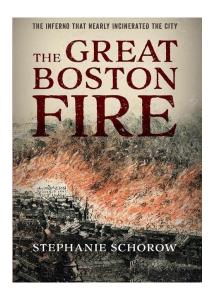


# Your newsletter for non-halogen fire safety solutions n° 146 February 2023

EVENTS	1	Calculating cost-benefit of fire protection	5
2 <sup>nd</sup> pinfa-NA Lunch & Learn 22 <sup>nd</sup> March	1	Innovation	6
6 <sup>th</sup> Workshop on FRs for Plastics (AIMPLAS)	1	PIN FR polycarbonate (PC) for 3D-printing	6
Fire Retardants in Plastics USA 26-27 April	2	PIN FR for recyclable tubing	7
FRPM23, Switzerland, 26-29 June – pinfa	2	PIN FR chosen for eco-friendly textiles	7
Policy	2	Phosphorus FR for safer car seats	8
Cefic welcomes EU chemical industry	_	Breeding plants for inherently FR cotton	8
Transition Pathway	2	Non-halogenated PIN FR for PC film	9
Consultation on CLP revision to 18th March	3	Polymeric silica PIN FRs	9
Consultation on Ecodesign to 25th April	3	Coal fly ash tested as PIN FR for epoxy	9
Fire safety	4	DOPO-silanes as PIN FRs for cotton	10
Home fires caused by electrical equipment	4	Other news	10
Micro e-mobility fire challenges event	4	Publisher information	12
Ongoing debate on FRs in furniture	5		

# **EVENTS**



# 2<sup>nd</sup> pinfa-NA Lunch & Learn 22<sup>nd</sup> March

150 participants joined the first fire and FRs learning webinar. The second will recount the 1872 Boston Great Fire with journalist and author Stephanie Schorow, free, Wed. 22<sup>nd</sup> March 2023, 11h30-12h30 EST (17h30-18h30 CET). For two days during November 1872 a massive fire swept through Boston, Massachusetts, leaving the downtown in ruins and the population traumatized. Boston's inferno turned out to be one of the most expensive fires in US history. Using witness statements, period artwork and photographs, Stephanie Schorow will recount the history of 150 years ago including decisions that contributed to the conflagration. Increase your understanding on how modern building codes, fire codes and standards were shaped by events as far back as the 19<sup>th</sup> century!

"The Great Boston Fire – the Inferno that Nearly Incinerated the City", S. Schorow, Globe Pequot, 2022 ISBN 978-1493054985 <a href="https://www.globepequot.com/books/9781493054985">https://www.globepequot.com/books/9781493054985</a>

Register for the webinar: <a href="https://www.pinfa-na.org/">https://www.pinfa-na.org/</a>



# 6<sup>th</sup> Workshop on FRs for Plastics (AIMPLAS)

Valencia, Spain, 19<sup>th</sup> April (with pinfa), followed by the pinfa General Assembly (pinfa members) on 20<sup>th</sup> April. The workshop will address formulation of polymer compounds with FRs for different applications, processing optimisation, compounding simulation and sustainability aspects (bio-based materials, recycling).

https://www.aimplas.es/plasticsacademy/convocatoria/vi-workshop-sobre-formulacion-procesado-y-sostenibilidad-de-los-retardantes-de-llama-2







**AMI** Events

# Fire Retardants in Plastics



# Fire Retardants in Plastics USA 26-27 April

12<sup>th</sup> edition of AMI Fire Retardants in Plastics, 26-27 April 2023, Philadelphia, PA, USA. For industry professionals from across the supply chain to learn, share knowledge and network on flame retardants and polymers,

www.ami.ltd/event-fire-USA

# FRPM23, Switzerland, 26-29 June - pinfa

19<sup>th</sup> edition of the European Meeting on Fire Retardant Polymeric Materials (FRPM). Early bird to 15<sup>th</sup> march 2023. pinfa Awards (1500 € - 500 €) will be made to the best papers on PIN flame retardants by students and young researchers

