pinfa

Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 88 February 2018

The 12th AMI Fire resistance in Plastics Conference, Cologne, 6-7 December 2017, brought together over 160 participants, mainly from the polymer, compounding and plastics additives industries. This pinfa Newsletter Special Edition summarises presentations relevant to PIN fire safety and presents interviews with a selection of companies present. Previous AMI FR conferences are summarised in pinfa Newsletters n°s 61, 76, 80.

The next AMI flame retardant conferences will take place in Pittsburgh **10-11 April 2018 and in** Cologne **10-12 December 2018**.

Günter Beyer, Kabelwerk Eupen, opened the conference by identifying flame retardant development trends from an overview of scientific publications on flame retardants. All the trends noted concern PIN fire safety. He noted the increase in publications from China, now over 50% of scientific articles and patents. He highlighted 10 recent scientific papers, mostly addressing improving performance of LS0H (Low Smoke Zero Halogen) formulations. PIN synergists studies in these papers include: layered double hydroxides, zinc borates, carbon nanoparticles (fullerenes), polymeric compatibilizing agents, zinc hydrostannate, silicates, polysiloxanes, glass frits. He noted the potential of additives which improve char resistance by ceramification, and of technologies for coating polymer foams to ensure fire protection. : He also discussed possible questions around toxicology of nanofillers, noting that carbon nanotubes are under scrutiny for toxicity, whereas organoclays are non problematic, because they only become nanodispersed within the compounding step by extrusion (no risk in processing); in fire emissions probably the nanodispersed fillers collapse to larger scale (so are no longer nanoscaled).

Smoke toxicity

Guillaume Capon, CREPIM (fire research and testing, France), presented the initial review of published scientific data on whether PIN flame retardants impact the toxicity of smoke emissions, prepared for pinfa (see pinfa Newsletter n°85). 135 relevant scientific articles were identified after a thorough search of scientific publications from the last 30 years, with 22 being identified as containing evidence or data. The conclusion is that smoke is always toxic, that the nature of the material burning can impact toxicity by a factor of up to 10, but that this is considerably less important than the fire conditions (ventilation = oxygen available) = factor of up to 100. Acute smoke toxicity is caused mainly by carbon monoxide, emitted by any material burning in under-ventilated conditions (as is almost always the case in accidental fires), whereas chronic toxicity (long term, concern for fire fighters) is mainly caused by small particles of soot, related to PAHs and dioxins/furans. Non flame retarded materials will generally burn more, so causing more toxic emissions. PIN flame retardants may in some case act in the gas phase, but they do not contribute to the generation of highly toxic polyhalogenated dioxin/furan emissions. The action of PIN flame retardants in the solid phase will help to trap gases and soot, and so reduce toxic emissions. The positive effect of PIN FRs is conditional on using the right FR, adapted specifically to the polymer. However, the main conclusion of this initial science review is

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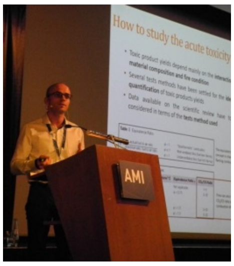
that data is lacking, particularly concerning soot emissions, and particularly as regards data from large scale fires or testing.

Discussion session on smoke toxicity



A discussion session with conference participants, on smoke toxicity, was organised by AMI and pinfa following the CREPIM report presentation.

Participants underlined:

- Smoke is always toxic. Previous major studies have concluded that it is not meaningful to attempt to differentiate low smoke materials, for example the University of Pittsburgh methods developed for New York State were never implemented into regulation (see https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4914232/pdf/jresv97n2p245_a1b.pdf)
- The importance of smoke opacity in hindering escape, and so in fire safety
- Variation in regulations and standards for smoke, covering opacity, total smoke particle emissions, smoke corrosivity, smoke toxicity
- Regulations addressing smoke toxicity only look at acute toxicity (carbon monoxide, irritant and asphyxiant gases). Results may not be indicative of real fire situations.
- The environmental impacts of accidental fire smoke and gas emissions should be considered, and not only their immediate toxicity
- To where does the phosphorus from P-containing PIN FRs go in fires? Experts present indicated that it is generally not found significantly in fire gases, and is probably retained in char as phosphate or polyphosphates. This indeed is usually the objective, because it is the presence of this phosphorus which accelerates char formation.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Study 1901/01/166 – How PIN FRs affect gas and soot toxicity of smoke in case of fire? Review of the literature.
28 April 2017

