This can be achieved by using materials based on halogenated polymers. Fluorinated polymers were chosen historically because of the good FR properties but also their very good resistance to chemicals: Kerosene, oils, solvents (MEK), and the good release/lubricant properties. Other materials, including seat covers or flooring materials were made from PVC (poly vinyl chloride). The risk with these fluorinated and chlorinated polymers is that they release corrosive and toxic gases in case of fire – which is particularly dangerous in the passenger cabin and cockpit – and can also impact electronic equipment. Hence, significant efforts are underway to replace these materials with non-halogen containing polymers equipped with PIN-flame retardants. An example is the replacement of flooring in aircrafts from PVC to silicones or highly filled EPDM. But there are many other applications, each with numerous, demanding requirements and specifications, resulting in strong innovation in PIN FR solutions.

<sup>29</sup> [www.alstom.com/solutions/rolling-stock/coradia-iliint-worlds-1st-hydrogen-powered-train](http://www.alstom.com/solutions/rolling-stock/coradia-iliint-worlds-1st-hydrogen-powered-train)

<sup>30</sup> [www.railway-technology.com/projects/bombardier-talent-3-battery-train/](http://www.railway-technology.com/projects/bombardier-talent-3-battery-train/)

#### 9.1.4. MARITIME

Like in any transport where it is difficult to escape, fire represents an important risk on ships. 24% of the accidents on board are caused by fire. Most of them are starting in engineering spaces. Fire is causing 130% more fatalities than any other accident.

To limit the risk of fire development, IMO standards were launched several decades ago. All materials on ships must be self-extinguishing and even for high-speed crafts (e.g. high-speed ferries) they need to be non-combustible.

However, part of the fatality is not only related to the fire spread but also to the design of ships and behaviour of crews. Modern models are allowing simulations considering these three parameters to develop safer vessels.

As in other transportation modes, alternative propulsion methods are appearing for less pollution:

- In small ships, hybrid propulsion is coming, so bringing the specific risks associated with Li-ion or Li-polymer batteries.
- In larger vessels, the fuel cell is considered as a new power source with the associate risk of storage of flammable gases (hydrogen) or liquid with low flash point temperature (like methanol).

To take into account these new risks, some of the IMO standards have been amended.

### 9.2. RECYCLED POLYMERS IN TRANSPORT APPLICATIONS

As mentioned in section 1.1.1, the automotive industry has ambitious targets for the content of recycled polymers in cars, this includes not only fibres for carpets and upholstery but also materials for cables, ducts and injection moulded parts. For this reason, the EU has sponsored the project Car E Service ([www.careserviceproject.eu/](http://www.careserviceproject.eu/)) which is a study to give second life to plastic and metals at the end of vehicle life. The project has highlighted that besides significant drop in mechanical properties, costs for sorting, cleaning, and regrinding the plastic components can be up to 40% higher than oil-based materials, so limiting the opportunities to introduce this solution.

### 9.3. 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 (10–50kg) per vehicle. According to the German Association of Automobile Industry, such construction parts have even more advantages. As a rule, they are CO<sub>2</sub> 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 tons/year and carbon dioxide emissions by around 15 metric tonnes/year. Now, the focus lies on natural fibre-reinforced polypropylene containing 25-60% flax, sisal, kenaf, hemp, wheat straw, and others.

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 natural fibre mats and natural fibre-reinforced foams are used 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 non-halogen flame-retarded thermoplastics and thermosets were developed in the last 20 years, there is still today only limited information on the fire behaviour and flame retardancy of newly developed natural fibre-reinforced plastics. Here, there is considerable need for R&D. Non-halogen solutions for PLA-based reinforced and non-reinforced materials exist already.

