pinfa

Innovative and Sustainable Flame Retardants in Building and Construction

Non-halogenated phosphorus, inorganic and nitrogen flame retardants

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

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

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

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Dr. Morgan has over seventeen years of experience in the areas of materials flammability, polymeric material flame retardancy, fire science, fire testing, and fire safety engineering with an emphasis on chemical structure property relationships and fire safe material design.
He has helped academic, government, and industrial customers solve their flame retardant and fire safety needs in a wide range of applications. Dr. Morgan is on the editorial review boards for two fire safety journals (Fire and Materials, Journal of Fire Science), and is a member of ASTM, Sigma Xi, International Association of Fire Safety Scientists, and the American Chemical Society.

Dr. Morgan is the group leader for the Applied Combustion and Energy Group, leads a group of 11 professionals, including Ph.D. researchers and technicians.

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1 Introduction

Mike Klimes
Vice Chairman of Pinfa

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Fires are a constant hazard of our daily life. Even if for the vast majority of people this is a non-event, or something we hear from news, fire and consequent fire damages are threatening our daily life. There are numerous examples of devastating fires which occurred in the far or closer past history of humanity.

As a natural consequence of these events, we are trying to protect ourselves and our buildings in the best possible way from fire and potential damages while keeping them comfortable and energy efficient, but safe.

To achieve this several techniques and means are available within the fire safety toolbox.

With this brochure, the pinfa team (Phosphorus, Inorganic, Nitrogen flame retardants association), is willing to put together available information about the different techniques used to prevent or retard the ignition of materials or in the event of a fire, to slow the spreading of fires, giving more time to people to escape and to firemen to intervene.

Examining the materials involved in buildings and constructions, allow us all to clearly understand the complexity of the components used at making the buildings we occupy for most of our time.

These modern complex materials, thanks to the progresses of technology are becoming more and more efficient in terms of comfort, energy, and safety. Many materials used in the buildings can burn. Therefore techniques and additives such as the flame retardants have been developed to avoid fire starting, or if fire starts, to avoid spreading.

Of course before being applied the different techniques will need extensive testing and the material will need to comply with actual regulations aimed at keeping the highest fire safety standards, while respecting environmental constraints. This brochure is not meant to be exhaustive, but presents a panel of flame retardant solutions applied to materials which are utilised according to the intended uses of the buildings and constructions, as well as the fire tests and standards involved.

Dear reader, as pinfa team members we hope you will find in this brochure, answers to some of the questions you may have about Flame Retardants used in building and construction (and about flame retardants in general), and we would be happy to answer to you if you would have more questions about flame retardants and pinfa.

On behalf of the pinfa team, we would like to thank all key contributors who took part in the production of this brochure and made it possible.

2 Fire Tests

2.1 INTRODUCTION

Building products need to meet a variety of performance requirements. Although there are few fire performance requirements for building products in one-family dwellings, such requirements are significant for commercial, industrial, and multi-family buildings. Depending on the type of materials and intended application, specific fire performance properties of building materials are tested by use of different test methods.
When designing a building a very important consideration is how it will behave in fire and ensure the elements of structure will not collapse but remain standing or hold back the fire for a prescribed time. The building regulations stipulate the rules and the degree of fire resistance of the elements of structure.

2.2. CLASSIFICATION AND TESTING OF FIRE PERFORMANCE OF BUILDING MATERIALS

2.2.1. EUROPE: THE CONSTRUCTION PRODUCT DIRECTIVE

A new classification system for the reaction to fire properties of building construction products has been introduced in Europe by COMMISSION DECISION (2000/147/EC) of 8 February 2000 implementing Council Directive 89/106/EEC (Ref. OJ L 50, 23.2.2000). It is important to outline that the second essential requirement of the Directive is that "buildings have to be fire safe".

Regarding reaction to fire, it is often called the Euroclass system and consists of two sub systems, one for **construction products** excluding **floorings**, e g wall and ceiling surface linings, and another similar system for **floorings**. Both sub systems have classes A to F of which classes A1 and A2 are non-combustible products. The new system is replacing the earlier national classification systems, which have formed obstacles to trade. The Directive is going to be substituted by the **Construction Product Regulation (CPR)** that will enter in force in July 2013, being since that moment compulsory for all member states.

2.2.1.1. EuroClass

The 'Reaction to fire' classes test three properties of the building material: spread of fire, smoke intensity and burning droplets. There are 7 EuroClasses.

The product testing for the EuroClass system is performed in accordance with test methods, defined in European harmonized standards published by the European Standardization body, CEN.

The next tables contain the classes of reaction to fire performance for construction products, flooring and cables.

TABLE 1: REACTION TO FIRE PERFORMANCE FOR CONSTRUCTION PRODUCTS

EuroClass	Test method	Classification criteria	Typical products
A1	EN ISO 1182 and EN ISO 1716	Temperature rise; Mass loss Gross calorific potential Duration of flaming	Stone, Concrete
A2	EN ISO 1182 or EN ISO 1716 and EN 13823	Temperature rise, Mass loss, Gross calorific potential, Duration of flaming, FIGRA, Flame spread, Total heat release	Gypsum boards (thin paper), Mineral wool
B	EN 13823 and EN ISO 11925- 2	FIGRA, Flame spread, Total heat release, Smoke production, Flaming droplets	Gypsum boards (thick paper), Fire retardant wood, Fire retardant polymers
C	EN 13823 and EN ISO 11925 -2	Smoke production, Flaming droplets FIGRA, Flame spread, Total heat release	Coverings on gypsum boards, Fire retardant polymers
D	EN 13823 and EN ISO 11925 -2	FIGRA, Flame spread, Total heat release, Smoke production, Flaming droplets	Wood, Wood-based panels
E	EN ISO 11925 - 2	Flaming droplets	Some synthetic polymers
F	No performance determined		

TABLE 2: REACTION TO FIRE PERFORMANCE FOR FLOORINGS

EuroClass	Test method	Classification criteria
A1fl	EN ISO 1182 and EN ISO 1716	Temperature rise, Mass loss, Duration of flaming, Gross calorific potential
A2fl	EN ISO 1182 or EN ISO 1716 and EN ISO 9239-1	Temperature rise, Mass loss, Duration of flaming, Gross calorific potential,Critical flux
Bfl	EN ISO 9239-1 and EN ISO 11925 -2	Critical flux, Flame spread
Cfl	EN ISO 9239-1 and EN ISO 11925 -2	Critical flux, Flame spread
Dfl	EN ISO 9239-1 and EN ISO 11925 -2	Critical flux, Flame spread
Efl	EN ISO 11925 - 2	Flame spread
Ffl	No performance determined	

The Commission decision on the European classification for the reaction to fire performance of cables is dated 27 October 2006 and was published in the Official Journal of the European Union on 4.11.2006.

The decision stated that "*separate classes of reaction-to–fire performance should be established for electric cables*".

TABLE 3: REACTION TO FIRE PERFORMANCE FOR CABLES

EuroClass	Test method	Classification criteria
Aca	EN ISO 1716	Gross calorific potential
B1ca	FIPEC20 Scen 2 EN 60332-1-2	Flame spread, Total heat release, FIGRA, Combusted length of the cable
B2ca	FIPEC20 Scen 1 EN 60332-1-2	Flame spread, Total heat release, FIGRA, Combusted length of the cable
Cca	FIPEC20 Scen 1 EN 60332-1-2	Flame spread, Total heat release, FIGRA, Combusted length of the cable
Dca	FIPEC20 Scen 1 EN 60332-1-2	Flame spread, Total heat release, FIGRA, Combusted length of the cable
Eca	EN 60332-1-2	Combusted length of the cable
Fca	No performance determined	

2.2.1.2. Test methods for EuroClass

2.2.1.2.1 EuroClass A1 and A2

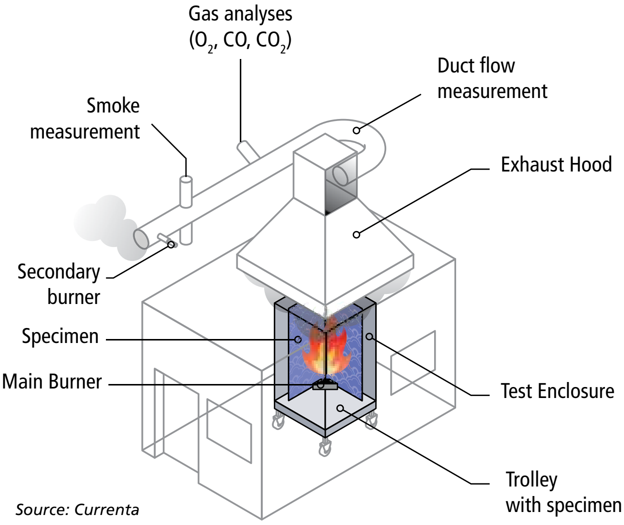
- **EN ISO 1716 Calorific Potential:** determines the maximum total heat release of a product when completely burning in a bomb calorimeter.
- **EN ISO 1182 No combustibility Test:** determines the temperature rise, mass loss and duration of flaming in a furnace kept at 750°C

2.2.1.2.2 EuroClass A2, B, C and D

- **Single Burning Item Test (SBI)**: The SBI test simulates a single burning item burning in a corner of a room. The total exposed specimen surface area is 1,5 m x 1,5 m. The specimen consists of two parts (height 1,5 m, width 0,5 and 1,0 m) which form a right-angled corner. A triangular shaped propane diffusion gas burner running at 30kW acts as heat and ignition source representing a burning waste paper basket. It is placed at the basis of the specimen corner.

The performance of the specimen is evaluated during 20 minutes.

The combustion gases are collected in a hood and transported through a duct. The duct contains a measurement section with a differential pressure probe, thermocouples, a gas sample probe and a smoke measurement system, to measure heat and smoke production.



Source: Currenta

TABLE 4. SBI CLASSIFICATION CRITERIA

EU Classification	Fire Growth Rate/ Total Heat Release/ Lateral Flame Spread		Smoke Growth Rate/ Total Smoke Release		Flaming droplets/ particles classification
A2 and B	FIGRA<= 120W/s; THR 600s<= 7,5 MJ LFS <edge of specimen	S1	SMOGRA ≤ 30 m^2/s^2 TSP600s ≤ 50 m^2	d0	No flaming droplets
C	FIGRA<= 250W/s; THR 600s<= 15 MJ LFS <edge of specimen	S2	SMOGRA ≤ 180 m^2/s^2 TSP600s ≤ 200 m^2	d1	No flaming droplets/ part. persisting > 10 s
D	FIGRA<= 750W/s	S3	-	d2	-

2.2.1.2.3 EuroClass A2, B, C, D and E

- **EN ISO 11925-2 Ignitability Test:** the specimen is subjected to direct impingement of a small flame. The test specimen of size 250 mm × 90 mm is attached vertically on a U shaped specimen holder. A propane gas flame with a height of 20 mm is brought into contact with the specimen at an angle of 45°C. The application point is either 40 mm above the bottom edge of the surface centreline (surface exposure) or at the centre of the width of the bottom edge (edge exposure). Filter paper is placed beneath the specimen holder to monitor the falling of flaming debris.

Source: Currenta

The classification criteria are based on observations whether the flame spread reaches 150 mm within a given time and whether the filter paper below the specimen ignites due to flaming debris. In addition, the occurrence and duration of flaming and glowing are observed.

TABLE 5. IGNITABILITY TEST CLASSIFICATION CRITERIA FOR CONSTRUCTION PRODUCTS

EU Classification	Flame spread
B	Fs<150mm within 60s
C	Fs<150mm within 60s
D	Fs<150mm within 60s
E	Fs<150mm within 20s

2.2.1.2.4 EuroClass A2fl, Bfl, Cfl ,Dfl and Efl

TABLE 6: IGNITABILITY TEST CLASSIFICATION CRITERIA FOR FLOORING

EU Classification	Flame spread
Bfl	Fs<150mm within 20s
Cfl	Fs<150mm within 20s
Dfl	Fs<150mm within 20s
Efl	Fs<150mm within 20s

- **EN ISO 9239-1 Radiant Panel Test:** a test specimen of size 1050 mm × 230 mm is placed horizontally below a gas-fired radiant panel inclined at 30°. The radiant panel generates a radiant energy flux distribution ranging from a nominal maximum of $11 kW/m^2$ to a minimum of $1 kW/m^2$. A pilot flame front is applied to the hotter end in order to ignite the specimen. The duration of the test is 30 minutes. The classification criterion is the critical heat flux which is the distance burned until flame-out is reached and converted, by calibration, into an equivalent critical radiant flux, in kW/m^2. The smoke development during the test is measured on the basis of light obscuration by smoke in the exhaust duct.

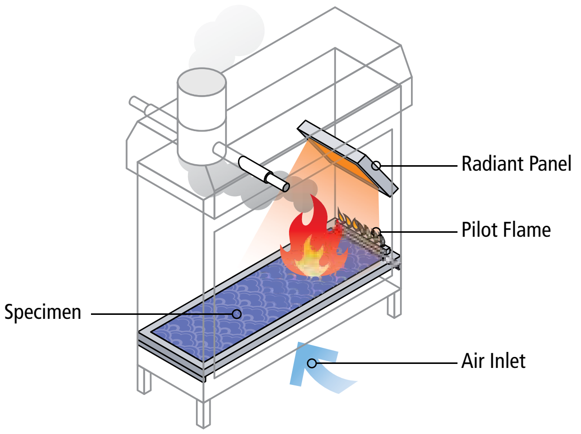


TABLE 7: RADIANT PANEL TEST CRITERIA

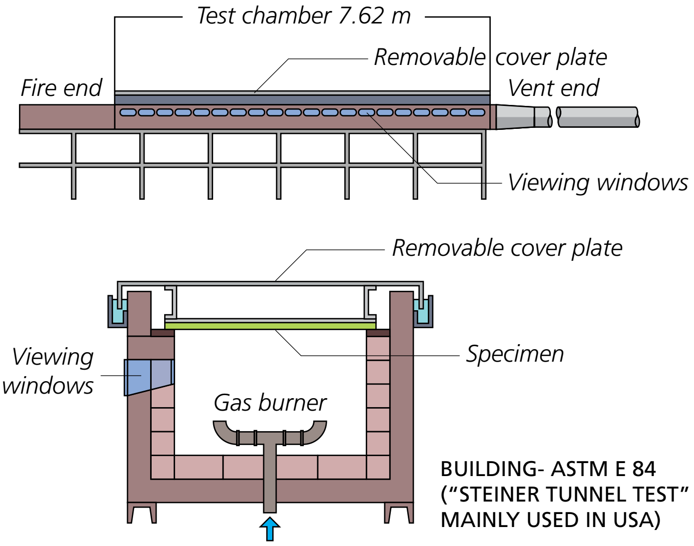
EU Classification	Flame spread
A2 fl	>= 8,0 kW/m^2
Bfl	>= 8,0 kW/m^2
Cfl	>= 4,5 kW/m^2
Dfl	>= 3,0 kW/m^2

2.2.2. USA

In USA fire testing and classification are based on certain parameters such as no combustibility, fire resistance, ignition temperature, flame spread, smoke development. Most tests have been issued by American Society for Testing and Materials (ASTM), other by NFPA (National Fire Protection Association) or UL (Underwriters Laboratory).

2.2.2.1 ASTM E 84-00a
Surface Burning characteristics of Building Materials

ASTM E 84-00a is the most used fire test standard to characterize flammability of plastics. In the test, a specimen (7.3 m x 0.56 m,), either in one unbroken length or in separate sections joined end to end, is mounted face downwards so as to form the roof of a horizontal tunnel. The fire source, two gas burners, ignites the sample from below with a 89 kW intensity and the combustion products are carried away by a controlled linear air velocity of 73 m/min. Flame spread index (FSI) and a smoke-developed index (SDI) are measured.



