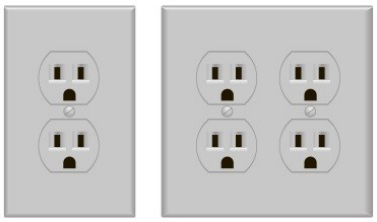
pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 73 December 2016

For events listing, see www.pinfa.eu

Innovation continues in development and commercial implementation of PIN fire safety solutions. This Newsletter presents new products and applications using PIN flame retardants to improve fire safety in cables such as optic fibres, power, fire safety alarm cables, in wood in buildings, automobile technical polymers, electronics resins, rubber, textiles. Innovation also continues towards environmental performance, with PIN FRs offering low smoke emissions, and new approaches to recycling including use of PIN FRs to ensure fire safety of recycled textile products or synthesis of PIN FRs from chemical industry by-products. This is recognised, as shown by the company examples below, in prizes (such as the TURA Toxic Use Reduction Act prize in the USA) and ecolabels (EPAT, LEEDS, Blue Angel, EU Flower, Nordic Swan).



Electrical faults lead to million $ property damage

NFPA (the US National Fire Protection Association) reports fires and in some cases the cause has been identified. Recent reports include an electrical failure in a power strip or plug, mounted on a timber beam, which led to major fire in a hangar at an airport in Washington, USA. Eight aircraft and several other vehicles were destroyed, with total damage estimated at over one million US$. The hangar did not have sprinkles. In another case, an electrical fault, leading to arcing in a ceiling void, led to over two million US$ damage in a multi-tenant commercial building in Maine, despite being detected by smoke alarms and despite sprinkler operation. Such cases show the importance of fire safety treatment of electrical installations (including power cords, in-wall plugs and sockets) and of surrounding materials (such as insulation or decorative materials) to reduce the likelihood that an electrical fault will lead to a fire.

NFPA Journal "Firewatch" September 2016

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Reducing fire risks from wood in buildings and furniture

Wood is an aesthetically pleasing, sustainable and widely used material in buildings (structure and finishings) and furniture, but is in all cases potentially flammable. When subject to heat the natural polymers in wood (cellulose, hemicellulose and lignin) decompose to volatile gases, tar (levoglucosan) and aromatic carbons. Fire safety protection of wood is therefore necessary to avoid ignition and prevent fires starting and spreading, reduce toxic smoke emissions and protect the structural properties of timber in construction. This complete overview of wood flammability behaviour summarises wood fire chemistry, testing methods and regulation and developments in wood fire retardant systems. All the flame retardants identified as solutions for sustainable wood fire safety are PIN, including combinations of phosphorus, nitrogen and silicon based compounds, metal salts, metal hydrates and carbonates, graphite / expandable graphite and bio-sourced materials such as whey proteins.

"Review: Flammability behaviour of wood and a review of the methods for its reduction", L. A. Lowden & T. R. Hull, Fire Science Reviews 2013, 2:4
http://www.firesciencereviews.com/content/2/1/4

Recycling industry phosphorus by-products to PIN FRs

Phosphene (PH_3) is a dangerous tail-gas, generated in significant quantities in certain phosphorus chemical industry processes. To avoid risk, it is converted to THPS (tetrakis (hydroxmethyl)phosphonium sulphate). China produces c. 50 000 t/y THPS, but only around one fifth is sold for industry applications, so that PIN flame retardant production from THPS enables phosphorus recycling. Two different P-containing amines were combined with THPS in a three step process to generate P-benzoxazine polymers (TBOz and BBOz). These show very high char formation capacity, and so interesting potential as phosphorus PIN FRs, with possible economic and environmental advantages because based on industrial by-products.

"Phosphorus-containing polymers from THPS. IV: Synthesis andproperties of phosphorus-containing polybenzoxazines as a greenroute for recycling toxic phosphine (PH3) tail gas", Z-W Tan et al., J. Hazardous Materials 2016 (in print)
http://dx.doi.org/10.1016/j.jhazmat.2016.10.021

Novel application of APP to jute/polypropylene blend

The phosphorus – nitrogen inorganic chemical APP (ammonium polyphosphate) was tested as a PIN flame retardant for jute / polypropylene (PP) 1:1 blend fibre nonwoven felt. APP and PP powder were spread on both sides of the felt then combined into it by hot pressing. This treatment showed better fire performance (LOI limiting oxygen index, HBR horizontal burning rate) than application of APP by soaking and sodium hydroxide treatment. The optimal fire performance was with 10% APP / zero PP added by surface treatment.

