pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 165 November 2024

PINFA IN ACTION

Recycling of plastics in electric vehicles

pinfa workshop with automotive industry experts concludes need to develop knowledge and technologies for recycling, 18th September 2024, Munich. Participants included pinfa members including PIN flame retardant manufacturers, polymer compounders and distributors, as well as around twenty experts from the automotive industry, ranging from raw material producers to Tier 1 suppliers. In six sessions, the state of the art of automotive plastics recycling and challenges for the future were discussed. The workshop identified as a priority the optimisation of sorting, dismantling and recycling stream management. This is complex, because of the wide variety of cars (age, materials used, type of engine). Economy of scale is a significant obstacle, and a challenge is the development of technologies to separate different polymer types with different additives, including different flame retardants. The advantages and disadvantages of dismantling vehicles prior to shredding were discussed: dismantling increases labour costs, but facilitates separation, and so improves recycling as mixing of materials can be reduced. The workshop noted that material stabilisation and upgrading was important to enable recycling to technical applications with demanding requirements from OEMs. The workshop concluded that implementation of recycling of end-of-life automotive technical plastics is a real challenge for the future. We need to start working on potential solutions now in cooperation throughout the whole value chain. Participants concluded on three actions:

- Mapping of flame retardants used in different polymers across automotive applications.
- Analysis of ‘heavy’ and ‘light’ shredding fractions, from different vehicle end-of-life operators, and comparison with literature data, to identify which flame retardants are present and what are the recycling options.

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- Mechanical recycling trials using real car parts, produced with representative polymers and adjusting flame retardant and other additives levels.

"Exploring Sustainable Solutions – Flame Retardant Additives and Plastics Recycling in the Automotive Industry", technical workshop for pinfa members, 18th September 2024, Munich. Information contact: pinfa secretariat pinfa@cefic.be

1 000 downloads PIN FR smoke toxicity study

Science publication of pinfa study on PIN flame retardant polymer smoke emissions downloaded more than 1 000 times after eighteen months. Already 1 500 views were clocked several months ago, now the paper has also exceeded 1 000 full reads online or downloads. The paper in 'Fire & Material's', by authors from CREPIM France and pinfa, presents results of tests on 72 formulations of 10 polymers. Results showed no significant increase in smoke density or toxicity with PIN FRs. See pinfa Newsletter n° 149.

"The impact of halogen free phosphorus, inorganic and nitrogen flame retardants on the toxicity and density of smoke from 10 common polymers", H. Feuchter, F. Poutch, A. Beard, Fire and Materials. 2023;1–21, https://doi.org/10.1002/fam.3145

FIRE SAFETY

Firefighters new voice for policy

New association representing firefighters across Europe aims to influence fire and safety regulations and policy. The new group is led by the global organisation CTIF (International Association of Fire Services) and was launched with fire services from 25 EU member states in Brussels on 5th - 6th November with online participation of European Commission President, Ursula Von Leyen. The organisation will consult national fire services across Europe to develop unified positions to input to EU policy.

Pinfa notes that there already exist a Federation of European Fire Officers (FEU), a European Fire Fighters Alliance (EFFUA), the European Fire Safety Alliance (EuroFSA, an alliance of fire professionals extending beyond fire fighters) as well as the Confederation of European Fire Safety Associations (CFPA).

"CTIF will be the voice of a new firefighters association with the power to influence EU politics – European Firefighters Summit in Brussels November 2024", CTIF, 11th November 2024 https://ctif.org/news/ctif-will-be-voice-new-firefighters-association-power-influence-eu-politics-european

Photo Credits: Cover Photo shows Roman Sykora, General Secretary in CTIF, and Milan Dubravac, CTIF President.