BUILDING- ASTM E 84
("STEINER TUNNEL TEST"
MAINLY USED IN USA)

TABLE 8:
ASTM E 84-00A CLASSIFICATION OF THE INTERIOR FINISHES

Class	Flame spread	Smoke index
A	0-25	0-450
B	26-75	0-450
C	76-200	0-450

2.2.2.2 ASTM D 2859-96 Ignitability Test

Is applicable to all types of carpets (natural or synthetic) used as floor coverings material.

2.2.3.3. ASTM 648-99
Critical Radiant Flux of Floor Covering

Describes a procedure to measure the critical radiant flux of horizontally mounted floor covering exposed to a flaming ignition source of 11 kW/m2. The test method assesses the critical incident flux (which is measured by comparing the distance between the ignition source and the point where flame propagation stops to a calibration curve).

The following table 10 summarizes the two methods:

Flooring Radiant Panel

TABLE 9: ASTM 648-99
CRITICAL RADIANT FLUX CLASSIFICATION CRITERIA

Critical flux	Class
4.5 kW/m²	I
2.2 kW/m²	II

TABLE 10: CRITICAL RADIANT FLUX OF FLOOR COVERING

	ASTM D 2859-96	ASTM E 648-99
Specimens	8 x 230mm x 230mm	3 x 254mm x 1070mm
Specimen position	horizontal	horizontal
Ignition source	Methenamine reagent tablet, 0,15 g	Radiant heater inclined at 30°C Flux= 1,0-0,1W/cm²
Test duration	Until flames extinguish or reach the edge of the steel frame	5 min preheat, 5 min pilot burner contact; until flames go out.
Conclusions	Passes if charred area is <25mm from frame for 7 out of 8 specimens.	Radiant flux measurement

Measures the "Critical radiant flux" at the flameout for carpeting and flooring materials used in public buildings and public transit vehicles (ASTM E648, NFPA 253, ISO 9239-1, ISO 9239-2).

2.3. RESISTANCE TO FIRE OF BUILDING ELEMENTS

The evaluation of the resistance to fire determines **how long the elements will resist** the fire effect maintaining the design properties.

Basically we can consider two segments which are structural behaviour, e.g. columns, beams, loaded walls and partition elements, e.g. fire doors, penetration gaps. In all cases the resistance is measured in time (minutes) and the parameters depend on each application.

For steel structural elements, **resistance to fire is the time** that will take for the steel to reach 500ºC (EN 13381) when the stiffness of the steel will not be able to resist the expected load bearing capacity.

In the case of fire doors, **resistance to fire it is the time** during which the door will lose its integrity, leaving smoke and fire to pass through.

Therefore always in front of any time number, the initials FR (Resistance), FI (Integrity) indicate the concept for the resistance to fire.

The evaluation of the resistance to fire determines **how long the elements will resist the fire effect** maintaining the design properties.

2.3.1 EUROPE

The former CPD (Construction product directive) and now the CPR (Construction Product Regulation), legislates the performance requirements for the building elements when tested to the standards of reference. Moreover, CPR will force to use only products with CE mark when proceedings to get the mark are available. Single elements, like fire doors, are easy to label, since they have to have a given performance only by themselves, like a TV or a refrigerator. Labelling becomes more complex when the expected performance depends on various materials, like in the case of structural steel fire protection, where the element to be tested is a column protected with a reactive paint: it is not only the paint, but its application that will lead to a certain performance.

This is why today to get the CE marking it is necessary, besides a test report and the related classification, to have an ETA (European Technical Approval) after evaluation processes defined by the ETAGs (European Technical Assessment Guides).

2.3.1.1 Standard testing methods.

2.3.1.1.1 Protection of Load Bearing Elements

- ENV 13381 Part 1 to 7 for covering walls, concrete structures.
- ENV 13381 Part 8 for steel elements.

Furnace for testing columns

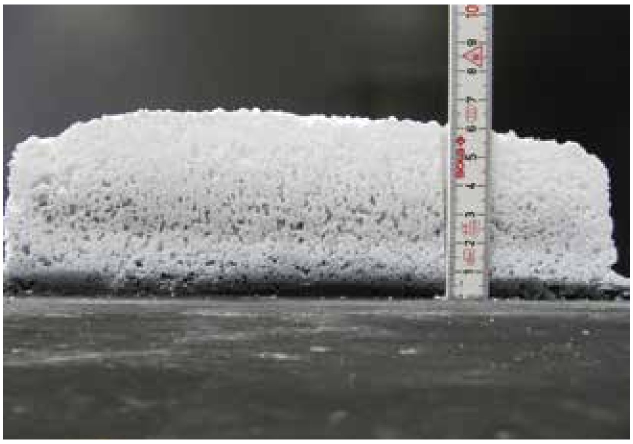
©Ralf Baumgarten, BAM and Clariant

The building element, column / beam, is submitted to the ISO standard time/temperature curve in a furnace of 4x4 meters under loading conditions. Thermocouples are placed direct to the steel element and temperature and flexion of the element is recorded.

As the average temperature reach 500°C or one of the thermocouple reaches 550 °C, the clock stops and the time is determined. Same if the flexion exceeds of 1/20 of the length or the height of the element: whatever will be first.

A set of complementary tests are run in the small scale furnace of 1x1 mts to test different thicknesses of the protective product and different steel element sections. The measured time is corrected by a factor obtained in the 4x4 mts furnace test.

This standard enables architects to define the Dry Film Thickness (DFT) for the application of reactive paints according to the different steel section that are in the building.



Steel plate coated with intumescent after a furnace test. The coating expands up to 100 times of the dry film thickness.

(Source: Clariant)

This testing method is applicable to reactive coatings (intumescent) in Part 8, sprayed vermiculite or mineral wool mortars or bolted silicate panels in Part 4.

- EN 13.501 Part 1: Classification standard that determines the FR time (30, 60, 90,..)
- ETAG 018 Part 2: ETA for the CE marking for steel structures

2.3.1.1.2 Partition Elements (partition walls, fire doors)

- **EN 1364 Part 1 to 4: standard for non load bearing elements**
- **EN 1365 Part 1 to 6: standard for load bearing elements**
- **EN 1634 Part 1 to 3: standard for doors, shutters, windows**

The test method uses same furnace as above described, the element to test is mounted and fixed on a FR wall in a well-defined manner (part of the test report).
Temperature on the cool side should be lower than 180°C or an average of 140°C.

2.3.1.1.3 Service Installations: ducts, dumpers, penetration gaps and others.

- **EN 1366 Part 1 to 10: Installations are divided in 10 groups.**

Sealants for penetration gaps are tested with same standard in Part 3. In this application the furnace is closed with a FR wall up to 3h and gaps are left simulating a penetration in a wall for ventilation pipes, cable trays. The sealing elements (intumescent bags, collars for plastic pipes, mastics for cable trays,) are placed and the test starts following the development of the heating rate as per the above mentioned ISO curve. As soon as the integrity is lost (smoke, heat,..) the clock stops.

- **EN 13501 Part 2 to 5: to classify any of the above test results.**

Penetration gap protected with intumescent bags. (Source: Hilti)

2.3.1.1.4 Extended Applications

For the big number of construction possibilities, either different product combinations or different fixing and mounting, there are EN norms covering Extended Applications (EXAP) which take the basic data from the main test and specify only a complementary testing or an assessment process for each particular case.

TABLE 11: EXTENDED APPLICATIONS (EXAP)

Standard	Application
EN 15080/12	Masonry walls
EN 15080/8	Beams
EN 15254	Non load bearing walls, including sandwich panels
EN 15269	Doors, Shutters
EN 15725	General
EN 15882	Services, Ducts and penetration seals

2.3.2 USA

TABLE 12: FIRE RESISTANCE METHODS

Standard	Application
UL 263 / ASTM E119-12/ NFPA251 UBC7-1	Resistance to fire of building elements
UL 1709	Rapid rise fire tests of protection materials for structural steel
E2226	Hose stream resistance test

The UL 1709 is a very stringent test because of the rapid rise of temperature during the test. The furnace temperature reaches 2000°F/1103C° in 5 minutes and maintained at this level until failure. Temperature for steel failure is reached when it goes over 1000°F/538°Crange for 1, 2, 3 or 4 hours depending on the thickness of the coating and requirement of the installation. It may range from 0,8 mm to 13 mm. In some cases resistance to hose stream is required and E2226 applied.

It is mainly used in the petrochemical industry, off shore facilities, etc.

UL 263/ASTM E-119 is a testing procedure that rises the temperature in steps from 1000ºF/538ºC for 5 minutes to 1700ºF/927ºC for 1 hour. Higher temperatures and longer times are used if required by the installation criteria. Failure is determined in most cases as 1000ºF/538ºC depending on the shape and construction of the steel.

This test is for residential and low risk industrial B&C.

There are also accelerated heat aging tests for intumescent coatings that involve subjecting the coating to 135 days at 80ºC or 270 days at 70ºC. The coating must perform 80% of the original coating.

2.3.3 JAPAN

- **JIS A 1304 for structural elements**: the max temperature allowed for protected steel specimens is 400ºC and an average of 350ºC. The test is run always with the same steel profile, with a maximum section of 120 cm^2 for columns and 100 cm^2 for beams. The specimen dimensions are 240 cm for loaded tests and 150 cm for non-loaded.

The test of water resistance and impact resistance are also included in this standard. Both tests are conducted after 30 min of heating and the aim is that the protective material should not fall off.

As an example, a reactive coating is classified as 2h LWS, when a loaded element has resisted 2 hours and has passed the water and shocking test.

2.3.4 KOREA

- **KS F 2257 part 1 to 7**

Part 1 deals with general conditions and 6 and 7 with beams and columns respectively.

The test is a single specimen test, defining only the length: 3 meters for columns and 4 meters for beams. The test end when the average temperature of thermocouples in the specimen reach 538ºC as average and 649ºC as maximum tests are run always under loading condition. Calculation of the load is made based on the end use design.

2.3.5 CHINA

- **GB 14907-2002**

The protective coating has to be applied at a fix thickness according to the desired classification:
- ultra-thin coating 1,5 mm for 1 hour rating
- thin coating 3,5 mm for 1 hour rating
- thick coating 25 mm for 1 hour rating

The test specimen is a beam of 4 m length under load and the test ends when the bending is superior to 1/20 of its total length.

Smaller specimens (1 m length) are submitted to aging, corrosion, and other tests and compared afterwards with a blank specimen. This is a 1 m protected beam which is taken as reference when the temperature reaches 538ºC as average. The other specimens are allowed to have a 35% deviation compared to the blank.

Classification: you pass or don’t pass the test.

3. Profiles & composites

Plastic materials have enjoyed growing use in B&C over the last decades due to their enhanced durability and easy maintenance (corrosion resistance, cleaning and repair) compared to other materials such as wood or metals.

More recently, reinforced plastics (composites) have developed and continued to displace traditional building materials in a growing number of areas. Glass (or carbon) filled thermosets offer high strength properties and excellent durability, and are increasingly used to produce light-weight load-bearing structures such as bridges/walkways or even balconies.

Thermoplastic based Wood Plastic Composites also represent a recent class of materials that are increasingly used in B&C, allowing the combination of aesthetic properties of wood with the physical performance of plastics, while being largely based on recycled materials, thus meeting customer's needs for products with a reduced environmental footprint.
In the building industry there is also a growing trend to replace traditional materials with thermoplastic and thermoset composites that replicate the look of natural materials but have the added benefits of polymeric materials; design, color and other enhancements. Some of these enhancements include metallic additives, embedded objects e.g. shells, reeds, buttons, etc.

Flame retardants are needed in interior applications like wall partitions, counter tops, panels and translucent or transparent skylights and covers. The most common test is ASTM E 84, Class A, B, C.

There are also bio-content polymers incorporated within these categories of resins to provide even greener solutions. Owing to their flammable nature, the polymers used need to be treated with FR in order to comply with fire safety regulations, which can be more or less severe depending on the final use (flooring material vs. vertically oriented vs. suspended articles).

3.1. THERMOPLASTIC BASED PROFILES AND COMPOSITES

Thermoplastic based profiles & composites are produced by extrusion or by injection molding. The addition of the flame retardants occurs mainly during the compounding stage. In a few cases, they can be added in form of master batches during the production of the final article.

TABLE 13: FLAME RETARDANTS FOR PROFILES AND COMPOSITES

Materials	Application	FR additives
Rigid PVC	Profiles- window, doors, trim	Stannates, zinc borate, ATH, AOH (boehmite), MDH
ABS, PC blends, Polycarbonate	Profiles- Trim	poly(phosphonate-co-carbonates) Silicone compounds Phosphate esters Potassium perfluorobutane sulphonate (KPBS) Potassium diphenyl sulphone sulphonate (KSS)
HDPE, PP	Pipes	Intumescents (with some limitations), ATH, MDH, boehmite
PP	Cable trays, skirting boards	Intumescents, EDAP, Melamine pyrophosphate, melamine Polyphosphate, ATH, MDH, AOH (boehmite)
Wood-Plastic Composites (WPC)	Decking, railings, roofing shingles, fencing, facings	APP, Melamine pyrophosphate, Melamine polyphosphate, Alkyl phosphonates, Melamine cyanurate
Aluminium Composite Panels (ACP) – inner layer made of PE, PE/EVA, Ethylene-co-polymers	Facade decoration	ATH, MDH

Wood Composite profiles offer good strength to weight ratio, are durable with good dimensional stability, and are relatively inexpensive. Specialty grades can offer water, insect, corrosion and mildew resistance making them ideal for outdoor applications. Wood Composite profiles may be colored and provided with a wood grain although no surface finishing is necessary. Wood Composite profiles may be sanded, drilled or painted giving them great flexibility in the building industry. Wood Composite profiles are good for the environment because they can be comprised mostly of waste products.

Profiles

The use of wood in thermoplastic extrusion is a relatively new technology with extensive market growth over the last decade or so. Wood Composite profiles are extruded using Wood Plastic Composite (WPC) resins. WPCs are compounded using 30-60% wood filler in the form of wood flour or wood fibre both of which are available from recycled sources. These wood fillers are combined with plastic resins like High Density Polyethylene (HDPE), Polypropylene (PE), PVC, and ABS and are processed by extrusion into variously shaped profiles (both hollow and solid) that retain many of the favourable qualities and aesthetics of wood but offer enhanced properties provided by the thermoplastic.

Aluminium Composite Panels (ACP) are used for façade decoration. They are made of two layers of aluminium-metal with an inner layer of polymer. These panels are normally offered in total thicknesses of 3 – 6mm. In multi storey buildings these panels have to fulfil fire tests according to construction product standards. Mineral flame retardant fillers are used at 65-70wt.-% (acc. to DIN 4102 B1) or even up to 90% (acc. to DIN 4102 A2).

3.2. THERMOSETS BASED PROFILES & COMPOSITES

In contrast to thermoplastics, the manufacturing process used to produce final parts based on thermosetting resins has a major influence on the choice of suitable FRs. So do composites made by BMC (Bulk Moulding Compounds) typically support high amounts of filler-type FRs, whereas composites produced by pultrusion only allow a limited content of solid FR in order to keep an acceptable viscosity.

More recent techniques, such as resin infusion or VARTM (vacuum assisted resin transfer moulding) do hardly accept any fillers, since these may be filtered when the resin will be diffused through the fabrics.Thus the FR choice is limited to either liquid FR (which have undesirable plasticising properties) or reactive FRs, which actually remain the most technically viable option, but usually do not offer much choice in terms of chemistry, or speciality grades of ATH, which are designed for to give very low viscosity increase and filtration tendency.

In total, there are about 20 different continuous or discontinuous manufacturing techniques available for low, middle or high volumes applications, each with respective strength and limitations, and a different impact on the choice of additives. For these reasons, thermoset composites include a large variety of different formulations that are usually based on a combination of different PIN FR in order to be compatible with the process, while achieving a certain set of properties.