https://www.frpm-23.org/

#### **POLICY**



# **Cefic welcomes EU chemical industry Transition Pathway**

EU long-term plan for chemical industry includes investment, innovation and regulation to support green transformation. The new EU "Transition Pathway for the Chemical Industry" is a 75-page short- and long-term plan to transition to Green Deal objectives, including, technology objectives, a regulatory calendar and some 200 actions. Key themes are innovation, clean energy supply and feedstock diversification, with objectives of circular economy, use of waste and bioresources and increased supply resilience, despite the recognised complexity of international chemicals supply chains. Investment support will refer to the **EU Taxonomy**, which will define criteria for which processes can benefit from green funding. Proposed actions include targets for recycled and bio-based content of feedstocks. The regulatory roadmap includes Taxonomy to support the Chemicals Strategy for Sustainability, CLP – GHS and REACH revisions, Restrictions Roadmap and Generic Risk Management approach, SSbD (Safe and Sustainable-by-Design chemicals), EcoDesign, Industrial Emissions Directive revision. Cefic has said that the Transition Pathway is a milestone for the sector towards meeting Green Deal goals and that the chemical industry in Europe stands ready to help make it happen, underlining that tens of billions of investment will be needed.

"Transition Pathway for the Chemical Industry", European Commission, January 2023 <a href="https://single-market-economy.ec.europa.eu/sectors/chemicals/transition-pathway\_en">https://single-market-economy.ec.europa.eu/sectors/chemicals/transition-pathway\_en</a>

"A milestone moment for the European chemicals industry: The EU Chemical Industry Transition Pathway helps define the sector's path to 2050", Cefic, 27 January 2023 <a href="https://cefic.org/media-corner/newsroom/a-milestone-moment-for-the-european-chemicals-industry-the-eu-chemical-industry-transition-pathway-helps-define-the-sectors-path-to-2050/">https://cefic.org/media-corner/newsroom/a-milestone-moment-for-the-european-chemicals-industry-the-eu-chemical-industry-transition-pathway-helps-define-the-sectors-path-to-2050/</a>









#### Consultation on CLP revision to 18th March

Proposed CLP Regulation revision would establish new hazard classes for endocrine, PBT, vPvB, PMT, vPvM chemicals. "M" is a new category "Mobile". P, B and T are Persistent, Bio-accumulative and Toxic as at present.. The proposed regulatory text also includes changes aimed at improving labelling both on-packet and online. Cefic has reacted that introducing new EU Classifications which diverge from the internationally recognised GHS framework will pose problems in value chains and that the new classifications will trigger restrictions and bans under REACH and under product legislation whereas clarification on how to scientifically support new classifications for complex endpoints such as endocrine disruption and mobility is yet to be developed. The proposed revised Regulation is open for comment until 18th March.

"Cefic Statement on the Publication of the Delegated Acton CLP" 19<sup>th</sup> December 2022 <a href="https://cefic.org/media-corner/newsroom/cefic-statement-on-the-publication-of-the-delegated-act-on-clp/">https://cefic.org/media-corner/newsroom/cefic-statement-on-the-publication-of-the-delegated-act-on-clp/</a>

European Commission short summary of proposed changes in the revision of the CLP Regulation 19<sup>th</sup> December 2022 <a href="https://ec.europa.eu/commission/presscorner/detail/en/qanda">https://ec.europa.eu/commission/presscorner/detail/en/qanda</a> 22 7776

"Revision of EU legislation on hazard classification, labelling and packaging of chemicals", including access to the regulatory proposal open for public comment to 18<sup>th</sup> March 2023 <a href="https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12975-Revision-of-EU-legislation-on-hazard-classification-labelling-and-packaging-of-chemicals">https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12975-Revision-of-EU-legislation-on-hazard-classification-labelling-and-packaging-of-chemicals</a> en



# Consultation on Ecodesign to 25th April

EU roadmap consultation on which products and aspects should be priorities for fixing EcoDesign criteria under ESPR (EcoDesign for Sustainable Products Regulation). The Commission is looking for input on which products or horizontal measures should be priorities for defining criteria, what product environmental and circularity aspects can be improved and how ESPR criteria can be technically feasible and implemented through the value chain. Proposed horizontal measures are: Durability, Recyclability, Post-Consumer Recycled Content. Proposed priority products are: Textiles & Footwear, Furniture, Ceramic Products, Tyres, Detergents, Bed Mattresses, Lubricants, Paints & Varnishes, Cosmetic Products, Toys, Fishing Nets & Gears, Absorbent Hygiene Products, Iron & Steel, Non-Ferrous Metals, Aluminium, Chemicals, Plastic & Polymers, Paper, Pulp Paper & Boards, Glass.

