pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 127 June 2021

PINFA WEBINAR 7TH JULY

Product sustainability and fire safety

Can flame-retardant materials be Safe and Sustainable by Design ? Is fire safety an essential use ? Interactive discussion with the European Commission, EU experts, OEMs, Plastics Europe, NGOs.

Wednesday 7th July 15h – 16h30 CEST. Registration
https://www.eventbrite.be/e/what-does-product-sustainability-mean-for-tomorrows-fire-safety-tickets-160171803175

POLICY

EU Zero Pollution Action Plan published

This confirms the Green Deal's targeting of endocrine disruptors, persistent and hazardous chemicals. The Zero Pollution Action Plan is presented as a "*compass for including pollution prevention in all relevant EU policies*", targeting both production and consumption (e.g. by the Sustainable Product Initiative and Product Environmental Footprint). A Zero Pollution Hierarchy is emphasised: 1) prevent pollution by clean-by-design production and the circular economy, 2) minimise releases and exposure, 3) eliminate and remediate. Emphasis is placed on combining environment with economic prosperity and jobs, and on implementation and enforcement. Little is said about chemicals, beyond stating that the already published Chemicals Strategy (see pinfa Newsletter n°119) will "phase out the most harmful chemicals – like endocrine disruptors and persistent substances – especially in consumer products". It is also stated that the EU will promote international actions on "hazardous chemicals, persistent organic pollutants"

European Commission "Pathway to a Healthy Planet for All. EU Action Plan: 'Towards Zero Pollution for Air, Water and Soil", SWD(2021)140 - SWD(2021)141, 12th May 2021
https://ec.europa.eu/environment/strategy/zero-pollution-action-plan_fr

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Swedish chemicals tax proposed changes

Swedish authorities publish proposals to take into account flame retardant safety properties based on assessments. The Swedish chemicals tax on most electrical and electronic goods was introduced in 2017. An official report in 2020 concluded that it has been largely ineffective in modifying flame retardant use, is not cost-effective, has increased prices for consumers and is burdensome for companies (see pina Newsletter n°118).

In their final report on how to modify the tax, Sweden's Tax and Chemicals Agencies now propose to:

- reduce the tax rate (95% exemption instead of 90%) for products not containing FRs considered problematic,
- take into account hazard assessment of FRs, such as CLP classification or Green-Screen™ ratings, in defining tax rates, as well as presence of bromine, chlorine, fluorine or phosphorus and reactive/additive,
- clarify definitions, including for "flame retardant" and for "reactive" and "additive" FRs, plus various other technical changes.

The report notes that "*FRs containing bromine, chlorine and fluorine (halogenated flame retardants) should be considered as a single group, as regards hazard, which should be phased out*".

The recommended tax rates, depending on the characteristics of FRs present in the E&E product sold are as follows:

- zero tax deduction (i.e. highest tax rate) for products containing additive FRs with high hazard level or identified as 'Phase-out' on the Sweden KEMI PRIO list. Also, if containing additive halogenated (bromine, chlorine, fluorine) FRs for which hazard data is insufficient for assessment.
- 50% deduction if containing additive FRs identified as "Priority risk-reduction" in PRIO or Green-Screen Benchmark 2, or if containing hazardous or PRIO "Phase-out" reactive FRs. Also, if containing the following FRs with inadequate hazard data: phosphorus containing additive FRs, halogenated reactive FRs.
- 95% deduction if containing additive FRs which are not identified in CLP as "particularly hazardous", are not PRIO "Priority risk-reduction" or are Green-Screen Benchmark 3 or 4, or if containing reactive FRs which are "Priority-risk assessment", Green Screen Benchmark 2, or reactive halogenated or P-FRs with inadequate hazard information.
- The 95% reduction is also applicable to products NOT containing FRs, that is all products pay a minimum 5% tax.

The report also proposes to extend the tax to a wider range of products, including printers, memories, keyboards, etc. Legal wording is proposed to implement these proposals into regulation. These proposals will now be considered by the Swedish government.

A joint statement between pinfa and IT&T (Sweden's IT and telecom industry organisation) regrets that it is not proposed to withdraw this tax, which is recognised to be ineffective, and calls for zero-tax for products containing only best-in-class flame retardants.