Wood plastic composites

TABLE 14: FLAME RETARDANTS FOR THERMOSET COMPOSITES

Materials	Application	FR additives
Unsaturated Polyesters (UP)	Laminate structures, Pultruded profiles	ATH, APP, Intumescents, Phosphonate oligomers, DMPP, Various melamine derivatives
Vinylester (VE)	Laminate structures, Pultruded profiles	ATH, APP, Intumescents, Phosphonate oligomers, DMPP
Epoxy (EP)	Laminates, Panels, Adhesive layers, Tubes/pipes (filament winding)	ATH, AOH (boehmite), APP, Phosphonate oligomers, DOPO, Intumescents, Melamine phosphate, Melamine polyphosphate, Cyclic phosphonates, Phosphinates.
Polyurethane (PU)	Castings, Coatings, RIM parts	ATH, AOH (boehmite), APP, Phosphate esters, Phosphonate oligomers, Various melamine derivatives, Intumescents, Phosphorus Polyols, Alkyl phosphonates
Phenolics (PF)	Laminates and profiles	Excellent FST (fire, smoke, toxicity) performance without the use of FR additives. Sometime need addition of APP, Zinc borate, Melamine borate to improve smoke or suppress afterglow
Melamine resin (UF)	Laminates, wood particle boards	Excellent FST (fire, smoke, toxicity) performance without the use of FR additives.

Facades made of ACP

4. Cables

4.1. INTRODUCTION

Cables transmit energy and an ever growing amount of data. Large numbers of cables are installed to connect rooms horizontally and floors vertically in multi-story buildings. Cables are also found in elevators connecting these floors from the basement up to the top of the building, where cables are used to collect and transmit electrical energy produced by photovoltaic modules installed on roofs. Low up to medium voltage cables, telephone and LAN cables are part of all residential premises. Lift, fire alarm and emergency lighting cables are additionally found in industrial and public buildings, which are very often multi storey constructions.

Independent from the conductor / transmitter material used, all cables generally contain a substantial amount of inherently flammable polymer materials as insulation, sheathing, or bedding. Cables can therefore represent a significant quantity of fuel for fires. Besides being a potential source of ignition due to overheating, arcing, short circuiting or other electrical faults, cables can tremendously contribute to the spread of fires, simply because they form an interpenetrated network in modern buildings.

Flame retardants provide an important function in cables. For example, flame retardants prevent / delay the spread of flame so that a localized ignition does not develop to endanger a whole building and those in it. Secondly, they prevent / reduce the accumulation of toxic gas / smoke; particularly in high occupancy buildings like schools, hospitals, airports and transport stations. The ultimate result of a successful flame retardant is to win time; allowing people to escape from the building and the fire authorities to extinguish the fire in its early stages.”.

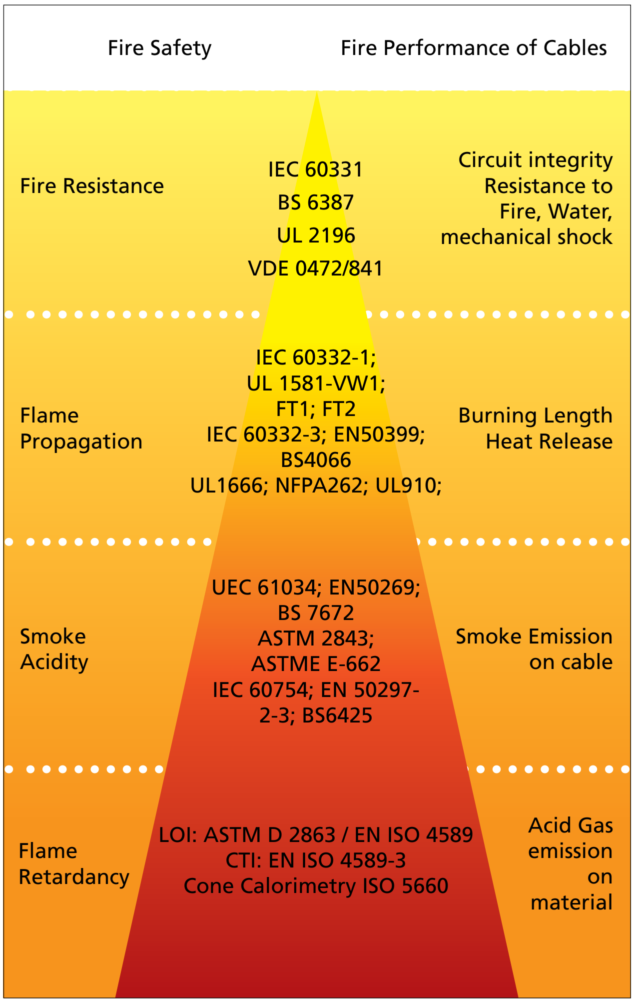
4.2. FIRE SAFETY OF CABLES

Figure 1 shows a pyramid of commonly applied cable standards for buildings. The rowing of the standards was done according to the fire safety level of cables.
Fire resistant or fire rated cables continue to operate in the presence of a fire and have to guarantee circuit integrity for a certain period of time and intensity of fire. Fire alarm and emergency lighting cables fall under this highest category and have to fulfil severe performance tests also under quenching water and mechanical stress.

Essential for all cables applied in buildings is their resistance to flame propagation, as this is the most important hazard originating from cables. Different standards and test regimes exist worldwide, but all of these tests have burning length and heat release criteria included.

The presence and intensity of smoke influences the escape and survival probability of fire victims and has therefore found entry in many standards. Low acid gas emission is a criteria frequently requested by insurance companies. This is because emitted high levels of acid gases will cause significant consequential damage in conjunction with fire fighting water. Acidic gases are also irritant and may hinder fire victims to escape easily.

FIGURE 1: PYRAMID OF COMMONLY APPLIED STANDARDS FOR WIRE & CABLES “CONNECTING” FIRE PERFORMANCE OF CABLES (RIGHT) AND FIRE SAFETY (LEFT).



Terms like fire resistance and flame propagation are closely connected with real life scenarios in buildings. The correlating cable performance parameters verified in large scale tests are not only influenced by the polymer material, but also by the cable design. Smoke generation, acid gas emission and flame retardancy on the other hand side are material properties, determined by the choice of raw materials.

4.3. MATERIALS – CABLE COMPOUNDS

Halogen free PIN-flame retardants (FRs) are used in a wide variety of base polymers. These polymer matrices can of course be halogen free, but also when used in halogenated polymers like e.g. PVC, PIN-FRs can significantly improve the environment and health profile of the end product.

4.3.1 PVC CABLES

Plasticised PVC (Poly-vinyl-chloride) is still the most important polymer material used in the cable industry. While showing a high degree of inherent flame retardancy as such, the presence of flammable plasticisers in soft PVC makes non flame retardant PVC cables an important fuel source in buildings.

Antimony trioxide (ATO) is a very effective flame retardant for flexible PVC when ignitability and flame propagation is considered. Unfortunately, besides the critical environment and health profile of ATO, the smoke generated by PVC flame retardant with ATO is a weak point. PVC cables containing ATO release significantly more black smoke than non-flame retardant PVC cables.

Modern Low Smoke Flame Retardant (LSFR) PVC compounds are made by incorporating metal hydrate flame retardants like Aluminium (tri-)hydroxide (ATH) or Magnesium (di-) hydroxide (MDH). Also Zinc Hydroxystannates and Zinc borates are additionally used in lower quantities as synergistic FRs. Zinc Hydroxystannate acts as a synergist in PVC, acting in conjunction with chlorine to prevent the spread of flame and also to reduce smoke by char formation.
Based on these flame retardants sheathing materials with low smoke generation and low Hydrochloric (HCl) acid emission can be designed, also fulfilling the commonly requested ignition and flame propagation criteria (see table 15).
Table 15 summarizes PVC and other halogenated base polymer, the relevant PIN-FRs and cable end applications.

TABLE 15: PIN FLAME RETARDANTS USED IN PVC CABLE COMPOUNDS AND OTHER HALOGENATED POLYMERS

PIN-Flame retardant	Working Function	Polymers/compounds	Main Applications
Aluminium tri-hydroxide (ATH) Magnesium di-hydroxide (MDH) Zinc-borates Zinc Hydroxystannates	In case of a fire, these mineral flame retardants decompose • absorbing energy • releasing water (thus reducing fire intensity and diluting fire gases). • creating an oxide layer which adsorbs soot particles and HCl Zinc Borate is a smoke suppressant that works in the condensed phase by forming a glass-like char. Zinc Hydroxystannate works both in the gas phase (flame) and in the condensed phase (smoke) simultaneously	FR-PVC Flame Retardant PVC LSFR-PVC Low Smoke Flame Retardant PVC CPVC Chlorinated PVC CR Chlorinated Rubber	Electrical cables • Low voltage • Medium voltage Information cables • LAN cables • Telephone cables • Plenum cables • Plenum cables
Phosphorus flame retardants Aryl phosphates Aryl alkyl phosphates	Flame inhibition of phosphorus-based materials reduce the flammability of polymers.	LSFR-PVC *Low Smoke Flame Retardant PVC* CPVC Chlorinated PVC CR Chlorinated Rubber	Information cables • LAN cables • Telephone cables • Plenum cables Control Cables

Highly flame retardant PVC compounds can also be used in one of the most severe constructive situations found for fire retardant cables: plenum spaces. Plenum describes the space between the structural ceiling and a dropped ceiling. Plenum cables are laid in these plenum spaces of buildings. Two factors make this constructive situation critical for fire propagation:

- Spaces are actively ventilated as they are used for air circulation and heating / air conditioning systems, and they can be a duct for the fire,
- Over the lifetime of office and functional buildings many new cables, especially new generations of data cables are installed in such plenums, while abandoned cables are commonly not dismantled. Consequently the load of burnable mass increases over the years. In USA cables used in Plenums are regulated under NFPA 90A. Besides fluorinated ethylene polymers only speciality PVC compounds containing large amounts of flame retardants can meet these requirements.

TABLE 16: TYPICAL COMPOUND FORMULATION OF LSFR-PVC

Component	phr	Properties
PVC, K=70	100	Tensile Strength > 12 MPa Elongation at break > 200% LOI > 32%O_2
DINP	50	
Ca/Zn stabiliser	5	
PE-wax	0.5	
ATH	75	
Zinc Borate or Zinc Hydroxystannate	5	

4.3.2 HFFR CABLES

Halogen-free flame retardant (HFFR) 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, their working function and main cable applications, are displayed in table 15.

By far the most important compounds by volume used for HFFR wire and cables (W&C) are based on blends of EVA (Poly-ethylene-co-vinyl-acetate) and LLDPE (Linear Low Density Poly-ethylene) using fine precipitated ATH as the sole flame retardant filler. The fine grades of ATH have particle sizes of approximately one micron and are used at loadings of 60 – 65wt.-%. Coupling agents are used to guarantee the required physical properties (see table 4.4). These compounds are applied by standard extrusion processes without any crosslinking.

Thermoset type or cross linkable compounds are used, whenever special requirements in regard to abrasion and chemical or temperature resistance are required, like e.g. for lift / elevator cables or cables used for photovoltaic modules. Elastomeric type of compounds based on EPDM (Poly-ethylene-propylene-diene-copolymer) or EVM (EVA grades with high contents of vinyl-acetate) are an option. Cross-linking is induced by peroxides. These compounds do also contain ATH at loadings of 50 – 60wt.-%, sometimes combined with Zinc-borates as FR-synergist and inherent mineral fillers. The latter are used to achieve strength and hardness.

Alternatively thermoplastic compounds may also be cross-linked by E-beam cure after wire / cable extrusion. Depending on the process temperatures, sometimes magnesium hydroxide (MDH) is preferred over ATH. E-beam cross-linking is a standard procedure for the production of photovoltaic cables, where resistance against sun light and high temperatures are most crucial requirements.

Last but not least, thermoplastic base materials like TPU (Thermoplastic Poly-Urethane) give inherently good abrasion resistance. In this case the combination of PIN-FR is an established technology. Melamine derivatives, organic phosphate, phosphinates and metal hydrates, ATH or MDH, are used in different ratios depending on the manufacturer's technology.

TABLE 17: PSELECTED PIN-FR USED IN HFFR CABLE COMPOUNDS AND MOST IMPORTANT END APPLICATIONS.

PIN-Flame retardant	Working Function	Polymers/compounds	Main Applications
Aluminium trihydroxide (ATH) Magnesium dihydroxide (MDH) Aluminium oxide-hydroxide (AOH, boehmite) Zinc-borates Zinc-Hydroxystannates	IIn case of a fire, these mineral flame retardants decompose -absorbing energy. -releasing water (thus reducing fire intensity and diluting fire gases). -creating an oxide fire barrier against heat from the flame and to prevent burnable polymer decomposition products from reaching the flame.	**Polyolefins** Low-density polyethyl ene (LDPE) Polyethylene vinyl-acetate copolymer (EVA) Polyethylen-co-butene Polyethylen-co-octene **Elastomers** Natural Rubber (NR) Poly-Ethylene-Diene-Rubbers (EPDM) Poly-Styrene-Butadiene-Rubbers (SBR) Silicone rubbers (SiR) Thermoplastic Elastomers (TPE)	Electrical cables • Low voltage • Medium voltage • PV cables • Emergency lighting Control cables • Fire alarm cables Information cables • LAN cables • Telephone cables
Phosphorus flame retardants Phosphate esters (eg. Tricresyl phosphate TCP) Intumescent products based on: ammonium polyphosphates (APP), Polyphosphonates, metal phosphinates, aryl phosphates, Melamine Derivatives Red phosphorus	Flame inhibition and charring properties of phosphorus-based materials reduce the flammability of polymers. A char on the surface prevents heat transfer and protects the polymer below.	Used in fire-resistant coatings for cables Polyolefins Polypropylene (PP) Elastomers Thermoplastic Elastomers (TPE), Thermoplastic Poly Urethanes Thermoplastic Polyesters	Electrical cables • PV cables Control cables • Lift cables • Fire alarm cables

TABLE 18: TYPICAL HFFR-COMPOUND FORMULATION BASED ON PE/EVA-BLENDS

Component	wt.-%
LLDPE	10
EVA	24.8
PEgMA (coupling)	5
Stabiliser / Antioxidant	0.2
Aluminium hydroxide	60
Characteristic data	
Tensile Strength [MPa]	>12 MPa
Elongation at Break [%]	> 200%
LOI [%O2]	> 32

5 FILMS & SHEETS

5.1. INTRODUCTION

Films, sheets and tapes used in B&C cover a large variety of different articles that can be made of different materials, synthetic or of natural origin. They can have one or more functionalities, which can be roughly segmented as follows:

- protective: i.e. building scaffolds, construction films, confinement films, tarpaulins etc.
- functional: i.e. vapour barrier films, adhesive films, greenhouse films, artificial grass, etc.
- structural: roofing sheets, wind barriers, films or sheets for space partition, etc.
- decorative: banners, printed films, artificial plants/trees, etc.

Depending on their final use (residential building vs. public places vs. industrial buildings), they can be subject to different fire safety regulations. In terms of fire safety, most thin films represent a relatively low mass of fuel and thus a limited fire load compared to other flammable materials used in B&C. However, they are often made of highly flammable materials and are thus relatively easy to ignite, and also pose secondary fire risks in regard to fire propagation, both through vertical and horizontal surface spread of flame and through the potential formation of burning drips.

In contrast, thicker sheets are normally more difficult to ignite (requiring a higher energy source) but then pose other hazards in terms of heat release and smoke. For thermoplastic based sheets, the formation of burning droplets also remains an important safety factor in regard to fire propagation.

A variety of PIN flame retardants is available to treat a large number of materials. Very often, different PIN FRs are combined to achieve synergistic effects, which help to achieve a particular set of properties (i.e. mechanics, transparency) or to optimize costs.

This chapter will address PIN FRs used in most of the relevant materials and applications, but will exclude films and sheets used as waterproofing membranes or specific articles, such as films and back sheets used in photovoltaic panels.

5.2 MANUFACTURING FILMS & SHEETS

Films and sheets are produced using different techniques, including, but not limited to extrusion, calendaring and lamination. Very often, films are further processed to make more complex products. Apart from the nature of the base polymer(s), the respective production and application parameters all have an influence on the selection and formulation of FR additives.