"New product priorities for Ecodesign for Sustainable Products", EU consultation open to 25th April 2023, input = free text of up to 4000 characters plus upload document <a href="https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/13682-New-product-priorities-for-Ecodesign-for-Sustainable-Products\_en">https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/13682-New-product-priorities-for-Ecodesign-for-Sustainable-Products\_en</a>

European Commission page "Ecodesign for sustainable products" <a href="https://commission.europa.eu/energy-climate-change-environment/standards-tools-and-labels/products-labelling-rules-and-requirements/sustainable-products/ecodesign-sustainable-products en

Image: European Commission <a href="https://op.europa.eu/en/publication-detail/-/publication/ef3f214c-b040-11ec-83e1-01aa75ed71a1">https://op.europa.eu/en/publication-detail/-/publication-detail/-/publication/ef3f214c-b040-11ec-83e1-01aa75ed71a1</a>







# FIRE SAFETY



#### Home fires caused by electrical equipment

US NFPA says electrical wiring, lighting and related installations cause 5 000 home fires, cost 250 M\$ per year. Data for 2015-2019 identifies nearly 33 000 home fires caused by electrical distribution and lighting equipment (for the period), leading to 430 civilian deaths and 1.5 billion US\$ direct property damage. Wiring accounted for two-thirds of these home fires, with peak months in winter, suggesting that overloading of wiring by heating appliances are a significant cause, along with faulty wiring, which is often hidden so that initial problems are not visible. The item identified as first ignited in around a third of the fires was wiring, and building parts in a further third, underlining the importance of not having combustible building materials in proximity to electrical wiring or equipment.

"Home Fires Caused by Electrical Distribution and Lighting Equipment", Richard Campbell, NFPA Journal Winter 2022 https://www.nfpa.org/journal and report February 2022 https://www.nfpa.org/News-and-Research/Data-research-andtools/Electrical/Electrical



# Micro e-mobility fire challenges event

Fire Department of New York (FDNY) conference shows need to address major new fire risks of e-bikes and e-scooters. The two-day symposium brought together firefighters, stakeholders and researchers and was sponsored by FNDY, UL's Fire Safety Research Institute and US NFPA. New York is now seeing an average of more than one micro-mobility device battery fire per day (e-bikes, e-scooters), often in homes as people bring the device or its battery to charge. The symposium heard firefighters' recount ferocious fires started by batteries and were given live demonstrations of burning batteries shooting flames and debris. Joseph Loftus, an FDNY battalion chief: "We have guys with 20 years of experience ... who respond to e-bike fires and tell us afterwards that it was something they've never seen before. They haven't seen smoke like that before, haven't felt heat like that, haven't seen fire go up like that."

"Emerging Issues. Full throttle. A. Verzoni, NFPA Journal Fall 2022 https://www.nfpa.org/News-and-Research/Publications-and-media/NFPA-Journal/2022/Fall-2022/Features/E-bikes

"You need to be ready. FDNY-hosted event underscores the urgency for continued guidance on e-bike fire hazards". NFPA Journal Winter 2022 https://www.nfpa.org/journal

Listen to FDNY Chief of Fire Prevention Joe Jardin discuss the e-bike fire problem, NFPA Podcast https://nfpa.libsyn.com/e-bike-and-e-scooter-fire-

FNDY symposium <a href="https://www.fdnypro.org/symposium/">https://www.fdnypro.org/symposium/</a>

