pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 149 May 2023

PINFA ACTIONS

pinfa General Assembly regulatory update

Members discussed with ECHA the 'Flame Retardants Strategy' and other chemicals, safety and fire safety developments.

Some thirty representatives of fifteen pinfa member companies met at the pinfa General Assembly in Valencia on 20th April (after the Aimplas Flame Retardant workshop, see below) and online.

pinfa members were able to dialogue with **Jesus Vazquez Rodriguez and Maarten Roggeman of ECHA**, who presented the recently published ECHA Flame Retardants Strategy (see pinfa Newsletter n°147), underlining that FRs are useful and value-added chemicals, but that some are problematic. ECHA's assessment started from an inventory of some 350 chemicals identified as used as FRs, then focussed on halogenated and organo-phosphorus FRs, for which ECHA then defined eleven "groups" containing some 220 chemicals. ECHA intends to propose regulation by "group" to avoid regrettable substitutions. ECHA considers that the objective should be to have only low-hazard FRs, or FRs with low mobility and closely controlled end-of-life. Several groups of organo-phosphorus FRs are identified as non-hazardous or of low hazard, for others data is still being developed. As well as regulatory restrictions by REACH, certain groups of FRs may be banned through EcoDesign. EU authorities may also promote fire safety standards which allow solutions other than FR use. Discussions underlined the need to develop data on release of FRs from articles and so exposure and the need for EU standardised analysis methods to enforce regulation on restricted FRs in imported articles (<0.1%). Without such verification, EU industry will be penalised and problematic chemicals will be imported in articles meaning that the EU consumer and environment are not protected.

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A sector group of Cefic

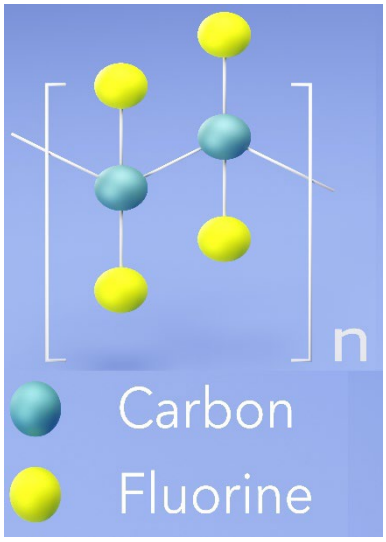
pinfa members also discussed ongoing work on inorganic FRs (regulatory questions around inhalation risk definitions), melamine compounds (see Q&A on www.pinfa.eu), recycling of polymers containing PIN FRs, smoke toxicity, monitoring of traces of organophosphorus FRs in the environment and training and education actions on PIN FRs in Europe, North America and China.

www.pinfa.eu

Free webinar: chemical hazard assessments

ChemForward pinfa-NA webinar 14th June 11h30 EST (17h30 CEST) chemical hazard assessments and regulatory trends. With Lauren Heine and Chris Bartlett, ChemForward. This webinar will explain drivers for chemical alternatives and how a shared chemical hazard assessment repository can support proactive design to anticipate regulatory trends.

Information and registration: https://www.pinfa-na.org/hazardassessment



Alternatives to poly(tetrafluorothylene)

Expert paper, with pinfa-NA, assesses possible non-halogenated solutions to reduce melt-drip fire risk in plastics. Melt-dripping of plastics can propagate fire from burning plastic to other materials. The UL 94 fire performance test therefore requires absence of flaming drips for V0 or V1 rating. The halogenated polymer PTFE (polytetrafluoroethylene, as in Teflon) is widely used at low dosages (e.g. 0.5%), in synergy with flame retardants, to avoid melt-drip in plastics and acts by shearing-inducing fibrillation within the polymer under heat, which increases viscosity. Problems of dispersion of PTFE in plastics are addressed by using e.g. SAN coating (styrene acrylonitrile). However, PTFE is included in the wide class of chemicals "PFAS" (per- and polyfluoroalkyl substances) currently subject to a proposed "Restriction" in the EU. This study discusses a range of PIN compounds which improve the structure of char which can hinder melt-dripping or which increase polymer viscosity (talc, clays, metal hydroxides, zinc borate, silicones, acrylic acid polymers, carbon nanomaterials) as well as other possible solutions such as multilayer coextrusion of different polymers. Some bio-based compounds may also have anti-drip effects, such as lignin, saccharide-based compounds, phytic acid, probably due to char formation. The paper concludes that anti-drip agents are essential for plastic fire safety, that there is rapid development of char-promoters which can somewhat reduce dripping, but that there is today no solution available to replace PTFE in many polymer FR compounds.