5.2.1 MOST RELEVANT PRODUCTION PROCESS FOR FILM & SHEETS

5.2.1.1 Blown film extrusion is one of the most popular processes to produce thin films.
Plastic granules are fed into an extruder, melted and homogenised before being pumped through a circular blown film die. The formed tube is pulled from the die, inflated and simultaneously cooled in order to solidify quickly.

5.2.1.2 Rigid sheet extrusion / cast film extrusion
Is a similar process, with the difference that the molten polymer is fed through a flat die onto a chilled roller so that it cools down extremely quickly. Generally speaking, extrusion temperatures tend to be higher than in blown extrusion. Once the plastic has solidified, it is wound onto a reel.

5.2.1.3 Calendering
Is a specialty process for the manufacture of large-volume and high-quality products, mainly vinyl (PVC) films and sheets. Modified PE, PP, ABS, and other thermoplastics can also be calendered.

5.2.2 FURTHER PROCESSING STEPS

Rigid sheets are normally not further processed (except by cutting, mounting and fixing). In contrast, flexible films can be subject to additional processing or assembly steps with other components to produce the final articles.

Differences in modifications and material build-ups are as varied as films applications are. For example, the final articles can be made of single or multiple layers. In case of multi-layer products, the composition can be homogenous (different layers of the same polymer), made from different materials (polymeric or others, i.e. plastic coated paper), or may contain reinforcements, i.e. weaves. If not suitably treated with FRs, the weaves can act as a candle wick and adversely affect the flammability of whole composite film.

Films can be stretched to obtain a lower thickness than the original film produced, obtaining by this way also modified mechanical properties, i.e. to produce woven flat tapes or weaves. These films can be mono- or bi-axially oriented, in order to fine tune the mechanical properties for particular applications. They can also be shrunk by application of heat (although rarely relevant for flame retardant applications), glued or laminated onto a substrate (i.e. nonwoven, wood etc.) or used on its own (i.e. roofing underlay). Additional steps can be perforation, printing, coating to obtain specific properties.

There are various ways how each of these factors, and combinations thereof, can influence the flammability of the final article and thus the FR formulation:

- Flammability aspects must be considered. So do multilayer articles ignite burn or drip somewhat differently compared to the fire behaviour of each single layer. In additions, films are not always tested alone but often in a configuration that comes close to the final application. So are films applied on substrates rarely classified on their own, but the whole composite must satisfy the FR test. The FR solution in the film may thus have to be adapted to the reaction to fire of the substrate.
- It is fairly common that the addition of FR additives not only modifies the flammability of materials, but also their physical and mechanical attributes. So behave non-melting FRs like fillers in the polymer matrix. Depending on their chemical nature, their dosage and their affinity to the host polymer, the addition of filler-type FRs may or may not negatively influence the stretching or shrinking behaviour of the film, or its physical properties (i.e. transparency, elongation at break, puncture resistance etc.) or other specified parameters. For high stretching ratios for example, melt-blendable FR additives may be preferable.

5.2.3 FLAME RETARDED COMPOUNDS FOR FILM AND SHEET

In the following table 19 are listed the most common materials used for film and sheet with the respective PIN FR that can be used.

TABLE 19: FLAME RETARDANTS FOR FILM AND SHEET

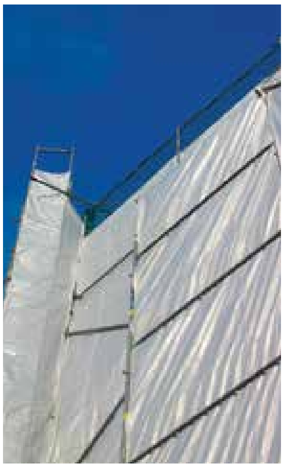
Material	Application	PIN Flame Retardants
Paper	Decorative, advertising	Water soluble phosphates and alkyl phosphonates
Flexible PVC	Films: Tarpaulins	Phosphate esters, Stannates, Zinc Borate, ATH
Polycarbonate and blends	Sheets: Roofing, Glazing, Lighting	Poly(phosphonate-co-carbonates), Silicone compounds, Phosphate esters, Potassium perfluorobutane Sulphonate (KPBS), Potassium Diphenyl Sulphone Sulphonate (KSS)
Unsaturated polyester	Sheets	ATH, Intumescents, Melamine Cyanurate, Melamine Phosphate (opaque applications), DMPP, Cyclic phosphonate, Phosphonate oligomers (transparent applications)
Polyolefins (PE, PP, EVA, others)	Thin films: roofing underlay, vapour barrier, scaffold sheeting etc.	Amino-ether HALS, Alkyl phosphonates, Hypophosphite salts
Polyolefins (mostly HDPE, PP)	Rigid sheets: Aluminium Composites Panels, building scaffolds (walk ways)	ATH, MDH, Intumescents
TPU	Thin films: roofing underlay	Alkyl Phosphonates, Polyphosphonates, Phosphate esters
PA12	Thin films for particular niches	Alkyl phosphonates substrate
Copolyesters, Copolyamides	Breathing film: roofing underlay	Polyphosphonates, Metal phosphinate

Recent developments and outlook

For a majority of thick sheets, the polymers can be flame retarded with mineral FR or char forming additives but are not appropriated for thin films. Mineral fillers are used at high loadings reducing the physical and mechanical properties of the material and intumescent systems require by nature a certain thickness to develop their FR mechanism.

For particular niche applications in thin polyolefin films and fibres, special amino-ether HALS (hindered amine light stabiliser), so-called NOR-HALS permits to reach DIN 4102 B2. Combinations with newly introduced alkyl phosphonates flame retardants offer options to develop non-halogen containing articles, reducing the number of technical gaps.

Nevertheless, halogen-free solutions are still missing in some cases i.e. for particular resins and/or to pass certain fire tests while retaining certain performance criteria, such as transparency or mechanical properties. In other cases, the presence of other fillers (notably pigments such as carbon black) can also bring some technical limitations.



Protection-films

(Source: iStock)

6 INSULATION

6.1. INTRODUCTION

There is a growing worldwide awareness of energy consumption helping to minimize the fossil fuel depletion as well as to reduce the global warming. Insulation of buildings helps to reduce the energy consumption and thus contributes to a more sustainable society.

Various materials are used for insulation in the building and construction industry, such as mineral wool, rigid polyurethane, polystyrene, polyolefin or natural based materials, e.g. cellulose fibres.

All these different materials have to provide strong insulation properties while fulfilling stringent fire safety requirements in order to be used as building materials. Certain materials, such as mineral wools (including rock and glass wool), offer inherent good fire properties combined with good insulation properties. Other organic materials such as polyurethane and thermoplastics show superior insulation properties and lighter weight, but combined with inferior fire properties. Flame retardants must therefore be added to these organic materials to comply with the required fire standards. This particularly applies to foamed materials as they present a pre-mixture of fuel and air in their physical structure, and tend to ignite more easily and burn more vigorously than non-foamed materials.

6.2 POLYURETHANE FOAMS

A major group of insulation material is based on rigid polyurethane (PU) foams due to the excellent insulation properties of this material. Insulation material based on rigid polyurethane can be produced and applied in several ways such as:

- continuous or discontinuous production of insulation boards with flexible (e.g. aluminium foil) or rigid facings (e.g. metal sandwich)
- insulation of surfaces in place by spraying the reactive PU formulation on the surface (e.g. roofing)
- filling gaps in walls, by applying PU formulation via a can ("OCF" or "one component foam")

Rigid PU foams are inherently flammable like most of organic materials. The fire performance of rigid PU foams is influenced by several parameters such as used raw materials (nature of the polyols, used blowing agent etc.), foam density and ratio between polyols and isocyanates, known as index.

Rigid PU foams with a low index, so called PUR foams, show a higher flammability than rigid PU foams with a high index. These so called polyisocyanurate (PIR) foams offer an inherent better fire resistance due to the higher amount of isocyanurate structures in the foam.

In order to pass various fire standards, including criteria for flammability, flame spread and smoke density, flame retardants have to be added to the PU foams. Beyond the required level of fire safety, the flame retardants used have to meet additional criteria such as:

- No impact on the curing of the PU formulation
- No impact on the shelf life of the PU formulation
- No impact on the mechanical properties of the foam (hardness, resilience)
- No impact on the insulation properties of the foam

These requirements can be fulfilled by several different halogen free flame retardants. Phosphorus based flame retardants are the most commonly used, especially liquid substances. Generally speaking, flame retardants used for rigid PU foams can be classified in three families:

- Additive liquid flame retardants: On the one hand, this group of products can be easily incorporated into the foam by adding it to the polyols, as most of the raw materials are handled as liquids. On the other hand, they can impact the mechanical properties owing to their plasticising properties.
- Reactive liquid flame retardants: This group of products is incorporated into the polymer chain, usually by a reaction with the isocyanate. Thus they become integral part of the polymer, do not show a plasticising effect. However, their processing window is often narrower and some of them may impact curing of the PU foam.
- Solid flame retardants: These substances behave like filler in the foam. Therefore they tend to influence the physical properties of the foam, as well as the insulation properties. They can be incorporated as dispersion or blended into the liquid raw materials. They are often combined with liquid flame retardants.

An overview of common halogen free flame retardants for rigid PU foams is presented in Table 20.

TABLE 20: OVERVIEW OF COMMON HALOGEN FREE FLAME RETARDANTS FOR RIGID PU FOAMS

Flame retardants	Chemical name	Appearance	Phosphorus content [%]	Viscosity at 25°C [mPa.s]
TEP	Triethyl phosphate	liquid	17.0	2
DEEP	Diethyl ethyl phosphonate	liquid	18.6	2
DMPP	Dimethyl propyl phosphonate	liquid	20.3	2
CDP	Cresyl diphenyl phosphate	liquid	9.1	45
Reactive P/N polyol	N,N-Dihydroxyethylamino-methan phosphoric acid ester	liquid	12.1	175
Reactive P-Polyol 1	Proprietary	liquid	11.5	< 500
Reactive P-Polyol 2	Proprietary	liquid	19	2.200
APP	Ammonium Polyphosphate	solid	31% P (15%N)	n.a.
EG	Expandable Graphite	solid	-	n.a.

The insulation material based on rigid PU foams has to meet different fire standard depending on the region, where they are used.

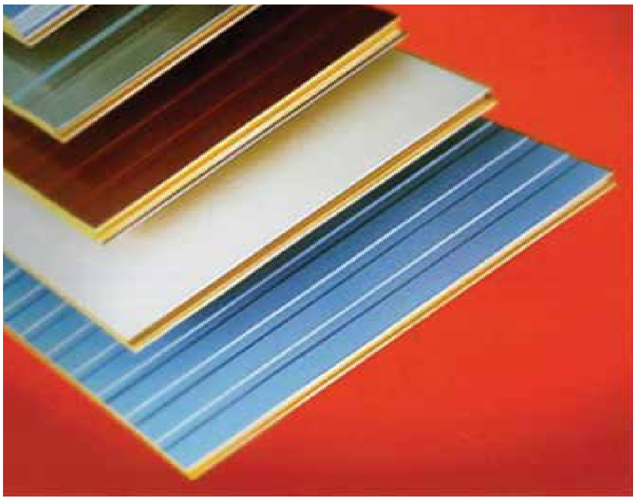
In Europe all materials for building and construction, including rigid PU foams, have to meet the fire requirements according to EN 13501. This fire standard defines various EuroClasses for building materials. Rigid PU foams with flame retardants can achieve classification from class E to C depending on density, blowing agent and type of facing. It is also possible to achieve class B in some cases.

The European fire test EN 13823 (SBI test) also includes a classification for smoke density. Flame retardant rigid PU foams can typically achieve s3 or s2 rating for smoke.

Building materials in the USA have to be tested according to ASTM E 84 (Steiner tunnel test), which assesses flammability and smoke development. ASTM E 84 defines three classes (A to C) for flame spread, as well as for smoke density.

Rigid PU foams containing flame retardants can achieve class A, the highest rating, for both criteria.

In order to pass European and North American fire standards, flame retardants are typically used at dosage levels between 5 and 30 php (parts per 100 parts polyols), depending on the foam density, raw materials and final application.



6.3 THERMOPLASTIC FOAMS

6.3.1 EXPANDED POLYSTYRENE (EPS) FOAM

Polystyrene foams are good thermal insulators and are therefore often used as building insulation materials. EPS is a rigid and tough, closed-cell foam. It is usually made of pre-expanded white polystyrene beads. Thermal resistivity and thermal conductivity are key properties which shall not be negatively impacted by flame retardants. The high flammability of polystyrene materials cannot yet be satisfactory overcome with PIN FR's.

6.3.2 EXTRUDED POLYSTYRENE (XPS) FOAM

XPS consists of closed cells and offers good surface toughness and high stiffness and reduced thermal conductivity. Water vapour diffusion resistance of XPS makes it more suitable to weather exposure than EPS. Mainly used in architectural applications, the flame retardancy norms to fulfil are stringent and are nearly not achieved with PIN FR's.

6.3.3 POLYOLEFIN FOAMS

Polyolefin foams include a variety of products with different densities (from approx. 20 kg/m³ up to 400 kg/m³) and available in different physical forms (beads, sheets, rolls). Depending on the final requirements, they can be made of polypropylene (PP), polyethylene (PE) of different densities, or, to a lower extent, on ethylene vinyl acetate (EVA). Very often, mixtures of different resins are used to obtain a particular set of properties.

Their major use in building is in HVAC applications (heating, ventilation, air conditioning), such as thermal insulation of pipes (both hot and cold fluids) and/or for sound insulation, but these versatile foams also find many other applications where fire safety requirements apply.
Polyolefin foams can be produced by different methods which may have an influence on the choice of PIN FR:

a) foamed beads: the polymer is first compounded and granulated in order to obtain mini-pellets having specific dimensions and weight. The pellets are then transferred into an autoclave, heated and impregnated with a physical blowing agent under pressure until saturation is reached. When these pellets are suddenly released into atmospheric conditions, spherical foamed particles (beads) with a multitude of micro-cells are formed (similar to EPS foams), which can further be processed (i.e. by "steam chest moulding") to produce the final parts.

b) extruded sheets / rolls: also include a first compounding step, in which the blowing agent, FR additives and sometimes other components (i.e. Pigments, dyes) are added to the polymer. In a second step, the resulting compound will be extruded to produce sheets or rolls of different thicknesses (typically from 0,2 to 40 mm). Under the influence of heat, the blowing agent will release an inert gas that will provoke the foaming during the extrusion of the sheets. The so produced sheets and rolls can be further processed, i.e. by cutting, welding etc.
Depending on the final requirements, polyolefin foams can be cross-linked (by electron beam or chemically) and the cell structure can vary from closed to open.

TABLE 21: FLAME RETARDANTS FOR POLYOLEFIN FOAMS

Flame retardants	Chemical name	Appearance	Phosphorus content [%]	Nitrogen content %
Alkyl Phosphonate 1	Proprietary	Solid	19.5	17.5
Alkyl Phosphonate 2	Proprietary	Solid	14	37
Amino-ether HALS 1	Proprietary	Solid melting range 110 to 125°C	0	Not specified
Amino-ether HALS 2	Proprietary	Slightly Yellow Waxy solid with a melting range 95 to 105°C.	0	Not specified

6.4 OTHER INSULATION MATERIALS

6.4.1 INSULATION MATERIALS OF NATURAL ORIGIN

Natural products are increasingly popular for building insulation due to their "green image" (recycled materials based on renewable resources), but are on the other hand also limited due to their fire performance. Owing to their organic character, they have a calorific potential that makes them unsuitable for requirements such as EuroClass A1 or A2, which, at least in Europe, are almost mandatory for use in public locations and high-rise buildings. This substantially restricts their use to residential homes, which are less regulated and require EuroClass E (acceptable contribution to fire) or even EuroClass F (no fire safety). Natural materials include raw materials of animal origin (i.e. short fibres from wool, not suitable for textile applications) or vegetal, such as cellulosic fibres. Cellulosic fibres can be obtained from hemp, flax, cotton, waste wood fibres or from recycled paper ("loose fill cellulose").

