pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
January 2016 – No. 60

PIN flame retardants in thermoplastics recycling

Fraunhofer Institute for Structural Durability and System Reliability LBF, Germany, with support from the German Federation of Industrial Research Associations (AiF) and pinfa, launched a project to demonstrate the recyclability of several thermoplastics formulations using PIN flame retardants. They will test polypropylene, PC/ABS, polyamides (PA-6 and PA-6.6), and polyethylenes, using phosphorus, nitrogen and mineral based PIN flame retardants provided by pinfa member companies Adeka, BASF, Budenheim, Clariant, Nabaltec. The project also involves compounders and recyclers Material quality after multiple extrusion and after accelerated ageing will be studied, as well as maintenance of fire performance (UL-94) and mechanical properties, polymer and additive degradation and potential for reformulation (re-stabilisation, compatibility). The project was approved by AiF in October 2015, and will run to the end of 2017.

UK to prescribe fire safety for children's costumes

Following action from MP Ann Main, the UK government has announced that regulations will be introduced to require all children's fancy dress costumes to be flame-retardant. The announcement by Chancellor George Osborne, December 2015, follows decisions already announced by several UK retail chains to require fire-safety for dress costumes in their shops and media coverage of burns suffered by the daughter of Strictly Come Dancing host, Claudia Winkleman, after a Halloween costume brushed against a candle (see pinfa Newsletter 53). MP Ann Main says that the proposed legislation is needed to improve fire resistance and labelling requirements and that although a multi-billion-pound industry had grown around supplying children's fancy dress and play costumes: "our children are less protected than if they were wearing nightwear … In the United States, a child's dress-up garment offers a much higher level of protection: it must not catch fire for at least 3.5 seconds after exposure to a flame." She quoted the British Retail Consortium, which warned that the currently applicable flammability test EN71-2 was no longer fit for purpose.

"The Prime Minister has been urged to support a bill championed by St Albans MP Anne Main, aimed at preventing children's clothing from catching alight." *21/12/2015*

"All children's fancy dress costumes to be flame-retardant", Toy World Magazine, 11/12/2015

Non FR foam rejected from building code

Proposals to allow non flame retardant plastic foams in residential construction have been rejected by the International Code Council (ICC, for the International Building Code IBC). At present, IBC requires that polymer foams used in building conform to the ASTM E84 Steiner Tunnel Test Class B. The proposals (FS170, FS171) concerned only foams separated from building interiors by concrete or masonry. They were rejected, amongst other reasons, because of risks of confusion on building sites resulting in use of dangerous non flame retardant foams in building interiors, so posing fire risks. Similar proposal were already rejected in 2013 IRC and 2014 IgCC discussions.

International Building Code

US NFPA Railway standard fire safety improved

Final agreement has been reached on a number of improvements in fire safety requirements in the US NFPA 130 Standard for Fixed Guideway Transit and Passenger Rail Systems, mainly resulting from public comment proposals. Improvements include: the requirement that insulation materials in stations must be located behind thermal barriers, gypsum or concrete and must meet building code requirements; new fire safety requirements for rail ties, interior

finishes and protective cover boards; testing of adhesives and sealants in rail vehicles for smoke, flame-spread, dripping. Also, after discussion, the current requirement that wires, cables and other materials be halogen-free was maintained.

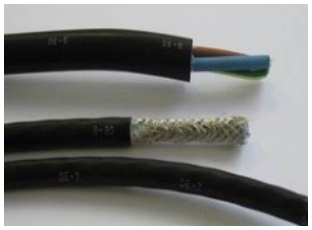
NFPA 130 Standard for Fixed Guideway Transit and Passenger Rail Systems

1.3 million fires in the USA in 2014, + 5% from 2013

The US National Fire Protection Association (NFPA) has published its annual report on US fire losses covering 2014. Fire fighters responded to nearly 1.3 million fires, up 4.7% from 2013, with nearly 3 300 civilian fire deaths, 16 000 civilian fire injuries and 12 billion US$ property loss. Nearly 500 000 of the 1.3 million fires occurred in buildings, up 1.3% from 2013, and 74% of these occurred in homes. Nearly 170 000 fires (with fire service call) were in road vehicles and 610 000 were outside. Home fires caused nearly 12 000 civilian injuries and 2 700 civilian fatalities.

