pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

# Your newsletter for non-halogen fire safety solutions n° 123 March 2021


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## PINFA


## pinfa sustainability strategy

**pinfa's General Assembly discussed directions for PIN FRs in the context of the new EU Chemicals Strategy** and the Green Deal. Online 3rd March 2021, the meeting brought together 41 participants from 21 pinfa members companies, along with representatives of pinfa North America and pinfa China. Pinfa's two major recent projects, on recycling of plastics containing PIN FRs and on smoke toxicity of flame retarded and non flame retarded synthetic and natural materials will deliver full reports shortly. Discussion is engaged with downstream user industries on a position on FRs and recycling.

**pinfa is now actively working on opportunities for PIN FRs under the new EU Chemicals Strategy** (see pinfa Newsletter n°119). Discussions included how to address the questioning of whether FRs are needed for fire safety and the meaning of "Essential Use" in the Chemicals Strategy, demands for more toxicity / ecotoxicity data, and how to take forward opportunities for EU support for innovation in new sustainable PIN FR solutions. Collaboration with science and NGOs is seen as important to independently validate sustainability of PIN FRs, and with industry and users to implement FR innovation along the value chain (production, compounding, use, products, recycling).


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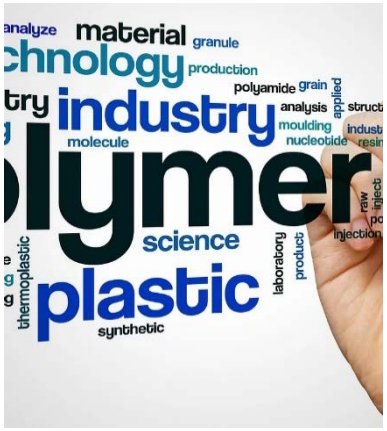
## Fire, smoke & toxicity for transportation

**Pinfa-NA – sampe (Society for the Advancement of Material and Process Engineering) free online event, 28 April 2021**. This session will look at fire, smoke and toxicity (FST) requirements for transport applications, in particular aviation. Speakers from FAA, Boeing, Underwriters Laboratories, Safran, Southwest Research Institute.

*Fire, smoke & toxicity requirements for transportation composites, 28 April 2021 online, SAMPE – pinfa-NA, 18h00 CEST*
*https://www.nasampe.org/events/EventDetails.aspx?id=1496426*




## Training to formulate fire safe materials

**Four interactive webinars will provide insight into flame retardant product design for formulators and compounders**. The training is organised by pinfa North America, in collaboration with SPE (Society of Plastics Engineers), online, from June 1st, 8th, 15th and 22nd, 2021, this four part training series will look at flame retardant mechanisms, selection and formulation, to meet application and fire safety specifications, including sustainability and circular economy, as well as fire performance testing. Thermoplastics, elastomers, thermosets, textiles, adhesives, sealants and coatings will be covered by instructors with decades of industrial experience in formulating and compounding.

*Information, detailed programme, registration www.pinfa-NA.org*

# PIN FRs IN ECOLABELS

TCO CERTIFIED

## More PIN FRs on TCO accepted list

**Sixteen PIN FRs are now on the TCO Certified list of safer alternatives**. TCO Certified, the health, environment and worker protection label for office and home electronics, has updated its list of "alternative safer substances" to now include 16 PIN flame retardants, including mineral FRs (inc. ATH, MDH), siloxanes and similar, nitrogen polyphosphates FRs (MPP, APP), aluminium phosphinate (AlPi) and several organophosphorus FRs. TCO Certified inclusion on the "accepted substance list" is based on GreenScreen® assessments with benchmark of 2 or higher.