"Utvärdering av skatten på kemikalier i viss elektronik, del 2. Redovisning av regeringsuppdrag" Fi2019/04008/S2
"Evaluation of the tax on chemicals in certain electronics, part 2. Reporting of government assignments", Sweden Tax Agency and Sweden Chemicals Agency KEMI 17/5/2021, in Swedish with English summary
https://www.skatteverket.se/download/18.3016b5d91791bf546791837/1621318436048/Utv%C3%A4rdering%20av%20skatten%20p%C3%A5%20kemikalier%20i%20viss%20elektronik%20del%202.pdf

Joint statement pinfa and IT&Telekomföretagen www.itot.se "Proposed chemical tax revision is appreciated – necessary steps in the right direction, but complete withdrawal should still be considered", 4 June 2021
https://www.pinfa.eu/mediaroom/proposed-chemical-tax-revision-is-appreciated-necessary-steps-in-the-right-direction-but-complete-withdrawal-should-still-be-considered/

Safe and Sustainable-by-Design (SSbD)

For chemicals, the EU emphasises safer plastic additives, product performance, recycling, harmonised approaches. A number of recent European Commission publications and workshops address the objective of "safe and sustainable by design" fixed by the new EU Chemicals Strategy.

A European Commission briefing on Sustainable-by-Design Plastics specifies "*Plastics free from hazardous chemicals e.g. safer alternatives to current additives and coating*" and refers to product performance (e.g. lightweight, strength, antimicrobial), to sustainable production and to recycling.

The European Commission (DG Research and Innovation) has also published a mapping study for defining criteria for "Sustainable-by-Design". This addresses both finished products (articles, textiles, …) and chemicals. This concludes that hazard of substances used in products is the main driver for existing criteria (such as Ecodesign, Ecolabels), but that Sustainable-by-Design criteria should address production, use (e.g. durability, functionality) and end-of-life. It is proposed to develop a methodology and then apply this to define criteria for specific sectors or applications of chemicals in 2021-2022.

A briefing from the European Environment Agency underlines the need for an LCA approach considering health and environmental impacts of chemicals, exposure, end-of-life, but also benefits for product sustainability (e.g. chemicals which make products more durable).

At a first stakeholder workshop Kestusis Sadauskas, DG Environment, underlined that "Safe and Sustainable by Design" is the structuring backbone of the new EU Chemicals Strategy, driving innovation, and will require a clear definition of what this means. DG RTD outlined the Commissions plans for developing criteria: starting with a framework, then definition of criteria and a community of experts and stakeholders. Two first priority materials have been already identified: polymers, metal coatings. This first Commission workshop will be followed by a stakeholder survey to identify safety and sustainability dimensions to be covered and a second workshop Q4 2021.

European Commission briefing document (2 pages) on "Plastics Sustainable-by-Design" 21/9/2020 https://op.europa.eu/en/publication-detail/-/publication/e1e5fcad-fc84-11ea-b44f-01aa75ed71a1/

"Mapping study for the development of Sustainable-by-Design criteria", European Commission DG Research & Innovation, 2021 https://ec.europa.eu/info/publications/mapping-study-development-sustainable-design-criteria_en

European Environment Agency (EEA) briefing (10 pages) 4/2/2021 "Designing safe and sustainable products requires a new approach for chemicals" https://www.eea.europa.eu/publications/designing-safe-and-sustainable-products

European Commission – Advanced Materials webpage "Sustainable-by-Design approach: towards a sustainable future" https://ec.europa.eu/info/research-and-innovation/research-area/industrial-research-and-innovation/key-enabling-technologies/advanced-materials_en#sustainable-by-design-approach-towards-a-sustainable-future

European Commission Research & Innovation Days 22/9/2020 session video (50 mins.) "Sustainability-by-Design. Embedding sustainability criteria in life cycle of products and processes" https://www.youtube.com/watch?v=Y_NnR3A-7Ik

European Commission first stakeholder workshop 19/3/2021 "Safe and Sustainable-by-Design criteria for chemicals, materials and products" (3 ½ hours) https://www.youtube.com/watch?v=alXzLtwu8WE