pinfa President, Adrian Beard, Clariant, noted that pinfa is not "campaigning" for the introduction of smoke toxicity requirements in regulation. In the current reassessment of the EU Construction Products Regulation, pinfa has submitted that "the EU should also continue to develop harmonised fire safety, smoke and sustainability standards to address the risks of modern constructions and the challenges of the circular economy" without referring to "toxicity" (see pinfa Newsletter n°84).

pinfa notes however that many companies (flame retardant producers, compounders) claim low smoke toxicity (e.g. "FST" fire – smoke – toxicity) for PIN flame retardant solutions and compounds, and that it would be appropriate to have data to justify these claims (comparison of PIN FR materials to neat polymers). **pinfa invites transmission of any such product smoke toxicity data** (to CREPIM, under appropriate anonymity/confidentiality conditions).

Innovative PIN FR systems

Jan-Pleun Lens, FRX Polymers (pinfa member), presented new applications of the company's phosphonate PIN FR technologies, available as polymers, oligomers with tailored functional end-groups, and polycarbonate co-polymers. Developing applications include in polyesters (film and fibres, including synthetic hair)), , polycarbonates, thermoplastic polyurethanes, and thermosets like epoxies and polyurethanes. Performance advantages can include transparency, low processing viscosity and good mixing (enabling production of very thin, transparent flame retardant films), very low fogging, and a smooth and attractive surface appearance. Specific oligomeric phosphonates can react into epoxies, improving mechanical properties, offering good adherence properties, high electrical performance and low moisture uptake. Other specific oligomers are developed for polyurethane foam, offering improved ageing and mechanical performance because they react into the foam.

Christian Schmidt, Clariant (pinfa member), presented new non-halogenated FR systems for transport fire safety. The new EU railway materials standards EN 45545-2 sets demanding fire, smoke and toxicity (FST) requirements, as do national requirements for railways in other countries (e.g. NFPA 130 in the USA) and requirements for aviation and shipping (FAR 25.853 and ABD 0031). PIN flame retardants are the best choice to achieve these requirements, because they can offer reductions in flammability, low smoke and gas corrosivity and density, whilst ensuring material performance and processing compatibility (avoid release of acid in extrusion). Solutions presented included combinations of ATH with long molecular chain APP and PIN synergists in polyethylene and polyurethane (structural composites, fibres), and organophosphorus FRs with PIN synergists in flexible polyurethane foams (enabling achievement of aviation specifications).

Birgit Fassbender, Budenheim (pinfa member), presented new PIN FR systems for reinforced thermoplastics for electrical and electronics equipment. These high-tech applications require fire resistance (because of fire risks due to arcing or over-heating) tested by Glow Wire and UL94-V0, easy and fast processing including to produce increasingly thin parts for miniaturisation and absence of corrosion of processing equipment, electrical properties, durability, and absence of corrosive gases in case of heat or fire (avoid safety risks related to deterioration of circuits). Budenheim melamine derivative PIN FRs in combination with phosphorus-based PIN FRs achieve these objectives in polyamides and glass-fibre reinforced polyamides, at loadings of below 25%. They also offer no discoloration, low smoke and smoke toxicity (toxicity 3 times lower than specification under DIN 5510-2), high stability and low migration.

Gérard Lips, BASF (pinfa member), underlined that flame retardants must enable product fire safety requirements whilst also respecting objectives for environmental and health safety and for recyclability. For films used in the construction industry, they must also offer durability (ranging from few years up to 15 years), high flow processing (thin film extrusion) and not reduce material performance characteristics (elongation at break). He presented developments in PIN FRs polypropylene and polyethylene films, for applications such as protective weather wraps for vehicles, protective films for construction sites, artificial grass, offering light stability and pigment compatibility, low processing corrosivity and no processing odour, recyclability and effective fire performance achieved by both runaway effect in condensed phase and release of a non-halogen radical scavenger in the gas phase.

