pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 63 March 2016

Pinfa Twitter account launched @pinfa_eu

pinfa has launched its Twitter account @pinfa_eu. This will provide occasional professional information only: announcement of events or publications, regulatory developments, links to new information and news relevant to fire safety and flame retardants. We invite you to follow @pinfa_eu for concise, selected and up-to-date information links. pinfa invites you to inform us about your news, events, developments and new applications for PIN flame retardants and fire safety which pinfa can Tweet. Please also link @pinfa_eu to your company or organisation's Twitter account.

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Additives | flame retardants

Fighting fire on every front

Demand for flame retardants is growing fast but increasingly tough performance and environmental requirements present tough challenges for FR additive manufacturers. **Peter Mapleston** reports

Compounding World update on FR developments

'Compounding World' magazine published a 7 page special article, which includes visions of plastics industry experts on innovation challenges for polymer fire safety and flame retardants. The overview of flame retardant developments underlines the triple challenge of increasing market demand, tightening performance demands and environmental challenges. The global market for flame retardants is expected to grow at 5-10% yearly over the coming decade. Regulators are pushing for increasing fire safety, requiring products to resist ignition and to burn with lower heat release in order to delay 'flashover' and increase escape time for building occupants and reducing risks for fire fighters. At the same time, FRs must respond to environment and health requirements, including end-of-life requirements, and addressing impacts of smoke and soot on fire professionals. Interviews include Adeka, Huber Engineered Materials, Fraunhofer LBF, Nabaltec, NKAB Minerals, Polymer Dynamix, Paxymer, Thor, MPI Chemie, Daihachi Chemical, ICL, Chemtura and pinfa.

"Fighting fire on every front", Peter Mapleston, 7 pages, Compounding World, December 2015
http://content.yudu.com/A3y4ga/CWDec15/resources/17.htm

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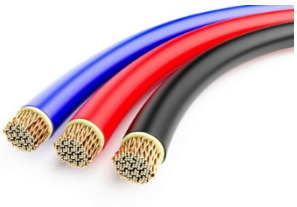
Milan Prato chemicals safety commitment

Twenty leading Italian fashion and textile companies from Milan's Prato district have together signed Greenpeace's 'Detox' commitment to eliminate "hazardous" chemicals, defined as meaning any chemical which is bio-accumulative and toxic (PBT), carcinogenic, mutagenic or toxic for reproduction (CMR), endocrine disruptive or has "properties of equivalent concern." The commitment specifies 11 families of chemicals considered as "*priority hazardous*". The joint supply chain commitment covers production of 4.5 million metres of fabric per year. Implementation will be undertaken by the regional industry federation, Confindustria Toscana Nord, which represents Europe's largest textile district. The federation stated that the commitment will "*further green a supply chain that proudly provides global brands with the highest standard in the textile industry*."

Greenpeace International press release 11/2/2016 "Italy's largest fashion supply chain pledges to Detox hazardous chemicals". Photo Andrea Guermani / Greenpeace.



Tolsa ADINS® clay synergists for PIN FRs

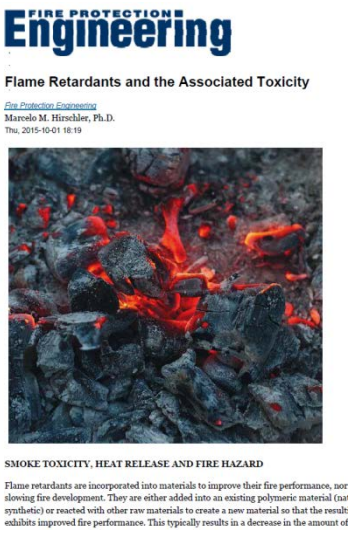
Tolsa Group, Madrid, a leading supplier of additives for wires, cables and electronics, has widened the polymer applications for its ADINS® fire safety synergists, to cover EVA/PE, PP, PA and expanded polystyrene foams. The products are based on natural silicates doped with phosphorus compounds (ADINS Fireproof) and sepiolite clays (ADINS Clay), modified with a range of specific compounds including ammonium salts and silanes, to offer different polarities and tailored performance benefits and polymer processing compatibility. They constitute an inorganic technology, which can help PIN flame retardant packages ensure fire performance and low smoke, low fire gas toxicity, whilst offering reduced environmental impact. They can act as synergists with mineral PIN flame retardants such as ATH (aluminium trihydrate) and MDH (magnesium hydroxide) and also support char formation and improve char mechanical properties, improving fire protection in non-halogenated flame retardant systems.