*PIN FRs included in the February 2021 TCO "TCO Certified Accepted Substance List": Aluminum diethylphosphinate, Aluminum Hydroxide, Red Phosphorus, Substituted Amine Phosphate mixture, Triphenyl Phosphate, Tetrakis (2,6-dimethylphenyl)-m-phenylene biphosphate, Siloxanes and silicones - di-Me - di-Ph - polymers with Ph silsesquioxanes, Magnesium Hydroxide, Phenoxyphosphazene, Melamine Polyphosphate, Resorcinol Bis-Diphenylphosphate RDP, Ammonium Polyphosphate, Octaphenylcyclotetrasiloxane, Aluminum oxide, Resorcinol Bis-Diphenylphosphate, Bisphenol A diphosphate*

*TCO "Safer alternatives to hazardous substances listed here", updated 18 February 2021 https://tcocertified.com/accepted-substance-list/*

# FIRE SAFETY

## Fire dangers from objects near buildings

**Bench fire destroys school and again shows risks of outside furniture or decorations not covered by building regulations**. In the editorial to Fire Safety & Technical Bulletin (FS&TB) February 2021, Marcelo Hirschler shows that around 3% of reported fires in the US occur in structures which are not buildings (there are also many fires occurring in vehicles). Fake palm trees around an outside pool on a roof caused a major fire in the Cosmopolitan Hotel, Las Vegas, in 2015 (pinfa Newsletter n°60), injuring two people with smoke. This has led to the inclusion of fire test requirements for "artificial vegetation" (only) permanently installed on roofs or near buildings in the IFC Code. A fire deliberately started in clothing placed on a plastic composite bench attached to a school wall under a wooden overhang, on February 3, 2013, in Vancouver, WA, led to the complete destruction of the school. Fire tests conducted to reconstruct the event showed that plastic composite benches, without flame retardants, resulted in very high heat release (> 4 MW) and burning of the overhang within minutes of bench ignition (as shown in the first photo), whereas both an alternative flame retarded plastic composite bench and a wooden bench performed much better (the pine wood bench actually self-extinguished). Mr Hirschler considers that fire codes should require fire testing for improved safety of large, fixed objects placed on roofs or near buildings.

*Fire Safety & Technical Bulletin (FS&TB) February 2021*
*http://www.gbhinternational.com/fire-safety-and-technology-bulletin/*

# INNOVATION

## Eastman announce polyester recycling plant

**100 000 t/y of waste polymers will be broken down by methanolysis to chemical building blocks for new quality plastics.** The new 250 million US$ plant in Kingsport, Tennessee, is expected be completed in 2022 and will reduce greenhouse gas emissions by 20-30% compared to plastics production from oil. Input materials will be end-of-life polyester, such as carpets, and polyethylene terephthalate packaging. Eastman already markets a copolyester containing up to 50% recycled content from the company's recycling technologies. Flame retardants and other additives are generally not an obstacle to chemical recycling processes.

*"Eastman invests in methanolysis plant in Kingsport, Tennessee", 1 February 2021 https://www.recyclingtoday.com/article/eastman-chemical-recycling-plastics-investment/*


## Halogen free flame retardant PC blends

**Romiloy 7410® is a non-halogen rubber-modified PC blend offering mechanical, UV and fire performance** (UL94-V @1.5 mm). The new PC-blend material from Romira (ROWA Group) is suited to applications in electronics and electrical industries, consumer goods, medical technologies, both indoors and outdoors. It offers high notched impact strength and temperature resistance. Romiloy state that the absence of halogenated FRs and antimony synergist reduces migration, so improving surface quality, and avoids problematic catalytic degradation of the polymer matrix. The ROWA Group, with 60 years' experience in plastics, comprises six companies, each specialist in different areas of plastics innovation, technology, production and trading, including technical plastics and blends, masterbatches, foils and coatings, pigments and additives.

