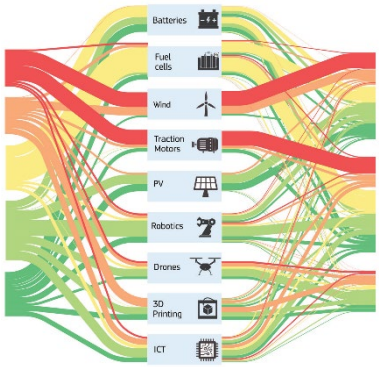
pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 150 June 2023

CONSULTATIONS AND CALLS



Call to add P to Strategic Raw Materials List

pinfa calls for phosphorus to be identified as crucial for fire safety for all of the identified EU "Strategic" industries: batteries, renewable energy, electrical systems, circuit boards, electronic, power and data cables, aerospace. pinfa has submitted to the **EU public consultation to 30th June** underlining that fire risks are increasing in these industries, that phosphorus flame retardants (PFRs) are needed to meet fire safety standards and that a number of PFRs have been have been validated as low-risk and preferable for use by independent assessments, including the European Chemicals Agency (ECHA) in their recent FR strategy The EU has no P_4 production and is dependent on imports from just three countries. pinfa calls for "Phosphorus (P_4 and derivatives)" to be added to the proposed list of EU "Strategic Raw Materials".

Your company or organisation can input to the public consultation until 30th June here: https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/13597-European-Critical-Raw-Materials-Act_en

pinfa input submitted 22nd June 2023 https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/13597-European-Critical-Raw-Materials-Act/F3426840_en

ELSEVIER

Call for flame retardants book contributions

Industry expert input is invited for new Elsevier book on "Flame Retardant Selection for Polymers", covering FR selection, formulation and regulations. Chapters cover FR formulation and processing in different types of polymer, applications for specific sectors including cables, textiles, foams, E&E, transport, 3D-printing, and regulations in different regions of the world. If you are interested to contribute with practical industry expertise, please contact the editors as below.

Editors: Henri Vahabi, University of Lorraine, Günter Beyer, Fire & Polymers, and Mohammad Reza Saeb, Gdańsk University of Technology.Contact: henri.vahabi@univ-lorraine.fr

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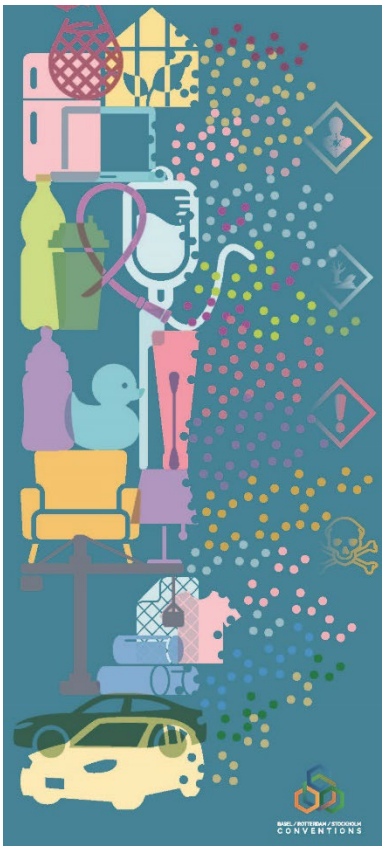
Open to 4th August 2023 HERE.

Further information see pinfa Newsletter n°149

POLICY AND REGULATION

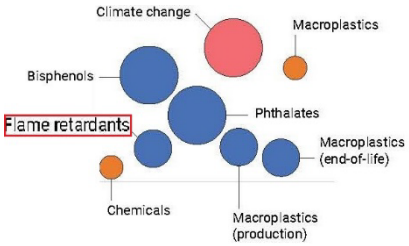


UNEP reports on chemicals in plastics

Document for UN Plastics Treaty on plastics identifies certain specific flame retardants as one of ten chemical concerns.