See also: "Recommendations and guidelines to foster sustainable design" for buildings, European Commission JRC Technical Report 2018 https://publications.jrc.ec.europa.eu/repository/handle/JRC112809

pinfa webinar: ***What does product sustainability mean for tomorrow's fire safety?***
Wed. 7th July 15h – 16h30 CEST: Registration https://www.eventbrite.be/e/what-does-product-sustainability-mean-for-tomorrows-fire-safety-tickets-160171803175

UK Fire Safety Act 2021

New regulation, following the Grenfell catastrophe, extends fire safety obligations but leaves unclear who will pay the costs. Fire Safety Orders for buildings with two or more dwellings will now extend to the structure, walls, doors, windows. The Act also introduces the concept of "risk-based guidance". However, the Act does not specify who must pay for work necessary for fire safety compliance, in particular replacement of unsafe cladding materials. A subsequent Bill is still under discussion whereby leaseholders / tenants in buildings over 18m high (4 – 6 stories) would not face costs, but tenants in lower buildings would have to pay UK£50 per month. The UK has also opened a public consultation on a proposed new residential property developer tax intended to help fund cladding remediation works.

UK Residential Property Developer Tax: consultation, open to 22 July 2021 https://www.gov.uk/government/consultations/residential-property-developer-tax-consultation

UK Fire Safety Act 2021
https://www.legislation.gov.uk/ukpga/2021/24/contents/enacted

Ballymore UK£ 20 m for fire safety

UK property developer Ballymore has announced a UK£ 20 million fund for replacing flammable ACM cladding (aluminium composite material). This follows a fire in Ballymore's New Providence Wharf building, East London, May 2021. Ballymore say that the ACM cladding did not burn in this incident and that work to remove the cladding had already started before the fire. It is not clear how much of the total cost of replacing flammable ACM on flats built by Ballymore will be covered by this UK£ 20 million, how much by the UK Government fund (see above) and how much will remain for "leaseholders" of flats. In the UK, many individual owners of flats and houses do not own the property, but only a 100 year "lease" from the developer.

"Ballymore to spend £20m on fire safety repairs" BBC, 18 May 2021
https://www.building.co.uk/news/ballymore-to-spend-20m-on-fire-safety-repairs/5111865.article

FIRE SAFETY AND STANDARDS

Fire safety of photovoltaic systems

Review shows significant numbers of fires in PV on buildings, but inadequate reporting and poor data on fire and smoke risks. Over 300 publications on PV fire safety were reviewed. Two reports from Italy and Germany suggest 1600 fire incidents per 590 000 PV installations and 430 per 1.3 million respectively (numbers are not per year, so not comparable). Different factors can cause fire in PV systems: physical degradation, overheating, arc faults, faults in

inverters, by-pass diodes, bridging and arrays or power unit, as well as fires starting elsewhere in the building. Although the semi-conductor in PV panels is silicon, other layers and backsheets are generally made of flammable polymers, as are cables and electronic structures and housings. There is today limited published research on PV fire behaviour, but with some increase over recent years. In particular, research is lacking on fire behaviour of panels integrated into the building structure (compared to attached panels), on smoke emissions and on fire propagation and heat transfer.

"A state-of-the-art review of fire safety of photovoltaic systems in buildings", M. Arem et al., Journal of Cleaner Production 308 (2021) 127239 https://doi.org/10.1016/j.jclepro.2021.127239

Updated EU railway fire standard published

A new version EN 45545-2-2020 of the European railway materials fire safety standard is published. New standards for fire behaviour of a complete seat EN 16989 and toxicity test of materials and components EN 17084 are created replacing annexes A-B and C. Standardised substrates by EN 13238 and various clarifications are also made. The updated and the existing standard will co-exist for a transition period of three years to give time for the sector to adapt, and so that certificates with the previous version remain valid for this time.

"New version of EN 45545-2 published", RISE Brandposten n°61 2021 https://www.ri.se/sites/default/files/2021-05/RISE_Brandposten_61_Digital.pdf

Freight ship fire standards

Safety investigator calls for new fire resistance requirements for conveyor belts in bulk transport ships. The Australian Transport Safety Bureau (ATSB) has investigated the fire on the Iron Chieftain which caught fire whilst self-unloading the mineral dolomite (an inert calcium magnesium carbonate) in Port Kembla, News South Wales, June 2018. A fire starting in a rubber conveyor belt, probably because of friction caused by a bearing failure, spread along the rubber conveyor belts, igniting the external discharge boom, and then heavy fuel oil when nearby tanks cracked. The fire took five days to extinguish and the ship was declared a total loss. ASTB has called to modify International Maritime Organisation standards, to add requirements for fire detection systems and fixed fire extinguishing systems in the self-unloading cargo spaces and fire resistant conveyor belts to prevent fire spread.