NFPA "Fire Loss in the United States During 2014", H. Haynes, Sept. 2015

See NFPA "The Total Cost of Fire in the United States" in pinfa Newsletter n° 42 and NFPA "Fire loss in the United States during 2012" in pinfa Newsletter n° 35

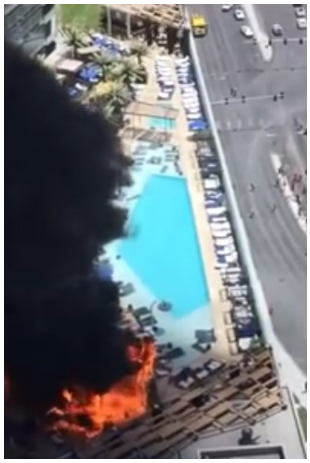


DEROCA: carbon nanotubes PIN FR synergies

The EU-funded (FP7) project, DEROCA, has developed five new PIN flame retardant system prototypes, combining industrial multiwall carbon nanotubes (MWCNTs) with phosphorus-based and other commercially-available PIN FRs. The objective is to replace halogenated FRs, in order to reduce toxicity and corrosivity of smoke, in electrical wires and cables, insulation foams, heating – ventilation and air conditioning applications, corrugated pipes and consumer goods. Market potential for new non-halogenated fire safety solutions is estimated at over 2 billion €/year worldwide. The MWCNTs act in synergy with the PIN FRs by improving the resilience of the protective char layer developed in case of fire, so reducing heat release from burning polymers and composites. The DEROCA project includes new, cost/rapidity optimised fire testing methods, cost competitiveness and mechanical performance in applications. Project partners are the European Commission JRC Service (Joint Research Centre), Leoni Studer (wire and cable), Akyuz Plastik Turkey, NMC Group Belgium, Vamptech Iberica, Lille School of Engineering Chemistry, SP Sweden and University of Central Lancashire UK and project leader, Nanocyl Belgium.

"Keepers of the flame", International Innovation, Issue 187, 2015
http://www.internationalinnovation.com/keepers-of-the-flame/

DEROCA Development of safe and eco-friendly flame retardant materials based on CNT co-additives for commodity polymers www.deroca.eu

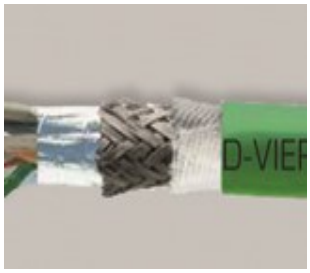


Fake palm trees in Las Vegas hotel fire

Firefighters said that artificial palm trees went up in flames "like 20-foot-tall cans of gasoline" near a 14th floor outside swimming pool at the Cosmopolitan Hotel, Las Vegas, 25th July 2015. The fire broke the glass of one hotel room and black smoke spread inside the hotel. Fortunately nobody was seriously injured. The trees were made of non flame retardant plastic foam, within a hard plastic coat, around a steel core structure. Because the trees were near an outside pool, they were not subject to fire safety regulations. Contact13 TV video online shows a comparison (NFPA 705 test) between non flame retardant and flame retardant fake palm plants (although the material in the pot was not FR and did burn), showing the non flame retarded plant resulted in "burning material on fire raining down, … the foam core acting like a torch" and "toxic fumes coming off … a hazard to anybody."

Photo from Cosmopolitan Hotel fire video YouTube

"After The Cosmopolitan fire, Contact 13 does artificial tree fire test" D. Spears, ABC Contact TV News 25/9/2015



PIN FR cables for increasing rail safety

SAB Bröckskes offers rail FRNC (Flame-Retardant Non-Corrosive) cables conform to the new European rail standard EN 45545-2, which requires that all cables must be self-extinguishing. The FRNC cables respect R15 (EL1A) requirements under this railway standard for hazardous applications. The new cables are conform to the data cables standards categories CAT 5eR, CAT 6A, CAT 7A R for applications in Ethernet or gigabit Ethernet cross-linking in rail vehicles information systems, controls or e-ticketing. The cables respect standards EN 50306-1 + EN 50264-1, EN 50267-2-1 (development of HCl hydrogen chloride 0.5%), EN 50267-2-2 and EN 60684-2 for non-halogenated, EN 61034 for smoke density and EN 50305 for toxicity.