The United Nations Environment Assembly (UNEA) Resolution 5/14 (10th May 2022) started the process to develop an "international legally binding instrument on plastic pollution, including in the marine environment" (see also update from 2nd International Negotiating Committee on this UN Plastics Treaty June 2023).

A technical report to support development of this UN "Plastics Treaty" summarises relevant knowledge and proposes policy actions. Flame retardants are identified as one of ten families of chemicals of concern in plastics. FRs cited as problematic are: halogenated FRs (in particular PBDEs, HBCDD, HBB, TBBPA, Dechlorane Plus, BTBPE, DBDPE, HBBz, SCCPs, MCCPs) and organophosphorus FRs (in particular TDCPP, TBOEP, TPhP). The report also suggests that there are "concerns about the efficacy of flame retardants because their use in some applications does not provide additional protection" and that brominated FRs "can increase the toxicity of smoke due to smouldering, which releases more carbon monoxide (CO)". Policy action proposals include restricting hazardous chemicals to specific applications ("essential use"), avoiding regrettable substitution, improving plastics chain transparency, updating chemical testing to address combinations of chemicals and bioaccumulation in the environment and improvement of waste management policies.



A second report addresses reducing plastics pollution and improving circularity and proposes "three shifts: Reuse, Recycle, Reorient and Diversify". Flame retardants are indicated as one of three chemical types with high "scientific consensus that harm is caused by plastic-related exposure" (fig.3, page 5). This is taken from a publication from the Minderoo Foundation, an NGO whose objectives are to "eliminate the negative impacts of plastic on people and the planet" and is based on the NGO's assessment of a literature review. The UNEP report also indicates economic damage estimates of plastic pollution (table 1, page 6), again taken from Minderoo. In this case, UNEP incorrectly cites more than 100 billion USD/y as damage from FRs. In fact, the Minderoo estimate for FRs is 10-100 bnUSD/y (fig.6, page 28) and covers the whole plastics life cycle (not only end-of-life plastic pollution). The UNEP report estimates that in total plastics pollution costs 300 – 1500 billion USD/year. It estimates that waste management and circularity policies could reduce virgin

plastic use by over 50%, increase plastics recycling to nearly 30% and reduce environmental losses by over 80%.

The Minderoo Foundation NGO report cited by UNEP (see above), is an NGO document, authored by the NGO's own Head of Finance and a Senior Advisor, which claims to show that societal costs of plastics pollution (environmental clean-up, impacts on ecosystems, human health and life expectancy) are more than 100 billion US/year. This is somewhat confusing as the document also suggests that the health impacts of micro/nano plastic particles, bisphenols and phthalates in plastics alone are each > 100 bnUSD/y (Annex 1, table 1, page 24). The "damage cost" of FRs (incorrectly) cited by UNEP seems to come principally from Annex 1, table 1, page 24, of the Minderoo report which suggests societal health costs of FRs as "low" except for endocrine & immune and development impacts (both medium, estimates of 47 and 26 bn USD/y respectively). This Minderoo document also models (page 38) US industry expected litigation liabilities as "moderate probability" 10 bnUSD for brominated FRs and "low probability" 4 bnUSD for phosphorus FRs.

"Chemicals in plastics. A technical report", 144 pages, United Nationals Environment Programme (UNEP) 2023, ISBN: 978-92-807-4026-4 https://www.unep.org/resources/report/chemicals-plastics-technical-report

"Turning off the Tap. How the world can end plastic pollution and create a circular economy", 88 pages, United Nationals Environment Programme (UNEP) 2023, ISBN: 978-92-807-4024-0 https://www.unep.org/resources/turning-off-tap-end-plastic-pollution-create-circular-economy

Minderoo Foundation "The price of plastic pollution. Social costs and corporate liabilities", Merkl & Charles 2022, 48 pages plus 166 pages of three annexes. https://www.minderoo.org/no-plastic-waste/reports/the-price-of-plastic-pollution/