Photo from video on dangers of lithium-ion battery fires: FDNY website









#### Ongoing debate on FRs in furniture

How do flame retardants improve furniture fire safety, depending on effects: prevent ignition, reduce heat, smoke? Two recent issues of the PolyFlame newsletter (French Chemical Society) present three different positions on whether, or in which conditions, flame retardants in furniture may contribute to save lives. A paper by J. Fleming (consultant and previously fire-fighter and Boston City Fire Marshall), in PolyFlame n°25, suggests that FRs effect of delaying high heat release (the pinfa infographics are shown) may have little benefit, because escape is most often hindered by smoke (visibility, toxicity), and gas-phase FRs can increase initial smoke emission. This same n°25 includes an article by Marcello Hirschler, fire safety expert (from PolyFlame n°9, 2016) who argues that smoke toxicity of materials containing FRs is not significantly different from non-FR materials, and that time to peak heat release is key to fire lethality (see also Hirschler, Fire Protection Engineering, in pinfa Newsletter n°63). A third article in PolyFlame n°26, by K Rodgers, Boston University, argues that the decrease in furniture fire deaths in the USA since 1980 (fewer such fires), whilst at the same time furniture fires have become deadlier, and data on fires started by open flames and smoking materials, suggest that the national standard requiring resistance to ignition by a smouldering cigarette is appropriate to improve fire safety (see also summary of Rodgers et al. 2019 in pinfa Newsletter n°104).

PolyFlame Newsletter <a href="http://gcf-scf.lmops.univ-lorraine.fr/">http://gcf-scf.lmops.univ-lorraine.fr/</a> (see in top menu on this page). Relevant articles are in English.



# Calculating cost-benefit of fire protection

Major international report proposes cost-benefit methodology for building fire protection measures with five case studies. The 125-page report was commissioned by the US NFPA (National Fire Protection Association) Research Foundation and carried out by Ghent University Belgium, Utah State University and Johns Hopkins University Maryland. NFPA is the recognised source of information on economic impact of fires by its periodic studies on fire losses (see e.g. pinfa Newsletter n°143). These studies identified in 2017 costing of fire losses as an area needing further research. This report is based on a literature review (40 studies identified) and analysis of the identified methods including their data needs. It develops a holistic calculation method for evaluating total benefits and costs of fire protection features in buildings. Benefits include estimates of fire loss and replacement costs. Building structure is often only around ¼ of costs, with higher economic impacts relating to building functions. Five case studies are presented, implementing this methodology for: sprinklers in single-family dwellings; sprinklers and compartmentation in warehouses; fire detection system and extra staircase in an administrative building; passive fire protection in a commercial office building; sprinklers and passive fire protection in multi-family timber building.







Further research is considered necessary in eight areas including: retrofitting of existing buildings, indirect fire costs, costs of fire injuries, environmental costs and benefits, insurance effects.

"Show me the money. A new project takes aim at quantifying the true cost of fire and the fiscal benefit of fire protection"; Birgitte Messerschmidt, NFPA Journal, Winter 2022 <a href="https://www.nfpa.org/News-and-Research/Publications-and-media/NFPA-Journal/2022/Winter-2022/Columns/Research">https://www.nfpa.org/News-and-Research/Publications-and-media/NFPA-Journal/2022/Winter-2022/Columns/Research</a>

"Economic Impact of Fire: Cost and Impact of Fire Protection in Buildings", R. Van Coile et al. for NFPA Research Foundation, FPRF-2022-13, August 2022 <a href="https://www.nfpa.org/-/media/Files/News-and-Research/Fire-statistics-and-reports/US-Fire-Problem/RFEconomicIImpact.ashx">https://www.nfpa.org/-/media/Files/News-and-Research/Fire-statistics-and-reports/US-Fire-Problem/RFEconomicIImpact.ashx</a>

#### INNOVATION



# PIN FR polycarbonate (PC) for 3D-printing

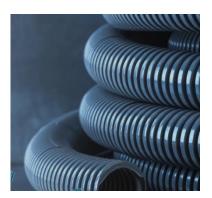
SABIC launches non-halogenated flame retardant PC for PFAM 3-D printing for railway fire safety and smoke requirements. SABIC's new carbon-fibre reinforced compound may be used for PFAM (Pellet Feed Additive Manufacturing) and is certified to produce 3D-printed parts in compliance with the EU and US railway standards (EN45545-R1-3 and NFPA-130). These standards assess the flame spread, heat release, smoke density and smoke toxicity of the materials according to specified requirements depending on the end application e.g. seat shells, wall cladding etc, and the type/category of train in use e.g. normal, double deck, sleeping. The compound delivers good processing, dimensional stability and low warpage, creep resistance, high strength and stiffness and temperature resistance. Potential applications include external parts and interior cladding parts such as panels, ducts and partitions, as well as seat backs and shells for railway and other transport applications. Production of large parts by 3D-printing can enable small production runs or production of replacement parts rapidly, flexibly and economically.