"ATSB: Fire on Self-Unloading Bulk Carrier Highlights Inadequate International Fire Safety Standards and Regulations", 18 May 2021 https://gcaptain.com/atsb-fire-on-self-unloading-bulk-carrier-highlights-inadequate-international-fire-safety-standards-and-regulations/

Covid oxygen fire risks in hospitals

The EU (JRC) documents increased fire risk in hospitals linked to Covid oxygen use, with 36 hospital fires worldwide. These fires killed over 200 people, not including indirect deaths from resulting oxygen supply cuts. The number of incidents since the start of the Covid pandemic far exceeds those before. The EU JRC (Joint Research Centre) Bulletin aims to raise awareness of fire risks related to oxygen-rich environments in hospitals. JRC is working on recommendations for managing these risks. An increase in oxygen levels in air from 21% to 24% is sufficient to cause risks, and additionally infection units have low air-exchange. This brings the Limiting Oxygen Index fire test starkly into real life.

"Risk of oxygen-related fires in hospitals treating Covid-19 patients", European Commission JRC Lessons Learned Bulletin, updated 3 May 2021
https://minerva.jrc.ec.europa.eu/en/shorturl/minerva/llb_on_risk_of_oxygen_related_fires_in_hospitals_treating_covid_19_patients

INNOVATION

Superior surface quality PIN FR polyamide

Asahi Kasei has launched PIN flame retardant (FR) and glass-fibre reinforced semi-aromatic polyamides. Their aesthetic surface gloss and moisture-resistant strength are suitable for automotive and E&E applications. Although with a glass-fibre content of up to 50%, the materials offer high quality appearance without additional surface treatment or coating. Their tensile strength is higher than that of general glass-fibre reinforced PA66 FR grades and is maintained also in a conditioned state (23℃, 50%Rh equilibrium). Applications include automotive powertrain items, and E&E parts that require flame retardancy, such as connectors, magnet switches, or relay blocks. The halogen-free flame retardant grade achieves UL94-V0 flammability (at 0.75 mm thickness) and meets the European railway fire safety standard EN 45545 Hazard Level 3 (highest) in the categories R22 (interior parts) and R23 (exterior part). It is particularly suitable for E&E applications where a high flame retardancy is required. In addition, the materials also offer excellent laser printability and low mould deposit.

Webinar (Omnexsus SpecialChem) "How to achieve high safety and clear laser printability with new halogen/red phosphorous-free, HL3 certified PA66FR" https://omnexus.specialchem.com/webinar-video/new-halogen-red-phosphorous-free-hl3-certified-pa66fr?lr=clientpromotion

Webinar (Omnexsus SpecialChem): "PA66 FR with superb laser printability for high performance applications" https://omnexus.specialchem.com/webinar-video/new-halogen-red-phosphorous-free-pa66-fr-with-superb-laser-printability

PIN FR labels for fire-safe electronics

Polyonics continues to improve its non-halogen flame-resistant labels for miniature, high-power electronics. Component and material labels in electronic equipment and batteries are essential to enable component and material identification, quality control, commercial traceability, maintenance and dismantling – recycling. They must resist high temperature, demanding conditions over time, without contributing to fire risk. Polyonics proprietary label systems combine polyimide and polyester (PET), with specific pressure-sensitive adhesive and printable coating formulations. Heat transfer and release of flammable gas in case of fire is limited by generation of char layers, achieving UL94 VTM-0, FAR 25.853, BSS 7238/7239 or DOT FMVSS302 fire, smoke and toxicity standards. The latest line of barcode labels and tags is designed for tracing hot metals through processing and is rated up to 700°C using specific non-yellowing PIN FR polymer, coating and adhesive system.

