pinfa

Newsletter for non-halogen fire safety solutions

January 2015 – N° 48

Innovation

Presafer, pinfa's first member from China

Presafer (Qingyuan City, Guangdong, China) has become pinfa's first Asia-based member company. Presafer is a specialized producer of environmentally friendly, halogen-free flame retardants, based on phosphorus (P) and nitrogen (N). The largest volume product is high-degree polymerised ammonium polyphosphate. The company's main products include Prepiphor™, Nitrophor™ and Phoniton™ and combine performance, long-term stability in products and fire safety effectiveness. These products are used in applications including textiles, transport, electronics and construction. The company is ISO 9001 (2008), ISO 14001 (2004) and OHSAS 18001(2007) registered and supplies a worldwide market. Presafer have joined pinfa to contribute to promoting PIN solutions for fire safety, with health and environment profiles preferable to halogenated flame retardants in Europe, America, Asia and Australia, and to collaborate in improving access to information and developments in PIN flame retardants.

Photos: Top: furnace test of cellulose insulation material with Presafer PIN FR. Below: Application of Presafer PIN FR in an electrical socket unit. www.presafer.com

Full-scale furnished room fire tests show limited escape time

For the first time for a decade, new experimental work is published assessing **tenability (how toxic gases and heat prevent escape and kill)** using full-scale furnished rooms. The authors, Guillaume et al., from LNE (French National laboratory for testing and metrology) and LCPP (the Paris Police district Central Laboratory), measured temperature, heat flux, opacity and a range of toxic fire gases in five test fires in a furnished domestic bedroom and adjacent corridor. The room contained a bed (pine), mattress and bedding, furnishing and daily items (wardrobe, desk, table – all wood/fibreboard, rug, clothes, towels, books, CD cases, papers, food packets) and fittings (flooring, electrical ducting). The room was 3m x 3m x 2.5m high, with non -flammable walls and ceiling, and PVC flooring and fittings. Temperatures were measured at heights from 0.8m to ceiling and toxic gases (by FTIR) at height 0.6m to ceiling. The room was fitted with a smoke alarm on the ceiling. In the first three tests, different fire sources were placed on the bedding and the room door remained closed, simulating a fire starting whilst a person is asleep in bed (under ventilated fire). In the last two tests, fires of different sizes were started in waste paper baskets under the desk and the door of the room was opened, simulating a person escaping rapidly.

The paper also summarises previous fire tenability studies carried out on full-scale room set-ups (Grand et al. 1985, South West Research Inst.), Morikawa et al. (1987, 1993), Purser 2000, Gann et al. 2003, single furniture items (Sündstrom 1987) or tenability modelling (Peacock et al. 2004), underlining the **lack of data from full-scale tests relevant to assessing capacity of occupants to escape and risk of toxicity injuries**.

In the first two tests, a smoldering cigarette and a match were placed on the bedding (on the quilt, cotton-polyester fabric, polyester lining). **In both cases, the quilt did not catch fire and did not significantly smolder**. It should be noted that domestic bedding in France is subject to legal fire safety regulations requiring resistance to ignition by a burning cigarette (Décret 2000-164 du 14/2/2000). In the third test (under ventilated, door closed), a small fire (small crib, BS6807 #5, equivalent to a burning ball of paper) is placed on the bedding. No flames are observed for 10 minutes, but **carbon monoxide levels start to rise significantly from 2 minutes**, at which time the smoke alarm activates in the room. The smoke reaches a density such that escape would be compromised for an unknown travel path after c. 3 minutes Concentrations of oxygen fall to levels which would compromise tenability (occupant survival) after c. 4 minutes and carbon monoxide and hydrogen cyanide reach levels which would compromise tenability after c. 6 minutes.