"The flame retardancy and mechanical properties of jute/polypropylene composites enhanced by ammonium polyphosphate/polypropylene powder", Y. Dou et al., J Applied Polymer Science 2016 http://dx.doi.org/10.1002/app.43889

US CSPC tests furniture fire barriers

TH US Consumer Product Safety Commission has published results of over 100 full-scale tests on mock-up upholstered chairs, comparing fire development with 5 different fire barrier materials (and no barrier) and different covering textiles. The test chairs used solid wood frames, non flame-retardent polyurethane foam and covering textiles of light cotton, heavier cotton (denim) or cotton – polyester blend (Jaquard), on top of polyester batting. The fire barrier textiles were based on glass fibre, silicon fibre, halogenated fibres and antimony. 60 of 84 chair fire tests with barrier materials ignited with an open flame (small butane flame) and only one of the five barrier materials (based on glass fibre) significantly prevented ignition (ignition in half the tests with this barrier). The peak heat release was significantly lower with barriers (15 – 50% lower) and time to peak heat release was increased by 10 to 16 minutes. A majority of chairs tested (13/20) showed to transition more rapidly (than chairs with no barrier) from smouldering to open flame with cigarette ignition, and CPSC notes that this is an issue requiring further assessment. CPSC concludes that fire barrier textiles show promise for preventing fires in upholstered furniture, or reducing fire intensity, but that more work is needed to find effective barriers for the wide range of furniture design geometry and different materials and coverings.

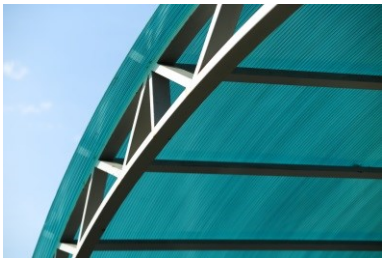
US CPSC "Memoranda on Full-Scale Upholstered Furniture Testing, 2014-2015", total 133 pages, A. Lock, April 2016 https://www.cpsc.gov/s3fs-public/FY14_Chair_Study_Memos.pdf

Alternative fire safety for upholstered furniture

A report by SP Sweden looks at options for fire safety in upholstered furniture other than use of flame retardants. The report starts by underlining that upholstered furniture does represent a fire risk because it is composed of large amounts of easily ignited and very combustible materials. Small scale foam/covering sample tests and furniture mock-up test (three small c. 30x30cm, 7.5 com thick cushions in a corner) were carried out for fire ignition and fire development, using cotton, wool, polyester, PVC, leather and blend fabric covering fabrics, polyester wadding, light or dense glass-fibre or aramid-fibre barrier and polyurethane cushion foam. Results were variable. For most covering materials, time to ignition was increased somewhat when barriers were used (but not for cotton/viscose blend). For most coverings, barriers reduced, peak heat release and total heat release were also reduced with the dense glass-fibre (80 g/m^2) and aramid barriers, but often not effectively with the light glass-fibre (25 g/m^2). Total smoke production was significantly reduced for nearly all barrier – covering combinations. The report concludes that light barriers may have a positive effect in combination with some textiles only, and that heavy barriers can reduce heat and smoke release in most cases, but that an case-by-case assessment of the barrier – covering fabric combination is always needed, and concludes that further research is needed into both barriers and design aspects to reduce furniture fire risks. This research should assess impacts on quality, comfort, cost and fire safety.

"Fire safe upholstered furniture. Alternative strategies to the use of chemical flame retardants", K. Storesund, SP Sweden, report A15 20124-2, 2015

"Fire safe upholstered furniture - alternatives to the use of chemical flame retardants", in SP Brandposten n°54 2016



Phosphorus – sulphur FRs for polycarbonate

Three different phosphonium sulphonates (PhSs) were synthesised and tested as PIN FRs for polycarbonate, a performance polymer widely used in a range of engineering plastics applications. The phosphonium sulphonates were tested at 5-10% loadings in polycarbonate, with in al cases 0.1% anti-dripping agent ETFE*. UL-94 V0 (3mm) was achieved for all three PhSs at 5% loading, with optimal increase in LOI (limiting oxygen index) at 10% loading (LOI 34 compared to 25 for non(FR polycarbonate). Investigations suggested that the PhSs acted both by char formation and by flame inhibition. The most effective of the three PhSs tested included an alkene group.

** ETFE = ethyl tetra fluoro ethylene. "Phosphonium sulfonates as flame retardants for polycarbonate", S. Hou et al., Polymer Degradation and Stability 130 (2016) 165e172 http://dx.doi.org/10.1016/j.polymdegradstab.2016.06.004*

PIN FRs enable Euroclass textile revalorisation

The French used cloth and clothes public collection points NGO "Le Relais", with CREPIM and Thor, has developed the Métisse® building insulation material made of shredded and processed mainly cotton textile waste, using clothes which cannot be re-used. The blowable insulation material offers high levels of both sound and heat insulation and is fire safety treated using AFLAMMIT® HML, inorganic phosphorous and nitrogen salts based PIN flame retardant. Euroclass C S_2d_0 fire safety performance is achieved (Construction Products Directive), enabling use of the product in thermal and sound insulation of public buildings. The PIN FR treatment also enables achievement of A+ classification in the French official material indoor air labelling system. The solid Métisse® eko baffle panels made of the same material offer acoustic sound-absorption for buildings such as meeting rooms, show halls, canteens, restaurants, public spaces. Waste textiles are today being diverted from incineration to production of these ecological insulation materials by Le Relais in France, Belgium and The Netherlands.