DEPARTMENT OF ECOLOGY
State of Washington

Washington State FR restrictions

Ban of all halogenated FRs in E&E casings and of halogenated FRs and five phosphorus FRs in some polyurethane foams. Preparation of this Washington State "Safer Chemicals" regulation was summarised in pinfa Newsletter n°140. The regulation is now enacted, effectively banning all organohalogen flame retardants from plastic enclosures of electrical and electronic equipment intended for indoor use (with exemptions for certain types of equipment) by from 1st January 2024, and requiring reporting for equipment for outdoor use. For polyurethane (PU) foams in covered flooring or in uncovered recreational products, all organohalogen FRs are banned from 1st January 2025, as are five specific phosphorus FRs*, and reporting is required for covered PU foam recreational wall padding.

** Ethylhexyl diphenyl phosphate (EHDPP), Isopropylated triphenyl phosphate (IPTPP), Tributyl phosphate (TNBP), Triorthocresyl phosphate (TCP), Triphenyl phosphate (TPP).*

"WAC 173-337 - Washington State Department of Ecology. Chapter 173-337 WAC – Safer Products Restrictions and Reporting" HERE.

Electronics industry position on FRs

DIGITALEUROPE says FRs "provide essential fire protection" and prefer RoHS to REACH for regulation of FRs in electronics. The European digital industry federation (representing over 45 000 businesses) position on the ECHA regulatory strategy on flame retardants (see pinfa Newsletter n°147) "welcomes the balanced phased approach to addressing specific groups of FRs … focus on ensuring that the appropriate safe chemistry is used – the right FR for the right use". The position underlines that FRs are "essential for electronics safety", particularly by stopping small ignition events becoming larger fires. DIGITALEUROPE recommends that FR regulation should be sector-specific and that the RoHS (Restriction of Hazardous Substances) Regulation would be a better tool than REACH for the electronics sector, because it has proven effectiveness (high compliances), allows for repair-as-produced (circular economy) and manages time-limited exceptions. DIGITALEUROPE recommends to define under RoHS thresholds and chemical identifiers for FRs to be restricted.

"DIGITALEUROPE views on upcoming proposal for EU REACH restriction of flame retardants", May 2023
https://cdn.digitaleurope.org/uploads/2023/06/DE-position-on-proposal-for-EU-REACH-restriction-of-flame-retardants.pdf

COMMUNICATIONS

Questioning phosphorus FR toxicity

Discussions article by polymer chemicals researcher suggests effective phosphorus flame retardants may have low toxicity. Bob Howell, an expert in polymers and additives at Central Michigan University, suggests that studies of toxicity of phosphorus FRs often group very different molecules, often also including phosphorus-containing halogenated FRs, resulting in "muddled conclusions". Professor Howell considers that more data is needed on complex organophosphorus FRs, whereas much existing data concerns simple alkyl and aryl phosphate esters. He suggests that the toxicity of "more effective" organophosphorus FRs (that is, with a lower level of oxygenation at phosphorus: phosphonates, phosphinates, phosphine oxides) "exhibit no or minimal toxicity …" and that compounds with low levels of phosphorus oxygenation show little toxicity (e.g. DOPO). He suggests that to support future FR design and use, the relationships between oxygenation levels of phosphorus and toxicity, and between structure (size of molecule, branching) and toxicity should be investigated, including investigating whether toxicity can be related to thermal degradation pathways which have been widely studied to inform fire behaviour.

"Toxicity of organophosphorus flame retardants", J. Fire Sciences, vol. 41, issue 3, 2023 https://doi.org/10.1177/07349041231161493

Fire safety crucial for energy storage

Industry experts say US will need 100 GW of battery grid storage by 2030 and fire safety is needed to enable this. The 100 gigawatts grid storage capacity is needed if the US is to reduce greenhouse emissions by 50% and ensure grid resilience with use of renewable generation by solar and wind and in case of extreme climate events impacting the electricity grid. Expanding battery storage will mean installations in urban areas, in densely populated areas as well as wildfire interface risks. Fire safety standards and testing need to extend from existing single cell runaway considerations to address multiple cell runaway, explosion risk and full energy storage facility life cycle, including design, construction, commissioning, operation, maintenance and decommissioning.