In the last two tests, small fires were lit in waste paper bins under the desk. In one test, the fire was lit in a metal bin containing 500 g of crumpled paper (in this test, the fire burned out in the wastepaper without spreading to the desk). In the second test, the fire was lit in one such bin with a second bin also containing 500g of crumpled paper next to it (the fire spread to the second bin). In this second test the fire alarm activates at 3 minutes 15 seconds, gas toxicity does not reach untenable levels until around 6 minutes and smoke density does not compromise escape (for unknown route) until 5 minutes whereas **temperatures threaten survival from c. 4 minutes.**

The authors conclude that in these full-scale tests smoke alarms in the room where the fire is situated activate in time to make escape possible for a healthy individual. However, **in both cases an individual with inhibited movement (invalid, old or young children) would be at significant risk as there are only 1 – 2 minutes** between smoke alarm activation and both smoke density levels impeding escape and conditions becoming untenable for occupant survival (because of toxic gases in the under ventilated room – door closed, because of temperature in the ventilated room – door open). The authors note that results are highly specific to fire conditions, materials involved in the fire, and risk to occupants are highly dependent on their reaction and mobility in the face of the fire event. In all cases, occupants would be at high risk of death if smoke alarms were not operational or in case of late detection of the fire.

"Real-scale fire tests of one bedroom apartments with regard to tenability assessment", E. Guillaume et al. (Laboratoire National de Métrologie et d'Essais and Laboratoire Central de Préfecture de Police, Paris), Fire Safety Journal 70, pages 81-97, 2004 http://dx.doi.org/10.1016/j.firesaf.2014.08.014

EPA United States Environmental Protection Agency

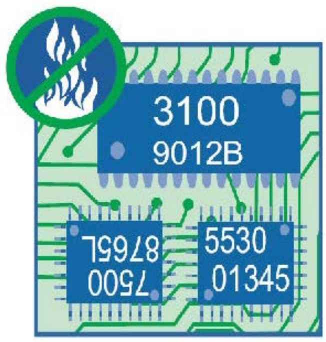
Design for the Environment U.S. EPA

EPA Design for the Environment: alternatives to TBBPA

The US Environmental Protection Agency has published an update of the Printed Circuit Boards Partnership report (DfE: Design for the Environment) on alternatives to the brominated flame retardant TBBPA used in printed circuit boards. **Public comment is open until 15th February 2015**. Most printed circuit boards (PCBs) for consumer electronics are so-called FR-4 boards, which means that they are based on glass-reinforced epoxy laminate sheets and fulfil certain performance requirements including the UL94-V0 fire safety standard. The report, updated from the first publication in 2008, assesses ten flame retardants: TBBPA, 2 reactive and 5 additive PIN FRs and two polymeric FRs (one brominated, one P-based). High persistence is indicated for all flame retardants and is linked to the required chemical stability for their function. Two of the mineral PIN FRs (aluminium and magnesium hydroxide ATH, MDH) achieve “low” or “very low” for all relevant toxicity and environmental end-points (persistence/biodegradability not applicable to inorganics/metals) and two other PIN FRs (dihydro-oxy-phosphaphenanthrene-oxide DOPO and aluminium diethylphosphinate DEPAL / Alpi) show only low to moderate concerns for all other criteria. For some PIN FRs questions regarding long-term health impacts or bioaccumulation suggesting that further optimisation is possible or that data is inadequate.

The updated study looked at smoke and toxicity emissions in different combustion conditions, reflecting both end-of-life incineration and accidental fires. Smoke release was around twice as high for brominated FR boards than for phosphorus FR boards in both combustion scenarios. Emissions of particles were also 25 – 50 higher with brominated FR boards. Brominated FR boards emitted 2-3 times more PAH (poly aromatic carbons) than phosphorus FR boards in both incineration and open fire conditions. Brominated dioxins/furans (PBDD/F) were detected in all scenarios with brominated FR boards.

The report underlines that material performance characteristics are essential for selecting alternative halogen-free flame retardants for circuit boards, including electrical and mechanical parameters, cost and reliability and refers to the iNEMI and HDPUG studies of halogen-free materials, including halogen-free flame retardants. The EPA press release accompanying concludes that “industry trade groups tested alternative non-halogenated flame retardants and found that they function equally as well or better than TBBPA-based circuit boards for certain products”.