Le Relais http://www.lerelais.org/aussi.php?page=metisse

PIN FR ABS for automobiles

Shenzhen Jindaquan Technology and Hangzhou JLS Flame Retardants have launched a PIN flame retardant solution for ABS parts for automobiles, in cooperation with YULONG Automobiles. The new P24C PIN FR combines UL-94 V0 fire performance with impact strength. Shenzhen Jindaquan expects all ABS automobile parts to be required to be low halogen within several years, <1000 ppm or much lower. Hangzhou JLS develops and produces non-halogenated flame retardants and masterbatches including for intumescent coatings, polyolefins, epoxy resins, PBT, HIPS and PC/ABS

"Hangzhou G20 Summit might focus more on environmental protection of Cars", Jindaquan Technology Co Ltd news Hangzhou JLS Flame Retardants Chemical Co Ltd summary

Phosphorus, nitrogen and silicon FR action in cotton

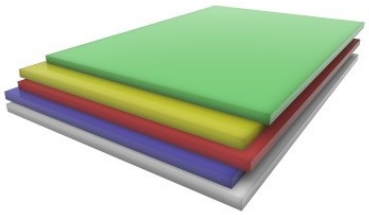
Cotton fabrics were modified to take up 1-4% phosphorus (P) plus 0-0.8% nitrogen by phosphorylation (application of phosphoric acid, urea, potassium hydroxide, sodium xylenesulphonate and heat treatment) and 0-1% silicon by a sol-gel process. These processes showed good durability (resistance to textile washing). Increased P content generally resulted in better fire performance. Si and N addition improved fire performance (LOI) for the same P content. Addition of only N did not do so at low P content. The authors suggest that urea (N source) acts by improving accessibility of hydroxyl groups in the cotton fibre and silicon by forming stable silicates in char. These PIN flame retardant treatments reduced smoke density very considerably (75% lower specific smoke density with 2% P).

"Synergistic effects in the pyrolysis of phosphorus-based flame retardants: the role of Si- and N-based compounds", S. Deh et al., Polymer Degradation and Stability 130 (2016) 155e164 http://dx.doi.org/10.1016/j.polymdegradstab.2016.06.009

SP Sweden looks into wind power fire safety

Wind power electricity generation is a growing source of renewable energy. Fire in turbines can disrupt production, destroy expensive equipment and be a safety issue. Yet to date, there has been little research in this area and there are currently no rules or recommendations concerning fire safety in wind turbine design. A new report from SP Sweden looks at wind generator fire safety, particularly in offshore wind farms, concluding that there is nearly no data, that fires can lead to considerable material damage, and that fire safety should be included early in the design phase. At a workshop on 20th September, Copenhagen, with Offshore Väste, work was launched to promote research and innovation into wind power fire safety.

"Fire safety in wind power stations an unexplored area", IFP International Fire Protection Magazine 13th September 2016. Further information: Anne.Dederichs@sp.se



De Grandi PIN FRs for rubber and plastics

Started in 1936 producing rubber products for shoe making, De Grandi S.r.l. (Vigevano, Italy) today produces non halogenated flame retardants for polyolefins, polyethylene, EVA and polypropylene. The DG-HF2000 product is a micronized powder, based on phosphorus and nitrogen and offers high solubility in polymer matrices, so producing a homogenous intumescent char and enabling fire performance (resistance to ignition and to flame propagation). The product achieves UL94 V-0, and reduced emission of toxic gases in case of fire (very low optical opacity, low corrosivity, negligible emissions of toxic gases). Advantages include ageing and UV resistance, colour stability, polymer property conservation, low compound density and relatively low flame retardant loadings.

"Halogen-free flame retardants", De Grandi http://www.degrandisrl.it/flamretatdanthalogenfree-eng.html

Why are fire deaths not decreasing in Sweden?