"Fire safety is crucial to the growth of energy storage in 2023", N. Warner and D. Furlong, Energy Storage News (Solar Media), 8th March 2023

Virtual reality for fire awareness

US Fire Administration, FEMA and META, launch virtual reality experience tool to promote fire safety awareness. The free tool lets users with VR equipment or using a desktop version practice fire escape skills and create a fire escape plan at home, at work, in public buildings, anywhere with internet connectivity. META say "While the Escape Plan is a virtual experience, the impact will be real". This VR tool "The Escape Plan" adds to existing FEMA (US Federal Emergency Management Agency) digital tools including an online form to help develop escape plans and a mobile app.

"New Virtual Reality Experience Tests Users' Fire Safety Skills", 16th May 2023 https://www.fema.gov/press-release/20230516/new-virtual-reality-experience-tests-users-fire-safety-skills

RESEARCH AND INNOVATION

PIN flame retardant resin for 3D-printing

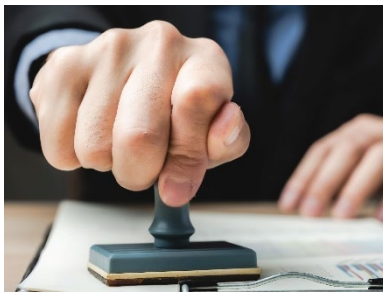
Formlabs' new non-halogenated performance resin achieves UL 94 V-0, is self-extinguishing, low smoke and low toxicity, enabling 3D-printing of performance components for aviation, railway and other transport applications, E&E, industrial parts, etc. The PIN FR resin is certified UL 94 V-0 (@ 3 mm) and FAR25.853(a), is self-extinguishing, low smoke and low toxic gas emissions in fire. Printed parts are dimensionally stable, creep resistant and functional at high operating temperatures. Formlabs' computer design platform and support for 3MF files enable direct CAD to product for complex and detailed parts.

"Formlabs announces new Flame Retardant Resin, BuildPlatform 2L, and 3MF file support at RAPID + TCT", 2nd May 2023 https://formlabs.com/uk/company/press/formlabs-announces-new-flame-retardant-resin-build-platform-2l-and-3mf-file-support-at-rapid-tct/ and website https://formlabs.com/uk/store/materials/flame-retardant-resin/

Performance PIN masterbatch for PE foams

Tosaf launches new phosphorus flame retardant for polyethylene foams for insulation, packaging, construction. The new non-halogenated PIN FR is effective at 10 – 15% loading and acts by a phosphorus gas-phase mechanism, inhibiting burning by blocking free radicals. It offers effective dispersion in foam and does not impact foam nucleation or cross-linking, so preserving mechanical and thermal insulation properties, and can be used in both crosslinked and non-crosslinked foams. Polyethylene foams offer corrosion resistance, dimensional stability, and thermal insulation and are increasingly used in acoustic and mechanical dampers, pipe insulation, flooring, and transport packaging. Because the foam is highly flammable, flame retardants are necessary to respect fire safety requirements in construction, shipping, buildings, or other applications. The new PIN masterbatch can achieve this without using halogenated chemicals. Tosaf is a leading developer and manufacturer of additives, compounds, and colour masterbatches for the plastics industry (see interview in pinfa Newsletter n°144).