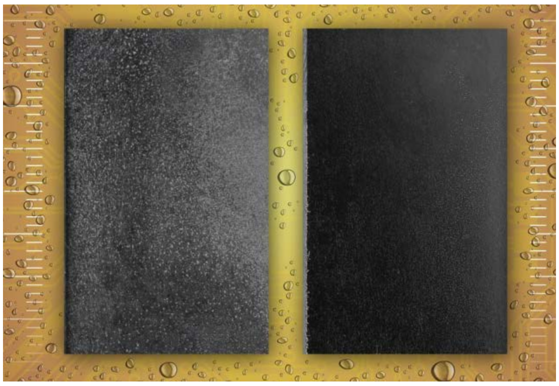
FRs considered in the report: 1 reactive brominated FR (TBBPA); 2 reactive P-based PIN FRs (DOPO, Fyrol PMP); 5 additive PIN FRs (aluminium diethyophospinate, ATH, MDH, melamine polyphosphate, amorphous silicon dioxide); 2 reactive polymeric FRs (DER 500 series - brominated, Dow XZ-92547 - P-based)

“Flame Retardants in Printed Circuit Boards Partnership”, US EPA (Environmental Protection Agency) Design for the Environment (DfE) http://epa.gov/dfe/pubs/projects/pcb/

“Flame Retardants in Printed Circuit Boards – Updated draft report”, December 2014
http://epa.gov/dfe/pubs/projects/pcb/141215_pcb_flame_retardants_report_updated_draft_full_report_and_appendices.pdf

*Public comment on this draft report is **open until 15th February 2015**:*
http://www.epa.gov/dfe/pubs/projects/pcb/index.htm

BASF launches glass fibre reinforced PIN FR polyamide



BASF's new Ultramid® A3U42G6 is a PIN flame retardant, glass fibre reinforced polyamide (PA) offering light colorability and easy processing (low deposits, low corrosivity). The material meets UL 94 requirements for the V-0 flammability class at wall thicknesses as low as 0.4 millimeters. With an RTI for dielectric strength (UL 746B) of 140 °C at a wall thickness of 0.4 millimeters and even 150 °C at thicknesses starting at 0.75 millimeters, the new Ultramid A3U42G6 is especially well suited for use at higher temperatures. The new flame retardant system shows no migration effects and thus ensures component surfaces of higher quality. It also contains no halogen or antimony components. This allows favorable smoke density and toxicity values to be attained. The product is particularly adapted to connectors and for thermally stressed industrial automation parts, such as switches and contactors.

Photo: testing of migration effects: right = Ultramid® A3U42G6

BASF Engineering Plastics:
http://www.plasticsportal.net/wa/plasticsEU~en_GB/portal/show/content/products/engineering_plastics/engineering_plastics

BASF News Release P361, 14th December 2014 "Improved flame retardant grade for E&E applications"
http://www.plasticsportal.net/wa/plasticsEU~en_GB/portal/show/common/plasticsportal_news/2014/14_361

See also pinfa Newsletter n°38 and n°6

pinfa responds to consultation on ammonium salts

pinfa has submitted information to the ECHA (European Chemicals Agency) consultation on the use of ammonium salts to reduce fire risks of cellulose building materials (see pinfa Newsletter n° 46). pinfa emphasises that ammonium salts are recognized to be non-toxic and have been developed as safer alternatives to previously used chemicals. The only risk with their use is a possible release of ammonia gas in conditions of high humidity and temperature, pH. In enclosed spaces, this gas can cause potential irritation to the respiratory tract and eyes but has no long-term or chronic toxic effects. Ammonia salts and ammonia gas are not carcinogenic, mutagenic, teratogenic or impacting on the immune system. Ammonia gas occurs naturally e.g. from animal excretions. pinfa considers that a use restriction should target ONLY situations where a risk of ammonium emissions susceptible to cause irritation may occur, so should be limited to the 3 specific ammonium salts proposed by France*, and should not apply to forms of ammonium salts which are processed or applied such that gas emissions cannot occur (stability or encapsulation systems, polymer forms), in order to enable continuing use of ammonium salts (a recognized, non-toxic, effective fire safety solution) and to not prevent positive innovation.

