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Upcoming events

- 25-26 April, Pittsburgh PA, USA , AMI Fire Retardants in Plastics 2017 http://www.amiplastics-na.com/events/Event.aspx?code=C809 addressing the American and international markets and supply chain, including a panel discussion on "Formulating with non-halogenated flame retardants"
- 26-28 Sept., Dearborn, MI, near Detroit, USA, pinfa NA 5th annual workshop: Fire Safety Requirements in Automotive Design. This workshop, co-organised with SAMPE (Society for the Advancement of Material and Process Engineering) will assess how trends in automobile design will impact flame retardant selections and will include car manufacturers and suppliers, regulatory and materials technologies experts. Info: Timothy.Reilly@clariant.com

For full events listing, see www.pinfa.eu

Life-span energy efficiency, product design and performance requirements all call for increasing use of polymers in buildings, transports and other applications. These materials are flammable, so fire risks must be addressed. Flame retardants are a key part of today and tomorrow’s toolbox of solutions to achieve this, alongside preventive design engineering, building regulations, smoke alarms, sprinklers and education. Consequently, global society’s need for flame retardants will continue to expand to respond to progressive tightening of fire safety regulations in many regions of the world. A number of recently published studies confirm that the global demand for flame retardants will continue to grow over the next five years. PIN FRs seem to be preferred, because of performance, regulation and demand for improved health and environment profiles. This is shown by several studies referenced below, and in particular the 6th Freedonia report on the world flame retardants industry and markets. This indicates a strong increasing demand for flame retardants in regions such as India and Eastern Europe, as well as a continuing but more moderate increase in China. The demand for flame retardants is linked to rising standards of living, which push societal demand for performance and quality products and for high levels of fire safety.
SP proposes fire classification hierarchy for furniture

In the editorial of Brandposten #55 (page 2), the magazine of RISE (Research Institutes of Sweden, previously SP), Björn Sunderström, highlights the current rise in concern about home fire deaths, pointing to actions or calls by the Swedish Civil Contingencies Agency (MSB) and the Federation of the European Union Fire Officer Associations (FEU). He reminds that similar calls in the 1990’s led to the major EU furniture fire testing programme CBUF (Combustion Behaviour of Upholstered Furniture) but suggests that legislation did not result “due to a strong lobbying element, the claims of which included assertions that fireproof furniture would require the use of hazardous flame-retardants”. Things seem not to have changed today, despite (pinfa suggests) the development of safer PIN flame retardant solutions. The SP article suggests that one option could be “a classification system, similar to that which exists for surface materials in buildings, that would allow more expensive, high-performance products to be selected for applications that truly require them, and products with lower fire safety requirements to be used in other, less demanding areas. The EU regulation on construction materials works perfectly well, and could easily be adapted for use in this field.” RISE is also working with FEU on an EU-funded project to consult industry, regulators and stakeholders and then propose fire safety testing methods for furniture (Brandposten #55, page 11).

“Domestic fires back in the spotlight” and “Focus on the risks presented by furniture fires”, SP Brandposten #55 2017

LCA of renewable polymer - PIN FR aircraft panels

A detailed LCA (life cycle assessment) compares forward-looking aircraft interior panels made of renewable or recyclable polymers, natural fibres, and PIN flame retardants, to conventional glass fibre reinforced polymer panels with halogenated flame retardants. The four non-conventional panels were based on geopolymer (kaolin + silicate), polymerised epoxidised linseed oil, polypropylene and polylactic acid (PLA), in each case reinforced with flax fibres. The flame retardants considered were decabromodiphenyl ether (DecaBDE) and or different combinations of PIN FRs for the different polymers: borax, organophosphorus compounds, ammonium polyphosphate, graphene, nanoclays, hetonite. The LCA considers materials used, panel manufacturing, transport, use in a Boeing aircraft, maintenance and end-of-life. The use phase accounted for 98% of environmental impact (aircraft fuel consumption and air emissions) and the lower weight of the non-conventional panels resulted in their showing overall much better environmental impact. The non-conventional panels also show significantly lower LCA combined factors for human health, ecosystem diversity and resource consumption. The authors note that these results do not take into account possible health impacts of end-of-life of the halogenated flame retardant.