High performance PIN FR masterbatches

Mark Hannah, Gabriel-Chemie, *underlines the need for stringent fire safety regulation or specifications to move the market. High fire performance masterbatches are today available, but at a cost. A good example is the sports stadium seating market, where stringent FIFA standards for fire safety of seats and installations mean that we can successfully offer state-of the art flame retardant solutions. At both the European Championships 2016 in France and the World Cup in 2018 in Russia the majority of the stadiums are equipped with FR, colour and UV protection combination masterbatch manufactured by Gabriel-Chemie. We have developed an extensive range of halogen-free flame retardants and see increased demand for these applications. End-user education is needed, so that consumers understand the environmental impacts of their purchases.*

Gabriel-Chemie, founded in 1950, offers a full range of masterbatches for plastics, including both colours and functional additives such as fillers, anti-flame, antistatic, processing and performance additives and laser marking. The family managed company has today around 550 employees, operations in ten countries in Europe, Russia and customers worldwide. http://www.gabriel-chemie.com

Inorganic flame retardant developments

Maryline Desseix, Polyone (pinfa member), presented development and testing of innovative solutions to combine PIN flame retardant performance in polymers with sustainability. Inorganic PIN FRs, such as ATH (aluminium trihydrate) and MDH (magnesium hydroxide) offer positive health and environment profiles, and are water soluble, which ensures that they are not bioaccumulative. However, these properties are also problematic for use as flame retardants, because water uptake impacts polymers' mechanical and electrical properties. Polyone tested surface treatment of ATH and MDH using different vinyl, silane, phenyl and siloxanes, then combinations of ageing, water contact and compounding in polyethylene/EVA polymer. Results showed potential advantages and significant variations between different solutions. The possible role of compatibilisers between the inorganic PIN FR and the surface coating merits investigation.

Klaus Rathberger, George H. Luh, presented applications of expandable graphite as a PIN flame retardant. See also AMI FR conference 2016 in pinfa Newsletter n° 61. Expandable graphite can be an effective flame retardant at 15-20% loading, either blended into polymers or applied as a surface coating, as well as being used in fire-protective coatings for structures, on textiles, on roof covering bitumens, in foams or in fire seals. Different grades offer expansion of 50x – 350x for different applications. Applications today include polyurethane foams in aircraft seats, polyurethane and polystyrene building insulation foams, automobile interior linings, special graphites for conductive applications. An issue is that some low quality expandable graphites on the market contain significant levels of chromium as an oxidising agent.

Fouad Laoutid, Materia Nova (Belgium), presented tests on calcium hydroxides (hydrated limes and hydrated dolomite limes) as flame retardants for polyethylene and EVA polymers, in combination with other inorganic PIN FRs (ATH and MDH). All of these inorganic compounds offer positive environment and health profiles. The calcium hydroxides are readily available, as they are today produced and widely used in both agriculture (soil liming to correct pH) and industry (glass, chemicals, flue gas treatment …). Calcium hydroxides release water at a higher temperature than ATH and MDH, so extending the temperature range of fire protection, and also contribute to increase char cohesion (by generation of calcium carbonate mineral char). Combination with zinc borate further reduced peak heat release and improved char cohesion.

However, calcium hydroxide is water soluble, so cannot be used as such as a flame retardant. In contrast, hydrated or partially hydrated dolimes ($Ca(OH)_2.Mg(OH)_2$ or $Ca(OH)_2.Mg(OH)_2.MgO$) are not water soluble. Using these calco-magnesian compounds was shown to reduce pHRR during cone calorimeter test and to generate a cohesive mineral residue during the combustion.