"SABIC to debut at InnoTrans a new EN45545 rail compliant additive manufacturing solution to help advance the transportation industry", 13<sup>th</sup> September 2022 <a href="https://www.sabic.com/en/news/36890-sabic-to-debut-at-innotrans-a-new-en45545-rail-compliant-additive-manufacturing-solution-to-help-advance-the-transportation-industry">https://www.sabic.com/en/news/36890-sabic-to-debut-at-innotrans-a-new-en45545-rail-compliant-additive-manufacturing-solution-to-help-advance-the-transportation-industry</a>









# PIN FR for recyclable tubing

Gabriel-Chemie's new non-halogenated FR offers performance and sustainability benefits for polyolefins. The masterbatches are EN 50642 for halogen-free material and antimony-free and can achieve IEC 61304-2 for low smoke and gas, Glow Wire IEC 60335/4 @ 960°C. They are particularly adapted for flexible tubing for electrical wires, offering fire performance and better recyclability than metal wire tubing. In addition, Gabriel-Chemie has launched a reduced  $CO_2$  white masterbatch based on a polyolefin carrier. The masterbatch material is processed using photovoltaic electricity produced onsite in Austria, offers reduced abrasiveness, full hiding power and is considered compatible with recycling. This masterbatch can be combined with a non-halogenated FR solution on customer request.

Gabriel Chemie has also now launched a new range of halogenfree flame retardant masterbatches for polyamides, for applications such as electronics, automotive and stadium seating.

"The new CO<sub>2</sub> reduced MAXITHEN white masterbatch", <a href="https://gabriel-chemie.svenso.dev/storage/CO2">https://gabriel-chemie.svenso.dev/storage/CO2</a> reduced whiteEDP NEW.pdf

"Gabriel-Chemie Develops Halogen-free FR Masterbatch Series for Electrical Cables", 14 November 2022 <a href="https://polymer-additives.specialchem.com/news/product-news/gabriel-new-halogen-free-fr-masterbatch-000229262">https://polymer-additives.specialchem.com/news/product-news/gabriel-new-halogen-free-fr-masterbatch-000229262</a>

"Gabriel-Chemie Launches Halogen-free FR Masterbatches Range for PA", 16th January 2023 <a href="https://polymer-additives.specialchem.com/news/product-news/gabriel-chemie-new-halogen-free-masterbatches-000229715">https://polymer-additives.specialchem.com/news/product-news/gabriel-chemie-new-halogen-free-masterbatches-000229715</a> and <a href="https://www.gabriel-chemie.com/en/node/397">https://www.gabriel-chemie.com/en/node/397</a>



# PIN FR chosen for eco-friendly textiles

**Industries** is exclusively using polyphosphonate PIN flame retardant in Recron® FS for fire safe, sustainable performance polyester fibres. Reliance Industries (over 100 billion US\$ group revenues), produce c. 3.5 Mt fibres and yarns annually and are probably the world's biggest producer of polyester staple fibre and filament yarns. The company's fire safe polyesters Recron FS use polymer phosphorus PIN flame retardant, which improves polyester textile tenacity (strength) and is compatible with 90% recycled polyester feedstock. The PIN FR is approved in Oeko-Tex Standard 100 for textile applications, as well as Green Screen Bench Mark 3, ChemForward, TCO. Depending on the amount of polymeric PIN FR blended with the polyester, 0.7 to 2.5 % phosphorus can be incorporated, enabling achievement of different customer fire safety specifications. Recent applications include furniture in the Paris CDG air terminal, Happers home furniture, Indian Rail.

Recron FS website <a href="https://www.recronfs.com/what-recronfs.html">https://www.recronfs.com/what-recronfs.html</a>
"Reliance Industries enhances polyester textiles with FRX Nofia technology", Composites World, <a href="https://www.recronfs.com/what-recronfs.html">7th November 2022</a>.

