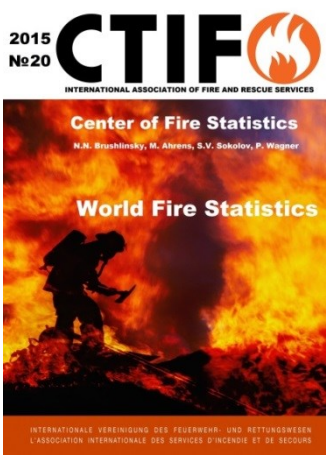
pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 67 June 2016

Upcoming pinfa events:

15 June	Brussels	pinfa General Assembly
17 June	Changchun, China	pinfa stakeholder & industry workshop at ISFRMT: fire safety and flame retardant standards, regulations and trends
For complete, up to date events listing, see www.pinfa.eu		

The world's fire and rescue services (VTIF) statistics show that fire continues to kill, injure and cause considerable economic damage. But the most recent statistics also show how inadequate is data globally, with no statistics from several of the world's largest countries. New information and tests also continue to demonstrate the fire dangers of various materials and applications: see below wood fibre board, student accommodation, buses and coaches, wood and polymer insulation materials, construction sites.



World fire statistics

The International Association of Fire and Rescue Services CTFI has published its annual report on world fire statistics. The 2015 report (n°20) brings together fire data from 32 countries. Its data indicates approximately 20 fire deaths per million population, with no clear trend since the 1990's (possibly because of changes in the declaring countries). Russia and Belarus have the highest fire deaths per population. Data may not be indicative of world averages because major countries are not included (statistics not available for e.g. China, India, Canada, Australia and all of South America). Direct and indirect losses from fires are estimated at an average 0.15% of GDP and fire protection (insurance, building protection, cost of fire services) at 0.19% of GDP.

CTIF "World Fore Statistics" 2015, n°20 (statistics to 2013) http://www.ctif.org/ctif/world-fire-statistics

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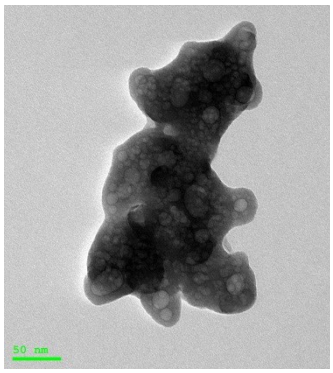
Reducing the risks of bus and coach fires

A presentation by SP Sweden summarises the need for improved fire safety standards in buses and coaches, and developments currently underway. Applicable regulations are UN ECE 118 for fire behaviour of interior materials (see J. Troitzsch in pinfa Newsletter n° 65) and UN ECE 117 for fire detection. Full scale tests show that UNECE 118 is inadequate: flashover occurs rapidly if fire reaches the passenger compartment, and toxic fumes become critical within minutes. Statistics show that bus fires are increasing (the number has doubled in Finland over the last decade), with 350-400 bus and coach fires per year in Germany and over 2 100 school bus fires in the USA. New systems are needed for detecting and fighting fires. Component failure is a key fire cause, and addressing this reduces operating costs. Fire standards' developments need to take into account the tendency towards lightweight materials and the importance of both flammability and of smoke toxicity.

"Reducing the risk of bus fires", F. Rosen, SP Sweden, 51 pages, Intersec Dubai 19th January 2016, online

***Upcoming conference**: 4th International Conference on Fires in Vehicles FIVE, 4-6 Oct. 2016, Baltimore, USA www.firesinvehicles.com*



TROVOtech glass particle PIN FR synergists

Produced with a specific high temperature extrusion process, TROVO® Powder B consists of porous borosilicate glass foam particles (diameter of a few microns) which are functional polymer additives. They are used as synergists with PIN flame retardants, such melamine cyanurate or phosphorus FRs. The glass particles can enhance or conserve (when FRs are added) polymer mechanical performance and contribute to intumescence. When used as carriers for inorganic ions they can provide durable antimicrobial and antifungal effects (silver ions) or smoke-suppression (zinc, tin, copper). They can also be used as carriers for organic catalysts. TROVOtech considers that their product offers environmental advantages by reducing resource consumption.

www.trovotech.com

Full scale fire tests in student bed-sits

SP Norway has carried out full-scale fire tests in mock-up furnished student bed-sits in a cross-laminated timber (CLT) building. The objective was to understand fire risks in the Trondheim Students Union (SiT) student housing, which is nine storey CLT. The test rooms contained a combination of a mattress and furniture and wooden pallets and heptane, to simulate real room contents fire load. The CLT structure was behind plasterboard and mineral wool insulation. The sprinkler system in the room was put out of action, but functioned in the adjacent corridor. Flashover was reached 4 minutes after a small fire (equivalent to burning paper) was started in the room. The results show that 10 cm CLT structural elements were burned through, faster than would be expected under Eurocode 5. However, the CLT provided very effective heat insulation.