** ammonium sulphate, ammonium dihydrogenorthophosphate, diammonium hydrogenorthophosphate*

ECHA public consultation on "Ammonium salts in cellulose insulation materials used in buildings" (closed 18/12/2014)
http://echa.europa.eu/restrictions-under-consideration/-/substance/6315/search/+/term

pinfa position: http://www.pinfa.eu/media/news/230-pinfa-position-on-ammonium-salts-in-cellulosic-insulation-materials.html

"Europe is Playing with Fire"

80 Members of the European Parliament (MEPs) and candidate MEPs have signed a pledge to work for a fire safe Europe, as proposed by the European Fire Fighters Unions Alliance (EFFUA). The fire fighters write that more than 4 000 people die annually in fires in Europe and that fires are becoming "*bigger and more dangerous*". Today a "small fire can become a blazing inferno in less than 3 minutes - injuring and killing the building occupants before the emergency services can arrive on the scene", whereas 40 years ago it would typically take 25 minutes for a fire to become out of control. The fire fighters' campaign emphasises that fire safety test methods need updating, in particular to better take into account smoke toxicity, which is responsible for more than half of fire deaths.

IFP Magazine E-Newswire, December 2014 *http://ifpmag.mdmpublishing.com/europe-must-tackle-fire-safety-flaws-says-new-white-paper/*

Fire Safe Europe / Fire Safety First *www.firesafeeurope.eu*

Fire Safe Europe white paper "Europe is playing with fire: a call to action on fire safety in buildings",2nd December 2014 *http://www.firesafeeurope.eu/uploads/Modules/Publications/europe-is-playing-with-fire-_-white-paper_fseu_03_12_2014.pdf*

Afumex LSX cables chosen for care village

Prysmian's Afumex LSX LS0H (Low Smoke Zero Halogen) cables a have been selected for the UK£ 1 million electrical installation at the new Edenholme Care Village, Scotland. The cables will provide small power and lighting circuits throughout the new development, designed to provide 21st century care to older people. Aberdeenshire Council underlined that the cables respect standards specifications. The services contractor Richard Irvin underlined the puncture protection offered by the cables. Afumex LSX low smoke zero-halogen cables are flame retardant to improve fire safety and to continue to provide power and control in case of fire. They emit low levels of smoke and of toxic fumes in case of fire and are particularly recommended for highly populated, enclosed public areas. They are designed to ensure compact installation, minimising space loss and maximising useful space in buildings.

http://www.afumexcables.co.uk/ *See also pinfa Newsletter n° 26.*

Biosourced PIN flame retardants

Research shows that two renewable PIN flame retardants can be combined: Phosphorus based phytic acid (widely present in plant seeds) and Nitrogen containing chitosan (derived from natural chitin, present in the structures of fungi, crustaceans …). The two renewable compounds were combined to produce a polyelectrolyte complex (PEC), which was then reacted onto EVA (ethylene-vinyl acetate) fibres. EVA is widely used in many applications, including wires and cables where fire safety and low smoke are required. A reduced peak heat release and total heat release were achieved, with a full and compact char layer, without deterioration of the fibres properties (ductility, tensile strength, viscoelacticity).

"Chitosan/Phytic Acid Polyelectrolyte Complex: A Green and Renewable Intumescent Flame Retardant System for Ethylene-Vinyl Acetate Copolymer", T. Zhang et al., Ind. Eng. Chem. Res. 2014
http://pubs.acs.org/doi/abs/10.1021/ie503421f

PolyFlame: Full scale fire gas tests of PIN FR cables

'PolyFlame', the newsletter of the French Chemical Society (SCF), has published results of full-scale fire gas emission tests on cables carried out as part of the OCDE Prism2 programme, with an objective of assessing cable safety in nuclear installations. The tests used one halogen-free FR cable (mineral PIN flame retardant ATH aluminium tri hydroxide) and two chlore-containing PVC cables. Several hundred metres of electrical cables were laid out horizontally on vertically-stacked racks, then subjected to fire in well-ventilated conditions. The PIN FR showed a significantly delayed CO_2 emissions peak, suggesting a longer delay before full development of fire (c 25 minutes compared to c. 5 minutes)The PIN FR also resulted in lower smoke toxicity with no detectable emissions of hydrochloric acid (HCl, which was emitted by the PVC cables, and considered by the authors to represent corrosivity), 10 – 15 times lower emissions of carbon monoxide (CO, often the most lethal fire gas) and significantly lower emissions of methane, ethylene, acetylene and benzene.