## ENVIRONMENT AND TOXICOLOGY

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

Additive flame retardants are physically mixed into the material they are meant to protect or brought onto the surface with a carrier or as part of a coating. These molecules must have a certain chemical stability to survive the processing of the target material which may occur at temperatures of up to and above 300°C for thermoplastics. Furthermore, a degradation of the flame retardant during the use phase of the finished article is not desirable. Construction materials or electric installations have a service lifetime of many years to even decades. This chemical stability relates to persistence of these materials in the environment. Therefore, there is some degree of conflict between desired functional properties and durability versus an ideal environmental behaviour. Temperature and hydrolytic stability limit the application of some PIN flame retardants in demanding applications, e.g. ATH, APP and organophosphate esters. It is also important to note that the concept of persistence is appropriate only for synthetic organic materials, where the ideal environmental fate is the degradation to carbon dioxide and water (and further oxidation products depending on composition). For inorganic materials like aluminium hydroxide or zinc borate this concept

does not make sense. Here the correct question to ask is whether they are naturally occurring or neutral in the environment and whether these materials react to form more toxic species in the environment over time.

Overall, PIN flame retardants mostly have a low (eco)toxicity profile and will eventually mineralize or are inert in nature. No PIN flame retardant was found to have a high potential for bioaccumulation, because they tend to not be very lipophilic, in contrast to some small molecule halogenated flame retardants. Due to these characteristics, none of the commercial PIN flame retardants are considered to be PBT or vPvB. Please refer to pinfa product selector guide for a legislative status overview of PIN FR's. (<http://pinfa.org/index.php/en/product-selector>).

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. 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 Clean Production Action (<https://www.greenscreenchemicals.org/> see figure).

| Chemical Name                                                                    | CAS                      | ECN       | Abbreviation | GHS Labelling | Reach |
|----------------------------------------------------------------------------------|--------------------------|-----------|--------------|---------------|-------|
| <b>2.2-Oxybis[5.5-dimethyl-1.3.2-dioxaphosphorinane]2.2-disulphide</b>           | 4090-51-1                | 223-829-1 |              |               |       |
| <b>3.9-Dimethyl-2.4.8.10-tetraoxa-3.9-diphosphaspiro[5.5undecane-3.9-dioxide</b> | 3001-98-7                |           | DMSP         | none          | 2018  |
| <b>Acrylic dispersion of P/N based FR-system</b>                                 | 78330-20-8.<br>2628-20-4 |           | DMSP         | H318          | 2018  |
| <b>Alkyl diphenyl phosphate</b>                                                  |                          |           |              |               | 2010  |
| <b>Aluminium monohydrate (Boehmite)</b>                                          | 1318-23-6                | 215-284-3 | AOH          | none          | 2010  |
| <b>Aluminium tri-hydroxide</b>                                                   | 21645-51-2               | 244-492-7 | ATH          | none          | 2010  |
| <b>Ammonium polyphosphate</b>                                                    | 68333-79-9               | 269-789-9 | APP          | none          | 2010  |
| <b>Ammonium polyphosphate (coated)</b>                                           | 68333-79-9               | 269-789-9 | APP          | none          | 2010  |
| <b>Ammonium polyphosphate (with synergists)</b>                                  | 68333-79-9               | 269-789-9 | APP          | none          | 2010  |

Figure 59 – Example extracts from the pinfa Product Selector.

On the pinfa website you find a “product selector”, a table which lists PIN flame retardants and their applications and regulatory information.

## 10.1. CHEMICAL REGULATIONS

### 10.1.1. EUROPE

In Europe chemicals are controlled by REACH, the Regulation on Evaluation, Authorisation and Restriction of Chemicals (1907/2006/EC). The major changes from the previous chemical legislation are the “no data, no market” and “reversal of the burden of proof” principles.

“No data, no market” means that the producer or importer of a chemical needs to provide sufficient information and test data on the product for a proper evaluation of its safety. All chemicals on the market need to be registered and information submitted to a central authority, the European Chemicals Agency (ECHA), who makes most of the data public (except commercial information). Under REACH, not only hazard data, but also data concerning emissions, uses and end of life are gathered.

The burden of proof is now on the producer to prove that a chemical is safe, whereas before the authorities had to demonstrate that there was an issue with a substance before any legal measures could be taken. REACH entered into force in 2006, by 2018 all chemicals down to those with small production or import volumes of 1 tonne had to be registered. This means that a wealth of information is available on all these chemicals including flame retardants. ECHA makes data publicly accessible here <http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances>.