SAB Bröckskes "Halogen-free cables" and "Industrial Ethernet Cables CAT 5e, CAT 6A and CAT 7A especially for use in rail vehicles" and "Higher standard regarding fire protection in rail vehicles" www.sab-cable.com

New @2spin PIN FRs for polypropylene textiles

Devan Chemicals, with ENSAIT (French National Textile facility), has developed a new family of phosphorus – nitrogen PIN flame retardants for textile products. The work was supported by Europe as part of the INTIMIRE project (development of new textile products with improved fire performance). The products combine new phosphinates with melamine cyanurate and have been tested for fire resistance and for impact on the textile performance and are now marketed by Devan Chemicals as @2spin PP 225 polypropylene masterbatches with different formulations adapted to different textile

configurations (nonwoven, knitted) and to different fire performance standard requirements. The new PIN FR solution offers the advantages of improving ultraviolet resistance of the polymer, and requiring no water in processing. The FRs are locked into the fibre, ensuring durability in washing.

"Devan Chemicals develops a new halogen free flame retardant masterbatch for Polypropylene Fibres" 1/6/2015 http://www.devan.net/news.aspx?id=6031

INTIMIRE (INTumescent materials with Improved fIRE retardant and flame resistant properties) http://intimire.ensait.fr/

ENSAIT (Ecole Nationale Supérieure des Arts et Industries Textiles, Roubaix, France) http://www.ensait.fr/

IED BAT BREFs wood treatment, textile coating

The EU has announced that work underway to update the 2006 BAT BREF for wood treatment will be extended to include not only preservative chemicals, but also application of other protective treatments including flame retardants. Separately, launch of work on a BAT BREF for textile coating is being proposed. BAT BREFs are official EU documents, elaborated after stake holder and Member State consultation, which define Best Available Technologies for different sectors of activity, under the IED Industrial Emissions Directive 2010/75/EU (previously the IPPC Directive). Implementation of BAT BREF specifications becomes obligatory for all industrial sites concerned in Europe when a BAT BREF is officially adopted.

List of and download of current BAT BREFs and status of those underway
http://eippcb.jrc.ec.europa.eu/reference/

TDK capacitors for electronics and automobiles

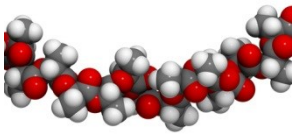
TDK has launched two new series of multi-layered ceramic capacitors (MLCCs), FG series and automotive FA series. The new products have a PIN flame retardant external resin coating, so achieving halogen-free to IEC 61249-2-21, and supporting use in environmentally friendly applications. The FG series covers voltage ranges from 6.3 to 630 V, is qualified to AEC-Q200 and includes models designed for temperatures up to 150°C. The FA series are adapted for use in automotive electronics: modern cars have maybe 100 small electric motors, and capacitors can suppress EMI (electro-magnetic interference) from these motors.

"Halogen-free leaded multilayer ceramic capacitors for automotive and general-purpose applications", TDK 27th January 2015:
http://www.global.tdk.com/news_center/press/files/pdf/20150127_04en.pdf

PIN fire safety for biosourced PLA polymers

Polylactic acid (PLA) is a biodegradable thermoplastic polymer which can be produced from bio-resources (crops and plant by-products), but it is highly flammable and can cause fire spread by flaming drips. Different PIN flame retardant solutions are proposed for PLA (pinfa Newsletters 29, 50). A new study assesses bio-sourced polymeric phosphorus PIN FRs, based on cellulose, and the bio-material and mineral-based PIN aluminium phytate. Microcrystalline cellulose MCC (obtained by partial depolymerisation of plant cellulose) and natural nanocrystalline cellulose NCC (extracted from ramie fibres = China grass) were tested. PLA / cellulose fibre composites (20 or 30% fibres) achieved UL94-V0 and reduced pHRR (peak heat release rate) using these PIN FR solutions. The nanocrystalline cellulose achieved target fire performance more easily because its high specific surface area enabled better char formation.