Photo: Paris Charles de Gaule Airport









#### Phosphorus FR for safer car seats

PIN FR can prevent ignition in synthetic leather, reduce flammability of polyester fabrics, improve car fire safety. Daihachi Chemical's non-halogenated aliphatic phosphoramidate (phosphate ester) flame retardant offers improved fire performance due to its high phosphorus content and action in both the solid and the gas phase. The PIN FR can be incorporated into polyester fibres, resulting in burn reduced from 50 mm (standard FR) to 18 mm (FMVSS302). When used in the adhesive back-layer of synthetic leather, FMVSS302 is passed with no ignition and no dripping. The product does not cause watermarking (low water solubility) and is solid so shows low-fogging (VDA278). The phosphorus PIN FR is effective in resins containing oxygen in their structure, such as epoxies and urethanes. It is adapted for large surface applications such as non-woven fabrics of artificial leather, polyurethane polyurethane/epoxy adhesives and polyurethane dispersion (PUD) applications.

https://www.daihachi-chem.co.jp/eng/technology/flame\_retardant.html https://flame-retardants.ip/products/daiguard-850/

Daihachi will present these products at the European Coatings Show 2023, 27-28 March, Nuremberg, Germany https://european-coatingsshow.nuernbergmesse.de/



# Breeding plants for inherently FR cotton

The USDA has bred a line of plants which produce inherently fire-resistant white cotton fibres. The breeding is selection, without genetic modification or gene manipulation. 257 interbred lines from 11 initial parent lines already were used (Multigenerational Advanced Generation InterCross methodology). The parent lines all produced flammable cotton. Using MCC (microscale combustion calorimetry), five lines with lower heat release were identified. Fabric c. 100 g/m<sup>2</sup> made from cotton from four of these showed to be self-extinguishing under ASTM D1230-17 (45°, open flame). The research analysed genomes of the cotton lines, identifying chromosome/gene positions common to the four fire-resistant lines, but not found in other lines. There was no investigation of chemicals present in the fire-resistant cotton plants, but not in others. One of the identified candidate genes has already been associated with fire resistance in brown cotton plants and is involved in flavonoid synthesis: these ring-based carbohydrates are considered to contribute to the FR properties of tannin. However, this gene alone did not explain the fire performance of the four identified lines. The authors suggest that the genes identified as contributing fire resistance would not modify agronomic performance or other cotton textile characteristics, but this was not experimentally tested.

"Flame resistant cotton lines generated by synergistic epistasis in a MAGIC population", G. Thyssen et al., USDA (US Dept. of Agriculture), PLoS ONE 18(1): e0278696. https://doi.org/10.1371/journal.pone.0278696





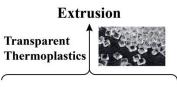


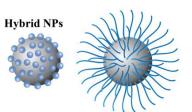


#### Non-halogenated PIN FR for PC film

CAI Performance Additives launches new PIN flame retardant for polycarbonate film, transparent, weather & water resistant. The new halogen-free flame retardant additive achieves UL 94 V-0 down to 0.25 mm in PC film, with < 1% w/w loading. The product also improves resistance of PC film to weathering and to yellowing, and resistance to hydrolysis in water-contact applications. The silsesquioxane based halogen-free flame retardant is very effective in polycarbonate films and sheets. With over fifteen years of experience, CAI Performance Additives supplies a range of plastics additives and masterbatches, including melt flow improvers, light and UV stabilises, chain extenders, laser marking, odour and VOC controllers, heat stabilisers and lubricants for a range of different polymers.

See <a href="https://www.caiadditives.com/st-sr487">https://www.caiadditives.com/st-sr487</a>



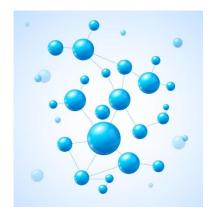


Nanocomposites / PBs-NPs

# Polymeric silica PIN FRs

Surface functionalised silica nanoparticles will be tested as PIN FRs for transparent thermoplastics, such as PMMA poly(methyl methacrylate) and PC polycarbonate. The project aims to develop a PIN FR with safe environment and health profile, compatible with high transparency, for e.g. automotive and aerospace applications, without migration out of the plastic matrix nor discoloration nor odor. Commercially available silica particles and those produced in the laboratory using the Stöber process will be tested. These will be surface functionalised with phosphorus and/or nitrogen FRs by grafting of small PIN FR molecules or of polymer brushes.