Report SPFR A15101 "Branntest av massivtr" (full scale fire test of CLT structure), K. Hox, 18th March 2016 30 pages, in Norwegian

Video shows why fire safety is essential for fibreboard

Medite is Europe's leading producer of MDF (medium density fibreboard) for use in buildings interior and exterior for furnishing, walls, decoration and insulation, with over 400 different specifications available. The company's products are CARB (California Air Resources Board) indoor emissions compliant (low formaldehyde) and use PIN flame retardants for fire safety. The company's online video shows the importance of flame retardancy for MDF panels, comparing two full-size furnished room tests simulating a hotel bedroom with MDF-based walls and ceiling. In the non flame retardant treated room (MDF Euroclass D), fatal conditions are reached in under 6 minutes after simulated paper wastebin fire in the room corner (temperature of 300°C and dense smoke) and flashover at 7 minutes (temperatures above 800°C with large flame, toxic burning gases, and a fire which would spread into other rooms). In the room using Medite Premier MDF (Euroclass B, using phosphorus and nitrogen PIN flame retardants from Ecochem) the waste bin fire never ignites the MDF walls, temperature only rises by 10°C in the room, there is little smoke and the fire self extinguishes when the flame source is stopped.

www.medite-europe.com/products/

"Demonstration of Medite Premier Flame Retardant MDF product performance Medite MDF and SmartPly DSB" This short video dramatically demonstrates the benefits of Medite Premier FR Flame Resîstant MDF wîthin a typical hotel bedroom. YouTube

Global specialist flame retardant markets

The world market for flame retardants in aircraft plastics is expected to grow from US$ 18 million in 2014 to 29 million in 2022, according to a study by GrandView Research. The development of PIN FRs is considered to have opened new areas of growth, including in applications subject to stringent regulations. For example, PIN FR carbon-fibre reinforced plastics (CFRP) are now used in aircraft cabins and empennage and a range of plastics are used in wings, fuselage, engines and interiors (including glass fibre reinforced engineering plastics, polyimides, polycarboxylates and epoxies. The report notes that regulatory pressures have led to the development of "non halogenated, non toxic" flame retardants, with Ecolabels further pushing in this direction. Carbon fibre reinforced plastics already account for 30% of the world aircraft plastic market and are expected to show an annual growth of nearly 6% CAGR. Other studies by QYResearch assess the world market for flame retardant fabric, with predictions for developments through to 2021, and the global PIN flame retardant market, summarising industry definitions and classifications, market development trends and industry structure.

"Flame Retardants for Aerospace Plastics Market Analysis By Product (Antimony Oxide, Aluminum Trihydrate, Organophosphate, Boron Compound), By Application (Carbon Fiber Reinforced Plastics (CFRP), Glass Reinforced Plastics (GRP), Polycarbonates, Thermoset Polyimides, Acrylonitrile Butadiene Styrene (ABS), Acetal/POM, Epoxies) and Segment Forecasts To 2022", Grand View Research, March 2016

"Global Flame Retardant Fabric Industry 2016 Market Research Report", QYR Chemical and Material Research Centre, February 2016

"Global Non-Halogenated Flame Retardant Consumption 2016 Market Research Report" (141 pages), March 2016

Seafood shell waste as natural flame retardants

Seafood consumption generates large volumes of shell waste, composed of calcium carbonate, mineral oxides and some organic materials. In a new study, ground and washed sea shells were tested as a flame retardant in ABS polymer. 25% loading did not significantly modify ABS mechanical properties and enabled a 40% decrease in peak heat release rate and a nearly 50% increase in time to ignition compared to pure ABS. The seashells improved fire performance somewhat more than pure calcium carbonate, suggesting a positive impact of the other minerals present, e.g. iron. Previous studies reported that a combination of ground oyster shells and a phosphorus PIN flame retardant (Clariant Exolit AP760) can provide fire performance for polypropylene.

"Highly flame retardant green composites using seashells", Moustafa, Duquesne, Darwish & Youssef, Plastics Research Online, 31st March 2016

"Clariant's Exolit® ensures protection for renewable polymers in oyster shell – reinforced polypropylene 20th January 2014 and pinfa Newsletter n°38.