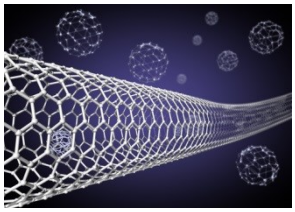
"Cellulose/phosphorus combinations for sustainable fire retarded polylactide", Eur. Polymer Journal 74 (2016) 218–228, L. Costes et al., University of Mons, Belgium.



High efficiency PIN FR for bio-sourced PLA

An innovative phosphorus and nitrogen based flame retardant showed to be highly effective in fire safety treatment of PLA (polylactic acid, a biodegradable polymer which can be renewably sourced from dairy byproducts). N, N'-diallyl-P-phenylphosphonicdiamide (P-AA) was produced by reacting PPDCl (phenylphosphonic dichloride) with TEA (trimethylamine) for several hours, subjected to filter separation and finally washed with water. It was then mixed into PLA by extrusion. Just 0.5% P-AA increased the LOI (limiting oxygen index) of PLA by nearly 40% and enabled passing of UL94-V0 at 3.2mm thickness. 1% P-AA enabled UL94-V0 at 1.6mm. The flame retardancy was considered to mainly result from a gas phase action of $PO^{\cdot}$ radicals released by thermal decomposition of P-AA. The 0.5% and 1% loadings of P-AA did not modify the key mechanical properties of the PLA polymer (tensile strength).

"A new super-efficiently flame-retardant bioplastic-poly (lactic acid): flammability, thermal decomposition behavior and tensile properties", X. Zhao et al, ACS Sustainable Chem. Eng. 2016



Nano not as big a problem as many may fear

After four years of assessment and 30 reports, the Denmark EPA (Environmental Protection Agency) has published conclusions regarding the safety of nano-materials for consumers and for the environment. The final report states that "most nanomaterials do not seem to be as big a problem as many may fear. However, there is still a need for more knowledge. It cannot with certainty be concluded that nanomaterials do not pose a risk to health or the environment [and that] with the knowledge we have today, and with the limitations of the assessments, the nanomaterials usually do not pose a health or environment risk when present in products in solid form. However, for some

uses without proper protective equipment, for example use of some spray products, or sanding of a painted surface containing nanomaterials, nanoparticles may be inhaled and cause a risk to consumers. Similarly, in the environment a risk may only occur under very special conditions." The possible risks are in a number of cases related to possible accidental uptake, for example ingestion of sunblock lotions. For the environment, questions are raised regarding local impacts near sewage works discharge points. The report considers that further information is needed about specific properties of nano-materials and also about where and how they are used. Experience with the Denmark nano-materials register indicates that companies have difficulties obtaining information from overseas suppliers. This report does not address nanomaterials in the working environment, which are being assessed separately by the Danish NanoSafety Centre.

"Better control of nanomaterials – summary of the 4-year Danish initiative on nanomaterials", Denmark EPA, Environmental Project no. 1797, 2015, 34 pages, ISBN 978-87-93352-89-6

PIN FRs emerging trend for biomaterials

A 34 page overview from Asia in the Review of Chemical Engineering shows that PIN flame retardants are key to enabling the development of biofibres, biopolymers and bio(nano)composites, demanded by industries such as automotive, construction, aerospace and electronics requiring "environmentally benign materials." Demand is for materials which are bio-sourced, to replace metals whilst reducing weight, and are non-halogenated. PIN flame retardants are essential to enable this whilst ensuring fire safety, reducing fatalities and property loss in case of fire. The authors underline the current number of fires in road vehicles (1.2 million per year in the USA). Trends in a range of PIN flame retardancy approaches are summarised, including layer-by-layer nano deposition, plasma FR treatments, sol-gel. Recent studies on PIN FR performance in bio(nano)composites, in particular PLA (polylactic acid) are presented, including both developments in application of known PIN FRs (e.g. ammonium polyphosphate, melamine polyphosphate, aluminium hydroxide) and new products such as zeolites, phosphorus-linked polymers and new phosphorus compounds, novel char promoters (e.g. TT4, PPLA), nanocarbons/nanographites, nanoclays.