Arkema performance PIN FR copolymer resins

Arkema’s HFFR (Halogen Free Flame Retardant) solutions for fire-resistant copolymers are based on ethylene – vinyl acetate or ethylene – acrylate copolymers, with selected mineral flame retardants (ATH or MDH) and coupling agents. These resins offer easy processing (fluidity), mechanical performance (ageing, softness, flexibility), chemical resistance, compatibility with other polymers, raw materials and fillers as well as printability, sealing and adhesion properties. High levels of fire performance and low smoke emission are achieved. The resins can be used for semi-conductive and strippable semi-conductive cable layers. Cross linking with peroxides, silane or e-beam enables high temperature resistance (e.g. for automotive T3 cables). Other applications include hot melts, adhesions, coatings, films and sheets, foams, solar panel encapsulation and cables.


Fire safety in wind turbines

Some 120 – 160 fire incidents occurred in wind electricity generating turbines in 2007-2012, and this can be expected to increase as more turbines are installed. A rate of around 1 fire per 2 000 turbines per year is estimated. Half the fires occur when there are people in the turbine nacelle, so that turbine fires imply risk to lives, loss of property and risk of wildfires (burning parts have been recorded falling from turbine fires). The highest cause of turbine fires is related to maintenance work, but fires are also caused by electrical failures, lightening strikes, hot surfaces. Combustible materials include the composites of the blades and structure, flammable liquids in the gear box and hydraulic system, lubricating oils and materials in mechanical parts and the electrical generator. Fire protection can include active systems (alarms, extinguishing systems) and passive systems (flame retardant materials, sections to prevent fire spread).


Millions of tumble driers pose fire risk

Over five million owners of clothes dryers sold in the UK under the brands Hotpoint, Creda, Swan, Proline and Indesit between 2004 and 2015 have now been told to stop using them, pending repairs. Previously, the manufacturer, Whirlpool, had asked owners to only use the machines when a person was in attendance. Fires have started in these tumble driers when fluff comes into contact with the heating element, including a fire in a tower block in London in 2015 which brought in 120 firefighters and left families homeless. The London Fire Brigade states that it attends a fire a day starting in electrical “white goods” and has been recommending users not to use the concerned tumble driers since the London fire. The London fire started in a machine awaiting repair and which was attended.

Electrical vehicle test shows batteries start fire

Two full scale fire tests of an electric vehicle show that the lithium-ion battery pack self-ignites after a simulated car crash, with the car in dense smoke after 2 minutes and engulfed in flames in less than 10 minutes. The cars used were a small Tata 4-door hatchback, rebuilt as electrical vehicles with a 12x30 cells, total 26 kWh, Nickel Manganese Cobalt Oxide cathode (NMC) Li-ion battery pack installed in a protective coating. In the first test the car was dropped from 20m height onto its rear, simulating a crash at c. 70 km/h. Smoke appeared from the battery immediately after the crash, with much dense smoke after 2 minutes. The battery started to burn after 6 minutes and the car was engulfed in flames after 9 minutes. In the second test, a small propane burner was placed under the car near the battery pack, and the car and battery caught fire after 10-12 minutes. After a first attempt to extinguish the fire after 14 minutes, using 100 litres of water, the car reignited. Some 550 litres of water were required to fully extinguish the car.

“Full scale EV fire test”, SP Sweden in collaboration with Skien Fire Department, Grenland Energy, University College of Southern Norway, A. Boe, SP Brandposten #55 2017

Keeping the Circular Economy clean

A 42-page paper by the European federation of environmental NGOs (EEB) with ClientEarth makes recommendations to improve integration of EU chemicals, product and waste legislation with the aim of facilitating the circular economy whilst ensuring health and environmental protection. The three key recommendations are to improve information of the supply chain concerning the presence of hazardous chemicals, to limit such chemicals entering the material cycle in the first place and to ensure that recycled products offer the same level of safety as virgin materials, in particular by decontamination in recycling. The paper summarises issues with chemicals, waste and product legislations (CLP, REACH, POPs, GPSD General Product Safety Directive, Toys, Food Package, RoHS, EcoDesign, Waste Framework Directive and End-of-Waste, WEEE. Two examples are assessed in detail: deconstruction and reuse of constituent parts of a mattress with DecaBDE in the ticking textile and HBCDD in the foam; recovery of materials from an LCD screen containing mercury.