REACH restricts the marketing and use of chemicals identified as problematic in different ways. Some restrictions for legacy hazardous chemicals were grandfathered into REACH via Annex 17. Chemicals evaluated based on REACH dossiers as candidates for “Substances of Very High Concern” (SVHC) are governed by Annex 14. A few flame retardants are included in these Annexes. In order to evaluate additional substances, ECHA runs a so-called Community Rolling Action Plan, the CoRAP working list, which contains around 400 substances suspected of posing a risk to human health or the environment, including a small number of flame retardants. Up to date lists of chemicals on these REACH Annexes and on the CoRAP list can be found on the ECHA website (as above) and pinfa provides updates regarding the few flame retardants concerned via our website [www.pinfa.eu](http://www.pinfa.eu)

Since 2021, manufacturers of finished articles have to provide information if SVHCs are present in their products in a public database (SCIP, substances of concern in products) maintained by ECHA.

Because commerce is global, REACH will affect flame retardant use beyond Europe. One issue with REACH and other European regulations has been the very limited controls and enforcement concerning imported products. This is recognised by the European Commission as part of the Chemicals Strategy for Sustainability announced in Oct. 2020.

### 10.1.2. USA

Since 2016 there has been regulatory activity on flame retardants under the Frank R. Lautenberg Chemical Safety for the 21<sup>st</sup> Century Act (LSCA) which substantially amended the Toxic Substances Control Act (TSCA) in the United States. In 2017 there was a data call on decabromodiphenyl ethers (DecaBDE) and phenol isopropylated phosphate ester (PIP) for assessment of their persistent, bioaccumulative and toxic (PBT) properties. Previous activities under TSCA included a “Work Plan” and an “Action Plan” on chemicals including FRs.

From 2005 to 2015, under their Design for Environment programme, the US Environmental Protection Agency (US-EPA) ran a series of extensive Design for Environment (DfE) projects which evaluated alternatives to the legacy brominated flame retardants pentabromo- and decabromo diphenylether, hexabromocyclo dodecane and tetrabromo bisphenol-A. This in-depth analysis of toxicity and environmental data, together with expert judgement and computer modelling, showed that there are no “bad hidden surprises” for the alternatives and that often halogen free alternatives exist with a better environmental and health profile. Although some chemical hazards were identified, these do not pose risks when taking into account potential exposures of consumers.

## 10.2. INITIATIVES AND PROJECTS ON SAFER CHEMICALS

### 10.2.1. GLOBAL AUTOMOTIVE DECLARABLE SUBSTANCE LIST (GADSL)

The automotive industry has set up a global database on chemicals in materials they use, the International Material Data System (IMDS). Related to this database, a Global Automotive Declarable Substance List (GADSL) was compiled by automotive parts suppliers and chemical/plastics industries with the intention to facilitate communication and exchange of information regarding the use of certain substances in automotive products throughout the supply chain. Substances on the list are either D = declarable or P = prohibited for use. The prohibited category generally covers substances which are banned by regulation in certain countries or regions already, e.g. PBDEs, TCEP.

The declarable category contains substances which are undergoing regulatory scrutiny or where there is specific interest in reporting. Flame retardants in this category are e.g. some aliphatic and aromatic phosphate esters, TBBPA and ATO.

### 10.2.2. GREENSCREEN®, TCO AND OTHERS

The environmental organisation “Clean Production Action” ([www.cleanproduction.org](http://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, bio-accumulative, and toxic) and CMR (carcinogenic, mutagenic, or toxic to reproduction) categories. They rank chemicals by their inherent degree of hazard. However, an assessment of risk is not included, i.e. the question of whether or not there is or can be any relevant exposure is not taken into account at all.

A study<sup>31</sup> by ToxServices LLC on phosphorus-based flame retardants comes to the conclusion that “based on the available data, both reactive and additive phosphorus FRs are relatively safe, as evidenced by GreenScreen® Benchmark scores of 2 or higher for specific reactive and additive phosphorus FRs” with the disclaimer that complete hazard assessments were not available for all of the phosphorus FRs identified in their literature search. In addition, “available data in the published literature do not support the conclusion that reactive phosphorus FRs are “safer” than additive phosphorus FRs.”

The Swedish ecolabel organisation TCO Certified have been using the GreenScreen methodology to define their “safer alternatives to hazardous substances list”. So far, halogen free flame retardants and plasticisers with a GreenScreen benchmark or 2 or higher are accepted, see table.