"Tosaf launches new additive for halogen-free flame retardancy (HFFR) of PE foams", 30th April 2023 https://www.tosaf.com/tosaf-launches-new-additive-for-halogen-free-flame-retardancy-hffr-of-pe-foams/



Durability of flame retardant materials

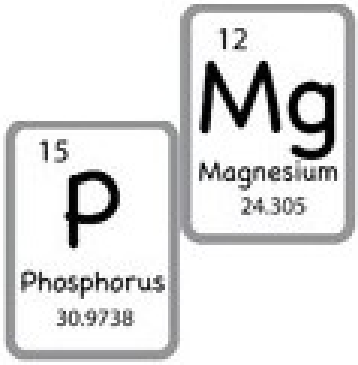
Expert review notes progress in FR durability over time, but research is needed on outdoor durability and recycling. Fire protection expert Jürgen Troitzsch analysed over fifty publications on ageing of flame retardant treated materials and on mechanical recycling. He notes that FRs play an important role in ensuring safety for lives and property. Studies analysed are based on artificial ageing, including exposure to heat, moisture, UV light, salt. Evidence is also provided from use in practice, documented by e.g. standards or guidelines for fire protection durability in buildings and in industrial installations, or by value certification of second-hand E&E equipment. This real-life experience shows lifetimes of FR materials of several decades or more. Dr. Troitzsch summarises conclusions for different families of FRs, noting that brominated FRs are themselves generally very durable but may cause deterioration over time of polymers and stabilisers, some PIN FRs may hydrolyse and/or leach out of materials so deteriorating fire performance, that certain PIN FRs (e.g. phosphinates) are highly stable ensuring long-term durability and that some PIN FRs can even show improvements in fire performance with ageing (e.g. ATH). Mechanical recycling has also been demonstrated for FR materials, but more research is needed on recycling of mixed end-of-life polymers containing FRs.

"Fire Performance Durability of Flame Retardants in Polymers and Coatings", J. Troitzsch, Advanced Industrial and Engineering Polymer Research, AIEPR 154, 2023 https://doi.org/10.1016/j.aiepr.2023.05.002

PIN FRs for recycled newspaper composite

PIN flame retardants were tested to enable fire safety of polypropylene – recycled newspaper fibre composites. Waste fibres can replace glass fibre to provide strength in plastic composites, enabling waste valorisation and also reducing tool wear and processing constraints. Magnesium hydroxide (MDH, $Mg(OH)_2$) was tested as PIN flame retardant, compounded into the polypropylene, on its own 25% and with zinc borate/ATO 5%, in composites of 50% polymer compound – 50% secondary fibres. The MDH alone provided the best fire performance improvement with a decrease in horizontal burning rate of >50% and an increase in LOI (limiting oxygen index) of nearly 25% compared to the PP-fibre composite without FR. The inclusion of the PIN FRs reduced mechanical performance of the PP-fibre composite only slightly or not significantly.

"Recycled Newspaper Fiber/Polypropylene Composites with Inorganic Flame Retardants: Flame Retardant and Mechanical Characteristics", H. Zaman & R. Khan, Adv. J. Sc. Eng. 2023; 4 (2): 042014. https://doi.org/10.22034/advjse042014



Biobased phosphorus – magnesium PIN FR

Magnesium hydroxide – phytic acid compound improved fire performance and reduced smoke loss in polyethylene. The natural inorganic compound, magnesium hydroxide, was reacted in water with phytic acid, a biological compound rich in phosphorus found widely in plants. The product (termed MHPA) was tested at 33% loadings of MHPA, MHPA+MH or MH, in high-density polyethylene (HDPE). UL 94 v-2 was achieved only with MHPA+MH, with peak heat release rate reduced by nearly -40% and total smoke production by -65% compared to neat HDPE. Mechanical properties (tear strength, tensile strength, shore hardness) were generally better when MHPA was included that with MH alone, but were significantly lower than for neat HDPE.