“Keeping it clean: how to protect the circular economy from hazardous substances”, ClientEarth and EEB (European Environmental Bureau), cofunded by MAVA (Fondation pour la Nature) and the European Union, 42 pages, February 2017

Si-P-N FR for renewable polylactide polymer

Polylactide (or poly lactic acid PLA) is a biodegradable polymer which can be sourced from agricultural by-products, see pinfa Newsletter n°50. However, a challenge for PLA use in many applications is to ensure fire safety, because the polymer is highly flammable and poses important melt dripping challenges. In this study, a cross-linked silicone-containing macromolecule (CSI-MCA), synthesised in a one-step reaction, was tested with ammonium polyphosphate (APP). APP is a Pin flame retardant recognised to offer high levels of health and environmental safety (see e.g. pinfa Newsletter n°74). A loading of 5% w/w CSI-MCA and 10% w/w APP in polylactic acid showed production of a compact and continuous protective char layer during
combustion, with peak heat release rate reduced by more than 50% compared to straight PLA, and achieved UL94-V0 at 3mm.

“One-pot” synthesis of crosslinked silicone containing macromolecular charring agent and its synergistic flame retardant poly(L-lactic acid) with ammonium polyphosphate*, Y. Guan et al., Polymers Advanced Technology 2017 http://dx.doi.org/10.1002/pat.4017

Macromolecular PIN FR for bio-sourced polylactide

In another study addressing on polylactide (PLA), a macromolecular nitrogen – phosphorus PIN flame retardant was synthesised in a 2-phase, single vessel reaction from THEIC (tris (2-hydroxyethyl) isocyanurate), polyphosphoric acid and melamine. THEIC is stated to be a non-toxic triazine derivative for which no corrosive gas or toxic by-products are released during production. The resulting product (tris(2-hydroxyethyl) isocyanurate polyphosphate melamine - TPM) was tested in combination with APP (ammonium polyphosphate) as a PIN flame retardant solution for polylactide (PLA). At 25% loading of APP-TPM (1/3 APP, 2/3 TPM) fire performance of PLA was significantly improved: LOI increased from 20% to 37%, peak heat release rate (pHRR) reduced by 2/3 and UL94-V0 (3mm thickness) was achieved without melt dripping. Analysis shows improved thermal stability of PLA with the PIN flame retardant addition and that fire resistance is probably resulting from the generation of a resistant intumescent char layer with combined carbon and phosphorus compounds.


Montmorillonite clay PIN FR synergists

BYK, pinfa member company and chemicals producer since 1873, offers clays, processed from natural mined montmorillonite (aluminium silicate) clays, as performance mineral synergists to PIN flame retardants. In fire cables, the clay acts in synergy with mineral flame retardants such as MDH (magnesium di hydroxide) or ATH (aluminium tri hydrate) generates highly stable char, reducing the total filler loading needed: for example from 65% filler to 55% plus 3% clay to achieve UL94-V0. This improves both processing and material properties. The products are compatible with the reduced smoke, low smoke toxicity offered by mineral PIN FRs. Since 2016, BYK offers also concentrates, both combinations of PIN FRs and masterbatches of PIN FR package with polymer. BYK sees the cables market as continuing to expand demand for PIN FR solutions, because of fire safety requirements and the replacements of PVC by low smoke emission and low smoke toxicity materials. New applications for montmorillonite mineral PIN FR synergists are also anticipated in construction and engineering polymers, with a continuing trend to combine different PIN FRs and synergists to offer optimal fire and material performance.