Traditionally, natural based insulation products, and in particular loose fill cellulose (being one of the most popular ones) have been treated with boric acid, which had the advantage of imparting the required level of flame retardancy while making the treated fibres resistant against fungus and acarians. The use of boric acid being more and more restricted, it must not only be replaced by suitable flame retardants, but also by approved biocides.

Suitable PIN Flame retardants include different mixtures of ammonium salts of various inorganic acids (i.e. Phosphate, Phosphonate, Sulphate, Sulphamate and others). While many building blocks are common for all types of materials, the nature and respective amount of the components of such mixtures must in fact be adjusted to each type of fibre and designed in a way to be compatible with the respective production process (i.e. FR for loose fill cellulose must be water-free). The here below table illustrates some materials, processes, and used generic chemistries.

TABLE 22: FLAME RETARDANTS FOR NATURAL MATERIAL

	Wet impregnation / Filtering / Drying	Application by spray	Application during fibre cutting
Flax	Ammonium salts of inorganic acids (P, S, or others)	Ammonium salts of inorganic acids (P, S, or others) Methyl Phosphonic Acid, Amido-urea salt	
Hemp	Ammonium salts of inorganic acids (P, S, or others)	Ammonium salts of inorganic acids (P, S, or others) Methyl Phosphonic Acid, Amido-urea salt	
Cotton	Ammonium salts of inorganic acids (P, S, or others)	Ammonium salts of inorganic acids (P, S, or others) Methyl Phosphonic Acid, Amido-urea salt	
Loose fill cellulose			Ammonium salts of inorganic acids (P, S, or others)
Wool	Ammonium salts of inorganic acids (P, S, or others)	Ammonium salts of inorganic acids (P, S)	

7 TEXTILES

7.1 INTRODUCTION

This section will deal with the more traditional uses of textiles in Building applications, thus excluding fibres used in reinforced plastics or fabrics used in composites.

7.2 TEXTILES AND FIRE SAFETY

Generally speaking, textile articles, due to their low mass, represent a relatively low quantity of fuel (‘fire load’) compared with other organic materials. However, most of them pose other fire risks, such as their ignitability, their potential to propagate the flame, and in particular their ability to melt and produce burning droplets.

The reaction to fire of textiles is essentially dictated by the composition of the fibre (natural or synthetic). The behaviour of non-FR treated textiles can therefore vary strongly when exposed to an ignition source (Table 23 and Table 24).

The fibre class can be inherently flame retarded (for example PTFE) or made to be flame retarded by:

1. Reacting a flame retardant into the fibre
2. Coating the fibre with the flame retardant
3. Melt blending a flame retardant additive.

TABLE 23: REACTION TO FIRE OF VARIOUS FIBRES

	Fibre	Flammability and fire behaviour
 Increasing fire hazard & need for FR treatment	Cotton Flax Silk	Ignite easily Burn heavily with white smoke formation Do not melt away from the flame
	Cellulosic Fibres Rayon	Burn rapidly like cotton May melt away from the flame (with or without burning)
	Acetates	Burn heavily May melt away from the flame without burning form burning drips
	Acrylics	Burn rapidly form burning drips form dense black smoke
	Polyamide Polyolefins Polyesters Other synthetic fibres	Burn slower while releasing a high amount of heat May melt away from the flame without burning form burning drips may continue glowing after flame extinction
	Wool	Difficult to ignite Burn slowly May self-extinguish under certain conditions
	Modified acrylics (“Modacrylics”)	Burn very slowly Tend to melt away from the flame without burning May self-extinguish under certain conditions
	Aramid	Does not burn, strong char formation

TABLE 24: FLAMMABILITY PROPERTIES OF POLYMERS ACCORDING TO DENKENDORFER FIBRE TABLES
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Fibre type	LOI-value (%)	"Melting point (°C)"	"External ignition (°C)"	"Self ignition (°C)"
Acrylic	18	215 - 260	225	515
Polypropylene	19	160 - 175		430 - 450
Cotton	19	-	350	400
Viscose	20	-	350	420
Polyamide	20	215 - 220	430	530
Polyester	21	255	390	510
Wool	25	-	325	590
Modacrylic	27	130 - 170		650 - 700
m-Aramide	28	-		675
p-Aramide	29	-		-
Carbon	>60	-		-

7.3 OVERVIEW OF TEXTILES USED IN BUILDING + CONSTRUCTION

Textiles are used for decorative and/or functional purposes.
The most common applications are summarized in Table 25.

TABLE 25: OVERVIEW OF FR TEXTILES USED IN BUILDING AND CONSTRUCTION

Application area	Uses	Fabrics
Home textiles	Curtains, draperies	Polyester, Polyamide, Cotton, Viscose
	Upholstery	Cotton, Polyester, Polyamide, Wool and their respective blends
	Carpets	Polyamide, Wool, Polyester
	Children nightwear (US)	Cotton
Public places	Curtains, drapes	Polyester, Polyamide, Cotton
	Upholstery	Cotton, Polyester, Polyamide, Wool and their respective blends
	Carpets	Polyamide, Polyester, Wool
	Banners, advertising	Polyester

7.4 WASH-PERMANENCY & APPLICATION TECHNIQUES OF FR ONTO TEXTILE PRODUCTS

Depending on their final use, textiles may be subject to cleaning under various conditions. Different levels of wash-resistance (relating to the permanency of the FR treatment) 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 can be retained after a minimum of 50 washing cycles with boiling water

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

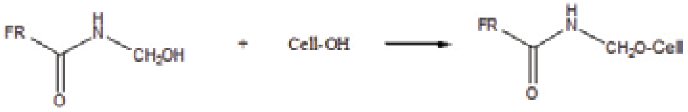
a) Non-durable treatment: The textile passes, in a continuous process, through a bath of flame retardant solution, in which it is pressed at a controlled pressure between two rollers. This process enables a pre-determined quantity of the flame retardant to be deposited onto the textile. The amount applied must be sufficient to provide the required performance. The textile is then dried, again in a continuous process, at temperatures in the range 100°C – 160°C depending on the material.

b) Semi-durable treatment can be obtained in two ways:

- Weak cross-linking of special FR salts onto the fibre: this is normally limited to a few textile/FR combinations, such as for 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 is only limited if fabrics have a sensitive face structure that could be damaged during processing. A paste or foam of FR and binder is applied onto the back of the textile using a system of rollers or scrapers to a deposit level to give the required performance. This is then dried and polymerised to enable the binder to provide the necessary durability, which is essentially influenced by the nature and characteristics of the binder.

c) Durable treatment can be obtained following six different techniques and processes:

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



Process-wise, the FR is applied in a liquid stage, before being dried and cured. Non reacted molecules are then neutralized and washed-off, before the fabrics can finally be dried.

- Self cross-linking: Polymerisation or poly-condensation of the FR onto the substrate, e.g. for FR treatment of knitted or woven fabrics.
- Thermal fixation: Deposition of the FR inside the fibre, e.g. post-treatment of polyester fibres.
- Transfer Coating: A polymer film, containing the flame retardants is cast onto a paper. The fabric is laminated to the polymer film prior to curing in an oven. The flame retardants are permanently encapsulated into the polymer and cannot be removed by laundering. Using this process, additional functionality can be built in to the textile (eg waterproofing) and the surface characteristics can be modified to create, for example a faux leather.
- Ionic linkage: Binding of negatively charged complexes onto positively charged basic groups, e.g. FR treatment of wool.
- Application by exhaustion from acidified liquor in a long liquor ratio. An exchange of ions between the FR and the fibre takes place. 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
  i. by adding a FR-co-monomer during the polymerization e.g. polyester fibres.
  ii. by designing polymer backbones with very high heat and flame resistance e.g. Polyaramide fibers based on Polyphenylene isophtalimide, polyamide-imide), Polyphenylene terephtalimide, Polytetrafluoroethylene (PTFE) and a few others.

These technologies relating to inherently flame retarded fibres are more connected with polymer chemistry than to textile treatment.

Melt blending a flame retardant additive

The addition of flame retardants (neat or via masterbatches) into the polymers prior to melt spinning is a well-known technique for improving the fire performances of textile materials.

[For more details on the above processes please refer to the pin*f*a Transportation brochure available through www.pinfa.org].

7.5 LIST OF PIN FR USED IN TEXTILES

The following table 27 shows a list of the substances that are most commonly used in textiles including building applications. Apart from a few exceptions, combinations of different substances must be used in order to meet the various requirements, which include the fire standard, but also other aspects such as functionality of the considered textile, wash permanency, handle (soft, hard), etc.

TABLE 27: FLAME RETARDANTS USED IN TEXTILES

Substance	Physical form	Use
Ammonium Polyphosphate	Powder	Back coating
Dipotassium fluortitanate	Powder	Reacted on fiber
Zirconium acetate in solution	Liquid	Reacted on fibre
Dipotassium hexafluoro zirconate	Powder	Reacted on fibre
Methylphosphonic acid, amidino-urea compound	Liquid	Back coating or impregnation
Amino-Ether-HALS structures	Melting powder	Added to polymer melt
Polyphosphonate homopolymer	Pellet	Added to polymer melt
Diethylphosphinic acid aluminum salt	Powder	Back coating or added to polymer melt
Diphenyl cresyl phosphate	Liquid	Added to polymer melt
Isopropylated triphenyl phosphate	Liquid	Added to polymer melt
Cyclic phosphonate	Liquid	Diffusion into fibre
ATH	Powder	Back coating or added to polymer melt
Zinc Borate	Powder	Back coating or added to polymer melt
Melamine	Powder	Back coating
Melamine cyanurate	Powder	Back coating or added to polymer melt
Melamine phosphate	Powder	Back coating
Melamine polyphosphate	Powder	Back coating or added to polymer melt
Guanidine phosphate	Powder in aqueous solution	Back coating or impregnation
Expandable graphite	Powder	Back coating or impregnation
Ammonium sulphate	Powder in aqueous solution	Back coating or impregnation
Ammonium phosphate	Powder in aqueous solution	Back coating or impregnation
Ammonium sulphamate	Powder in aqueous solution	Back coating or impregnation
Urea	Powder in aqueous solution	Impregnation
Red phosphorus	Coated powder in aqueous solution	Back coating

8. COATINGS AND SEALANTS.

8.1. GENERAL ASPECTS

Coatings and sealants are used in buildings and constructions to improve resistance to fire. They are therefore the essential technologies to achieve safer buildings and constructions by maintaining an aesthetic appearance at the same time. Although steel doesn't burn it loses its strength at temperatures higher than 500°C. The main task therefore is to fulfil relevant fire classes in passive fire protection by meeting the required Fire Resistance time of structural elements and fire sectors specified in the building codes and technical standards which are becoming ever-more stringent and demand careful consideration. At the same time these high performance coatings and sealants offer a high degree of architectural freedom in particular in modern designs in big spaces like airports, supermarkets, theatres, etc.

The worldwide demand for fire resistant coatings and sealants is driven by the safety level required in the national B&C codes. Additionally, insurance companies may require a higher level of safety to get lower fares. The demand is also linked to construction practices, in particular for coatings which are depending on the steel used in the buildings. UK is an example of one of the leading countries for the use of steel and fire safety regulations, while in France and US still the use of reinforced concrete as structural element prevails, which means a new potential due to the evidence of concrete spalling / cracking when submitted to the fire test. The increasing aesthetic demands of architects are supporting the use of visible steel structure in modern buildings, which drives the consumption of intumescent paints. Emerging economies, such as China, have a growing demand of steel for building and construction. In parallel the safety standards in these countries need to be further developed and adjusted to international levels. An important factor to improve fire safety is not only setting up higher standard levels but also its enforcement. Usually this is only done by third parties in fire safety inspections at relevant buildings where the quality level of applied coatings and sealants is checked.

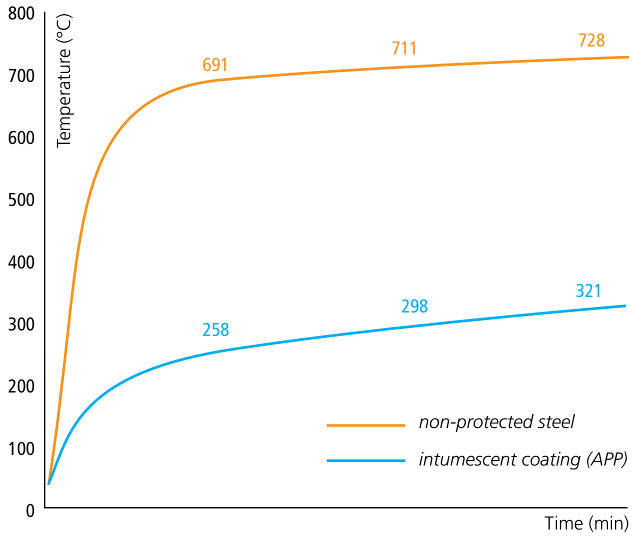
8.2 REACTIVE COATINGS

8.2.1 TECHNOLOGY AND APPLICATIONS

Reactive coatings are mainly intended to provide resistance to fire for structural steel and in some cases to improve reaction to fire of decorative wooden substrates. Most reactive coatings are based on the so called intumescent technology (chemical foaming process)and some of them on ablative coatings (physical foaming).

Example of a reactive (intumescent) coating of a structural steel element at Heathrow

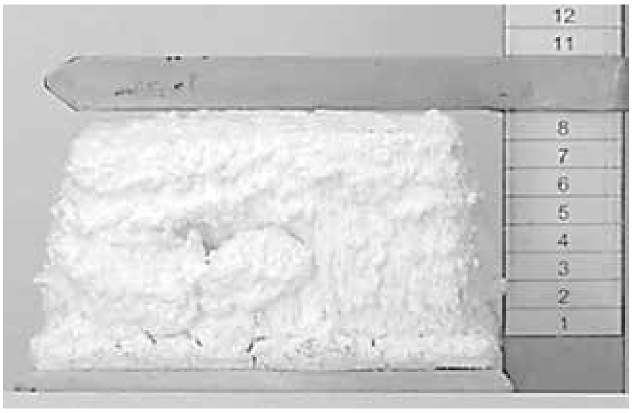
FIGURE 2 - TIME-TEMPERATURE CURVE OF UNPROTECTED AND PROTECTED STEEL SECTIONS WHEN BEING EXPOSED TO FIRE UNDER ISO 834 HEATING RATE (Source Budenheim)



Typical intumescent coating systems basically contain five basic synergistic ingredients:

- a binder/resin system, for instance acrylic resins, PVA resins, etc.;
- a source of carbon, i.e. a substance which can be charred (polyols, carbohydrates etc.);
- APP, which acts as a charring catalyst, i.e. a dehydrating agent
- a blowing agent that releases non-combustible gases, such as melamine.
- TiO$_2$ that builds the final white inorganic foam phase by reacting with APP.

The main additive for the intumescent coatings responsible for fire protection is ammonium polyphosphate (APP) in any of its different variations (coated or non-coated grades) according to the final application. If an intumescent coating subjected to an intense heat source such as a flame, the binding system first melts so that in the beginning, chemical reactions take place in a very viscous phase. Then the APP releases polyphosphoric acid and ammonia whereas the acid attacks any suitable carbon containing compounds such as pentaerythritol which will be dehydrated to a carbonized material. The blowing agent decomposes, e.g. melamine releases ammonia and the molten suspension of carbonized material swells up to form thick, solid, dense and carbon-rich foam, which protects the substrate from heat and further decomposition. Along the time, carbon is oxidized and the remains of the intumescent body are chemically bound white ashes obtained by reaction of polyphosphoric acid with TiO$_2$. There are basically two types of formulations: water based and solvent based. Water based systems are mainly intended for interior applications, due the VOC emission limitations and the safe drying with no risk of moisture or rain during the application time, while solvent based coatings are used in external applications mainly. Coated APP grades help to improve the moisture resistance of intumescent coatings, reduce the weight loss and help to minimize surface defects, especially when applied in external or humid environment type. The paints are typically applied by airless spraying in several layers till the desired thickness, as specified in the fire test report for the requested FR time, is achieved. A typical DFT (Dry Film Thickness) for FR60 rated column is around 1000 microns (HB180).