Sophie Duquesne, ENSCL (Ecole Nationale Supérieure de Chimie de Lille), presented applied research projects into PIN flame retardant applications. Development and testing of a lightweight carpet for aviation showed the complexity of smoke density and smoke toxicity, depending on the different elements of the carpet (pile, weft, warp, backing, backcoating) and on whether these are tested separately or together. In another project, phosphorus, silicon and nitrogen based compounds and sodium hydroxide were used to treat flax-PLA (polylactic acid) composites. In a third project, a silicone surface plasma treatment was tested to improve performance of high temperature resistant textiles.

tesa performance adhesives

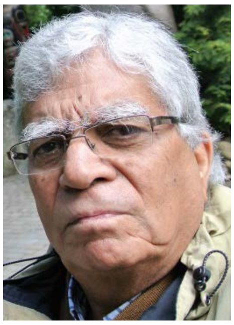
Cai Rong Lim, tesa, *is developing new performance adhesive solutions for industrial and professional customers as well as end consumers. Applications are developed for industrial sectors such as automotive, electronics, printing and paper, and building supplies. For effective brand and product protection, security labels are also part of tesa's assortment. Besides fixation, tesa is also developing novel solutions to meet new application requirements including chemical resistance, shock resistance, adhesion to demanding substrates as well as fire performance. Fire performance requirements include flame resistance and smoke emission, which must be demonstrated by various tests often with specific relevant material. It is important that the flame retardants do not impact key adhesive properties.*

tesa is one of the world's leading manufacturers of technical adhesive tapes and self-adhesive system solutions for industrial and professional customers as well as end consumers, with over 4 100 employees. Since 2001, tesa SE is a wholly owned affiliate of Beiersdorf AG (whose products include NIVEA, Eucerin, and la prairie). www.tesa.com

PIN synergists to improve PIN FR performance

Kathrin Lehmann, Evonik, summarised the advantages of organomodified siloxanes (OMS) as functional PIN synergists. Inclusion of specific functional groups onto the ends or sides or siloxane molecular chains enables either full polymer compatibility, or to ensure that part of the OMS molecule embeds in the polymer whilst part remains outside giving interface properties. OMS can thus improve melt flow behaviour, surface appearance or electrical performance of PIN FR polymer compounds and reduce "die drool" in cable extrusion. For example, 1% of specific OMS with inorganic FRs can enable to combine UL94-V0 with melt flow and CTI specifications in polyamides / glass fibre polyamides, TPO/polyethylene or polypropylene. This addresses applications such as thin wall electronics parts or performance cables.

Swaraj Paul, Paxymer, presented the company's development of PIN FR synergists based on carboxylic functional polymers and acrylate copolymers, which can be used with phosphorus, inorganic or nitrogen flame retardant systems. This enables PIN FR systems in polymers such as polyolefins which do not drip and release no toxic gases in fire [toxicity as tested by pyrolysis (pyr)/ gas chromatography (GC)/ mass spectroscopy (MS]. These systems function for example generation of a fire-protecting carbonaceous char, the stability of which is increased by generation of phosphorus oxynitride, and by release of phosphoramidic acid, a gas phase radical scavenger.



Bansi Kaul, MCA Technologies, presented his company's PPMT (poly(piperazinyl,morpholinyl)triazines) PIN FR synergists (see previous AMI conferences in pinfa Newsletter n°s 80, 76, 61). In addition to combining PPMT with calcium carbonate and ultracarb (a natural magnesium mineral), previously presented, he showed tests of PPMT in EVA (ethylene vinyl acetate) or HDPE (polyethylene) polymers with PIN FRs and synergists including: kaolin (a natural aluminium silicate clay), piperazine pyrophosphate, APP (aluminium polyphosphate) and siloxane-coated APP, zinc borate, ATH (aluminium trihydrate), MDH (magnesium hydroxide), montmorillonite clay and stearic acid (for intumescence and dispersion). The mechanism of PPMT is presented as the rapid production of resistant intumescent char (reduced shrinking and cracking) due to formation of oxynitrides, which ceramify char structure and increase heat dispersion.

De-Yi Wang, IMDEA Materials Institute, Madrid, Spain presented research into new functionalized nano-materials as PIN flame retardants (layered double hydroxides, nano-clays, nano-carbons, nano silicates, etc.) as well as composites combining e.g. minerals (such as iron or aluminium) into nano-materials, or use of nano-materials as interfacial catalysts for ammonium polyphosphate (nano silicates on the surface of APP). These combinations showed better fire performance in epoxies, EVA, PS, PLA etc. than non-functionalised nano-materials or flame retardants without nano synergists. In addition, a new flame retardant mechanism has been proposed.