EMS-GRIVORY flame retardant bio-based PPA

EMS-GRIVORY, High Performance Polymer business unit of the EMS-Group, operates worldwide with production sites in Europe, Asia and the USA. Grivory HT XE 4027 is a bio-based polyphthalamide compound, adapted specifically for processing by injection moulding, which enables parts to maintain their structure and shape even at very high temperatures. This is one of the EMS-GRIVORY polyamides in the GreenLine range based on renewable raw materials. Grivory HT XE 4027 provides low moisture absorption, high dimensional stability, chemical and hydrolysis resistance, good surface quality, stiffness and strength and achieves UL94 V0 rating for thin wall thicknesses using a PIN flame retardant. Grivory HT XE 4027 is especially suitable for injection molded components in electrical and electronic applications which require a flame classification of UL 94 V0. The material is suitable for lead-free SMT reflow soldering according to the standard JEDEC J-STD-020C (peak temperature 260°C). Components conforming to JEDEC MSL1 are also possible.


VELOX expands range of performance PIN FRs

VELOX, a European leader in raw material specialities for the polymer and coatings industries, has extended its range of low-density phosphorus-based PIN flame retardants. The range of P-based PIN products offers environmentally sustainable fire safety solutions for polyamides, EVA, PWC, latex and rubbers, epoxy, polypropylene and polyolefins. The new phosphorus flame retardant for polyolefins, based on a mixture of phosphorus salts with different condensation and valence number, achieves high fire performance (UL94-V0 at 3,2 – 1,6 mm in different polyolefins), low smoke emission as measured by NBS smoke chamber. The product also offers high resistance to humidity, good compatibility with glass fibres, ageing resistance, low tinting, thermal stability, easy dosing and processing. It is delivered as a white, colourable powder and its high phosphorus content ensures effectiveness at low loadings.


Yellow Card for PIN FR TPE compounds

Hexpol TPE, the global ThermoPlastic Elastomer compounding specialist, has obtained the UL (Underwriters Laboratory) Yellow Card certification for all colours of the UV FLAM TPE 60600 range (UL94-V0 3mm). The company considers that these TPE compounds provide alternative, non halogenated formulations, with mechanical and fire safety performance. The compounds have hardness 30 – 90 Shore A, good adhesion to thermoplastics (such as polypropylene, polyethylene) for overmoulding or co-extrusion, and can be offered with various colours, antistatic or electrical conductivity. Applications include electrical connectors and insulation, wall sockets, gaskets. The Lifoflex FLAM 700 series offers further improved fire safety performance, including DIN 5510-2-2009-05 for railway systems with flammability S2, drip formation ST2 and smoke formation SR2 and FED classification 0.14 (compared to maximum permissible 1) under DIN EN ISO 5659-2 for fume toxicity.

**‘Low smoke halogen free’ certified cable**

Hitachi Cable America (Hitachi Metals group) has obtained UL (Underwriters Laboratories) certification as ‘Low smoke halogen free’ (LSHF) for its NanoCore® optical cables, that is UL 2885 (based on IEC 62821-1, 2, 3). This UL standard covers both the complete cable and all components used in it, and enables third-party certification of producer claims, user and installer confidence, and installation conform to the US national electrical code. The NanoCore® cables are available multi-unit, dual jacket, as interconnectors and armoured, and are adapted to interior uses in walls, floors, plenum ducts, etc, where fire resistance is important to avoid spread of fire from one room to another and ensure continuity of communications and safety signalling. The PIN FR jacketing ensures resistance to stress during building works and installation and reliable and safe use over time.


**PIN flame retardancy integrated in DGEBA epoxy resin**

Reaction of PIN flame retardants into polymers avoids risk of migration of the FR out of the product into the environment, enables an optimal distribution of the PIN FR throughout the polymer, can avoid polymer mechanical performance deterioration and has also been show for some phosphorus PIN FRs to improve the fire protection performance. Tributyl(ethyl)phosphonium diethylphosphate (IL169), an ionic phosphorus-containing liquid, was shown to initiate anionic polymerisation and react into the resin of DGEBA (bisphenol-A-diglycidyl) epoxy resin, a polymer used in aircraft engineering applications. Resins were tested with 10 to 30% IL169 (1.5 – 3.7% phosphorus) showed no deterioration of resin thermal stability whilst significantly improving fire performance: peak heat release rate was reduced by nearly 75% and total heat release by c. 50%. Residue after burning was considerable (40% of initial weight) corresponding to formation of a fire-protecting layer of expanded char. The phosphorus content showed to also have a significant gas phase flame retardancy effect.