The role of the flame retardants in the intumescent formulations is to catalyse the char formation in the formulation. The result is a foamed layer that insulates the steel element from the heat source.

TABLE 28: TYPICAL FORMULATIONS OF SOLVENT AND WATER-BASED INTUMESCENT COATINGS.

Solvent (org. Solvent)	20,3	Water – 16,0
APP	27,0	25,0
Melamine	8.5	8,0
Pentaerythritol	8.5	8,0
Resin (binder)	14,0	25,0
Titanium Dioxide	11,0	10,0
Other additives	11,0	8,0

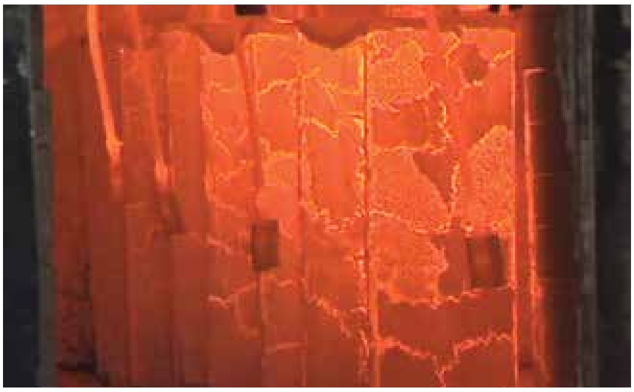
8.2.2 STANDARD TESTING METHODS

The most important standards used worldwide measure the beam/column load bearing capacity under high temperature conditions. Depending on the country, the maximum allowed temperature of the steel is between 350 °C (e.g. Japan) to 650 °C (e.g. Russia). EN standards define the average maximum temperature at 500ºC. The criterion for the temperature has to do with the local construction codes when they specify the safety coefficient for the structure e.g. the higher the coefficient, the higher temperature is allowed. At 500 ºC the load bearing capacity of a typical steel profile is reduced by 50% but as typical safety factors (??) are around 2, at this temperature the stiffness of the steel should be enough to avoid the collapse. Another factor which is considered in standard fire tests is the bending of beams when being submitted to a load and high temperatures. A bending above 1/20 of the length of the beam would represent the end of the test even if 500ºC are not reached as per EN 13381/8 for testing steel structures. Tests results are always, regardless of the standard, expressed in FR time in minutes, being qualified to a value just below to the actual obtained: if 33 minutes are reached, the qualification is the same as if 55 min are reached which is FR30.Some standards, as the EN, overcome this problem by expressing the result in a table in such a way that by data interpolation the thickness can be reduced to get the value – in this means: DFT - down to a real 30 min. Another common point in many standards used worldwide the furnace temperature: It is the ISO time/temperature curve described in ISO 834 for solid fuels (cellulosic fire curve).

Normally intumescent paints are used to cover up to a rating of FR90, sometimes FR120 can be reached. For higher rating values other means for fire protection, such as silicate panels or sprayed vermiculite mortars, are used.

In the EU testing standard for intumescent paints is given in EN 13381/8 whereas the guideline for the test set up is defined in ETAG018/2. Neither standard nor technical guideline are harmonized yet, therefore the obligation for the CE marking, so the fulfilment of both standard and guideline, will still be optional to the member states even after having same law, the new CPR, to be effective by mid-2013. To prevent this, a new mandate from the EC to CEN for the elaboration of a new standard by rewriting ETAG 018/2 in a single harmonized EN standard to make the CE marking mandatory for all EU member states, is in process.

The most developed standards for testing intumescent coatings are the EN standard and BS standard, mainly due to the fact that distinguishes between performances for different steel sections. Obviously a bigger column will need less film thickness than a thin column for the same FR time due to its inherent insulation capacity. Nevertheless this concept is not taken into account by most of the standards used worldwide: they consider a fix steel profile element for the fire test and the results are applied afterwards to any steel profile which is obviously not correct. Only China is now in the process of modifying their standard taking the EN model, same as they did with SBI and EuroClass regarding reaction to fire.



Non loaded set of intumescent paint protected steel columns with different sections by the end of the test 13381/8

8.2.3 TRENDS

The on-going CE marking of construction products will show the way: it defines and stimulates the future development of flame resistant products in the building industry. Coatings will have to be designed for the final use. Therefore, the mark will indicate if the paint is suitable for external, internal, for all applications, etc… which means an effort in developing higher quality paints than today. This is a needed topic since the risk of lowering quality can have an impact on reliability on coatings, can manage designers to look more for other alternative systems, such panels or sprayed material.

The fact that the CE mark must relate to a certain application will have as well implications on the quality of raw materials used in paints and coatings. The main active ingredient is ammonium polyphosphate, and the properties have to be in accordance to the final application defined by the CE mark. In external applications for example a higher resistance to moisture is necessary. In this application an ammonium polyphosphate with lower the solubility is needed.

8.3 SEALANTS

8.3.1 TECHNOLOGY AND APPLICATIONS

Sealants are intended to close, in a fire case, penetration gaps for services (cables, pipes,...) to secure the required FR time of the partition element. These materials can be applied as tapes as well as paste to close the gap between the door and its frame for FR rated doors. The chemistry for the foam expansion in sealants is much wider than the case of coatings: ablative systems, expandable graphite and intumescent reaction are the major technologies used.


Source: Hilti

For sealants the application conditions such as rain, frost.... is not generally an issue. The main point is to have a formulation stable enough as to be used in cartridges (very stable shell life), therefore, highly polymerized APP is used or low acidic expandable graphite.

A very wide system to close penetration of plastic pipes is the use of expanding collars. In case of fire, the intumescent material expands only inside the melting plastic pipe and closes the gap, as in the picture below.


Source: Hilti

8.3.2 STANDARDS

The applicable standards are the same as for intumescent paints in its concept: a furnace that can reproduce the ISO 834 curve and the sealing elements protecting penetration gaps with cables, pipes, etc. are tested on the partition wall that is build closing the open side of the testing furnace. Criteria's to be passed are: no smoke through, integrity of the whole system, and temperature on the back side below 180 °C.

In Europe the fire test is according to EN 1366-3combined with ETAG 018 part 1 to achieve a CE marking (not mandatory). In other countries the fire tests are generally very similar with minor variations like the measurement of smoke development, criteria for measuring external temperature, etc.

1m^3 furnace tests for some sealants closing penetration gaps. Source: Hilti

8.3.3 TRENDS

There are not clear potential improvements with the existing technologies, but it is on the systems. Sealing penetration gaps is something that needs a continuous monitoring, it is a living part of the building: new IT services means new cables through the partition walls, with a need of resealing this gap again. In many cases this is neither been done nor controlled. Inspection is as well important: who is responsible to check what is up behind a false ceiling? We manufacturers of the ingredients for these protection elements are here, not only to supply flame retardants, but to help them in lobbying for quality as well as better inspected and safer markets.

9. FLOORING

9.1. GENERAL ASPECTS

For building areas submitted to heavy traffic, hard-wearing coverings that are skid-proof, flame-resistant and which offer a long service life are needed. For hospitals, cafeterias and child care centres, hygiene has the highest priority. Outdoor areas call for weather and UV-resistant properties.
A range of different flooring materials are used to meet the above mentioned requirements in five typical application areas (Table 28).

TABLE 28 FLAME RETARDANTS USED IN TEXTILES

Application Areas	Material	Properties
Healthcare	Vinyl, Linoleum	Stain resistance, Chemical resistance, Color fastness, Flammability
Retail and Hospitality	Wood, Laminate, Linoleum, Vinyl, Rubber	Wear resistance, Stain resistance, Chemical resistance, Flammability
Offices and Education	Vinyl, Linoleum	Wear resistance, Chemical resistance, Flammability
Housing	Laminate, Wood, Linoleum, PU	Slip safety, Air quality and noise reduction, Flammability
Sport surfaces	Vinyl, Rubber, Linoleum	Antislip, Water proof, UV, Flammability

For the different market segments one can choose from the following types of flooring:

Flooring category	Material
Carpets	Hand and machine made
Textile coverings	Jute, Sea weed, Wool
Resilient coverings	Vinyl, PU, Linoleum, Rubber
Wood and parquet	Bamboo, Cork, Solid or soft wood, W.P.C

9.2 MATERIALS

Flammability is one of the safety criteria of the floor coverings. Most of the fire requirements are concerning the resilient group of floor coverings.
Resilient floor coverings are essential to the zero-dust environments of:
- clean rooms in the microchip industry
- treatment rooms of hospitals, where sterility is a must.

Recent advances in printing technology have made possible a virtually infinite selection of patterns and visual textures. Resilient floor coverings are also gaining ground in the residential segment – probably as a result of their easy-clean properties and the increasingly wide range of designs available.

9.2.1 VINYL (PVC)

Vinyl has evolved into one of the most widely used materials in industrial design. Coverings made of vinyl are not only wear-resistant but also durable and hygienic, are easy to install, to clean and maintain. Today, PVC flooring is available in a close to unlimited selection of designs, patterns and colours.

Due to the different manufacturing processes and the wide variability of the formulations and material combinations, a variety of PVC floor coverings is possible:
- Homogeneous PVC coverings are multi-layer floor coverings made of sheets of similar formulation. The manufacture of a single sheet is carried out by calendering. Two or max. 4 sheets are sealed together.
- Heterogeneous PVC coverings are produced similar to the homogeneous. The sheets are of different formulation.
- Cushioned vinyl, multi-layered constructions (the simplest having 4 layers) manufactured by mechanical or chemical embossing of the plastisols.
- Composites (except cushioned vinyl's) are made of PVC - plastisols in direct coating process. The multilayer plastisol is coated on a support and is responsible for properties such as wear resistance, UV, stain and lighting resistance.
- PVC tiles are a commonly used finish. Due to the small size of the tiles, usually 150 mm, 225 mm and 305 mm, any damage can soon be repaired by replacing individual tiles. The tiles are made of a composite of PVC and fibre, producing a thin and fairly hard tile.

The following table 29 gives a general overview of the different flame retardants used in the PVC flooring industry.

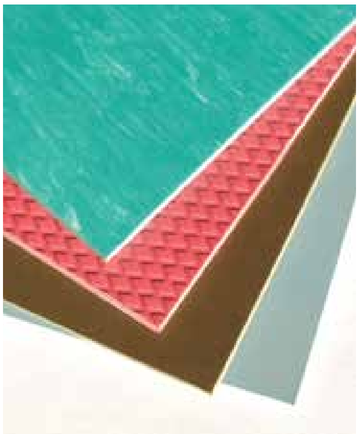

PVC tiles. Source: iStock

TABLE 29: FLAME RETARDANTS FOR PVC FLOORINGS

Flame retardant	Composition	Delivery form	Effectiveness
CDP	Cresyl diphenyl phosphate	liquid	flame inhibition and charring properties, plasticizing effect
TCP	Tricresyl phosphate	liquid	flame inhibition and charring properties, plasticizing effect
DPO	Diphenyl 2-ethylhexyl phosphate	liquid	smoke inhibitor, plasticizing effect
TOP	Tri (2-ethylhexyl) phosphate	liquid	plasticizing effect, cold flexibility
ATH	Aluminum tri-hydroxide	powder	flame inhibition through endothermic decomposition
ZHS	Zinc Hydroxystannate	powder	smoke suppression and flame inhibition

9.2.2 LINOLEUM

Linoleum flooring is made of largely renewable materials such as linseed oil, rosin, ground cork dust, wood flour and mineral filler such as calcium carbonate. It is easy to clean and very tough.

Composition of linoleum as well as its technical characteristics and their testing are now defined in EN standards.

The following FR are used in linoleum:

Flame retardant	Composition	Delivery form	Effectiveness
MDH	Magnesium hydroxide	powder	flame inhibition through endothermic decomposition
ATH	Aluminum tri-hydroxide	powder	flame inhibition through endothermic decomposition

9.2.3 ELASTOMERS

Blends of NBR (nitrile butadiene rubber) and EVA (ethylene vinyl acetate) are soft, and elastic. This makes them the ideal material for applications such as, gym mats and floor coverings. With suitable compounding, they also exhibit good flame retardancy. Properties such as strength and elongation, excellent weather and swell resistance are typical for these blends.

Flame retardant	Composition	Delivery form	Effectiveness
ATH	Aluminum tri-hydroxide	powder	flame inhibition through endothermic decomposition

9.2.3.1 Flame retardants

Materials made of wood can be treated with compounds containing nitrogen, phosphorus and ammonium phosphate.

9.3 FIRE TESTING

9.3.1 EUROPE

In Europe the classification of reaction to fire performance of the flooring materials is done in accordance to EN 13501-1. With the implementation of the Construction Products Directive (89/106/EEC) in the floor coverings sector, the new 'Euro-standard' test and classification system was being put into practice across Europe, superseding national standards.
EN 13501-1:2002 consists of four European 'reaction to fire' test methods that can be applied to floor coverings. One or more of the tests are used to obtain a classification from A1fl (no contribution to fire) down to Ffl (no performance determined).
For the requested tests please go to chapter 2.2.1

9.3.2 USA

The first attempts to regulate flooring materials used the existing Steiner Tunnel, a test for flame spread and smoke development developed by the Underwriter's Laboratory. Developed by Al Steiner for testing building materials, such as wood or gypsum board, at Underwriters Laboratories in 1944, the Steiner tunnel test has been standardized by the major North American standards writing organizations (ASTM E-84, NFPA 255, UL 723, ULC S102).
As this test did not provide the type of data necessary for evaluating flooring materials, it was subsequently replaced by the Pill Test (ASTM D 2859-96) and the Flooring Radiant Panel Test (ASTM E 648-99).
For a summary of the test please go to chapter 2.2.2.

10. WATERPROOFING MEMBRANES

10.1 INTRODUCTION

One of the functions of building structures is to form a watertight envelope, but other infrastructures, such as tunnels and bridges, also have to be protected against water. While many building materials, such as concrete or wood, can be easily treated to improve their behaviour against water (or vapour), conventional systems usually involve polymeric membranes to impair an additional layer of water protection, often coupled with other properties (i.e. elasticity, impact resistance, resistance against salts and chemicals, etc.).

Applications relating to roofing or flooring are typically subject to fire testing (EU: ENV 1187:2002 for roofing; EN 9329 for flooring; US: ASTM E648; E-84). A few other applications (i.e. waterproofing of oil, gas or chemical tanks/pipes) may be also subject to other fire safety regulations.

Traditionally, fishers treated the wood of the boats with tar products. A couple of centuries later, tar is still very popular, but more sophisticated bitumen products have been developed, as well as alternative polymer chemistries. The choice now includes films, sheets or rolls, as well as liquid applied membranes. All have in common: they need the addition of FR to meet the various fire standards

10.2 MEMBRANE CHEMISTRIES

The wide choice of waterproofing membranes reflects the variety of problems that are posed, both in terms of application (i.e. mounting + fixing, weather conditions during application), different type of construction in various regions (flat roofs vs. inclined roofs), climate (resistance to cold or hot temperatures, ambient moisture), productivity during installation, total costs of ownership and many other aspects (i.e waterproofing of bridges, with traffic and vibrations).

Distinction can be made between ready-made membranes, supplied as sheets or rolls, and membranes that are produced on site by application of liquid resins that cure once they have been applied.