P. Zavaleta & L. Audouin, IRSN (Institute for Radioprotection and Nuclear Safety), Saint Paul lez Durance, France, in PolyFlame Newsletter n°6, October 2014 (in French), Société Chimique de France www.polymer-fire.com

Phytate: from agriculture's problem to bio-sourced PIN FR

Much of the phosphorus present in crops (cereals in particular) is present as "phytate" ($C_6H_{18}O_{24}P_6$ see below). This form of phosphorus poses issues in agriculture and food, because it cannot be digested by mono-gastric animals (such as pigs, chickens, humans). Thus, the phosphorus content is not available, so in pig feed for example it is effectively lost to manure. Also, phytate bonds to metal ions (complexes), thus rendering important minerals such as calcium or iron non-available in animal or human foods. Scientists in Belgium, working on BioRefineries (making valuable products from agricultural wastes and non-food by-products) are looking at turning the phytate problem into a valuable, bio-sourced PIN flame retardant. Phytate has two properties which make it potentially interesting as a PIN flame retardant: its phosphorus content and its capacity for complexing with metals (to produce phosphorus-inorganic FRs). Different phytate – metal complexes have been tested as PIN flame retardants in the bio-sourced polymer poly lactic acid (PLA), with aluminium phytate salts showing the best fire performance (up to 40% reduction in peak heat release). The authors are also testing other bio-sourced PIN flame retardants, in particular microfibers of cellulose (CNC cellulose nano crystals) treated with urea and phosphoric acid (CNC-P), and synergies of these products with the phytate salts presented above.

F. Laoutid & P. Dubois, Service des Matériaux Polymères et Composites (SMPC), Université de Mons - Materia Nova, Mons, Belgique, in PolyFlame Newsletter n°6, Oct. 2014 (in French), Société Chimique de France www.polymer-fire.com

Proposed End-of-Waste criteria outline for plastics

The European Commission has published a report outlining proposed End-of-Waste criteria for waste plastics intended for conversion into recycled plastics products. The report indicates that "*Most additives in use [in plastics] are not known to have environmental or health risks*" but cites as identified as having environment/health risks "*a few problem substances*" including some halogenated flame retardants. The report notes that measures are already in place to identify and separate plastics containing halogenated FRs: these measures include the obligation to remove plastics containing brominated FRs from any separately collected electrical / electronics waste (EU WEEE Directive), non-mixing of such plastics (EU End of Life Vehicle Directive), classification in "Category C" of plastic waste containing halogenated FRs (in the UK). The report suggests that this separation is adequate to ensure safety of recycling of plastics containing flame retardants, subject to respecting legislation on hazardous materials, substances of very high concern and POP's.

European Commission Joint Research Centre "Technical proposals, End-of-waste criteria for waste plastic for conversion", October 2014, ISBN 978-92-79-40944-8
http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/33010/1/2014-jrc91637%20.pdf

Other News

Organophosphorus (OP) flame retardants: a review of environmental studies on OP substances used as plasticisers or FRs looks at human exposure to 3 halogenated OPFRs, 6 OP plasticisers and 3 non-halogen OPFRs. The non-halogen OPFRs were not bioaccumulative and human exposure through food or breast milk feeding was negligible. Exposure to additive OPFRs through inhalation of indoor air or through dust was considered to be of possible concern and further research on long-term health effects of low-level exposure is called for. Further development of "reactive" phosphorus FRs, which react into polymers and which do not risk emissions from products, would avoid these exposure questions.