Sweden tax on chemicals in E&E products in force

The Sweden tax on chemicals in certain electrical and electronic goods (Finances Ministry Act 2016:1067) enters into force on 1st April and is applicable from 1st July 2017. This is despite significant opposition from numerous stakeholders. For example, TCO, the international sustainability certification organisation for information technology products, criticised the tax (pinfa Newsletters 66 and 72) stating that “by also including all phosphate-based flame retardants, the current proposal does not achieve its desired goal. We believe the current proposal raises the risk that industry will not bother to substitute halogenated substances with safer alternative”. The tax will impact kitchen appliances (refrigerators, washing machines …), computers, telephones, etc. sold in Sweden, at SEK8 (around 1€) per kilogramme for kitchen appliances and 120SEK (c. 14€) for electronics (up to maximum 320SEK). The tax is reduced 50% for products which do not contain additive flame retardants using bromine, chlorine or phosphorus, and is reduced 75% for products which contain neither these additive FRs nor reactive halogen FRs.

http://www.riksdagen.se/sv/dokumentlagar/dokument/svenskforfattningsamling/lag20161067omskattpakemikalieriviss_sfs20161067
and TCO “Chemical tax on products misses the mark”, N. Rydell, June 2015 “Proposed chemical tax on electronics misses environmental target”
TCO 23 Sept. 2016

Phosphorus and inorganic fireproof paper

A research paper presents an experimentally developed phosphorus and inorganic based non-combustible nano-composite paper, using glass fibres (GF) coated with networked hydroxyapatite (calcium phosphate) ultra-long nano-fibres (HS-HANWs), generating a three-dimensional weave similar to cellulose paper structure. The HS-HANW/GF paper offers smooth finish, high mechanical (tensile) strength, bio-compatibility (hydroxyapatite is the structure of bones), stability up to 1000°C and good thermal insulation. Experiments demonstrated the effectiveness of the HS-HANW/GF paper as a refractory protection for optical fibre cables. Possible other applications, if the product can be industrialised, could include non-flammable printing papers, fire-retardant wallpaper and biomedical applications.


UN shows business advantages of safer chemicals

A report published by UNEP (United Nations Environment Programme) demonstrates the business advantages of pro-active positions on safer chemicals. Companies with active safer chemicals strategies reduce risk to problem chemical ‘surprises’ of hidden liability, and generate long-term value through increased sales, brand reputation and better supply-chain management. A positive example of chemical disclosure is presented as Seagate disk drives, in which the PIN flame retardant DOPO is listed.

PIN FRs for performance sandwich panels

Composite sandwich panels are increasingly used in transport (aviation, railways, shipping) and other high specification applications (e.g. bridges, offshore, wind turbines) because they offer low weight, mechanical and structural properties, fatigue and corrosion resistance. Fire performance must be ensured, including maintaining resistance to compression forces during fire. In this study, performance of panels using PVC core (low price benchmark), polyisocyanurate (PI) foam with glass fibre (stitching together the two panel skins) and balsa wood was tested at bench scale, with and without PIN flame retardant in the foam, applied to covering fabrics and on the panel surface. Intumescence from PIN FRs crucially increased the time to structural failure. Both PI foam and balsa offered significantly better time to failure than PVC foam. Balsa was better without flame retardant, but the best of all performance was using PI foam with PIN FR in the foam (better than balsa, where FRs could only be applied on the surface materials).

http://dx.doi.org/10.1016/j.compstruct.2016.11.027

Growing flame retardant market will benefit PIN FRs

The 6th edition of Freedonia’s “Global Flame Retardants Market” report estimates that the flame retardant market will continue to grow through to 2020, with slower growth in China offset by demand in India, Brazil and Eastern Europe. Rising standards of living will lead to improvements in product quality, e.g. for vehicles, resulting in demand for high-performance materials which include flame retardants. Other trends driving demand for FRs identified are the increasing use of plastics, stricter building safety standards, whereas wireless connectivity (replacing cables and desktop computers) will reduce demand. Phosphorus-based FRs will show the highest growth as PIN FRs replace phased out FRs. World FR use in construction will increase 3.2% per year through to 2020, to reach over 800 000 tonnes. Other major sectors covered in the Freedonia study are wires and cables, electronics, motor vehicles, textiles, furnishings, aircraft, marine and railway applications.