The DTNW, TU-Dortmund and HSHL Germany project is financed by AiF (German Federation of Industrial Research Associations) of the German government. <a href="https://www.dtnw.de/en/projekt/hybridnanoflam/">https://www.dtnw.de/en/projekt/hybridnanoflam/</a>



# Coal fly ash tested as PIN FR for epoxy

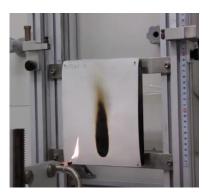
Industrial-grade coal fly ash hollow microspheres from a power station showed to improve fire performance of epoxy resin. Coal fly ash is mainly aluminium silicates, mostly as hollow microspheres c. 15 µm. Loadings of 2 – 10% w/w of flay ash with different densities were tested in epoxy resin CYD-128. The ash was first acidified in 3% oxalic acid then surface modified with silane coupling agent KH570 (3-(methacryloyloxy) propyltrimethoxysilane. Fire performance was significantly improved, e.g. peak heat release rate decreased by over one third with optimum 8% fly ash microspheres. Fire performance effect was due to generation of a complete and corrugated char layer. Flexural strength of the epoxy was however significantly deteriorated.

"Study on the effect of the density and incorporation amount of coal fly ash hollow microspheres on the fire performance of epoxy resin", J. Liu et al., Materials Today Communications 34 (2023) 105213 https://doi.org/10.1016/j.mtcomm.2022.105213









#### DOPO-silanes as PIN FRs for cotton

A new N P Si compound was synthesised and showed fire performance and semi-durability on cotton. The new compound, DOPO-AmdPTES, was compared to and showed better performance than similar DOPO-oxysilane (DOPO-ETES, see Vasiljević et al. 2015). Both compounds were applied to cotton fabric by sol-gel application and pad-dry-cure finishing. The curing at 130°C resulted in a silane polymer network on the cotton surface. DOPO-AmdPTES was synthesised by reacting DOPO\* with the commercially-available nitrogen silane compound isocyanatopropyltriethoxysilane (ICPTES). The treatment of the cotton resulted in 3.3% P and 5.5% Si on the cotton surface and a total c. 27% DOPO-AmdPTES w/w loading of the cotton and led the cotton to be self-extinguishing, with PHHR (peak heat release rate) 62% lower than untreated cotton and LOI (limiting oxygen index) 56% higher. Self-extinguishing is maintained after ten wash cycles, showing wash semi-durability, probably due to the hydrophobic properties of the DOPO-AmdPTES, covalent bonding of free silanol groups to cotton during curing and hydrogen bonding of amido groups. The flame retardancy is considered to be mainly due to catalysis of char formation and to a gas-phase dilution effect. The weaker P-bond, compared to DOPO-ETES, resulting in more rapid degradation in fire, probably explains the better fire performance.

\*DOPO = 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide "Flame-retardant finishing of cotton fabrics using DOPO functionalized alkoxy- and amido alkoxysilane", W. Ali, T. Mayer-Gall et al., Cellulose 2023 <a href="https://doi.org/10.1007/s10570-022-05033-3">https://doi.org/10.1007/s10570-022-05033-3</a>

#### **OTHER NEWS**



**EU HBMEU conclusions on flame retardant monitoring in children.** The large EU-funded population study has published conclusions of analysis of ten halogenated FRs in blood and four organo-phosphate metabolites in urine from 2136 children from nine European countries. Median levels of BDE-47 of c. 0.3 ng/g-lipid were found in children's blood in France and Norway, and median levels of Dechlorane Plus of 16 ng/g-lipid in Slovenia. The most widely detected organo-phosphate metabolite detected in children's urine was diphenyl phosphate (DPHP), found in nearly all samples, with a median of c. 2  $\mu$ g/g-creatine in several countries. However, as the study notes, DPHP is both used as such and is a metabolite of TPHP, which is used as a flame retardant but also in a wide





variety of products, including hydraulic fluids and nail polish. Other organo-phosphate metabolites were found much less frequently and at considerably lower concentrations (BDCIPP often detected, BCEP and BCIPP not often detected).