Circular economy

Elke Metzsch-Zilligen, Fraunhofer LBF, presented initial results of the pinfa – Fraunhofer LBF testing of recyclability of PIN flame retarded polymers, by multiple extrusion and ageing. Tests with polypropyleneand PIN FR piperazine pyrophosphate showed recyclability and conservation of fire performance and some mechanical properties for extrusion at 200°C. There was some loss of mechanical performance (elongation at break), significant loss of antioxidants, and loss of fire performance with extrusion at higher temperature (230°C). For polyamides (PA6 with melamine cyanurate PIN FR and glass fibre reinforced PA66 with aluminium diethylphosphinate PIN FR), fire retardancy was also conserved during recycling. There was again some loss of elongation at break, but this loss was lower than with the same recycling of the neat polymer (without PIN FR). Other tests are underway on cables (PE/EVA, LLDPE) and films (PP).

Ecodek wood-polymer composites

Luis Enriquez, Ecodek (Epwin Group), *develops wood-polymer composite materials for exterior applications such as fencing and decking. Fire resistance is not generally required today for such applications, but may be required where they are used on balconies or near to buildings, particularly as external thermal insulation is increasingly present. Fire performance of wood-polymer materials is currently being discussed in CEN 15534. Ecodek wishes to be ahead of developments with solutions for PIN fire safety treatment of its products. Ecodek is also today working on use of recycled materials, e.g. in Horizon 2020 projects SMART-Plant (fibres from sewage), GelClad (building insulation extruded aerogel from recycled polymers) and FISSAC (circular economy in the construction industry).*

Ecodek has been based in Wales, UK, since the beginning, back in 2002, and has produced over 2200 km of wood-polymer composite decking. Ecodek decking has achieved BS EN ISO 9239-1 and BS EN ISO 11925-2 2010 fire performance and BS EN ISO 9239-1 smoke emission standards. Ecodek has a proactive sustainability policy including independently verified carbon-negative production, use of recycled HDPE polymer, zero landfill objectives and work with local wildlife and landscape organisations. http://ecodek.co.uk/

Armacell PET structural foams

***Christoph Justen, Armacell**, provides rigid PET foams for applications requiring demanding mechanical properties and light weight, such as wind turbine blades and structural elements in transport applications. Armacell is producing such technical materials from post-consumer plastics waste (recovered PET bottles). PIN flame retardants provide solutions to achieve demanding fire performance and low smoke toxicity, for example to achieve EU railway requirements (EN45545, DIN 5510 or NF F 16-101). Customers are increasingly requiring testing of the foam itself, not only in the finished product (where the foam is behind protective cladding), so the performance of stand-alone product has to be increasingly improved. Therefore, challenges include identifying PIN synergists to further improve fire performance and reduce smoke emission.*

As the inventors of flexible foam for equipment insulation and a leading provider of engineered foams, Armacell develops innovative and safe thermal, acoustic and mechanical solutions that create sustainable value for its customers. Armacell is a global company: 3,000 employees, 25 production plants, 16 countries, four continents. Armacell´s products contribute to global energy efficiency making a difference around the world every day. The Advanced Insulation business focuses on insulation materials for technical equipment. The Engineered Foams business develops high-performance foams that are used in high-tech and lightweight applications. See www.armacell.com and http://www.armacell-core-foams.com

Thermal insulation

BASF polyurethane insulation

***Arne Klinkebiel, BASF** (pinfa member), specialises in polyurethane insulation, and underlines the importance of finding new PIN flame retardant solutions. Challenges include the need to respect demanding customer requirements on material and insulation performance and cost, in different polyurethanes all of which are specific, as well as meeting smoke toxicity specifications. To respond to this, BASF is looking at new flame retardants, combinations of FRs and synergists and modification of the polymer matrix itself to improve fire resistance. At the same time, insulation panel assemblies are becoming more complex, and can provide fire protection of the polymer, but the trend is towards testing of the polymer foam alone (not the assembly) in order to ensure the highest level of fire safety.*