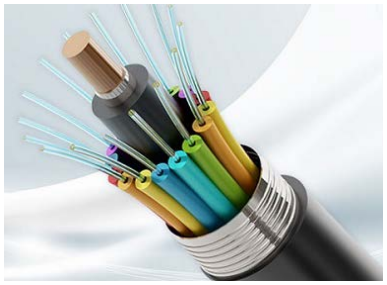
"Flame Retardant Label Materials Prevent the Propagation of Fire in Electrical Assemblies", 19 August 2020
https://polyonics.com/news/materials-prevent-fire-propagation-aug2020.php#

"New Polyonics HIGHdegree Tag and Label Materials Help Metal Processing Facilities Avoid Costly Expense of Recalls", 13 January 2021
https://polyonics.com/news/highdegree-jan2021.php

High temperature PIN FR 3D-printing resin

3D Systems has launched a new PIN FR resin for high accuracy parts for aerospace, automotive, defence, electronics. The manufacturer of 3D-printing systems, 3D Systems, as added to its range a high temperature black non-halogen flame retardant resin, offering surface quality, high rigidity and UL 94 V-0 @ 2mm, adapted for high-accuracy 3D-printing of parts for electronics and aerospace. US federal aviation fire standards FAR 25.853 and 23.853 are met at 3 mm. The material offers prolonged stability, tested for 8 years indoors and 1 ½ years outdoors as per ASTM D4329 and G139. Applications include printed circuit board covers, electrical housings and panels.

"3D Systems releases four new Figure 4 materials to 'revolutionize advanced production'", 26 May 2021
https://3dprintingindustry.com/news/3d-systems-releases-four-new-figure-4-materials-to-revolutionize-advanced-production-190586/



Teknor Apex recognised UL "halogen-free"

The global custom compounder Teknor Apex now has fifteen grades recognised UL AATJ2 low-smoke halogen free FR. The PIN flame retardant EVA-based cable compounds for control, data, fibre-optic and transit cables offer fire performance, heat shock and heat deformation resistance and processing throughput, compliant with UL 1685-FT4/IEEE 12020 vertical tray cable and UL 1666 riser

cable standards. PIN FR TPE-based cables are compliant with UL 62 and UL 758 for flexible appliance cords and wires, with oil and sunlight resistance.

"Four New Flame Retardant Wire and Cable Jacketing Compounds from Teknor Apex Receive 'Halogen-Free' Assessments from UL", 26 March 2021 https://www.teknorapex.com/flame-retardant-wire-and-cable-jacketing-compounds-receive-%E2%80%98halogen-free%E2%80%99-assessments-from-ul

GreenScreen Assessment Registry

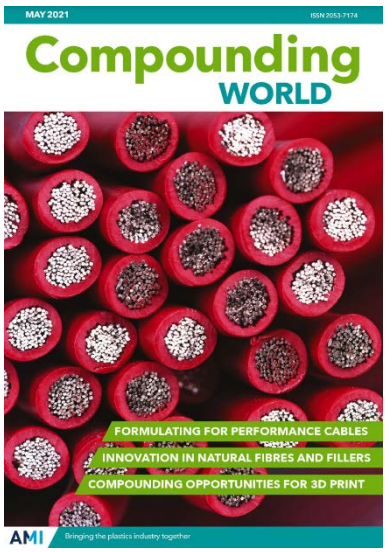
Clean Production Action has launched a Registry of chemicals for which a GreenScreen assessment has been carried out. There are today over 600 GreenSceen valid (not expired) assessments of different chemicals. On entering a CAS number, the Registry will indicate whether or not a GreenScreen assessment of the chemical is available, and if so provides a link to the assessment (if publicly available) or the name of the owner (if confidential). A number of PIN FRs have GreenScreen assessments with benchmark 2 or higher (see e.g. pinfa Newsletter n°123). GreenScreen also operates the GreenScreen List Translator, which compiles information from over 40 hazard lists compiled by scientific or regulatory bodies worldwide. This information can be accessed via websites of PharosProject and Toxnot, where chemicals can be searched for by name or CAS number.