"Tolsa Group Announces Latest Technical Developments for ADINS® Flame Retardant Synergists at NPE 2015" 5/4/2015 and www.tolsa.com/adins

Phosphorylated lignin as biobased PIN FR for ABS

Lignin is an abundant natural biological polyphenol polymer, found e.g. in wood and plant fibres. A number of studies have shown that the lignin's aromatic chemical structure supports char development, including in polypropylene, polylactide, polybutylene succinate and epoxy. In this study, phosphorus was reacted into lignin (4.1 % P). ABS was tested with 30% pure lignin and with 30% phosphorylated lignin (P-lignin). The peak heat release rate (pHRR) of ABS was reduced respective 43% and 58%. With both pure and P-lignin, however, time to ignition was reduced by nearly 40%. The flame retardancy effect of P-lignin was shown to be mainly by char generation and partly by gaseous phase action, probably of phosphorus species. The authors suggest that increasing the P content of the P-lignin could further improve its effectiveness as a biobased flame retardant.

"Phosphorylation of lignin to flame retard acrylonitrile butadiene styrene (ABS)", B. Prieur et al., Polymer Degradation and Stability (2016) .doi: 10.1016/j.polymdegradstab.2016.01.015


Fire Protection Engineering

Flame Retardants and the Associated Toxicity

Fire Protection Engineering
Marcelo M. Hirschler, Ph.D.
Thu, 2015-10-01 18:19

SMOKE TOXICITY, HEAT RELEASE AND FIRE HAZARD

Flame retardants are incorporated into materials to improve their fire performance, nor slowing fire development. They are either added into an existing polymeric material (nat synthetic) or reacted with other raw materials to create a new material so that the result exhibits improved fire performance. This typically results in a decrease in the amount of

Flame retardants and associated toxicity

An article by materials fire safety expert Marcelo Hirschler in "Fire Protection Engineering" provides an overview of toxicity questions related to different flame retardants and to fire smoke and gases. As summarised in pinfa Newsletter n°54, Mr. Hirschler first argues that the key to reducing fire injuries and deaths is heat release rate (how fast a fire gets hotter). Inhalation of combustion products is cause of death for 2/3 of fire fatalities, and a study of more than 5 000 fatalities in the USA showed that this is principally related to carbon monoxide (CO) asphyxiation. CO emissions are linked to the quantities of materials burned, at around 0.2 g CO per g material consumed. Mr. Hirschler writes "*The overall smoke toxicity of materials containing flame retardants is not significantly different from that of materials that do not contain flame retardants.*" Although FRs inhibit combustion, the level of CO is around 20% of fire gases irrespective of the materials burning in large fires. All fire smokes also contain, at very low concentrations, different chemicals which are potential carcinogens, in particular PAH (polycyclic aromatic hydrocarbons) the most toxic of which is BAP (benzo[a]pyrene). The author considers that the exposure hazard to professionals (e.g. fire fighters) regularly confronted by these known carcinogens in smoke is extremely high compared to relatively minor contributions resulting from halogenated flame retardants. He concludes that flame retardants "*are an essential first line of defence in terms of passive fire protection … Published data overwhelmingly shows that flame retardants do not contribute significantly to either acute or chronic fire toxicity in real fires. While some flame retardants have been removed from the market in recent years, the vast majority in commercial use do not present significant toxicological concerns*."