<sup>31</sup> ToxServices LLC (2018): Comparative hazard assessment of reactive and additive flame retardants (promoting the use of safer flame retardants under Sweden's tax on chemicals in E&E products). Prepared for: Apple Corp. ToxServices, 1367 Connecticut Ave., N.W., Suite 300, Washington, D.C. 20036, USA

| Substance name/Trade name                                               | CAS number                        | Benchmark |
|-------------------------------------------------------------------------|-----------------------------------|-----------|
| Aluminium diethylphosphinate                                            | 225789-38-8                       | 3         |
| Aluminium hydroxide                                                     | 21645-51-2                        | 2         |
| Aluminum oxide                                                          | 1344-28-1                         | 2         |
| Ammonium polyphosphate                                                  | 68333-79-9                        | 3         |
| Bisphenol A diphosphate                                                 | 181028-79-5; 5945-33-5            | 3         |
| Cross-linked phenoxyphosphazene                                         | 260408-02-4, 1184-10-7, 992-79-0  | 3         |
| Magnesium hydroxide                                                     | 1309-42-8                         | 3         |
| Melamine polyphosphate / Melapur® 200                                   | 15541-60-3; 218768-84-4           | 2         |
| Octaphenylcyclotetrasiloxane                                            | 546-56-5                          | 3         |
| Phenoxyphosphazene                                                      | 890525-36-7, 2791-22-2, 2791-23-3 | 3         |
| Red phosphorus                                                          | 7723-14-0                         | 2         |
| Resorcinol bis-diphenylphosphate                                        | 125997-21-9                       | 2         |
| Resorcinol bis-diphenylphosphate / Fyrolflex RDP                        | 57583-54-7                        | 2         |
| Siloxanes and silicones, di-Me, di-Ph, polymers with Ph silsesquioxanes | 68648-59-9                        | 2         |
| Substituted amine phosphate mixture                                     | 66034-17-1                        | 2         |
| Tetrakis (2,6-dimethylphenyl)-m-phenylene biphosphate                   | 139189-30-3                       | 3         |
| Triphenyl phosphate                                                     | 115-86-6                          | 2         |

Figure 60 - TCO Certified PIN FRs.

PIN FRs accepted in TCO Certified with GreenScreen® benchmark, status 2021-04,  
<https://tcocertified.com/accepted-substance-list/>.

In addition, there have been various independent, third-party evaluations of non-halogen 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  
[https://chemsec.org/app/uploads/2016/04/Studies\\_alternatives.pdf](https://chemsec.org/app/uploads/2016/04/Studies_alternatives.pdf)