*"New PC-blends with excellent properties", 15th October 2020*
*https://www.rowa-group.com/en/news/detail-view/news/new-pc-blends-with-excellent-properties.html*

*Photo: 3D-printed armrest component.*

## PIN FR 3D-printing for aviation

**Stratasys' ULTEM™ 9085 resin performance 3D-printing filaments meet aviation and railway fire, smoke and toxicity standards**. The material is polyetherimide-based with non-halogenated flame retardants. Printed on Stratasys F900 FDM (fused deposition modelling) 3D printers, is tested for flame, smoke and toxicity to 14 CFR 25.853, BSS 7238 and 7239, and AITM 2.0007B & 3.0005 and EN45545-2 (e.g. all hazard levels HL1/2/3), demonstrating suitability for use in production for the railway rolling stock industry. Aviation parts including seating, panelling and ducting can be manufactured rapidly and economically, enabling aircraft cabin customisation, and are already certified by and used by Airbus. The material can also be used for 3D printed applications in automotive and other industries. Stratasys invented FDM 3D-printing 30 years ago and is today a world leader in industrial-scale 3D-printing machines and materials.

*"Stratasys wins one of its largest ever aerospace orders", 13 August 2020*
*https://www.aero-mag.com/stratasys-am-craft-3d-printing-13082020/*

## Safe FR coating for furniture

**Annabel Furniture, with Flamaway, has launched a novel FR coating to achieve fire safety, e.g. on polyester fabrics**. The coating contains no halogen, no antimony and achieves with lamination crib 5 or crib 7 fire safety standards. It has a positive health profile (no cancer, reproduction, hormone effect) and is non bioaccumulative. It is ZDHC (Zero Discharge of Hazardous Chemicals) approved and Oekotex listed (ISO 17050-1). Colour proof textile treatment is compatible. Annabel Textiles develops and produces in Belgium innovative new fabrics since 1971.

*"Halogen Free FRC", Annabel https://www.annabeltextiles.com/our-range/finishing/halon-free-frc/*


## Loctite FR photopolymer for Asiga printers

**Henkel's halogen-free photo-curing resin is validated for Asiga 3D-printers, enabling ultra-fast, precision manufacturing.** Loctite 3D 3955 HDT280 FST is the first photopolymer that passes vertical burn and aerospace FST standards. This material can produce parts which meet low-smoke, UL94-V0 (3mm thickness), 30 and 60 second vertical burn tests and aerospace fire safety requirements, as well as meeting demanding performance requirements, including heat deflection up to 300°C. With Asiga's desktop MAX and large floor standing Pro4K printers, Henkel's material enables accurate, flexible and high-speed production of detailed and complex parts. For example, the Swiss electronics connector company has successfully used the 3D-printed backshells for printed circuit boards. Loctite 3955 HDT280 FST material also works well on OriginOne and EnvisionOne HT printers.

*Photo: Asiga 3D-printer*

*Henkel launches first photoreactive 3D printing material meeting aerospace fire, smoke and toxicity safety standards* *https://www.henkel.com/press-and-media/press-releases-and-kits/2019-11-15-henkel-launches-first-photoreactive-3d-printing-material-998268*

*"EnvisionTEC and Henkel to combine 3D printing and photopolymer material chemistry expertise for end-use parts", 23 November 2020* *https://www.henkel.com/press-and-media/press-releases-and-kits/2020-11-23-envisiontec-and-henkel-to-combine-3d-printing-and-photopolymer-material-chemistry-expertise-for-end-use-parts-1133134*

*"Flame Retardant 3D Printing Material from Henkel Now Validated for Asiga Printers", 10 February 2021* *https://www.etmm-online.com/flame-retardant-3d-printing-material-from-henkel-now-validated-for-asiga-printers-a-998947/*

*Hankel Loctite 3955 HDT280 FST* *https://www.loctiteam.com/aerospace/*
*Contact* *loctite3dp@henkel.com*

## Fire safe waterproof sun-protection

**Markilux has launched a halogen-free flame retardant polyester sun shading fabric for its designer awnings and blinds**. The polyurethane-coated polyester fabrics are waterproof, weather durable, SFC dirt-inhibiting, pliable even at cold temperatures, and transparent enabling full colour intensity. Fire safety to EN 13501-1 for public buildings, class B1, is achieved. The company says that combining waterproofing and flame retardancy in these sun protection fabrics required new chemistry, because the waterproofing treatment is inherently flammable, so that the new fabric is an industry first. Markilux Designer Awnings have been manufacturing quality awnings and outdoor textiles in Germany since 1972.