"Exposure to flame retardants in European children — Results from the HBM4EU aligned studies", V. van der Schyffet al., International Journal of Hygiene and Environmental Health 247 (2023) 114070 <a href="https://doi.org/10.1016/j.ijheh.2022.114070">https://doi.org/10.1016/j.ijheh.2022.114070</a>

Organophosphates and ADHD in children (Attention Disorder Hyperactivity Disorder). A population study of 260 children with pre-school ADHD was compared to a stratified control group of 549, with data of organophosphate metabolites in mother's urine at 17 weeks pregnancy. Statistically positive significant correlation was found between levels of DnBP (Di-n-butyl phosphate) and BDCIPP (Bis(1,3-dichloro-2-propyl) phosphate), whereas for BBOEP (Bis(2-butoxyethyl) phosphate) the correlation was negative for girls and positive for boys. The study notes that organophosphates are used for different applications, including as plasticisers and flame retardants.

"Gestational organophosphate ester exposure and preschool attentiondeficit/hyperactivity disorder in the Norwegian Mother, Father, and Child cohort study", A. Hall et al., Int. J. Hygiene and Environmental Health 248 (2023) 114078 https://doi.org/10.1016/j.ijheh.2022.114078

#### Organo-phosphates half-life 2 - 6 weeks in coastal sediment.

Lab incubation trials (in the dark) used coastal sediment and sea water collected from the Mediterranean (near the outlet of Marseille's sewage works) spiked with seven organo-phosphorus esters (list below) to c. 180 ng/g.dw for each of the OPEs. Ambient levels of the OPEs in the sediment before spiking were 1 – 85 ng/g.dw. For the different OPEs, half-lives varied from 3 to 11 weeks in abiotic conditions (sterilised at 120°C) and 2 to 6 weeks in biotic conditions. The OPEs slowest to degrade were TEHP and EHDPP.

OPEs tested: TiBP: tri-iso-butyl phosphate (CAS: 126-71-6)

TnBP: tri-n-butyl phosphate (CAS: 126-73-8)

TCEP: tris-(2-chloroethyl) phosphate (CAS: 115-96-8)

TCPP: tris-(2-chloro, 1-methylethyl) phosphate (CAS: 13674-84-5)

TPhP: triphenyl phosphate - (CAS: 115-86-6)

EHDP: 2- ethylhexyl-diphenyl phosphate (CAS: 1241–94-7)

TEHP; tris(2-ethylhexyl) phosphate (CAS: 78-42-2)

"Effective degradation of organophosphate ester flame retardants and plasticizers in coastal sediments under high urban pressure", J. Castro-Jiménez et al., Nature Scientific Reports (2022) 12:20228 https://doi.org/10.1038/s41598-022-24685-6

**Misleading paper confuses melamine with nitrogen flame retardants**. A paper from China presents data on eight nitrogen compounds in human urine (301 samples from 13 Chinese cities): cyanuric acid, melamine, ammelide, ammeline, benzoguanamine, 2,4,6-trimethoxy-1,3,5-triazine, 2,4-diamino-6-(4-methylphenyl) - 1,3,5-triazine, diphenyl amidophosphate. Only first four were widely found in urine. pinfa notes however that only a very small proportion







of the widespread use of melamine in consumer and industrial products is for fire safety; that some melamine compounds are used as flame retardants but that quantities are very small compared to the many uses of melamine in different applications, pinfa notes that FRs are < 5% of total melamine use, mainly as an intermediate for melamine compounds, several of which qualify for Ecolabels (see pinfa Newsletter n°129). There is no reason to suggest that flame retardants make any significant contribution to the presence of these nitrogen compounds in urine.

See also Shi et al. 2020

"Exposure to nitrogenous based flame retardants in Chinese population: Evidence from a national-scale study", Y. Shi et al., J. Hazardous Materials 445 (2023) 130653 <a href="https://doi.org/10.1016/j.jhazmat.2022.130653">https://doi.org/10.1016/j.jhazmat.2022.130653</a>

# PUBLISHER INFORMATION

This Newsletter is published for the interest of user industries, stakeholders and the public by pinfa (Phosphorus Inorganic and Nitrogen Flame Retardants Association), a sector group of Cefic (European Chemical Industry federation) <a href="www.pinfa.org">www.pinfa.org</a>. The content is accurate to the best of our knowledge, but is provided for information only and constitutes neither a technical recommendation nor an official position of pinfa, Cefic or pinfa member companies. For abbreviations see: <a href="www.pinfa.org">www.pinfa.org</a>

Subscribe / unsubscribe to this pinfa Newsletter (free) at www.pinfa.eu