## LIST OF ABBREVIATIONS

|                |                                                            |              |                                             |
|----------------|------------------------------------------------------------|--------------|---------------------------------------------|
| <b>ABS</b>     | Acrylonitrile butadiene styrene copolymers                 | <b>EP</b>    | Epoxy                                       |
| <b>AOH</b>     | Aluminium-oxide-hydroxide                                  | <b>EPA</b>   | Environmental protection agency             |
| <b>APP</b>     | Ammonium polyphosphate                                     | <b>EPR</b>   | Ethylene propylene rubber                   |
| <b>ATH</b>     | Aluminium-tri-hydroxide                                    | <b>EPS</b>   | Expanded polystyrene                        |
| <b>BDE</b>     | Diphenyl ether                                             | <b>ETFE</b>  | Poly(ethylene-co-tetrafluoroethylene)       |
| <b>BDP</b>     | Bis-phenol A bis (diphenyl phosphate)                      | <b>EVA</b>   | Poly-ethyl-co-vinyl acetate                 |
| <b>BET</b>     | Specific surface area according to Brunauer, Emmet, Teller | <b>EVM</b>   | Ethylene vinyl acetate elastomer            |
| <b>BFR</b>     | Brominated flame retardant                                 | <b>FEP</b>   | Fluorinated ethylene propylene              |
| <b>CAF</b>     | Conductive anodic filament                                 | <b>FPC</b>   | Flexible printed circuit                    |
| <b>CCL</b>     | Copper clad laminate                                       | <b>FSE</b>   | Fire safety engineering                     |
| <b>CDP</b>     | Cresyl diphenyl phosphate                                  | <b>FRP</b>   | Fibre-reinforced plastics                   |
| <b>CRP</b>     | Carbon fibre-reinforced plastics                           | <b>GADSL</b> | Global automotive declarable substance list |
| <b>CLP</b>     | Classification, labelling and packaging                    | <b>GHS</b>   | Globally harmonized system                  |
| <b>CLTE</b>    | Coefficient of linear thermal expansion                    | <b>GWFI</b>  | Glow wire flammability index                |
| <b>CMR</b>     | Carcinogenic, Mutagenic, or toxic to Reproduction          | <b>GWIT</b>  | Glow wire ignition temperature              |
| <b>CTE</b>     | Coefficient of thermal expansion                           | <b>HALS</b>  | Hindered-amine light stabiliser             |
| <b>CTI</b>     | Comparative tracking index                                 | <b>HBCD</b>  | Hexabromocyclododecane                      |
| <b>Df</b>      | Dissipation factor                                         | <b>HDT</b>   | Heat deflection temperature                 |
| <b>Dk</b>      | Dielectric constant                                        | <b>HIPS</b>  | High impact polystyrene                     |
| <b>DOPO</b>    | Dihydro-oxa-phosphaphenanthrene-oxide                      | <b>HTN</b>   | High temperature nylon                      |
| <b>DMPP</b>    | Dimethyl propane phosphonate                               | <b>IEC</b>   | International Electrotechnical Commission   |
| <b>E@B</b>     | Elongation at break                                        | <b>IMDS</b>  | International material data system          |
| <b>EDAP</b>    | Ethylene diamine phosphate                                 | <b>IPT</b>   | Inclined Plane Tracking                     |
| <b>E&amp;E</b> | Electrical and electronic                                  | <b>LDPE</b>  | Low-density polyethylene                    |
| <b>ELV</b>     | End-of-life Vehicles                                       | <b>LNE</b>   | Laboratoire National d'Essais               |
|                |                                                            | <b>LOI</b>   | Limiting oxygen index                       |
|                |                                                            | <b>LSFOH</b> | Low smoke free of halogen                   |

|               |                                                                      |
|---------------|----------------------------------------------------------------------|
| <b>MC</b>     | Melamine cyanurate                                                   |
| <b>MDH</b>    | Magnesium-di-hydroxide                                               |
| <b>MFI</b>    | Melt flow index                                                      |
| <b>MPP</b>    | Melamine polyphosphate                                               |
| <b>NEMA</b>   | National electrical manufacturers association                        |
| <b>NGO</b>    | Non-governmental organisation                                        |
| <b>OEM</b>    | Original equipment manufacturer                                      |
| <b>OSU</b>    | Ohio State University                                                |
| <b>PA</b>     | Polyamide                                                            |
| <b>PBT</b>    | Polybutylene terephthalate                                           |
| <b>PC</b>     | Polycarbonate                                                        |
| <b>PCB</b>    | Printed circuit board                                                |
| <b>PCT</b>    | Pressure cooker test                                                 |
| <b>PHR</b>    | Parts per hundred resins                                             |
| <b>PP</b>     | Polypropylene                                                        |
| <b>PPE</b>    | Polyphenylene ether                                                  |
| <b>ppm</b>    | Parts per million                                                    |
| <b>PTFE</b>   | Polytetrafluoroethylene                                              |
| <b>PVC</b>    | Polyvinyl chloride                                                   |
| <b>PBDE</b>   | Polybrominated diphenyl ether                                        |
| <b>pinfa</b>  | Phosphorus, Inorganic and Nitrogen Flame Retardants Association      |
| <b>PIN FR</b> | Non-halogen Phosphorus, Inorganic or Nitrogen Flame Retardant        |
| <b>REACH</b>  | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| <b>RoHS</b>   | Restriction of Hazardous Substances Directive                        |
| <b>Tg</b>     | Glass transition temperature                                         |
| <b>TSCA</b>   | Toxic Substances Control Act                                         |
| <b>WEEE</b>   | Waste Electrical and Electronic Equipment Directive                  |
| <b>xEV</b>    | Electric and hybrid vehicles                                         |





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