Legal action following fatal e-bike fire

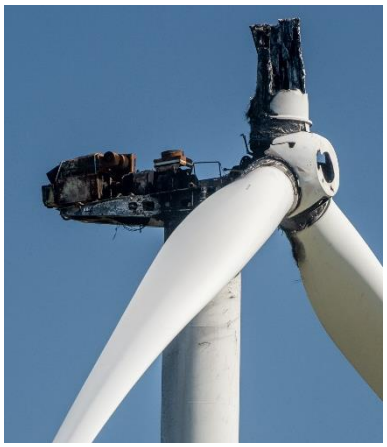
The fire in a flat in Shadwell, UK, 5th March 2023 is considered to have been caused by a charging e-bike battery. The 2-bedroom flat was occupied by around 20 men of Bangladeshi heritage, one of whom died in the fire. Twelve of the fire survivors have engaged legal action against the e-bike manufacturer, Leon Cycle Ltd, under the UK Consumer Protection Act, and against the flat landlords. The latter have already pleaded guilty to housing offences including absence of a gas safety certificate and overcrowding. The London Fire Brigade says there is an e-bike or e-scooter fire every two days, often related to unsafe or incompatible components. The UK Government has launched a "Buy Safe Be Safe" campaign urging the public to not buy e-bikes and e-scooters from "rogue online sellers" and proposes a new 'Product Regulation and Metrology Bill' to strengthen product safety and marketing regulations.

Photo : London Fire Brigade aftermath of an e-bike fire Shepherd's Bush, London, UK https://www.bbc.com/news/uk-england-london-66842516

UK Government a "Buy Safe Be Safe: avoid e-bike and e-scooter fires" https://www.gov.uk/guidance/buy-safe-be-safe-avoid-e-bike-and-e-scooter-fires

UK proposed 'Product Regulation and Metrology Bill' https://bills.parliament.uk/bills/3752

"Ebike battery fire survivors in London initiate legal claim over fatal incident", International Fire & Safety Journal, 30th October 2024 https://internationalfireandsafetyjournal.com/ebike-battery-fire-survivors-in-london-initiate-legal-claim-over-fatal-incident/



Study on fire risks of wind turbine blades

Wind turbine blades were fire tested and fire risk calculated, showing risk of blade blocks, ground fires and air pollution. Development of fire protection and suppression systems is considered urgent. Commercial wind turbine blades, made of glass fibre reinforced unsaturated polyester resin composites, were fire tested for heat release, limiting oxygen index, vertical flame test, smoke and carbon monoxide emissions, showing UL 94 NR (non rated), that is not fire resistant. Fire hazard risks were calculated, based on real fire scenarios. Conclusions are that such non fire resistant turbine blades would deform and disintegrate in fires, with possible blade blocks and with burning fragments causing spotting fires, ground fires and local air quality problems (soot, fragments, liquid and gas emissions including corrosive and toxic substances).

"Thermal and non-thermal fire hazard characteristics of wind turbine blades", N. Wang et al., Journal of Thermal Analysis and Calorimetry (2024) 149:10335–10351, https://doi.org/10.1007/s10973-024-13462-4

Wind industry should prioritise fire safety

Report says wind farms need to address fire safety as concerns are expressed by regulators and by the public. The report is by FireTrace, a company providing fire suppression systems for wind turbines. It points to the high downtime cost in case of fire on a windfarm, increasing public concern expressed during licensing procedures, and increased fire risk and possible consequences as windfarms integrate battery storage. Fire safety regulations for wind turbines are indicated to already be in place in Australia, Denmark, Germany, Japan, South Korea, UK and some states in Canada and in the USA. Some operators are adhering to the voluntary guidelines of CFPA-Europe (Confederation of Fire Protection Associations). These guidelines specify that "fire resistant components" shall be used.