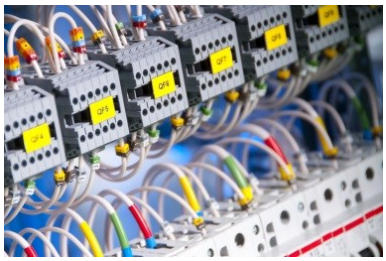
Arnoud 90 people die each year in fires in Sweden, and this number has not decreased over the last two decades despite information campaigns and an increase in home fire extinguishers and smoke alarms. A report by SP Sweden for the Swedish Civil Contingencies Agencies tries to assess why. Fire death rates are decreasing in most developed countries, according to CTIF (CTIF "World Fire Statistics" pinfa Newsletter n° 67), but improvements are particularly strong in Estonia, Germany, Latvia, Russia, the UK and the USA. Declines in the ex-Soviet countries are suggested to be probably due to social changes following the end of Communism here. The assessment concludes that the UK and the USA show increases in smoke alarms and sprinklers comparable to Sweden, and that their reductions in fire deaths are due to fire safety regulations for children's sleepwear and particularly for upholstered furniture.

"International Fire Death Rate Trends", D. Winberg, SP Sweden, SP Rapport 2016:32

ENVECO: economic and environmental impact of fires

The US – Sweden – UK project ENVECO is developing a tool to enable local fire services to assess the "prevented impacts" of interventions at fires. The toll will estimate the impacts which the fire would have had if firefighters had not prevented its development, including both environmental impacts (global warming, acidification, eutrophication, ozone depletion, smog, eco-toxicity and energy use) and economic impacts (property damage, job and business disruption, rent reduction). A prototype to date covering only warehouse fires is available for testing by local fire services. The objective is to develop this to cover other types of fire.

US Fire Protection Research Foundation (FPRF), SP Sweden, Worcester Polytechnic Institute USA "Instant impact. A new tool calculates the economic and environmental impact of fighting fires" NFPA Journal, Sept-Oct 2016 and "Development of an Environmental and Economic Assessment Tool (Enveco Tool) for Fire Events", FPRF, 27 May 2016



Phosphorus – nitrogen FR for polyethylene

Low density polyethylene (LDPE) is a widely used polymer in many fields, offering "low toxicity", electrical insulation, chemical resistance, mechanical performance and processing facility. However, used alone, it has "high flammability" and melt drips, so readily spreading fires. Here, a one-component intumescent PIN flame retardant (PA-APP) is proposed, based on phosphorus and nitrogen, obtained in a single step reaction between piperazine (a carbon – nitrogen organic ring) and ammonium phosphate –inorganic P-N compound). The PA-APP combines in one component the acid source, blowing agent and charring agent necessary for intumescent flame retardancy, with 7% carbon content. A loading of 30% PA-APP achieved UL94-V0 (3.2mm) but did not prevent dripping. Although this FR loading is quite high, it is better than total loadings of multiple-component intumescent FR systems. This loading of PA-APP significantly modified the polymers mechanical properties, and further work may be needed to address this.

"An Efficient Halogen-free Flame Retardant for Polyethylene: Piperazine modified Ammonium Polyphosphates with Different Structures", Liao et al., Chinese Journal of Polymer Science Vol. 34, No. 11, (2016), 1339−1353 http://dx.doi.org/0.1007/s10118-016-1855-8 See also PA-APP in polyethylene in Dong et al., pinfa Newsletter n°67.

Bavaria government information on fire toxicity

A document published by the Bavaria Environment Ministry provides information about toxic residues after fires for the attention of professionals or householders carrying out post-fire clean-up. Bavaria's fire services are called to 18 000 fires per year, with most occurring in homes. The document reminds that all fires emit toxic gases including carbon monoxide, nitrogen oxides, sulphur dioxide, hydrogen sulphide, ammonia, and halogenated compounds. Dangerous emissions can also come from asbestos, synthetic mineral fibres and wood protection chemicals. After the fire, a number of toxic compounds may be present in deposits and soot, and the document particularly cites: PCDD/F, PBDD/F, PCBs, PAC (polycyclic aromatic hydrocarbons). The document describes the type of cleaning and protection from toxins in soot which are appropriate after different scales of fire. For smaller fires, private individuals can carry out cleaning but should use protective clothing and take other measures to avoid contamination. For larger fires, or fires involving significant quantities of halogenated plastics, specialist cleaning companies should ensure decontamination.

"UmweltWissen – Schadstoffe bei Brandereignissen", Bayerisches Landesamt für Umwelt ("Environment information – dangerous substances following fires", Bavaria Environment Ministry), LfU ref. 12, updated Oct. 2014
http://www.lfu.bayern.de/umweltwissen/doc/uw_15_brandereignisse.pdf

Cuba bar fire, Paris – update

The pinfa Newsletter n°71 presented the tragic fire at the Cuba Bar, Paris, in which 14 young people died when non flame retardant interior sound insulation caught fire, ignited by candles on a birthday cake. The police statement after the fire indicating that this was polystyrene foam has now been corrected. The sound insulation foam in question is now reported to have been polyurethane, sold by a do-it-yourself retailer as sound insulation. The Club owner accepts responsibility and states that the material did not have fire warnings on the label, only an indication to "keep away from heat".

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For abbreviations see: www.pinfa.org

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