"Flame retardants and the associated toxicity", M. Hirschler, Fire Protection Engineering, 2015-10-01 http://www.sfpe.org/?page=FPE_2015_Q4_2

New bio-based FR solutions for textiles

An overview from the Fashion and Apparel Technology department of CET, India, assesses the need for textile flame retardancy, and summarises natural bio-based FRs and solutions with positive environmental profiles. Both natural and synthetic fibres can burn easily, and synthetic fibres pose specific dangers by melting and causing burns. Textile fire performance is particularly important in applications such as furniture (to protect the foam or filling material from fire), transport and aircraft interiors, heat protective clothing and military applications. Developing new solutions for textile fire protection presented include nano FR application: nanoparticle adsorption onto fibres (minerals such as hydrotalcite, titania, silica, cloisite, octapropylammonium POSS, carbon nano tubes, alumina silicate), LbL (layer-by-layer) nano-coatings of fibres combining negatively and positively charged minerals or polymers and sol-gel nano application processes. Natural materials used in nano-FR application include mineral clays, chitin, kaolin, phytic acid. Plant extracts presented as natural textile fibre flame retardants include cyclodextrin (plant derived cyclic polymer), banana pseudostem sap (BSP); spinach juice, whey extracts (from dairy industry), hydrophobins (produced by lamentous fungi) and DNA. The flame retardancy effect of these natural molecules results from their reaction with the textile fibre surface or from their natural content of phosphorus, nitrogen and minerals.

"Green Flame Retardants for Textiles", A. Khandual, in Environmental Footprints and Eco-design of Products and Processes, Springer, 2016

Global flame retardant market to grow 5.9% per year

The world market for flame retardants is predicted to grow nearly 6% per year from 2015 to 2020, from US$ 7 to 10 billion, according to a new Market study by ResearchAndMarkets. Today, Asia has today nearly 50% of the world FR market, and is the fastest growing. The electronics and cables markets are expected to grow fastest, driven by rising demand for consumer electronics. The worldwide increase in the standard of living will increase demand for flame retardants, because fire safety requirements are linked with increases in standards of living. PIN flame retardants will benefit from market changes and regulation. In particular, inorganic FRs, including nanocomposites and expandable graphite, are expected to expand markets, because of positive health profiles and effectiveness for smoke suppression.

"Global Market for Flame Retardant Chemicals Segmented by Application, Composition and Geography (2015-2020)" *http://www.researchandmarkets.com/reports/3618564*

Match dropped on carpet causes fatal fire

One women died and her husband was injured in a fire in a 5th floor flat in the Ménilmontant area of central Paris, 22nd February 2016, after a match dropped on the floor whilst lighting a cigarette set fire to the carpet. The fire spread to the rest of the flat whilst one of the occupants went outside to alert neighbours. Firefighters were able prevent the fire spreading to other flats but one occupant died and another was injured. This shows how the protection of materials against small ignition sources such as a match flame can be vital for fire safety and to save lives.

http://www.leparisien.fr/paris-75/paris-un-incendie-fait-deux-blesses-dont-un-grave-a-menilmontant-22-02-2016-5568473.php

Fire safe kid's clothes at 1° Vision fashion show

In February, the leading British textile manufacturer, Heathcote Fabrics, launched a new range of flame retardant dress fabrics at the Première Vision Fabrics show in Paris in February, in response for demand for fire-safe children's dressing-up and play costumes. The Heathcote 1808 Flare-Free nets, tulles and costume fabrics are conform to EN71 part2, and offer better fire protection than the nightwear standard BS5722. A demonstration video shows a typical child's tutu going up in fire seconds after contact with a candle flame, whereas the Flare-Free fabric does not burn. Heathcote states "*There is a definite need for more stringent controls over flame spread. The Federation of British Retailers has proposed recommendations to modify EN71, but it would be good to see more stringent legislation specifically relating to apparel, similar to BS5722*."

Heathcoat Fabrics launches new flame retardant range at Première Vision Fabrics" 17/2/2016
http://www.innovationintextiles.com/heathcoat-fabrics-launches-new-flame-retardant-range-at-premire-vision-fabrics/#sthash.BVLuu8Ok.dpuf

Video https://www.youtube.com/watch?v=oeczfYk1K6U

Optical smoke detectors react too slowly

Tests for Norway's Civil Protection Directorate conclude that optical smoke alarms can take 2 – 3 hours to sound in case of smouldering fires, whereas during this time the carbon monoxide (CO) accumulation could be sufficient to prevent occupants from awakening. Norway legislation requires smoke alarms to be installed in all homes, and optical alarms are recommended. In a separate survey of 624 dwellings in Norway, 98% had a smoke alarm installed, and 90% of these were correctly operational.