PIN FR synergy for low smoke polyurethane

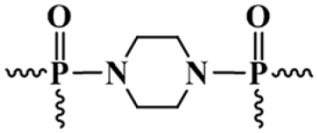
A combination of zinc hydroxystannate [$ZnSn(OH)_6$] inorganic zinc tin compound ZnHS) and ammonium polyphosphate (APP) was tested in thermoplastic polyurethane (TPU) with 12-15% loading of APP and 0-3% ZnHS. 1% ZnHS plus 14% APP showed optimal mechanical characteristics (better tensile strength than other combinations but still worse than pure TPU, better elongation at break than pure TPU or other combinations) and best fire performance (peak heat release rate PHRR < 12% of pure TPU, highest LOI Limiting Oxygen Index. All APP-ZnHS combinations achieved UL V0 (pure TPU did not). Inclusion of ZnHS at all tested levels significantly reduced the smoke density (c. 50% reduction after 8 minutes) and both of the two measured toxic gases in smoke (carbon monoxide, hydrogen cyanate, both reduced by more than 15%).

"The influence of zinc hydroxystannate on reducing toxic gases (CO, NOx and HCN) generation and fire hazards of thermoplastic polyurethane composites", B. Wang et al., Journal of Hazardous Materials http://dx.doi.org/10.1016/j.jhazmat.2016.04.029

Inorganic tin flame retardant and fire suppressant guide

A new technical guide to uses of inorganic (PIN) tin compounds as flame retardants and smoke suppressants includes information on fire performance and testing and on chemical regulation (e.g. REACH status) and a global inventory of 134 suppliers of different inorganic tin chemicals. Around 1 000 tonnes per year of inorganic tin chemicals are used in fire safety, that is c. 15% of global inorganic tin chemical use. Fire safety use is growing as tin compounds can be effective synergists, reducing smoke emissions, with other PIN flame retardant systems. Chemicals covered in this guide are: Tin (II) chloride, Tin (II) oxalate, Tin (II) oxide, Tin (IV) chloride, Tin (IV) oxide, Calcium stannate, Potassium stannate, Sodium stannate, Zinc stannate (including for all hydrous / hydroxy forms).

"2016 Inorganic Tin Chemical Flame Retardants and Smoke Suppressants: Global Suppliers Guide and Technical Overview", S. Blunden & P. Cusack, 2016
http://www.tinindustries.com/frchemicals.html



Experimental polymeric P – N flame retardant

A phosphorus and nitrogen polymer, poly(piperazinyl phosphamide) (PPMA) was synthesised by a one-step reaction by progressively combining acetonitrile, piperazine, trimethylamine and phosphorus oxychloride. The resulting polymer was tested as a flame retardant in EVA (ethylene vinyl acetate) with APP (ammonium polyphosphate). PPMA alone generated over 45% char residue in air at 600°C. EVA with 25% APP and 5.5% PPMA achieved UL94-V0 (3.2mm). The PPMA polymer showed very efficient char production and flame retardancy was improved by synergy with APP, in that APP delayed the breaking of the carbon – nitrogen bond in the PPMA polymer. In a previous paper, a similar N-P polymer, piperazine-modified ammonium polyphosphate PA-APP was shown to be an effective PIN flame retardant in polypropylene, achieving UL94-V0 (3.2 mm).

"Poly(piperazinyl phosphamide): a novel highly efficient charring agent for an EVA/APP intumescent flame retardant system", L-P. Dong et al., RSC Advances 2016, 6, 30436–30444 https://dx.doi.org/10.1039/c6ra00164e

"An Efficient Mono-Component Polymeric Intumescent Flame Retardant for Polypropylene: Preparation and Application", Z-B. Shao et al., ACS Applied Materials & Interfaces, 2014, 6, 7363−7370 https://dx.doi.org/10.1021/am500789q

PIN FRs for recycled plastic – wood composites

Wood – plastic composites combine natural fibres (e.g. sawdust or other timber production by-products) with polymers. The authors indicate that applications include construction and automobile, with a tendency to prefer PIN flame retardants because of low smoke and reduced toxic gases in case of fire. Here, recycled polyethylene – sawdust (wood flour) composite was prepared with different PIN FRs (APP ammonium polyphosphate, ATH aluminium trihydrate, melamine, zinc borate). Without flame retardants, the sawdust contributed to combustion, whereas with PIN FRs it acted as a char source, enhancing fire resistance. The PIN FRs used in combination with polyethylene graft polymers (GPE, GPW) enabled to achieve UL94-V0 (4 mm) whilst maintaining high mechanical performance.