"Wind industry must urgently prioritise fire safety, amidst growing public concern", Strategic Risk Global .com, 24th September 2024
https://www.strategic-risk-global.com/energy-power-and-utilities/wind-industry-must-urgently-prioritise-fire-safety-amidst-growing-public-concern/1453115.article

FireTrace report "Ahead of the game. Benefits of early installation of fire suppression systems in wind turbines" (14 pages)
https://www.firetrace.com/benefits-of-early-installation-of-fire-suppression-systems-in-wind-turbines

"Wind turbines fire protection guideline", CFPA-E Guideline No 22:2022 F Confederation of Fire Protection Associations https://cfpa-e.eu/app/uploads/2022/05/CFPA_E_Guideline_No_22_2022_F.pdf

PIN FR INNOVATION

PIN FR for lightweight battery enclosures

Fraunhofer WKI and IWU aim for PIN flame retardant composite EV battery enclosures for low weight, heat dissipation. The COOLBat project, funded by the German Federal Ministry for Economics and Climate, will develop carbon fibre composite electric vehicle battery enclosures integrating structural strength and heat dissipation (phase change material and cooling channels), foam for protection from impacts and accidents and fire safety, using a non-halogenated (PIN = phosphorus, inorganic, nitrogen) flame retardant coating. This has been developed at Fraunhofer WKI and tested at Fraunhofer IWU. The aim is to achieve a 60% weight reduction compared to steel enclosures, with space reduction and comparable performance, for batteries in electric vehicles, ships, aircraft and targeted energy storage applications.

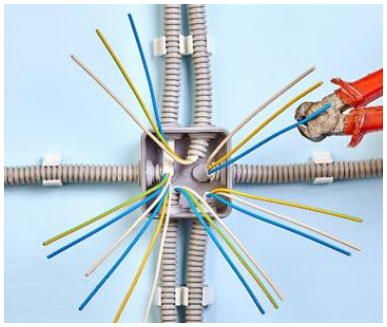
"EV Battery Enclosures with Lower Carbon Emissions", 2nd September 2024 https://www.fraunhofer.de/en/press/research-news/2024/september-2024/ev-battery-enclosures-with-lower-carbon-emissions.html

Photo: Fraunhofer IWU "Aluminum foam sandwich base panel with integrated cooling structure"

FRs for tomorrow: PIN, bio-based, safe

Materials expert Bob Howell says flame retardants of future will be bio-based organophosphorus, reactive or oligomeric. PIN phosphorus-based FRs are seen as the solution to ensure polymer compatibility and so material performance, fire safety, to avoid toxic and leaching halogenated substances and with accessible costs. Nitrogen PIN FRs can bring fire performance cooperative effects. The most effective P FRs are designed to include phosphorus with low level of oxygenation of the phosphorus and a structure conducive to release the phosphorus radical PO which can contribute to both charring, ensuring solid phase fire protection of the materials, and flame quenching in the gas phase. Sustainable organophosphorus PIN FRs can be produced by combining phosphorus derivates into bio-based compounds such as starch, cellulose, isosorbide (derived from carbohydrates), compounds recovered from wine or food processing. Tomorrow's phosphorus PIN FRs must also be non-migrating (not leach out of materials) and this can be achieved by either covalent bonding into the polymer matrix (reactive PIN FR) or by developing oligomeric phosphorus PIN FRs (large, often highly branched molecules, which tangle with the polymer matrix preventing migration). Examples are given of innovative research proposing new PIN FR molecules in these directions.

"Flame retardants of the future: biobased, organophosphorus, reactive or oligomeric", Bob A. Howell, Central Michigan University, USA, Front. Chem. 12:1500782, https://doi.org/10.3389/fchem.2024.1500782

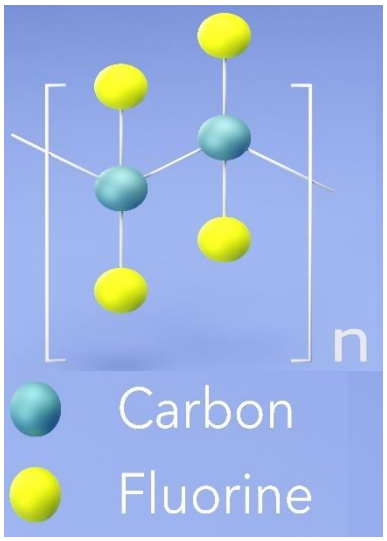


Ampacet launches PIN FR masterbatches

Ampacet, global leader in masterbatches, launches PIN FR formulations for polypropylene for building and construction. The new masterbatches respect IEC 61249-2-21 and EN 50642 halogen and antimony limits in order to reduce toxic and corrosive emissions in case of fire. They are available in natural colour pre-coloured, and can achieve UL 94 V-2 and Glow Wire Index in compliance to EN 50642 and IEC 61249-2-21 standards.