"Kartlegging av gasskonsentrasjoner, effekt av dødluftsrom og effekt av alternativt deteksjonsprinsipp ved ulmebrann" (Measuring gas concentrations, effect of dead-air space and effect of alternative detection principles in the case of a smouldering fire) www.spfr.no

"Kartlegging av bruk av røykvarslere i boliger" (Mapping the use of smoke detectors in Norwegian dwellings) www.spfr.no

N-P-graphene FR for polylactic acid foam

Microcellular foams were produced using the bio-sourced polymer PLA (poly lactic acid) and UL94-V0 fire performance achieved using a nitrogen, phosphorus and graphene (nano carbon plate polymer) based PIN flame retardant system. PLA is a bio-sourced polymer with increasing applications, particularly in markets for "green" and biodegradable packing and films, but it is inherently highly flammable. Here, PLA microcellular foams were produced using 4 MPa pressure, CO2 and water bath foaming. The PIN flame retardant 100D (Starbetter, China), containing 21%N and 23%P was tested at 5 – 30% dosing in the PLA and graphene at 0.5 – 1.5%. Even at 5%, the PIN FR PLA foam achieved UL94 V-0 fire performance, with higher PIN FR loadings leading to increased foam expansion. The addition of graphene improved anti-dripping and reduced foaming, so resulting in more uniform foam cell structure

"Preparation of microcellular poly(lactic acid) composites foams with improved flame retardancy", K. Wang et al., Journal of Cellular Plastics, 2016, http://dx.doi.org/10.1177/0021955X16633644

PIN FRs for recycled insulation material

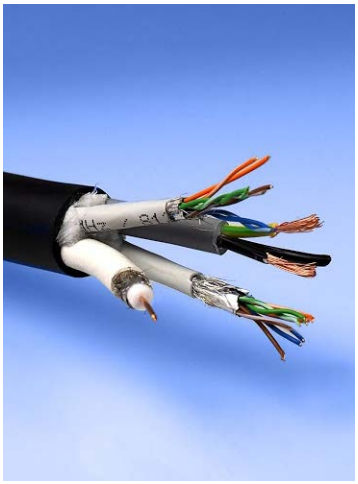
Interiorproject Ltd's PIN flame retardants are used to ensure fire safety of sustainable building thermal insulation material. The insulation material, made of recycled textiles and textile wastes, was developed by scientists working with Habitat for Humanity Bulgaria and Habitat Social Business Solutions Ltd to allow people of lower-income levels access to affordable energy-saving solutions. The product won the Grand Innovation Prize awarded by the Bulgarian Union of Inventors in November 2015. The insulation material achieves Class C fire performance under EN13823:2011 and has already been applied in a number of stand-alone houses, built by Habitat for Humanity Bulgaria for social housing purposes. Interiorproject's PIN FRs (see pinfa Newsletter n° 58) combine P (phosphoric acid), N (urea, triethanolamine, ammonia) and I (inorganic = silicon in polydimethylsiloxane) and can be applied to a range of porous materials including textiles, wood, leather, cellular and some foamed polymers.

Photo: volunteers install the thermal insulation prototypes in the attics of Habitat for Humanity Bulgaria`s houses http://www.interiorprotect.com/en/

PIN fire safety treatment for wood

Wood is a renewable sourced material for furniture and construction, but poses fire risks because "it is easily combustible, and when a fire occurs, the convection heat and radiant heat discharge decomposition gas over a long period". PIN fire safety treatments are widely used, and research continues to improve the low hazard, low smoke, low corrosive gases and heat resistance performance of PIN solutions. In this research, a combination of phosphorus and nitrogen PIN FRs based on piperazine, phosphonic and pyrophosphoric acids, were tested for fire retardancy on pine wood, using simple aqueous paint-on application. Time to peak heat release was more than doubled and effective heat of combustion reduced by nearly 20% for the optimal PIN FR combination tested.