FRs in a food web: in a study of FRs in an estuary food web in the Netherlands, OPFRs did not tend to accumulate in lipids in organisms, indicating that they do not bioaccumulate. Three of the OPFRs showed some trophic magnification (higher levels in higher organisms) in benthic (bottom dwelling) organisms, probably due to uptake from sediments.

PFR breakdown and excretion: a study of around 50 mothers and their children in Norway shows concentrations of di-aryl phosphorus esters (DAPs) in urine proportional to levels of tri aryl phosphorus PFRs (TAPs) in household dust and to time spent indoors. This confirms that these PFRs are broken down and their metabolites eliminated in urine.

"Review. Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human exposure", G-L. Wei et al., Environmental Pollution 196 (2015) 29e46
http://www.sciencedirect.com/science/article/pii/S0269749114003923

"Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web", S. Brandsma et al., Science of the Total Environment 505 (2015) 22–31
http://www.sciencedirect.com/science/article/pii/S0048969714012510

"Human exposure pathways to organophosphate triesters — A biomonitoring study of mother–child pairs", E. Cequier et al., Environment International 75 (2015) 159–165 http://dx.doi.org/10.1016/j.envint.2014.11.009

Agenda

Events with active pinfa - pinfa-na participation are marked: ►

2-4 Feb 2015	San Francisco, USA	Fire and Materials 2015 http://www.intersciencecomms.co.uk/html/conferences/fm/fm15/fm15cfp.htm
4-6 Feb 2015	Madrid	COST MP1105 Workshop on "Advances in Flame Retardancy of Polymeric Materials" and 7th Asia-Europe Symposium on Processing and Properties of Reinforced Polymers (AESP7) https://aesp7.org/fire-retardant-workshop/
18-19 March	Cologne, Germany	Green Polymer Chemistry 2015 www.amiplastics.com/events/event?Code=C637
26-27 March	Bucharest, Romania	COST MP1105 workshop "Advances in the synthesis and characterization of nanomaterials for flame retardant applications" COST.MP1105@UGent.be
26-27 March	Vienna, Austria	7th International Symposium on Fire Safety in Railway Systems http://www.railway-network.eu/english/fire-safety-2015.html
30 March – 2 April	Budapest, Hungary	7th European Combustion Meeting http://www.ecm2015.hu
14 April	Safety Harbor, Tampa, Florida	Fire Testing for Codes & Regulations, Marcelo Hirschler (GBH International) mhirschler@gbhinternational.com
15-16 April	Safety Harbor, Tampa, Florida	► Meeting Flammability Requirements for Commercial Buildings & Construction (**pinfa-na** and **The National Pollution Prevention Roundtable**) http://www.pinfa-na.org ***Preliminary speakers list now online***
12-13 May	Denver, Colorado	Fire Retardants in Plastics (AMI) http://www.amiplastics.com/events/event?Code=C648
17-20 May	Stamford, Connecticut	BCC Flame Retardancy Conference (18-20 May) and (17 May) industry seminar http://www.bccresearch.com/conference/flame
16-18 June	Nicosia, Cyprus	2nd European Symposium of Fire Safety Science http://www.iafss.org/2nd-european-symposium-of-fire-safety-science/
22-25 June	Berlin, Germany	►FRPM 15th European Meeting on Fire Retardancy and Protection of Materials http://www.frpm2015.bam.de/en/home/index.htm
28-30 Sept	Cambridge, UK	6th International Symposium Human Behaviour in Fire http://www.intersciencecomms.co.uk/html/conferences/hb/hb15/hb15.htm
5-7 Oct 2015	New Delhi	Fire India http://www.fire-india.com/
5-7 Oct 2015	Tsukuba, Japan	10th Asia-Oceania Symposium on Fire Science and Technology (AOSFST) http://www.iafss.org/10th-aosfst/

Calls for papers

Deadline:	15 Jan 2015	Fire Retardancy and Protection of Materials, FRPM, 22-25 June 2015, Berlin http://www.frpm2015.bam.de/en/home/index.htm

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