"Ampacet Introduces Low Halogen and Halogen-FreeFlame Retardant Masterbatches", 10th October 2024 https://www.ampacet.com/ampacet-introduces-low-halogen-and-halogen-free-flame-retardant-masterbatches/

Photo: Ampacet "Halolite 527 and Halofree 533 flame retardant masterbatches from Ampacet have been developed to comply with international standards IEC 61249-2-21 and EN 50642 regulating maximum halogen and antimony content"



Further non-PTFE anti-drips enter market

A number of companies are now offering non-PTFE (non-PFAS) anti-drip additives to achieve UL 94 V-0 fire safety performance. Tolsa (pinfa member) offers specialist organo-clays which enable PIN FR compounds to achieve V-0 in a range of polymers (EVA, polypropylene, EPDM, unsaturated polyesters, polyamides, PVC), see pinfa Newsletter n°156 and webinar. Avient (pinfa member) has also launched a non-PFAS flame retardant polycarbonate (see pinfa Newsletter n°154). LG Chemicals has announced a UL 94 V-0 PC/ABS, using without PFAS anti-drip, produced with over 50% recycled plastics, as well as V-0 non-PFAS PC and PBT. Elementis has launched organoclay PIN FR synergists to replace PTFE, as a processing aid (shear thinning, improving processing under high mechanical stress conditions), to improve product mechanical performance and anti-drip, with smooth white or darker colour products.

SpecialChem "Webinar: ADINS® Clay additives: A solution to replace the PTFE in flame retardant formulations", with Marta Sacristán Benito, November 2023 https://polymer-additives.specialchem.com/webinar-video/replace-the-ptfe-in-flame-retardant-formulations

"LG Chem Adds Eco-Friendliness to Flame-Retardant Plastics", 12th August 2024 https://www.lgcorp.com/media/release/27988

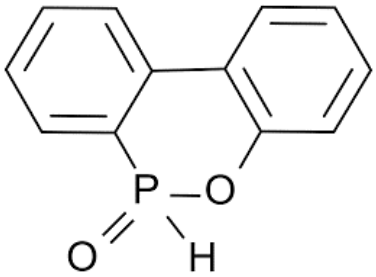
"Elementis expands its plastic additives portfolio with CHARGUARD™ fire retardant synergists", 17th October 2024 https://www.elementis.com/press-and-news/article/elementis-expands-its-plastic-additives-portfolio-with-charguardtm-fire-retardant-synergists/

PIN FR fabric for Global Green Tag blinds

Vertilux Euroscreen Eco sunscreen blinds obtain Global Green Tag Platinum Health with PIN flame retardant fabric. The blinds exceed Green Building Council Australia standards and meets Green Star, WBI WELL, USGBC LEED. The blinds ensure protection from heat, glare and from UV, without blocking the view, and with low VOC emissions. The Metallised Transparent fabric is treated with Trevira CS (phosphorus based, permanent, PIN FR textile treatment) to ensure fire safety

"Eurovision® Metallised Transparent", https://www.vertilux.com.au/product/eurovision-metallised-transparent/

RECYCLING



Recyclable reactive P-FR epoxy

Research tests show solvent recyclable DOPO-reacted itaconic acid epoxy resin (reactive PIN phosphorus flame retardant). At lab scale (250 ml), the P-FR DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) was reacted with itaconic acid (which can be derived from citric acid or by fermentation). This was reacted with a nitrogen-containing triazine derived from 2-aminothiophenol (ATP) and trimeythylpropane to give a

hyperbranched epoxy resin (IA-EHBP). This epoxy showed good strength and toughness. At 0.6% phosphorus content, the epoxy achieved UL 94 V-0 (3 mm). The organic solvent tetrahydrofuran with phosphoric acid was used to recycle the epoxy (8 hours) followed by sodium hydroxide neutralisation. This showed c. 80% recovery of DOPO itaconic acid and of ATP.