"Emerging trends in flame retardancy of biofibers, biopolymers, biocomposites, and bionanocomposites", Rev. Chem. Eng. 2015, C. Idumah & A. Hassan, Universiti Teknologi Malaysia,

Progress on fire risk standards

The International Standards Organisation working group ISO/TC 92/SC3 is defining recognised model methods for assessing the possible consequences of fires in buildings or vehicles on life (risk of casualty), health and the environment. These models provide regulators, safety engineers and researchers with tools to define when and how life safety in fires should be

evaluated, to analyse dangers of smoke and gases emitted in fires (quantity of smoke, inhibition of visibility and so of escape, toxicity, effects on persons exposed) and to assess when victims will be incapacitated by heat, gases or smoke. They define how to analyse and measure smoke in fires or fire tests and how to analyse how a fire which has occurred led to injuries or deaths. They also establish what factors should be taken into account to determine the environmental risk of fire gases and smoke. The aim is to improve both building and fire safety system design cost-effectiveness and to reduce the human consequences of fires.

"Fighting the toxic environment of fire with ISO standards", S. Tranchard, ISO News, 2/12/2015 December 2015

ISO 19702:2015 (August 2015) "Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy"

Other news

Modelling environmental fate of possible new flame retardants: 94 chemicals considered to be possible substitutes to PBDE (mostly other brominated FRs plus 20 non-halogenated phosphorus esters and melamine) were modelled for estimated potential persistence and LRT (long range transport). The authors note that physical and chemical properties vary widely depending on small changes in the molecules and functional groups. For around half of the 94 chemicals the model suggests potential persistence or LRT. This shows the need to assess these risks adequately substance by substance.

"Novel flame retardants: Estimating the physical-chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements", X. Zhang et al., Chemosphere 144 (2016), 2401-2407

Health and ecological risks of P-FRs: nine phosphorus flame retardants (five non-halogenated arly phosphates TNBP, TMPP, TPHP, TEHP, TBOEP and four halogenated TCEP, TDCIPP, TCIPP, TDBPP) were tested in vitro for possible thyroid effects and in vivo for effects on frog embryos. Only TNBP, TMPP, TCIPP and TDCIPP showed effects. Although the mode of action is unclear, the authors note that predictions using LigandFit molecular modelling were close to test results.

"Thyroid hormone-disrupting activity and ecological risk assessment of phosphorus-containing flame retardants by in vitro, in vivo and in silico approaches", Q. Zhang et al., Environmental Pollution 210 (2016) 27e33

QSAR chemical database updated: Denmark has updated the QSAR (Quantitive Structure – Activity Relationship) database. The database covers over 600 000 chemicals and gives model predictions of physico-chemical, health and environmental properties, by comparing chemicals with others of similar structure for which experimental data is available.

QSAR database, Technical University of Denmark's National Food Institute, with Danish Environmental Protection Agency and Ministry of Environment and Food, European Chemicals Agency (ECHA) and Nordic Council of Ministers
http://qsar.food.dtu.dk/

UL (Underwriters Laboratories) and Emory University are launching a study into both fire protection effectiveness and exposure to flame retardants from furniture and electronic products. Objectives are to identify routes to reduce exposure to chemicals of concern by management of sources, changing manufacturing processes or using safer alternatives, while also maintaining adequate flammability protection.

"UL Partners with Emory University to Conduct Research on Furniture Flammability and Human Exposure to Flame Retardants" 17/11/2015

Hoverboard fire risk concerns: Amazon.UK, has withdrawn from sale and told customers to throw away and will reimburse certain hands-free, self-balancing scooters (hoverboards). The three largest US airlines, BA and others have banned their transport. USPS and the US Postal Service have indicated that they will ship only overland. This follows reports that certain models are catching fire. The US CPSC (Consumer Product Safety Commission) has received reports of 12 hoverboards catching fire.