"Flame Retarded Polyethylene/Wood Flour Composites With High Performances: Satisfying Both Sides With Intumescent Flame Retardants and Synergistic Compatibilizers, Respectively", H. Hong, Polymer Composites, 2016 https://dx.doi.org/10.1002/pc.23970

Smouldering combustion of wood fibre insulation

A thesis from NTNU presents results of testing of four different loose wood fibre insulation materials with three different fibre structures (fibre length, thickness) and in once case a different level of PIN flame retardant (ammonium polyphosphate 4% or 9%). In these results self-sustained smouldering combustion starts at a lower temperature in the wood fibre with higher APP, but then progresses more slowly. The author notes that APP is not typical of FRs used in cellulosic insulation material and that further work is needed to assess the impact of FRs on the start of and development of smouldering, and so on smoke emission and fire safety.

NTNU (Norwegian University of Science and Technology) thesis "The Development of Smouldering Combustion in Combustible Building Insulation Materials", U. Jensen, January 2016, 86 pages https://brage.bibsys.no/xmlui/handle/11250/2385048

Fire emissions of polyurethane foams

A 27-page review of short term toxic gas emissions from polyurethane foams in fires is published in Fire Science Reviews. World use of polyurethanes (foams, solid) is estimated at c. 18 million tonnes (2016), up from 14 Mt (2010), with furniture foam and building insulation the main applications (28%, 25%). Polyurethanes are a widely varying family of polymers based on the nitrogen - carbon – oxygen urethane (carbamate) group. Like all combustible materials, polyurethanes emit toxic and/or irritant gases which can inhibit escape from a fire in case of incomplete combustion: carbon monoxide (CO), hydrogen cyanide (HCN), nitrogen oxides, isocyanates, hydrogen halides. Real uncontrolled fires, though, are always under-ventilated. The authors review data available, noting that there is a lot of fire test data but that toxic emissions depend strongly on fire conditions (temperature, oxygen availability, and development of these over time) making it very difficult to derive relevant information from bench tests. They also conclude that there is some contradiction in the literature concerning the impact of flame retardants on fire toxicity of polyurethane foams, but that "A large majority of the literature indicates that the addition of fire retardants does not increase toxicity of polyurethane foams."

"The fire toxicity of polyurethane foams", A Review, S. McKenna & T. Hull, Fire Science Reviews, 2016 (5:3), open access https://dx.doi.org/10.1186/s40038-016-0012-3

Other News

Respect of chemicals regulation improving: Sweden's chemical agency KEMI notes a "clear improvement in just a few years" regarding presence of banned chemicals in toys. Recent tests of 112 toys from 29 companies identified 15% which did not conform, of which 8 contained SCCPs (short chain chlorinated paraffins, a flame retardant / plasticiser which is banned in this application).

KEMI Sweden "Prohibited chemicals in every seven tested toys" 11th April 2016

Sustainable chemistry definition: the OECD website has published a definition of Sustainable Chemistry: "a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services. Sustainable chemistry encompasses the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes." The OECD underlines that Sustainable Chemistry stimulates innovation across all sectors to produce increased performance and added value, whilst meeting human health and environmental goals.

OECD Sustainable Chemistry Platform http://www.oecd.org/chemicalsafety/risk-management/sustainablechemistry.htm

Fire risk product recall: Homelite has recalled 860 000 electric vacuum blowers, used for blowing garden leaves, sold in the USA and Canada, because the equipment can overheat posing fire and burn hazards. A further 225 000 blowers sold at Walmart (OWT Industries blowers) have been recalled because of an overheat risk, leading to sparks and possibly catching fire. The US CPSC has received reports of blowers smoking, sparking and burning, resulting in user injury.

US Consumer Product Safety Commission CSPC recalls page http://www.cpsc.gov/en/Recalls/

Selection of sustainable chemicals: the new ASTM E3027 standard provides guidance for selecting sustainable chemicals. Relevant definitions are specified (e.g. hazard, risk, impact, LCA …). Different aspects of social, economic and ecological sustainability to be considered are listed. The importance of assessing the "product – chemical" pair is underlined (i.e. taking into account uses and exposures). Existing methods are referred (inc. GreenScreen, US EPA Design for the Environment DfE, LEED green buildings …) and regulatory schemes (e.g. REACH)

Source *http://www.astm.org/Standards/E3027.htm*

Publisher information:

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For abbreviations see: www.pinfa.org