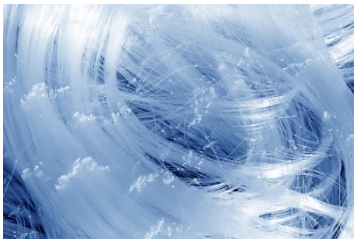
"Combustion characteristics of Pinus rigida specimens treated with 3 mixed phosphorus–nitrogen additives", E. Jin et al., Journal of Industrial and Engineering Chemistry, 2016 http://dx.doi.org/10.1016/j.jiec.2016.01.019



HELUEVENT flexible hybrid cable

HELUKABEL has launched the HELUEVENT HYBRID, an HFFR (halogen free flame retardant), bundled, hybrid cable combining sound, video and electrical components. The cable offers high flexibility, which is difficult to achieve in hybrid cables, and was developed for event control and mixing desks, cameras, studios, stage, building safety, surveillance or transport security cameras. The cable combines two data transmission cables, a JZ-500 control cable and a 75 Ohm 1.0/4.6 coaxial cable for video transmission. In addition to exceptional flexibility and PIN FR fire safety performance, which ensures low smoke, the cable is also weather and UV resistant for outdoor applications, and microbe resistant. HELUKABEL is a German-based, global provider of performance cable solutions with 24 locations worldwide. See also HELUKABEL's cleanroom PIN FR cables in pinfa Newsletter n° 51.

"New HELUEVENT Cable Bundles Video, Audio and Electrical Components", 8/2/2016 www.helukabel.de



Sulphur containing PIN FR for nylon

A polymeric phosphorus, nitrogen and sulphur containing PIN flame retardant was synthesised, based on polyphosphoric acid, an epoxy and thiourea, containing c. 2N:1P:1S. Using a water-soluble cross-linking compound, this PIN FR was applied to nylon fabric. Fire safety performance was compared to market-available P-based flame retardants for nylon. Fire resistance of the nylon fabric with the sulphur-containing FR (S-PIN FR), measured by LOI (Loss on Ignition) and length of charred fabric, was much better than untreated fabric, and was better, even after ten wash cycles, than with the market FRs. Results also show that the smoke density is significantly lower with the S-PIN FR than for untreated fabric, and that the emissions of various volatile carbon compounds were reduced (the S-PIN FR inhibited pyrolysis of the nylon fabric). Some sulphur containing PIN FR systems are already successful on the market, see e.g. Sony SORPLAS (recycled polycarbonate) in pinfa Newsletter n° 46.

"Synthesis and application of a sulfur-containing phosphoric amide flame retardant for nylon fabric", Y. Chen, Fie and Materials, 2016 http://dx.doi.org/10.1002/fam.2354

PFRs absent from most dust around new furniture

Dust collected from eleven student houses (Vasar Campus, New York), five furnished with old upholstered furniture (probably conform to TB117 fire safety standard) and six after replacement with new furniture conform to TB133, a more demanding fire safety requirement, following New York State regulations for fire safety in college accommodation. In dust around the old furniture, TDCIPP was found in 12 out of 20 samples, TCEP in just one sample and TPHP in 11 samples. Around the new furniture, TDCIPP and TCEP were not found in any of 29 samples, and TPHP was found in only 5 out of 29 samples. The conclusion is that the replacement of older furniture (by new flame retarded furniture) reduces TDCIPP and TCEP concentrations and may potentially reduce total phosphorus FR concentrations levels in dust.

"Organophosphate flame retardants in household dust before and after introduction of new furniture", A. Keimowitz et al., Chemosphere 148 (2016) 467-472
http://dx.doi.org/10.1016/j.chemosphere.2016.01.048

Upcoming pinfa events:

26-27 April	Montreal, Canada	►	pinfa-na industry seminar: flame retardancy of materials for surface transportation http://pinfa-na.org
15 June	Brussels	►	pinfa General Assembly

For complete, up to date events listing, see www.pinfa.eu

Call for papers:

Call for papers on **textile fire safety** for FLARETEX COST MP1105 final action and publication in MDPI Polymers Journal, themes: Novel Flame Retardants, Toxicological and environmental aspects, Processing and applications, Testing and standardization. Deadline 30/6/2016 COST.MP1105@UGent.be

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For abbreviations see: www.pinfa.org