*"A solar protection fabric offering new high-tech protection", 30 November 2020* *https://www.openpr.com/news/2198828/a-solar-protection-fabric-offering-new-high-tech-protection*


## LSHF cable for long term reliability

**Low Smoke Zero Halogen cables ensure low toxicity and high visibility in fire, operation up to 105°C and 70 years working life**. Mariotti Kabel, based in Karlsruhe, Germany, with operations worldwide, is producing power and communications systems and cables since 1948. The company's weak and strong current cables offer high corrosion and UV resistance, high temperature operation, anti-aging to ensure a lifetime which can reach 70 years or more and are produced with environmental and low-carbon objectives. PIN flame retardants ensure fire performance, releasing only water vapour in fire, so ensuring high visibility and low toxicity of smoke.

*"Low Smoke Halogen Free Flame Retardant Wire", Mariotti Kabel GmbH* *www.mariotti-gruppe.de/index.php*

## Aviation carpet with recycled binder

**Anker, Devan and Shark Solutions have developed a halogen-free FR carpet for aviation using 100% recycled PVB binder** (polyvinyl butyral) sourced from recycled vehicle and construction glass. Anker, a German professional carpet manufacturer, developed the product with Shark Solutions, a Danish cleantech company specialised in PVB sustainable solutions, and Devan Chemicals, a textile innovation company (see pinfa Newsletters n°s 60 and 113). The aviation carpet uses PIN FR back coating, achieving Airbus and Boeing fire safety standards.

*"Anker, Devan and Shark Solutions teamed up to create the world's first flame retardant aviation carpet that utilizes a 100% recycled binder", 13 October 2020 https://shark-solutions.com/worlds-first-flame-retardant-aviation-carpet/*

# RESEARCH

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SAFETY RESEARCH

## Toxic gases from electric vehicle fires

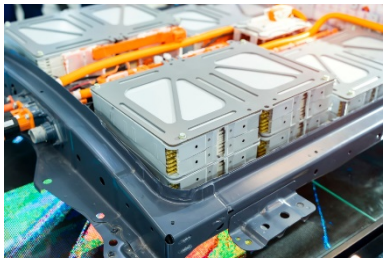
**RiSE report concludes EV fires have similar heat release to conventional vehicles, but specific additional toxicity risks**. The report presents full scale fire tests comparing two electric vehicles to a comparable diesel model, battery fire tests and data from a literature review. Heat release rate was similar for the electric and diesel vehicles (80% charge battery, 80% full diesel tank). Toxic gases are present in smoke from fires with both types of vehicle (e.g. CO, HF, HCl, $SO_2$) but smoke from e-vehicle fires also showed considerably higher levels of HF (hydrogen fluoride) and also presence of specific metals, depending on battery chemistry (Ni, Co, Li, Mn). The levels of HF were however lower than expected and achieved relatively low concentrations in a garage fire scenario.

*"Toxic Gases from Fire in Electric Vehicles", O. Willstrand et al., RISE Report 2020:90 http://ri.diva-portal.org/smash/get/diva2:1522149/FULLTEXT01.pdf*


## Challenges of lithium ion battery fires

**A review of 150 papers shows the high variability of LiB fires, importance of battery chemistry and of state of charges (SOC)**. Batteries with lithium iron phosphate cathodes show significantly lower peak temperature and lower risk of thermal runaway than those with lithium cobalt oxide or lithium nickel manganese cathodes. Heat release rate increases and time to thermal runaway decreases with SOC (i.e. with the energy held in the battery). The authors note that modelling of lithium ion battery fires is challenging, and that different battery testing protocols and different standards between battery manufacturers make data comparison difficult.