GreenScreen Assessment Registry
https://registry.greenscreenchemicals.org/

GreenScreen List Translator
https://www.greenscreenchemicals.org/learn/greenscreen-list-translator

PharosProject chemical hazards and List Translator (paying site)
https://pharosproject.net/

Toxnot & Clean Production Action https://content.toxnot.com/toxnot-and-greenscreen

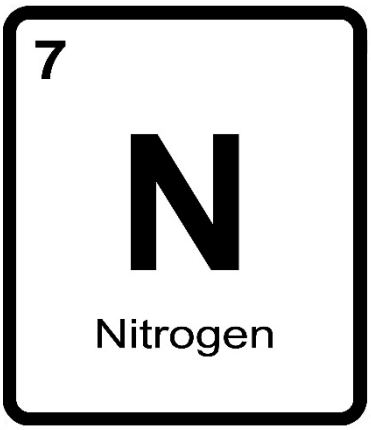


Increasing demand for HFFR in cables

Compounding World magazine points to PIN FRs as key innovation driver in cables, with processing and crosslinking. Compounders are looking for non-halogen solutions to achieve strict fire safety regulations for wires and cables and low smoke emissions, whilst ensuring processing productivity, with particular development in cross-linked halogen-free flame retardant materials. The magazine also notes the move to avoid antimony trioxide (ATO). Crosslinkable PIN FR solutions can offer oil and water resistance and high performance. Innovations include additives to improve mineral FR dispersion and to improve mechanical properties of cables with high mineral FR loadings. Companies cited are Avient, Benvic, Borouge, Buss, Europiren, Evonik, Hexpol TPE, Innospec Leuna, Nabaltec, Padanaplast, Tolsa, Viscospeed.

Compounding World, May 2021 "HFFR demands drive cable innovation"
http://www.compoundingworld.com/

RESEARCH



Mechanisms of nitrogen FRs in PUF

A review of PIN FRs for polyurethane foams notes the synergy of N and P FRs as an "eco-friendly", low smoke solution. Nitrogen-containing FRs can be additive or reactive in polyurethane foams (PUF) and are considered, with other PIN FRs, to provide future solutions with low toxicity, high thermal stability and low smoke, especially in PIN FRs combining nitrogen with phosphorus. Mechanisms of N-FRs are reviewed in detail. (1) N-FRs decompose with an exothermic reaction, absorbing heat. Melamine, for example, absorbs high amounts of heat. (2) N-FRs release ammonia, nitrogen, nitrogen oxides and/or carbon dioxide, which dilute fire gases. APP (ammonia polyphosphate) also releases water vapour. (3) Melamine compounds decompose to produce melamine salts (e.g. melem, melam, melon) which contribute to char stability. (4) Melamine compounds can react and modify the polyurethane decomposition process in fire, resulting in slower burning. (5) Some N-FRs in fire release radicals such as nitroxyl, alkyl, aminyl and alkoxy which inhibit the gas phase fire reactions. Combined with phosphorus, which causes char formation by release of phosphoric acid and can also act in the gas phase, nitrogen-based PIN FRs can delay ignition, reduce the release of heat and smoke.

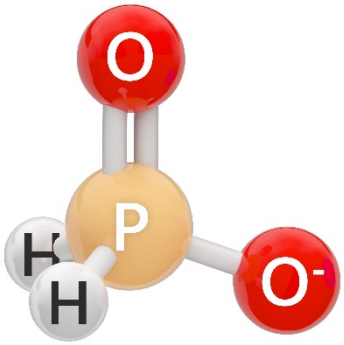
"Nitrogen-Based Ecofriendly Flame Retardants for Polyurethane Foams", N. Arastehnejad et al., chapter 6 in 'Polyurethane Chemistry: Renewable Polyols and Isocyanates', Gupta & Kahol, ACS Publications, 2021
https://dx.doi.org/10.1021/bk-2021-1380.fw001

NIST fire calorimetry database

US National Fire Research Laboratory has launched a publicly accessible database of nearly 400 fire test results. The tests range from small item to furnished room scale and include data (CSV format), videos, photos and graphed data. This can provide data on heat release, soot or carbon monoxide for different materials. The data base can be searched by specimen, test description, fuel type, and for each test a video is available.