"Amazon UK tells customers to get rid of hoverboards", "Statement from the U.S. CPSC Chairman Elliot F. Kaye on the Safety of Hoverboards"

Agenda

26-28 Jan	Coral Springs Florida		Thermoplastics Concentrates 2016 (AMI) http://www.amiplastics.com
1-3 Feb	Barcelona		COST MP1105 Training School "Strategies to study fire behaviours and fire retardant mechanisms" COST.MP1105@UGent.be
15-16 Feb	Torino, Italy		COST MP1105 Final Conference: Fire retardants & textiles: past, present and future COST.MP1105@UGent.be
1-2 March	Cologne, Germany		Sustainable Plastics 2016, from sourcing to end of life recovery (AMI) https://www.amiplastics.com
1-3 March	Cologne, Germany		AMI Cables 2016 https://www.amiplastics.com
8-10 March	Singapore		Masterbatch Asia (AMI) http://www.amiplastics.com/Events/Resources/Programme/MB%20Asia%202016.pdf
16-17 March	Mons, Belgium	►	1st International Conference on Eco-Friendly Flame Retardant Additives and Materials (ECOFRAM) http://www.greenwin.be
21-23 March	Preston, UK		Fire Toxicity 2016 (UCLAN) http://www.uclan.ac.uk/news/international-conference-fire-toxicity.php
5-6 April	Newark, New Jersey		PolymerFoam 2016 (AMI) http://www.amiplastics-na.com/events/Event.aspx?code=C712&sec=5546
6-8 April	Dublin		Sustainable Fire Engineering Benchmark Event (Regional SBE16/17) http://sustainable-firengineering.ie
14-15 April	Aalborg, Denmark		COFISH16 Conference on Fire Safety & Health http://www.cofish16.aau.dk/
26-27 April	Montreal, Canada	►	**pinfa-na industry seminar: flame retardancy of materials for surface transportation** http://pinfa-na.org
27-28 April	Poznan, Poland		COST Flaretex MP1105 final conference on Innovations in Flame Retardancy of Textiles and Related Materials http://www.iwnirz.pl/strona,160.html

3-4 May	Pittsburgh Pennsylvania		AMI Fire Retardants in Plastics http://www.amiplastics-na.com
11-13 May	Lund, Sweden		FSF 2nd Fire Safety of Facades Int. Conference http://www.facade2016.org
15-19 May	Lisbon		47th Annual Meeting of the International Research Group on Wood Protection http://www.irg-wp.com
23-25 May	Izmir, Turkey		7th European Conference on Protective Clothing http://www.ecpc2016.com/
23-26 May	Stamford CT		FLAME 2016: Recent Advances in Flame Retardancy of Polymeric Materials http://www.bccresearch.com
8-10 June	Princeton, USA		SiF'16 Structures in Fire http://www.structuresinfire.com
15 June	Brussels	►	**pinfa General Assembly**
12-16 June	Lund, Sweden		12th International Symposium on Fire Safety Science www.iafss.org
13-16 June	Las Vegas		NFPA Conference & Expo http://www.nfpa.org
21-22 June	Philadelphia		AMI Polymers in Cables 2016 http://www.amiplastics-na.com
4-6 July	London		Interflam 2016 (14th International Conference and Exhibition on Fire Science and Engineering) www.intersciencecomms.co.uk
21-26 August	Philadelphia		ACS Fire and Polymers VII www.acs.org or alexander.morgan@udri.udayton.edu
29-30 Sept	London		ICFSST 2016: 18th International Conference on Fire Safety Science and Technology https://www.waset.org
4-6 Oct	Baltimore		4th International Conference on Fires in Vehicles FIVE www.firesinvehicles.com
6-8 Dec	Cologne, Germany		AMI 11th Fire Resistance in Plastics https://www.amiplastics.com

Publisher information

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For abbreviations see: www.pinfa.org