*"A Review of Experimental and Numerical Studies of Lithium Ion Battery Fires", M. Ghiji et al., Appl. Sci. 2021, 11, 1247.*
*https://doi.org/10.3390/app11031247*



## Lithium ion battery fire toxicity

Thermal runaway and fire test of large cell battery shows high toxic emissions and dangers to firefighters. Seven tests were carried out on large (300 Ah, 0.54 kg) single cell $LiFePO_4$ cathode lithium ion battery, as used in buses or for energy storage. The battery was externally heated (500 W) to simulate thermal runaway. This did not cause spontaneous ignition. In some tests, fire was manually ignited when safety valves opened (after c. 25 minutes) releasing high-temperature vapours and aerosols. Around ten minutes after ignition, temperatures reached c. 600°C. The ignited batteries released high levels of carbon monoxide, which would be lethally toxic in the case of a bus fire in a garage. The authors conclude that high ventilation rates are needed to ensure safety in case of electric vehicle fires and that emissions under heating mean that extinguished battery fires may reignite. They note that large single-cell $LiFePO_4$ batteries may offer better safety than standard multi-cell lithium-ion configurations.

*"Thermal runaway and fire behaviors of a 300 Ah lithium ion battery with $LiFePO_4$ as cathode", Renewable and Sustainable Energy Reviews 139 (2021) 110717, https://doi.org/10.1016/j.rser.2021.110717*

## PIN FRs suppress smoke in polyurethane

**A combination of ammonium polyphosphate and magnesium-iron-LDH halved smoke density and toxicity of polyurethane**. Thermoplastic polyurethane was PIN flame retarded with APP (ammonium polyphosphate) and magnesium iron layered double hydroxide (MgFeLDH) at 20% loading of PIN FR (of which 0-4% MgFeLDH, 20-16% APP), plus control pure polyurethane (PU), and tested for heat release, smoke release and emission of organic compounds and toxicants such as HCN, carbon monoxide, isocyanurate … Smoke production and density was very significantly reduced with 20% APP only, and was even lower with a combination of APP and MgFeLDH, down to less than half that of pure polyurethane. Emissions of toxic gases and volatile organics

were also significantly reduced. The authors suggest that this is because of reaction between APP and MgFeLDH resulting in a compact char with fine microstructure.

*"Smoke suppressant in flame retarded thermoplastic polyurethane composites: Synergistic effect and mechanism study", H. Ren et al., Nano Res. (2021) https://doi.org/10.1007/s12274-021-3317-z*

## PIN FRs can reduce respirable fibres in fire

**Phosphorus PIN FRs tested in carbon-fibre reinforced epoxy reduced generation of respirable fibres in fire tests**. Samples were produced using epoxy resin* and carbon fibre fabric, with 0 – 15% loading of three different phosphorus PIN FRs** and also a combination of silicon dioxide nanoparticles with these. All three P-FRs showed flame retardant effectiveness, e.g. reducing MARHE*** from 242 to 194 – 230 (at 10% loadings), with the phosphazene and the phosphate showing the higher flame retardant efficiencies and acting respectively in the gas and condensed phases. All three P-FRs were effective in reducing levels of carbon fibres on the sample surface and also led to nearly two times higher average fibre diameter after testing (i.e. lower levels of respirable fibres), with the phosphate PIN FR showing the greatest effect against respirable fibres.