World flame retardant market to double by 2025

A report by GrandView Research suggests that the world flame retardant market will nearly double from 6.3 billion US$ in 2015 to around 12 billion US$ by 2025. Increasingly, FRs will be needed to fulfil fire safety regulations in construction, electrical and electronics and transportation. PIN FRs are expected to dominate the market as regulations phase out other products. Similar estimates are given by Zion Research, which estimates that the global FR market will increase at 10% per year from 2014 to 2020, reaching US$ 10 billion in 2020. Zion consider that growth will be driven by technological progress in fire safety solutions and by increasingly demanding fire safety regulation in construction and in automobiles, combined with an increasing use of plastics which are flammable and therefore need fire safety protection. Zion predict “toxicity issues related to halogenated flame retardants” to push towards higher value PIN solutions. Global Market Insights publish an estimate of the PIN flame
retardant market at US$ 3.45 billion by 2014, identifying as principal drivers environmental pressures to move to PIN FRs and increasing use of polymers in construction and automobiles. Technavio predict a 6% growth in the world FR market 2016-2020, with strong demand for PIN flame retardants particularly driven by emerging industries, enhanced safety requirements and regulatory requirements for less toxic chemicals.

“Flame Retardant Market Analysis By Product (Halogenated (Brominated, Antimony Trioxide), Non Halogenated (Aluminum Hydroxide, Magnesium Phosphorous))”, By Application, By End-Use and Segment Forecasts, 2014 - 2025”, GrandView Research


“Non Halogenated Flame Retardants Market Analysis By Product (Aluminum Hydroxide, Phosphorous Based), By Application (Polyolefins, Epoxy Resin, UPE, PVC, ETP, Rubber, Styrenics), By End Use Industry (Construction, Electrical, Transportation), Industry Analysis Report, Regional Outlook (U.S., Canada, Germany, UK, France, Italy, China, India, Japan, Australia, South Korea, Indonesia, Malaysia, Thailand, Brazil, Saudi Arabia, UAE), Application Potential, Price Trend, Competitive Market Share & Forecast, 2016 – 2024” Global Market Insights, August 2016


Other News

Declaration for an ambitious EU industrial strategy: cefic (the European Chemical Industry Council) has published a declaration, co-signed with ninety industry federations, asking the European Commission to confirm its commitment to reaching 20% of GDP from industry and to adopt and implement an action plan to achieve this. This will mean reversing the current decline in EU manufacturing which fell from nearly 19% to just over 15% 2000-2014, with a loss of nearly 4 million jobs.


EU restrictions on DecaBDE published: The European Commission has published an amendment of the REACH Regulation, restricting the use of bis(pentabromophenyl)ether (DecaBDE) following the EU Risk Assessment Committee opinion. The new Regulation states that DecaBDE “shall not be
Researchers find TDCIPP metabolites: An assessment of 14 US studies (total 741 persons) detected metabolites two flame retardants used to substitute brominated FRs (TDCIPP also referred to as TDCP, a chlorinated organophosphorus FR, and TPHP also referred to as TPP, a non-halogenated organophosphorus FR) in over 90% of samples. Concentrations suggested increases from 2002 to 2015, particularly for TDCIPP metabolite, but with wide variations and very low concentrations (around 1 part per billion). The authors conclude that research is needed to determine whether exposure levels may have health effects.

TDCIPP = tris(1,3-dichloro-2-propyl) phosphate (or TDCP). TPHP = triphenyl phosphate (or TPP). “Temporal Trends in Exposure to Organophosphate Flame Retardants in the United States”, K. Hoffman et al., Environmental Science and Technology 2017 http://dx.doi.org/10.1021/acs.estlett.6b00475