NIST Fire Calorimetry Database, US National Fire Research Laboratory (NFRL) at NIST (National Institute of Standards and Technology)
https://www.nist.gov/el/fcd

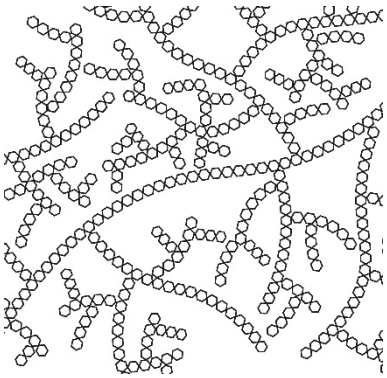
Presentation in FPEeXTRA Magazine
https://www.sfpe.org/publications/magazine/fpeextra/fpeextra2021/fpeextraissue63



Testing metal hypophosphite PIN FRs

An aluminium hypophosphite showed better overall performance in PA66 than magnesium or zinc hypophosphites. Lab scale tests of dicylohexyl hypophosphites of aluminium, magnesium and zinc were tested in polyamide 66 (PA66). The PIN FRs were blended into melted PA66 at 250°C, press moulded to sheets, then tested for fire performance (LOI, UL 94), tensile and flexural strength. All three metal salts showed a flame retardant effect in PA66. The magnesium salt showed the lowest thermal stability and lowest fire performance. The dicylohexyl aluminium hypophosphite showed the best overall performance, maintaining material strength and achieving UL 94 V-0 (3 mm) at 10% loading. LOI increased from 28% to 32% at 15% (nearly +50%) at 15% loading.

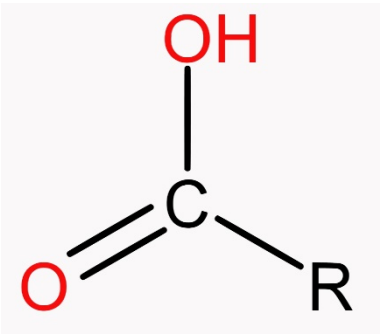
"Comparative Study on the Flame-Retardant Properties and Mechanical Properties of PA66 with Different Dicyclohexyl Hypophosphite Acid Metal Salts", H. Zhang et al., Polymers 2019, 11, 1956;
https://dx.doi.org/10.3390/polym11121956



Oligomeric aluminium phosphonate

Branched oligomeric PIN FR shows flame retardant and smoke suppression, smoke toxicity reduction in epoxy. The synthesised aluminium branched oligo(phenylphosphonate) (AHPP) had average molecular weight of 2 100 g/mol and oligomeric structure. This was blended into DGEBA before curing of epoxy at 2.5 – 7.5% With AHPP at 7.5% loading UL 94 v-0 (3 mm) was achieved, peak heat release was reduced by nearly 70% and LOI was increased from 23.5% to 30%. Smoke density was considerably reduced for the first 15+ minutes of combustion, total smoke yield was significantly reduced, as were toxic emissions (HCN, NO_x, carbon monoxide). Smoke reduction is considered to result from catalytic carbonisation of the polymers and formation of aluminium oxide layers on the surface of char residues.

"Facile synthesis of aluminum branched oligo(phenylphosphonate) submicroparticles with enhanced flame retardance and smoke toxicity suppression for epoxy resin composites", Y. Yuan et al., Journal of Hazardous Materials 381 (2020) 121233
https://doi.org/10.1016/j.jhazmat.2019.121233



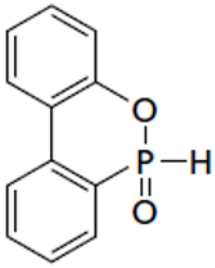
Biobased, hyperbranched PIN FR

Biobased itaconic anhydride (ITA), combined with DOPO, generated a polymeric P FR showed to be effective in epoxy. ITA is a dicarboxylic acid, derived from citric acid, which can be produced from renewable sources. It was here combined with DOPO* to generate a hyperbranched polymer (ITA-HBP), which was then dispersed in DGEBA and then cured into epoxy resin at 0 – 20% loading (0 – 0.93% P in final epoxy). 20% loading of ITA-HBP in exoxy increased LOI by nearly 60%, reduced peak heat release

by over 30% and reduced total smoke release by nearly 25%. Just 5% ITA-BHP was sufficient to achieve UL 94 V-0 (3 mm). Also, impact strength, fracture toughness and fracture energy were significantly improved.