** tetraglycidyl methylene dianiline and aromatic aminic hardeners.*
*** an oligomeric bis(phenoxy)phosphazene, a condensed adduct of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and salicylaldehyde [i.e. a phosphinate], an oligomeric resorcinol bis(diphenyl phosphate).*
**** MARHE = maximum average rate of heat emission.*

*"Prevention of the formation of respirable fibers in carbon fiber reinforced epoxy resins during combustion by phosphorus or silicon containing flame retardants", L. Greiner et al., Polymer Degradation and Stability 185 (2021) 109497 https://doi.org/10.1016/j.polymdegradstab.2021.109497*

# OTHER NEWS

**Human exposure to organophosphate esthers is within the reference dose (RfD).** A review of over 4 000 publications 2014-2020 identified 90 articles with useable data on organophosphate esther (OP) exposure covering OP's used in many applications (lubricants, food packaging, plastics, plasticisers, flame retardants, glues …) and exposure via air, water, dust and food. Intake data was found for eight OP esthers (chlorinated: TCEP, TCIPP, TDCIPP; non-halogenated: TPHP, TnBP, TBOEP, TEHP, EHDPP). The sum for total intake for these eight OP esthers by all exposure pathways was considerably lower than the reference dose (RfD) for any of the OP esthers, both for adults and toddlers. The main identified intake route as in food. The authors note that further research is needed, in particular into dermal uptake.

*"A critical review of human exposure to organophosphate esters with a focus on dietary intake", M. Remilekun Gbadamosi et al., Science of the Total Environment 771 (2021) 144752*
*https://doi.org/10.1016/j.scitotenv.2020.144752*

**BSEF report on impacts of brominated FRs on recycling**. The brominated flame retardant industry, BSEF, has published a report by SOFIES discussing brominated flame retardants in WEEE recycling. The report was presumably funded by BSEF (but this is not stated) and appears to be based on 50 references and input from around 12 stakeholders (not including BSEF member companies). It concludes that only around 9% of the 2.6 million t/y of WEEE plastics generated in Europe contain brominated FRs (BFRs) and that restricted BFRs only represent a small and declining fraction of BFRs found in WEEE. However, some 55% of BFR plastics are today not correctly separated and disposed of because of improper sorting by consumers or substandard WEEE treatment practices. Also, some BFR plastics are accidentally recycled (the report indicates 5% BFR ABS and BFR HIPS) because even where operated correctly (generally by density), sorting is not 100% reliable. The report suggests that non-halogen FRs, in particular phosphorus FRs, "are known to negatively impact the recyclability of WEEE plastics" but this is based on concerns expressed by WEEE recyclers (no references) and on two non-recent studies (Imai et al. 2003, funded by BSEF, and Statler et al. 2008). Neither of these studies support the statement made, see below. The report also ignores more recent studies which suggest that PIN FRs are compatible with plastics recycling (see two studies by Wagner et al., 2019, in pinfa Newsletter 110) and results of the studies carried out for pinfa by Fraunhofer IGB (pinfa Newsletter 105, 2019).

*"Study on the Impacts of Brominated Flame Retardants on the Recycling of WEEE plastics in Europe.", SOFIES, November 2020, published by BSEF https://www.bsef.com/wp-content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-WEEE-plastics-recycling-by-Sofies-Nov-2020.pdf*

*"Recyclability of Flame Retarded Polycarbonate: Comparison of Non-halogenated to Halogenated Flame Retardants", D. Statler et al., J Fire Sci 26, 331-350, 2008 https://doi.org/10.1177/0734904108090828 . In this study, polycarbonate flame retarded with brominated FR or with PIN FR potassium diphenylsulfone sulfonate (KSS) was subjected to eight recycles (granulating, melting, injection molding) concluding that the PIN FR resists as well as does the halogenated FR.*

*"Comparison of the Recyclability of Flame-Retarded Plastics", T. Imai et al., Environ. Sci. Technol., 2003, 37 (3), pp 652–656, https://doi.org/10.1021/es025771c In this study eight polycarbonate blends (PC/ABS or PC/HIPS) with phosphate ester PIN FR were compared to two ABS with brominated FR under four recycles (granulating, melting, extrusion). In that the polymers tested were different, no conclusion can be drawn concerning the impact of the FR system on recycling.*

## PUBLISHER INFORMATION

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