"Closed-Loop Recycling of Tough and Flame-Retardant Epoxy Resins", F. Wei et al., Macromolecules 2023, 56, 5290−5305, https://doi.org/10.1021/acs.macromol.3c00650

PIN FR ATH for recycling waste fibres

ATH and bentonite (inorganic flame retardants) for fire safety of recycled fibre – bio-based plastic compounds. Waste fibres from agave (sisal), coconut and leather industries were tested in combination with PIN FRs (ATH aluminium trihydroxide, modified bentonite nanoclay synergist) in a commercially available bio-based plastic (blend of TPS thermoplastic starch and the biopolymer PBAT polybutylene adipate terephthalate). At 50% loading ATH (100 phr), without fibres, UL 94 V-0 (3 mm). UL 94 V-1 was achieved with 25% recycled leather industry fibres and 90 phr ATH or 80 phr ATH plus 1 phr bentonite. Higher loadings of bentonite did not improve fire performance. The authors conclude that the recycled leather waste fibres, ATH and bentonite offer a readily implementable solution for valorising fibre wastes and in a fire-resistant bio-plastic compound.

"It's not waste, it's a resource: Utilizing industrial waste fibers/mineral fillers to attain flame retardant biocomposites", D. Rockel et al., J. Thermoplastic Composite Materials, 2024 https://dx.doi.org/10.1177/08927057241297083

PIN FR for plastic waste upcycling

Phosphorus PIN FR from THOR (pinfa member) with chain extender enabled upcycling of post-consumer PET. Secondary PET (polyethylene terephthalate) granules from post-consumer mixed plastic bottles was re-compounded (melted and extruded at 250°C) with an organic phosphorus PIN FR at 0 – 10% loading and a chain extender (a styrene-acrylic multifunctional epoxide oligomeric agent from BASF, pinfa member) at 0 - 1% loading. At 10% PIN FR, peak heat release rate of injection-moulded 5 mm thickness extruded samples was reduced by c.45% but smoke production increased by c.15%. Tests of foaming were also carried out, using carbon dioxide blowing agent, showing that the recycled PET with chain extender and PIN FR achieving up to 660 kg/m^3 with 7 µm cell size. The authors conclude that the combination of this phosphorus PIN FR and chain extender allow upcycling of post-consumer PET to performance rigid foam, with synergies between the chain extender and the PIN FR for both fire performance and performance and processing characteristics.

"Enhanced Flame-retardant Performance of Undervalued Polyethylene Terephthalate Waste as a Potential use in Foamed Materials", M. Santiago-Calvo et al., J. Polymers and the Environment, 2024 https://doi.org/10.1007/s10924-024-03424-0

ENVIRONMENT & HEALTH

Low PIN FR leaching from microplastics

Lab studies show low levels of PIN flame retardant leaching from microplastics under exaggerated artificial weathering.

Menger et al. tested leaching from 8 commercial plastics containing additives (of which 3 were PET or PVC containing FRs) after artificial UV weathering. Only five FRs were detected after leaching, of which the highest concentrations were TBBPA, with considerably lower levels of the only three PIN FRs detected (tri(butoxyethyl)phosphate TBEP, trimethyl phosphate TMP, triphenyl phosphate TPhP). The main use of TBEP is not as a flame retardant, but in polishes.

Zuo et al. tested leaching from polystyrene microplastics (ground to < 0.2 mm) in water and synthetic digestive fluids of two organo-P PIN FRs (triphenyl phosphate TPhP and tri-n-butyl phosphate TnBP). Conclusions are that only around 0.5% of the FR content in the microplastic particles, with leaching occurring in the first 24 – 30 hours. They concluded that leaching from such microparticles would not be a significant source of organophosphates, because it occurs mainly from the microplastic particle surface, but note that further leaching could occur later if the microplastic particles break down to smaller particles.