10.2.1 READY-MADE MEMBRANES

This family of products essentially includes sheets and films based on:

- tar membranes, with reinforcements as core material, and polymer bitumen coats on both sides.
- tar membranes (as above) modified with thermoplastic resins, to obtain a more plastic ("PYP") or elastic ("PYE") material
- ethylene-propylen-diene-monomers (EPDM)
- thermoplastic olefins (TPO)
- polyvinylchloride (PVC)
- high density polyethylene (HDPE)
- ethylene vinyl acetate (EVA)
- Polyisobutylene (PIB), also called butyl rubber

10.2.2 LIQUID APPLIED MEMBRANES

Offer the advantage that they can produce seamless membranes, avoiding the presence of joints, which are, besides the adhesion properties to the substrate, an important aspect of waterproofing designs. They have been traditionally used for repair and maintenance, but fast curing, spray able resins are finding more and more acceptance to be used as primary waterproofing systems. Different chemistries are also available:

- tar
- tar modified with thermoplastic resins
- polyurethanes (PU)
- polyurea (PUA)
- acrylates
- epoxy resins (EPR)
- unsaturated polyester resins (UPR)

And sometimes blends thereof ("hybrid systems")

10.2.3 PIN FR FOR WATERPROOFING MEMBRANES

TABLE 30 FLAME RETARDANTS FOR WATER PROOFING MEMBRANES

Resin chemistry	Possible PIN FR
Tar bitumen	ATH/MDH, inorganic P/S salts
EPDM	ATH/MDH, intumescents, APP, melamine phosphate
TPO	ATH/MDH, alkyl phosphonates, melamine phosphate, APP, intumescents
PVC	ATH, Zinc Borate, mixture of pyrophosphates
HDPE	MDH, intumescents, alkyl phosphonates
EVA	ATH, intumescents, ethylene diamine phosphate, melamine phosphate
PU	ATH, intumescents, OH term. phosphine oxides, expandable graphite
PUA (hot spray)	OH terminated phosphine oxides, melamine phosphate
EPR	ATH, intumescents, melamine phosphate, DOPO
UPR	ATH, intumescents, melamine phosphate, ethylene diamine phosphate
Acrylates	ATH

11. ENVIRONMENTAL AND HEALTH ASPECTS OF PHOSPHORUS, INORGANIC AND NITROGEN FLAME RETARDANTS

11.1 HAZARD VERSUS RISK

Whereas the previous chapters focused on the technical properties of PIN flame retardants in various application areas, this chapter discusses their environmental and toxicological properties. .. For PIN flame retardants, no official European risk assessments (according to Council Regulation (EEC) 793/93 on Existing Substances, now replaced by REACH) have been carried out, because they did not make it onto the so-called priority lists for high volume chemicals, which were the basis for carrying out risk assessments in Europe. Recently the European Risk Assessment Committee of the European Chemical Agency even removed environmental classification and labeling requirements of two PIN flame retardants. Similar observations have been made for PIN flame retardants under existing chemical regulations in countries around the globe, namely e.g. the United States of America, Canada, Japan, China, Taiwan, South Korea and Australia.

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 us whether a chemical can be hazardous, if man and environment are directly exposed to it. The next step is to assess the likelihood and occurrence of exposure for man (workers and consumers) and for environment. Only if both applies, hazard and exposure, a risk will be imposed. Hazard is a necessary but not sufficient precondition for risk. However, carrying out a full exposure and risk assessment is a lengthy and complicated task, so that some regulators but also 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. Very up-to-date examples of such an approach is e.g. the “Development of European Eco-labels Criteria for Office Buildings”, handled by the Joint Research Centre of the European Commission and the “LEED” (Leadership in Energy and Environmental Design) of the U.S. Green Building Council.

PIN flame retardants are feasible alternatives to other flame retardants under mandatory and voluntary evaluation regimes of national authorities, Eco-label bodies, NGOs and OEMs (Original Equipment Manufacturers).

11.2 EUROPEAN UNION: REACH (AND SVHC) & C&L (GHS)

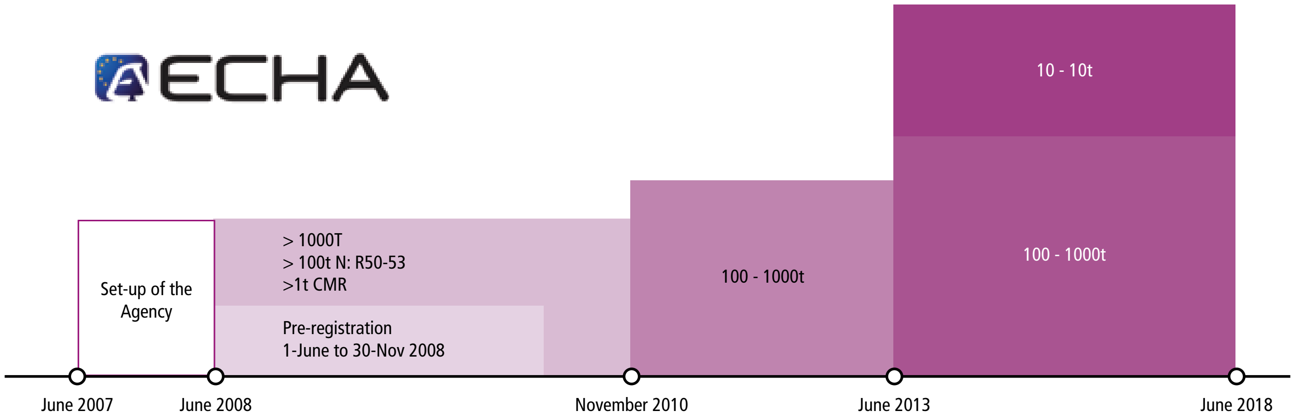
In Europe, regulation 1907/2006/EC on the registration, evaluation and authorization of chemicals (REACH,) came into force in June 2007. The basic idea of REACH is that a manufacturer or importer of a chemical has to supply basic physical-chemical, environmental and toxicity data on any substance before it can be placed onto the market (“no data, no market”). The amount of data which need to be supplied depends on the tonnage produced or imported (per legal entity) and certain hazard criteria. Furthermore, information on the intended uses of chemicals needs to be supplied, and registration is granted for certain uses only. Under the previous legislation, existing chemicals where grandfathered into the system and could be marketed with hardly any information on toxicity or environmental effects. Under REACH, the manufacturer or importer has to prove that a substance is safe to use and he is liable for product safety, whereas previously the authorities had to prove that a substance posed a risk before any restrictions could be implemented. Although REACH is a European regulation, it has had global repercussions, not only because of international trade relations, but also because other regions (e.g. USA, China and Japan) now are also considering updating their chemical legislation accordingly.

For flame retardants, in particular high volume products, a large amount of toxicological and environmental data have been compiled over the last years (e.g. for the European Risk Assessment procedure). These high production volume chemicals were due for registration by the end of 2010 (see Figure 1) and flame retardants manufacturers did submit their registrations on time. So called substances of very high concern (SHVC) have to undergo authorization under REACH, i.e. the authorities have to grant permission for defined uses which are limited in time.

At the end of 2008, another European regulation on the Classification, Labeling and Packaging of substances and mixtures was published (CLP 1272/2008/EC). This is the European implementation of the Globally Harmonized System (GHS) for classification and labeling of chemicals developed by the United Nations. The CLP regulation defines how chemicals need to labeled according to their hazardous properties. In the meantime, a central database (http://echa.europa.eu/informnation-on-chemicals/cl-inventory) has been established, where the classification and labeling information has been made publicly available for all chemicals on the market (there is no cut-off tonnage foreseen as in REACH). It must be noted that the information provided may show significant differences for the same chemical substance. Accordingly the information given in this database must be carefully considered before using it as a reference.

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

FIGURE 1: TIMELINE FOR IMPLEMENTATION OF REACH, THE EUROPEAN REGULATION ON REGISTRATION, EVALUATION, AUTHORIZATION AND RESTRICTION OF CHEMICALS (1907/2006/EC). THE GRAPH INDICATES WHEN SUBSTANCES HAVE TO BE REGISTERED DEPENDING ON THEIR PRODUCTION VOLUME AND / OR HAZARD PROPERTIES.



USA: TOXIC SUBSTANCE CONTROL ACT (TSCA)

The Toxic Substance Control Act (TSCA) was enacted in 1976. Under TSCA information on all new chemicals has to be provided by submitting a pre-manufacture (PMN) prior to manufacture or importation. The EPA is considering a revision of the TSCA.

One outcome of EPA's review of a pre-manufacture notice (PMN) for a new chemical substance is the issuance of an order under section 5(e) of the Toxic Substances Control Act (TSCA). Most TSCA section 5(e) orders issued by EPA are Consent Orders that are negotiated with the submitter of the PMN. When reviewing a PMN for a new chemical substance, the Agency can determine that use under certain specific conditions and with appropriate precautions would not pose an unreasonable risk, but that use under other conditions may pose an unreasonable risk. In addition, EPA may determine that the chemical substance may be produced in substantial quantities and will either enter the environment in substantial quantities or may result in significant or substantial human exposure. In such cases, EPA may develop a Consent Order based on a finding of potential unreasonable risk ("risk-based" order) or significant/ substantial exposure ("exposure-based" order).

CHINA: NEW CHEMICAL SUBSTANCE NOTIFICATION – MEP ORDER NO.7 (CHINA REACH) AND GHS (STATE COUNCIL DECREE 591)

MEP Order No.7 was enacted on October 15, 2010. This regulation is a significant update of previous measures enacted in 2003, the New Chemical Substance Notification (NCSN), and it introduces a number of new concepts as

Figure 1: Timeline for implementation of REACH, the European regulation on registration, evaluation, authorization and restriction of chemicals (1907/2006/EC). The graph indicates when substances have to be registered depending on their production volume and / or hazard properties.

found in the EU-REACH regulation, such as GHS-based criteria for hazard communication, notification according to annual tonnage bands and post-notification tracking, and acceptance of notifications only by legal entities within the jurisdiction of the regulation. This revised law is in line with international practices for a comprehensive chemicals management system addressing notification, evaluation, assessment, tracking and control.

By the State Council Decree No. 591 (published in March 2011 and entering into force on December 1, 2011) China implemented a regulation on the control of hazardous chemicals (Chinese GHS). The regulation introduces requirements for classification, labelling and material safety data sheets of hazardous substances. It also introduces the obligation to register identified hazardous chemicals prior to first-time manufacture or import at SAWS-NRCC (National Registration Center of Chemicals of the State Administration of Work Safety). Decree 591 applies to all legal entities in China that are engaged in the manufacture, storage, handle, transport or use hazardous chemicals.
The Ministry of Industry and Information Technology (MIIT) has launched a program (May 25, 2012) for the collection of information about "safe alternatives" of toxic and hazardous chemicals among the industry. The aim is to identify chemicals with lower toxicological properties and consequently a less hazard profile and enable industry developing and promoting such chemicals to reduce / eliminate pollution during production, handling and use. The focus is on heavy metals; organic persistent pollutants; persistent toxic pollutants; highly toxic, highly corrosive and highly irritant chemicals; carcinogens; chemicals with mutagenic and reproductive properties.

JAPAN: CHEMICAL SUBSTANCE CONTROL LAW (CSCL)

CSCL was introduced in 1973 and was amended and updated in 1986, 2003 and 2009 since then. With CSCL Japan maintains a strict pre-marketing evaluation scheme for chemical substances. The 2009 amendment went into force in two phases as of April 1, 2010 and April 1, 2011.
The amended law shifts the Japanese chemical control system from hazard-based to risk-based and is implemented in two phases. These changes require companies to evaluate and re-structure their chemical inventory management and communication processes through the supply chain.
Due to their properties PIN flame retardants are typically not impacted.

TAIWAN, SOUTH KOREA, MALAYSIA, INDONESIA, VIETNAM, THAILAND AND RUSSIA

An increasing number of countries in East Asia, including Taiwan, South Korea, Malaysia, Indonesia and Vietnam, are following the example of e.g. Japan by considering the introduction of notification requirements that would help create a national chemicals inventory, and, in some cases, plans for the registration of priority substances.
The identification and registration of priority substances in these countries may lead to the same chemicals (Substances of Very High Concern) as identified other major chemicals regulations as EU-REACH, or the Japanese- or U.S.-regulations, followed by restriction- and authorization processes.

11.3 ECOLABEL

EUROPEAN UNION

The European Commission's Joint Research Centre is developing Eco-label and Green Public Procurement criteria for office buildings. The proposed Eco-label will be a voluntary label awarded to the top 10 – 20% of office buildings, both new buildings and those undergoing major renovation. The Eco-label will be based on criteria for e.g. energy consumption, indoor quality, waste management, the selection of materials but also the use of hazardous materials including chemicals, as flame retardants. According to the latest DRAFT for the selection of materials and hazardous substances (DRAFT Development of European Eco-label Criteria for Office Buildings, criterion 7), "office buildings or any building element of it shall not contain substances referred to in Article 57 of the REACH regulation (EC) No 1907/2006 nor substances or mixtures meeting the criteria for classification in defined (35) hazard classes in accordance with the CLP regulation (EC) No 1271/2008.

USA

Since the year 2000, the U.S. Green Building Council has been the sponsor of an internationally recognized certification system called LEED (Leadership in Energy and Environmental Design). This independent third party certification provides verification that a commercial or residential structure meets the criteria for high performance in the areas of energy efficiency, human and environmental health plus material selection. Due to new pilot credits established during 2010, building owners can now earn green certification credit by using alternative materials that do not contain halogenated flame retardants (re. "PBT Source Reduction" and "Chemical Avoidance in Building Materials").

THIRD PARTY EVALUATIONS

In addition, there have also been various independent, third party evaluations of PIN flame retardants (Information from pinfa: fact sheets / product selector).
Pinfa has assembled a database of PIN flame retardants which shows their target applications together with essential environmental and toxicity information as well as REACH registration status. This database is available on the pinfa website at http://www.pinfa.eu/product-selector.html.
In addition, pinfa has summarized the environmental and toxicological properties for a number of flame retardants in fact sheets. The data in the sheets are typical hazard oriented data and should not be used as such to deduce risks. The sheets are divided into a Health and Environmental chapter, and also include an overall PBT / vPvB analysis to indicate the regulatory status. The fact sheets can also be downloaded from www.pinfa.org.

Please use these pinfa sources for information on classification and labelling of these flame retardants. The Classification & Labelling Inventory maintained by the European Chemicals Agency (ECHA) is an un-checked collection of submitted classifications from a vast number of submittants. The data are neither consolidated nor harmonised and therefore contain many errors so far.

FIGURE 2: THE PINFA PRODUCT SELECTOR ON HTTP://WWW.PINFA.EU/PRODUCT-SELECTOR.HTML IS A SEARCHABLE DATABASE WITH INFORMATION ON TARGET APPLICATIONS TOGETHER WITH ESSENTIAL ENVIRONMENTAL AND TOXICITY INFORMATION.

12. FUTURE TRENDS AND CONCLUSION - Alexander B. Morgan; PhD

12.1 PAST EVENTS AFFECTING FUTURE TRENDS

Before discussing the future trends that a user of Phosphorus, Inorganic, Nitrogen (PIN) flame retardants will encounter, it is important to quickly review the past, as reactions to historical events will show us what the future of flame retardancy is likely to be. Of course predicting the future is difficult, but since fire safety tends to be a reactive problem (fire safety addressed after a fire problem is found), there is a proven track record of looking to past events to determine what new fire protection solutions will be implemented in the future.

Material flammability has been a problem as old as recorded history, and for as long as humanity has suffered from fire damage, it has come up with flame retardant solutions. The solutions used over 2000 years ago (alum or vinegar to protect wood from fire) are not used today, and further, solutions being used today may be replaced by new chemistries or new forms in the future. One should not assume that flame retardants in use today or even in the next few years will be with us for decades or centuries later. New technologies and improvements will be found and implemented as science makes progress in discovering and solving new problems. In general, fire tests change as new fire risk scenarios are discovered, and also, new flame retardants are introduced in a constant aim to improve the efficiency and the health and safety profile of these substances. Flame retardant chemistry must be tailored to work in a specific polymer for a specific fire risk / regulatory test, and so new flame retardants or flame retardant formulations created to meet these new tests. Likewise, new ones with even more reduced environmental impact will be commercialized and used. So if we look to the recent past, we can see two specific trends that will affect the future. The first is new fire risk scenarios caused by flammable materials being used in building and construction applications to achieve energy efficiency (insulation), retrofitting of new construction into older buildings (plastic pipe), and dealing with wildland-urban interface fire scenarios. The second is the move to reactive and polymeric flame retardants to improve further their environmental profile. Each of these two issues will be discussed in turn.