** 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide*

"A bio-based hyperbranched flame retardant for epoxy resins", J. Zhang et al., Chemical Engineering Journal 381 (2020) 122719
https://doi.org/10.1016/j.cej.2019.122719



DOPO as a reactive PIN FR for epoxy

Two phosphorus compounds (DOPO, BICP) combine to cure epoxy, resulting in fire resistance and reduced smoke. DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and BICP (cyclotriphosphazene-modified benzimidazole) together showed to act as a curing agent for DGEBA, reacting into the epoxy resin. At a loading of 10% DOPO and 16.5% BICP (total P content in final resin: 2.6%), LOI was increased by nearly 70%, peak heat release was reduced by nearly 75% and total smoke production by over 50%. This flame retardant mechanism is considered to be a combination of phosphorus radicals active in the gas phase and generation of a highly intumescent, highly graphitised char layer.

"A highly fire-safe and smoke-suppressive single-component epoxy resin with switchable curing temperature and rapid curing rate", S. Yang et al., Composites Part B 207 (2021) 108601
https://doi.org/10.1016/j.compositesb.2020.108601

Bio-based PIN FR for wood fibre materials

Wheat starch modified with P and N showed to be an effective FR for wood fibres and industrially processable. Wood fibres are widely used in heat and sound insulation materials, and are recyclable, compostable and non-toxic, but are flammable. Industrial wheat starch is widely traded (global market c. 4 billion US$) and was here modified with standard nitrogen phosphorus compounds (e.g. the MAP mono ammonium phosphate, widely used as a fertiliser). Treatment of wood fibre at 10% loading of the P-N-modified starch resulted in improved fire performance comparable to a commercial flame retardant. Industrial applicability was tested at a plant of the insulation manufacturer GUTEX (Germany), with c. ½ tonne of FR processed, showing not significant foaming or clumping in processing and good dispersion. The authors conclude that this bio-based PIN FR could be a serious alternative FR solution for wood fibres.

"Flame Retardancy of Wood Fiber Materials Using Phosphorus-Modified Wheat Starch", S. Gebke et al., Molecules 2020, 25, 335;
https://doi.org/10.3390/molecules25020335

OTHER NEWS

Complexity of neurodevelopmental toxicity assessment. Fifteen brominated, chlorinated or phosphate ester flame retardants were tested using a battery of 22 different in vitro neurodevelopmental endpoint tests. Only one FR (TCIPP) showed no effect in all tests. The others showed effects in one or several tests, at concentrations of 0.6 - 20 µM. Results were not well predicted by ToxCast. Overall, EHDPHP and BDE-47 were rated as the most hazardous of the tested FRs, and TCEP and BBOEP as least. The authors conclude that real-life risk from these FRs is low (comparing to concentrations in breast milk) but that there is potential concern for risk from combined exposure.

FRs tested: TetraBDE (BDE-47), PentaBDE (BDE-99), Tetrabromobisphenol A (TBBPA), Triphenyl phosphate (TPHP), Tris (2-butoxyethyl) phosphate (TBOEP) and its metabolite Bis-(2-butoxyethyl) phosphate (BBOEP), Isodecyl diphenyl phosphate (IDDPHP), Triphenyl isopropylated phosphate (IPPHP), Tricresyl phosphate (TCP), Tris (1,3-dichloro-isopropyl) phosphate (TDCIPP), tert-butylphenyl diphenyl phosphate (t-BPDPHP), Tri-O-cresyl phosphate (TOCP), 2-ethylhexyl diphenyl phosphate (EHDPHP), Tris (1-chloro-isopropyl) phosphate (TCIPP), Tris (2-chloroethyl) phosphate (TCEP).

"Neurodevelopmental toxicity assessment of flame retardants using a human DNT in vitro testing battery, J. Klose et al., Cell Biol Toxicol 2021https://doi.org/10.1007/s10565-021-09603-2

Degradation products of TPP (TPHP). Degradation of the phosphate ester FR triphenyl phosphate (generally abbreviated as TPP, here as TPHP) were studied in experiments with green microalgae, invertebrates and fish, at exposure 100 µg/l (below the NOEC). 29 biotransformation products were identified, in particular diphenyl phosphate (hydrolysis product). Most of the decomposition products were predicted (using the ECOSAR model) to be less toxic than TPP itself, corresponding to biogenic "detoxification". However, 4 decomposition products were predicted to be more toxic than TPP with possible chronic effects.

"Identification of biotransformation products of organophosphate ester from various aquatic species by suspect and non-target screening approach", Y. Choi et al., Water Research 2021 https://doi.org/10.1016/j.watres.2021.117201

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