With over 50 years of experience, BASF is Europe's leading supplier of polyurethane basic products, polyurethane systems specialty elastomers. Applications include insulation, automobiles, shoes, furniture, electronics and the construction industry. http://www.polyurethanes.basf.de/pu/solutions/en/

Cables

Camillo Cardelli, iPOOL Materials Design, Italy, explained that cables in Europe today must undergo the EN 59399 vertical fire test for CPR (Construction Products Regulation), with demanding parameters for flame spread, non-dripping, smoke density, smoke corrosivity and smoke toxicity. He presented results of testing of a range of non-halogenated FR cable compounds (tested as tapes) in the "Mini SBI" (see SUSPI, pinfa Newsletter n°76), a non-regulatory, experimental set-up suitable to compare fire behaviour of different compounds and different raw materials. The formulations tested were based on polyethylene/EVA and POE (polyolefin elastomers) with stabilisers, hydrophobic and processing agents. Inorganic FRs tested were ATH, MDH, brucite, Böhmite, Calcium borate, and stearic acid or silane coated versions of these. Results showed many variations, but two possible conclusions were that all MDH containing recipes tends to give less flaming drips than does ATH (with collapse of char in fire), and that milled natural MDH gives good results comparable with fine synthetic MDH. Coatings applied on ATH or MDH could also positively or negatively affect the results of burning tests.

Thomas Fabian, Underwriters Laboratories, described different testing methods and possible correlations between results, noting the need for new testing methods to enable to rapidly fire test new materials under development and to ensure fire safety of new materials and new applications, for example in building and construction. He noted the difficulties of producing meaningful data on smoke emissions from testing, because smoke is mostly produced at the temperature of polymer degradation so emissions will depend on to what extent the material is near this temperature in the test. He also noted that when materials flow away from the heat source in testing this can result in a test pass despite a fire risk. Also, fire performance can deteriorate with ageing. He notes that today HFFR cables are available (non halogenated polymer, PIN FRs) which are "Plenum Rated by the Steiner Tunnel Test, that is the most demanding flame spread resistance rating.

Leoni cables for automobile

Werner Tecker, LEONI, *develops cables for performance applications, in particular automotive. Customer demand to move towards halogen free cable solutions in applications such as commercial buildings, domestic cables and automobile is challenged by cost restraints. Fire safety requirement in the car industry may become tighter. For example, at present, flame test requirements in the passenger compartment are lower than under the bonnet. Electric vehicles will also set new challenges: temperature resistance can maybe be lowered, but higher currents will pose safety issues in e.g. battery connection cables. High current loading combined with flexibility will favorise use of PIN additives such as silicones. New specifications will be needed for external charger cables (UV resistance, weathering). Increasing use of polyolefins in cable insulation will require new combinations of PIN flame retardants and synergists in order to meet fire performance, mechanical, water uptake and electrical requirements.*

LEONI: see pinfa Newsletter n°s 45, 74. LEONI, with over 80 000 employees in 30 countries worldwide, is one of the world's leading providers of wires, optical fibres, cables, cable systems, and related services to the automotive industry, electrical appliances and industrial applications. www.leoni.com

Prominvest low smoke, low toxicity cables

Dmitriy Lyashenko and Valery Moroz, Prominvest Cable Compounds, Ukraine*, noted that the market in both Russia and Europe is increasingly pushing for fire performance rated cables, in construction, transport and in specialised industries such as offshore and oil and gas. To combine this with mechanical and electrical requirements, and with cost constraints, new cable compounding solutions are being developed including new polymers, new flame retardants and PIN synergists. Challenges include flexibility at low temperatures, hydrocarbon resistance and low smoke toxicity, already today required in public buildings and in railway systems. Smoke opacity testing in Russia uses green light (coherent with emergency exit lighting) rather than red light in Europe. Prominvest is identifying opportunities to transfer to cable compounding innovative polymer / FR / synergist solutions developed in other applications.*

Prominvest is a leading producer of cables in the CIS (Eastern Europe and Russia) region, producing some 70 grades and formulations of cable compounds with capacity of 45,000 tons per year. http://prominvest.com.ua