12.2 NEW FIRE RISK SCENARIOS

The previous sections in this brochure covered a variety of existing regulatory tests which address current fire risk scenarios in a wide range of applications. New fire risk scenarios typically occur when a new technological advance or practice gets ahead of fire safety engineers. For example, increases in plastic in automotive cars for fuel efficiency has led to some unexpected fire risks in car parks and tunnels which can lead to catastrophic concrete failure when those cars catch on fire and give off large amounts of heat. For the building and construction market, the new fire risks will be driven by these new technology practices and material insertions to address non-fire risk needs. One example is the need to achieve better energy efficiency in the home. Another example would be where plastic materials are inserted into older construction as part of retrofit upgrades where ease of installation, not fire safety considerations, are the primary design driver. Finally, as more of human civilization moves into suburban and rural areas, there can be an increase in fire loss from natural fire causes, especially at the wildland-urban interface (WUI). The WUI scenario is somewhat country specific, with most of the problems in this area occurring in the USA and Australia, but it is possible it can occur in other more densely packed countries as well.

Before describing these three likely fire risk scenarios in more detail, it should be pointed out that one cannot predict the future of fire safety exactly. The best that can be done is to look in general at likely trends and then be prepared to deal with them as they happen. While it would be ideal to be proactive in dealing with fire threats, due to the inability to predict them, it may be impossible to tailor a solution to the problem until one has fully studied it and tests are developed for the flame retardant chemist / material scientist to design their product to meet the regulatory test need. With that caveat, here are three likely future fire risk scenarios that will drive new flame retardant material development.

- 1) Insertion of flammable materials into Building & Construction for energy efficiency: As part of efforts to achieve low carbon footprints and high energy efficiency in buildings, there is an increased drive to have improved insulation in all parts of the structure to moderate building temperature (heating and cooling) or any process where heat energy can be gained/lost in an antagonistic manner. Examples include typical insulation in roofs and walls for building temperature moderation, but also insulation around steam lines and hot water pipes / cooling water pipes for air conditioning needs. Higher levels of insulation prevent heating/cooling losses to the external environment which will keep heating/cooling energy costs (electrical, natural gas/propane, steam etc.) low. Some of the insulations with particularly high insulation values are polymeric in structure (polystyrene, isocyanurate rigid foams, etc.) and can be much more flammable than inorganic (rockwool, fiberglass) insulations. As more insulation is installed in modern buildings, the fuel load may begin to increase in that building. Each individual piece of insulation may not add that much, but combined it could be quite significant. Further, as open spaces behind walls and in attics get more filled with insulation, along with other building infrastructure (such as electrical wires) the potential for ignition events increases. Therefore we will likely see new fire risk scenarios where insulation may require higher levels of fire safety to address the total fuel load, or, to mitigate the increased chances of ignition due to more insulation being in contact with more electrical wires / ignition sources.

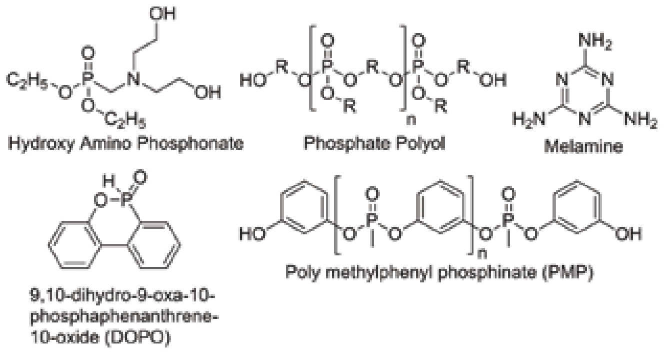
- 2) Retrofitting of older buildings with plastic components: Related to item #1 above, as houses age or need to be upgraded, the infrastructure of that house (electrical wiring, piping, ventilation ducts, etc.) may need to be replaced as well. Sometimes the replacement of that infrastructure can mean that entire walls and floors must be destroyed to reach the infrastructure, which can lead to significant cost and reluctance from the building owner to even bother with the needed upgrades due to the hassle of construction. One common example is piping for water, in which case semi-flexible plastic pipe can be of great interest to the homeowner as it flexible enough to snake along through existing HVAC vents or other small openings that may be present in the older building. However, much like the problems discovered early on when wiring began to be placed throughout homes, that plastic pipe could be a fire risk if the pipe is not sufficiently flame retarded. The fire scenario becomes more complicated in the case of water-filled plastic pipes. Specifically, the water in the pipe may prevent flame spread on that plastic pipe should the pipe melt or burn through, but the subsequent water release may lead to electrical short circuits if electrical infrastructure is nearby. Piping is not the only example of fire risk though. Spray insulation foam which is pumped into wall openings to provide insulation could also lead to a fire risk if the spray insulation coats/covers an electrical wire and later on that wire short circuits and fails leading to a smoulder or fire event in the wall itself. Flame retardancy of spray insulation foams may also be needed in the future, with needed protection against smoulder, electrical arc, and flame spread. Smoke release and gas release may also be fire risk requirements that have to be addressed in new flame retardant material design to ensure ease of escape in the event of a fire.

- 3) Wildland Urban Interface (WUI): For reasons ranging from climate change (increasingly dry vegetation) to urban sprawl (more homes moving into wild areas), there has been an increase in fire losses in WUI areas. As wildfires spread from forest or brush/outback during dry seasons, they quickly encounter homes and buildings in WUI areas, and very often lead to major losses of property as the fire rages through a neighbourhood. While many of the building materials present inside the home are flame retarded against various fire risks, not all exterior building materials may have the same level of fire protection. Certainly roofing shingles have fire protection requirements, but that protection may be against a much milder fire source than the ones typically seen in a raging wildfire. The same is true for exterior siding; a brick house will respond to a flame very differently than one with vinyl or wood siding. Therefore polymeric components or even tar-based roofing shingles may require higher levels of fire protection when they are installed in WUI areas. Even insulation behind the walls may have to meet more strict fire tests when the heat flux from a WUI fire impinges upon the wall of a structure. Right now the main approach to dealing with this fire risk in WUI areas is to propose changes in construction and surrounding landscaping, but this may not be sufficient and new building codes may dictate new fire tests which plastics will have to pass, and those tests will likely require high levels of fire protection and robust flame retardancy.

12.3 REACTIVE AND POLYMERIC FLAME RETARDANTS

While flame retardants must be somewhat persistent by design (they need to last throughout product lifetime), bioaccumulation and toxicity can be addressed through the use of polymeric and reactive flame retardants. Reactive flame retardants are molecules which not only have an active flame retardant chemistry present, but also have chemical groups which can react with the polymer during synthesis or during polymer processing to covalently bond the flame retardant to the polymer. This way the flame retardant cannot migrate out of the polymer during the lifetime of the product. Some examples of this are shown below in Figure 12.1, which includes phosphate polyols that can react with polyurethanes, melamine which can react with epoxies or polyurethanes, and DOPO which can react with epoxy.

FIGURE 5: REACTIVE PHOSPHORUS AND NITROGEN-CONTAINING FLAME RETARDANTS



Polymeric flame retardants are another future trend likely to be seen, as polymeric flame retardants are not easily bioaccumulated, and do not easily migrate out of a polymer that they have been blended into. A polymer/polymer blend presents a much better environmental profile than a polymer + small molecule blend. Currently, the only high molecular weight polymeric PIN flame retardant commercially available is the NOFIA group of polyphosphonates, but other polymeric phosphates have been reported in the literatures.

12.4 CONCLUSIONS ABOUT PIN FLAME RETARDANTS

This brochure on PIN flame retardants is a starting point for the end-user. It is meant to be a useful single-place guide for those wishing to determine how to use these flame retardants, but due to the complexity of optimizing a flame retardant formulation for each and every application, not everything can be discussed here. Therefore the user may need to consult additional papers and books on PIN FR chemistries and uses, of which there are several including:

- "Fire retardant action of mineral fillers" Hull, T. R.; Witkowski, A.; Hollingbery, L. Polym. Degrad. Stab. 2011, 96, 1462-1469.
- "Fire-Protective and Flame-Retardant Coatings – A State-of-the-Art Review" Weil, E. D. *J. Fire Sci*. **2011**, 29, 259-296.
- "Flame retardant challenges for textiles and fibres: New Chemistry versus innovatory solutions" Horrocks, A. R. Polym. Degrad. Stab. 2011, 96, 377-392.
- Fire Retardancy of Polymeric Materials, 2nd Edition. Eds. Wilkie, C. A.; Morgan A. B. Taylor and Francis. Boca Raton, FL ISBN 978-1-4200-8399-6.
- "Flame Retardants for Plastics and Textiles: Practical Applications" Weil, E. D.; Levchik, S. V. Hanser Publishers, Cincinnati, OH 2009, ISBN 978-1-56990-454-1.
- "Flame retardancy of silicone-based materials" Hamdani, S.; Longuet, C.; Perrin, D.; Lopez-cuesta, J-M.; Ganachaud, F. Polym. Degrad. Stab., 2009, 94, 465-495.
- "Fire Properties of Polymer Composite Materials" Eds. Mouritz, A. P.; Gibson, A. G. Springer-Verlag, The Netherlands, 2006. ISBN 978-1-4020-5355-9.
- "Zinc borates as multifunctional polymer additives" Shen, K. K.; Kochesfahani, S.; Jouffret, F. Polym. Adv. Technol. 2008, 19, 469-474.
- "Combined Fire Retardant and Wood Preservative Treatments for Outdoor Wood Applications – A Review of the Literature" Marney, D.C.O.; Russell, L.J. Fire Technology 2008, 44, 1 – 14
- "Fire retardant polymers: recent developments and opportunities" Bourbigot, S.; Duquesne, S. J. Mater. Chem. 2007, 17, 2283-2300.
- "Flame Retardant Polymer Nanocomposites" Edited by Alexander B. Morgan and Charles A. Wilkie. Book published by John Wiley & Sons, Hoboken, NJ 2007. ISBN 978-0-471-73426-0
- "A Review of Recent Progress in Phosphorus-based Flame Retardants" Levchik, S. V.; Weil, E. D. J. Fire Sci. 2006, 24, 345-364.

What can be said about PIN flame retardants is that they are potent protection against fire if used correctly. They are not a panacea for all polymers in all fire scenarios, but in many cases they provide superb protection against fire (P-N intumescent formulations) and smoke (inorganic water-releasing additives). This guide, plus many of the vendors of PIN flame retardants, can help the user meet their fire protection needs cost effectively and we hope you find it of value in development and sustainment of fire safe products.

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P.O. Box 43
6130 AA Sittard – The Netherlands
Phone: 00800-74663376
E-mail: CSC-Benelux.DEP@dsm.com
www.dsm.com

- Engineering plastics with PIN Flame Retardants

DuPont International Operations Sàrl

DuPont International Operations Sàrl
2,Chemin du Pavillon
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Switzerland
Phone:+41 22 717-5111

- PIN Flame Retardant Engineering Polymers and Elastomers

Everkem SPRL

Via Della Lirica 11
IT-48124, Ravenna
Italy
Phone: +39 02 67076.513
barbara.maresta@everkem.it
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- P/I/N based Flame Retardants

FRX Polymers™ Inc.

200 Tunrpike Road
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USA
Phone: +1 978 244 9500
info@frxpolymers.com
www.frxpolymers.com

- Polyphosphonate Homopolymers
- Copolymers
- Oligomers

CONTACT DETAILS

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Via Pietro Chiesa, 7/13
16149 Genova
Italy
Phone: +39 010 6420 81
n.gatti@italmatch.it
www.italmach.it

- Metal phosphinates
- Melamine cyanurate
- Red phosphorus
- Melamine phosphate
- Melamine borate

Lanxess Deutschland GmbH

Chempark
51368 Leverkusen
Germany
Phone: +49 214 30 37201
heiko.tebbe@lanxess.com
http://phosphor-chemikalien.de/fr/en/

- Cresyl diphenyl phosphate
- Tricresyl phosphate
- Reactive P/N polyol
- Dimetyl propane phosphonate
- Triethyl phosphate

Metadynea Austria GmbH

Hafenstrasse 77
AT - 3500 Krems
Germany
Phone: +41 22 751 90 10
Thomas.Zich@metadynea.com
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- Phosphorus based Flame retardants

Nabaltec AG

Alustraße 50 - 52
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Germany
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fillers@nabaltec.de
www.nabaltec.de

- Aluminium hydroxide
- Boehmite
- Magnesium hydroxide

Perstorp

Perstorp Specialty Chemicals AB
Industripark
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Phone: +46 435 380 00
david.james@perstorp.com
http://www.perstorp.com/

- Carbon source for intumescent systems

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Presafer Xiongxing Industrial Park, Qingyuan Hi-Tech, Industrial, Development Zone 511540 Guangdong China Phone: +86 763 3129090 tech@presafer.com www.presafer.com	• P/N based flame retardants
Solvay Rue de Ransbeek 310 1120 Bruxelles Belgium Phone: +32 (0)2 264 21 11 florence.schutz@solvay.com www.solvay.com/en/index.html	• P/I/N flame retardants for Polyamide based plastics
Thor GmbH Landwehstrasse 1 67346 Speyer Germany Phone: +49 6232 6360 jerome.deboysere@thor.com www.thor.com	• P/N based Flame Retardants for Plastics and Textiles
William Blythe Ltd Bridge Street Church, Accrington BB5 4PD Lancashire United Kingdom Phone: +44 1254 320196 john.williams@williamblythe.com www.williamblythe.com	• Zinc hydroxystannate • Zinc stannate

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- Bisphenol A bis (diphenyl phosphate)
- Diphenyldiol bis (diphenyl phosphate)
- P/N Intumescent systems

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- Phosphorus FR additives
- Metal Phosphinates
- Ammonium Polyphosphate and Intumescent formulations
- Red Phosphorus

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Polyphosphonate:
- Homopolymers
- Copolymers
- Oligomers

Huber Engineered Materials

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- Alumina Trihydrate
- Magnesium Hydroxide

Nabaltec AG

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Germany

Product Manager - Americas
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- Aluminum Hydroxide
- Boehmite
- Magnesium Hydroxide

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- Engineering and Specialty Compounds
- Blends and Alloys

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- Masterbatches, Engineeering and Specialty Compounds
- Wire and Cable Compounds

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J2C 7W3 Canada
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- Specialty resins

Pinfa-NA (North America) is a non-profit trade organization that brings to-gether and represents manufacturers and users of the major flame retardant technologies. We have two levels of membership:

- Full Members: Flame retardant manufacturers
- Associate Members: Synergists, Flame retardant compound formulators, fabricators and end-users.

Pinfa supports fire safety through innovative, reliable and sustainable fire performance solutions, using products based on halogen free phosphorus (P), nitrogen (N) and inorganic compound (metal ions, hydroxides).

Pinfa is a Sector Group of **Cefic** (the European Chemical Industry Council), and works with sister association **pinfa-na** in North America.

Pinfa Sponsors and participates in conferences on flame retardants and end uses, industry and regulatory organizations and we produce education-al brochures relating to flame retardant technology and markets.

Benefits of Joining: Be on the forefront of developments in the field of non-halogenated flame retardants, regulatory and environmental develop-ments impacting the field.

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

Pinfa also co-operates with national & supra-national organizations (EU, OECD, United Nations) & other industry associations, consumer organiza-tions & non-governmental organizations and will ensure the development of scientific knowledge related to the whole life cycle of PIN FRs.

www.pinfa-na.org

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