Li et al. review over 160 papers published over the last ten years, on leaching of chemicals from microplastics, scarcely mentioning PIN FR leaching. They conclude that antioxidants, flame retardant and plasticisers may leach, in particular bisphenols, and that fats and oils may accentuate leaching of liposoluble chemicals in the gut if ingested (the halogenated FRs PBDEs are severally cited). Photodegradation of plastics facilitates leaching.

Sun et al., in a modelling paper (based on published experimental data from Guo 2019, see pinfa Newsletter 132, and on theoretical diffusion coefficients), concludes that organophosphorus FR leaching from polypropylene and polystyrene microplastics contribute “minimally” in worms but leaching from polyethylene could be non-negligible. They suggest that leaching varies widely depending on the type of microplastic and that quantitative research is needed.

“Screening the release of chemicals and microplastic particles from diverse plastic consumer products into water under accelerated UV weathering conditions”, F. Menger et al., J. Hazardous Materials 477 (2024) 135256, https://doi.org/10.1016/j.jhazmat.2024.135256

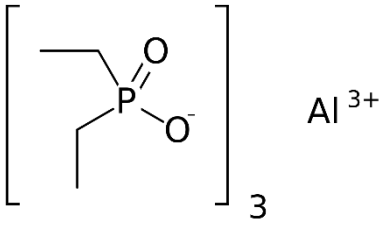
“Leaching of triphenyl phosphate and tri-n-butyl phosphate from polystyrene microplastics: influence of plastic properties and simulated digestive fluids”, L. Zuo et al., Environmental Science and Pollution Research (2023) 30:114659–114666, https://doi.org/10.1007/s11356-023-30229-w

“Leaching of chemicals from microplastics: A review of chemical types, leaching mechanisms and influencing factors”, Y. Li et al., Science of the Total Environment 906 (2024) 167666, https://doi.org/10.1016/j.scitotenv.2023.167666

"Leaching kinetics and bioaccumulation potential of additive-derived organophosphate esters in microplastics", B. Sun et al., Environmental Pollution 347 (2024) 123671, https://doi.org/10.1016/j.envpol.2024.123671

** "Leaching of polybrominated diphenyl ethers from microplastics in fish oil: kinetics and bioaccumulation. B. Sun et al., 2021, J. Hazard Mater. 406, 124726, http://refhub.elsevier.com/S0269-7491(24)00385-3/sref34*

"The leaching of additive-derived flame retardants (FRs) from plastics in avian digestive fluids: the significant risk of highly lipophilic FRs", H. Guo et al., 2019, J. Environ. Sci. 85, 200–207 https://doi.org/10.1016/j.jes.2019.06.013



PIN FR AlPi shows no gene or cytotoxicity

Independent study on aluminium diethyl phosphinate (AlPi, phosphorus PIN FR) concludes no cytotoxicity, not mutagenic. This study tested AlPi produced by Clariant (pinfa member). Mutagenicity was tested using the OECD 471 bacteria test (Ames test) with *Salmonella*. Cytotoxicity was tested for mitochondrial dehydrogenase activity (WST-1 test), for lactate dehydrogenase activity (LDH), and for in vitro cytokinesis -block micronucleus assay (invCBMN, OECD 487). Conclusions are that AlPi is neither mutagenic nor cytotoxic under the conditions tested but did show some genotoxicity (micronucleus induction, HepG2 cells) at the highest concentration tested (200 µg/ml = 0.2 g/l). Previous publications have found AlPi to be not toxic to PC12 and B35 cells (rat pheochromocytoma and neuroblastoma) (Hendriks et al. 2014) and to have low to moderate aquatic toxicity, developmental or reproductive toxicity (see references in paper).

Diagram: Wikipedia.

This study was funded by the State of Rio de Janeiro (Chagas Filho Foundation) with no industry funding.

"Genotoxicity analysis of a flame retardant, aluminum diethylphosphinate", T. Leoncio et al., Mutation Research - Genetic Toxicology and Environmental Mutagenesis 900 (2024) 503829, https://doi.org/10.1016/j.mrgentox.2024.503829

PUBLISHER INFORMATION

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