"Development of bio-based magnesium phosphate flame retardant for simultaneously improved flame retardancy, smoke suppression and mechanical properties of HDPE", X. Feng et al., J Appl Polym Sci. 2023;140:e53927 https://doi.org/10.1002/app.53927

PIN FR for secondary fibre brocade fabric

Ammonium poly phosphate PIN FR effective for durable fire safety for Varanasi brocade woven from waste pineapple fibres. Indian handloom Varanasi textiles are >80% exported so must meet fire safety standards. Secondary pineapple cellulose fibres can replace cotton, providing a sustainable, locally sourced and economically attractive material, but must be fire safety treated. Ammonium polyphosphate (APP, a phosphorus-nitrogen inorganic salt PIN flame retardant) was dissolved in water then applied to the pineapple-fibre fabrics with cyanoguanidine catalyst by soaking, curing at 150°C, rinsing then drying. Application of 15% APP, 5%

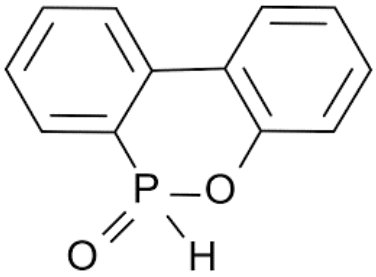
catalyst resulted in a 9% weight gain and increased N and P content of the fabric from near zero (untreated fabric) to 12% and 5% respectively. LOI was doubled, peak heat release rate was reduced by 98%, and there was no after-flame in vertical burn test. LOI remained > one third increased after 20 washes and there was no colour impact on the fabric. APP is considered to bind to the OH group of pineapple cellulose and to reduce flammability by intumescence, char formation and release of gas phase radicals.

"Application of ammonium polyphosphate as intumescent flame retardant on Varanasi brocade pineapple fabric", A. Kushwaha et al., Biomass Conversion and Biorefinery 2023 https://doi.org/10.1007/s13399-023-04274-x

Soybean PIN FR for bio-sourced polymer

Soybean protein dosed with phosphite gave a phosphorus-nitrogen PIN FR effective in bio-sourced PLA polymer. PLA (poly lactic acid) is a widely available bio-sourced polymer but is highly flammable. Soybean protein, naturally rich in nitrogen, was here reacted in water with the simple phosphorus compound dimethyl phosphite (non-classified, widely available) and formaldehyde (bonding agent). The resulting N-P PIN FR enabled PLA to achieve UL 94 V-0 (3 mm) at 7% loading (neat PLA is NR) and reduced pHRR by 15% at 15% loading. The soybean protein based PIN FR increased char formation, reduced flammable gas emission and diluted fire gases by emission of ammonia.

"Facile synthesis of soybean protein-based phosphorus-nitrogen flame retardant for poly(lactic acid)", L. Dong et al., Polymer Degradation and Stability 214 (2023) 110412 https://doi.org/10.1016/j.polymdegradstab.2023.110412



DOPO-based P-N-S-Cu PIN FR for epoxy

Organo-metal PIN flame retardant improved fire performance and reduced peak smoke emission by nearly 20%. The well-recognised phosphorus PIN FR, DOPO, was reacted with an amine compound, a sodium amino sulphate and optionally also copper sulphate, resulting in a phosphorus – nitrogen – sulphur – sodium or copper organometallic PIN FR molecules DCSA-Na and DCSA-Cu. This was cured into epoxy resin at 0 – 7% loading. At 5% loading of DCSA-Cu, peak heat release was reduced by 30%, peak smoke release rate by nearly 20%, UL 94 V-0 was achieved (neat epoxy was NR) and physical characteristics of the epoxy were not significantly modified. Fire performance is considered to result from char generation by phosphorus, cross-linking of the epoxy and reduced smoke toxicity from copper catalysis of conversion of CO to CO_2.

"An Organometallic Flame Retardant Containing P/N/S−Cu^{2+} for Epoxy Resins with Reduced Fire Hazard and Smoke Toxicity", J. Li et al., ACS Omega 2023, 8, 16080−16093 https://doi.org/10.1021/acsomega.2c08226

PUBLISHER INFORMATION

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