"Drip Suppressants in Halogen-free Flame Retardant Systems", Y. Zhang, G. Whek, R. Avakian, J. Zhou (Case Western University, pinfa-NA). Not yet published. Available to pinfa members. External parties may request a copy from dwagner@pinfa-na.org

pinfa Annual Report 2022

pinfa now has over thirty full and associate members active in 2022 on policy, recycling, communications and worldwide. pinfa's Annual Report 2022 provides a 30-page summary of actions on PIN flame retardants in the EU Chemicals Strategy for Sustainability and related EU regulatory developments, work on PIN FRs in recycling, active pinfa Task Forces on phosphorus- and melamine-based PIN FRs. The Annual Report highlights inputs from downstream users of PIN flame retardants (compounders, OEMs), researchers and other stakeholders. Actions of pinfa North America and pinfa China are summarised.

pinfa Annual Report 2022 *https://www.pinfa.eu/media-events/brochures-publications/*

AIMPLAS 6TH FLAME RETARDANT WORKSHOP

AIMPLAS
PLASTICS ACADEMY

How PIN FRs contribute to fire safety

Valencia, Spain, 19th April: eight pinfa members presented PIN fire safety solutions and regulatory developments: Adeka, Avient, Budenheim, Clariant, ICL, Imerys, Nabaltec, William Blythe. Workshop participants included compounders from across Europe and the workshop provided an expert training in formulation and compounding of fire performance polymers, as well as visits to Aimplas research lab and testing pilots.

Tobias Moss, Budenheim, reminded attendees why society needs flame retardants. Around 130 000 people die in fires worldwide each year, and fires cost around 1% of GDP. Flame retardants represent around one third of polymer additives with an annual world market of around 10 billion € growing at c. +6% per year, with PIN flame retardants showing the fastest growth.

Corina Neumeister, Nabaltec, summarised different fire performance tests and what information they bring, and outlined the mechanisms of PIN flame retardants, including char formation, intumescence, heat absorption, release of inert gases and gas phase flame inhibition. PIN FRs have the advantage of not releasing acid during processing, nor during use life, so protecting equipment or electronic circuits. Their mode of action results in low smoke toxicity and low smoke release, and this can be accentuated by synergies with PIN smoke suppressants.

Pascal Amiguoet, Avient, explained that flame retardants play several roles in fire protection, depending on their selection and combination in different polymers: prevent or delay the start of fire, reduce heat release rate, and maintain structure (for example by protecting steel or concrete from heat and so from collapse in case of fire, or by maintaining structure of cables so ensuring that power or data continue to be transmitted). Flame retardants always have impacts on polymer properties and cost, as do other additives, so a challenge is to identify what is really needed by the customer for the final product and to propose a formulation offering the best cost – performance balance whilst ensuring the required level of fire safety.

Begoña Galindo, Aimplas, presented the Aimplas Flame Retardant R&D group, created 2008, developing biobased flame-retardant additives, intrinsically flame-retardant polymers, recycling and fire testing. Processing is very important to ensure effectiveness of flame retardant additives. Twin screw extruders with distributive screw configuration and low specific mechanical energy avoid high temperature peaks along the process, so ensuring optimal mixing of the additive without degradation.

Ana Mangas Roca, Aimplas, presented reactive extrusion (REX) technology. This enables a high level of mixing and reaction control, but is complex to manage because many parameters must be closely controlled in one single installation. REX units can also operate mechanochemistry, that is reaction of solid components. Aimplas operates a full-scale pilot unit for testing and trials. Results are promising. To date there is little industrial application but applications are being sought.

Laurent Ratte, SCC Consultants, presented compounding simulation software. From inputs data (material and additives characteristics, screw design and operating conditions), simulation gives insights about material behaviour evolution and process efficiency. Software simulation enables to identify likely formulation ranges and so target testing. Test results are then used to improve the simulation and so material properties and process quality.

Laurent Ferry, IMT Mines Alès, outlined research into bio-based flame retardants. Many research papers have been published over recent decades, looking at flame retardant properties of natural phenolic carbon molecules (e.g. lignin, tannin), which can stabilise charring by cross-linking, natural molecules containing nitrogen and/or phosphorus (e.g. chitin, casein, phytic acid, DNA from fish waste), as well as bio-based carbon molecules doped with synthetically sourced phosphorus. Alginate can be used to produce fire resistant insulation foams. Phytic acid offers the advantages of being naturally widely available (in seeds), high phosphorus content, possibility to react with different metals for synergetic effects. To

date there is no significant industrial uptake of these bio-based PIN FRs. Some are widely and reliably available, but all pose challenges of water uptake, purity and cost. See pinfa Newsletter n°139, summary of ECOFRAM 2022 conference.

Mireia Fernández, Aimplas, outlined different processes for recycling of plastics, including chemical recycling, and how to apply them to FRs recovery.

- Solvent recycling: Dissolution and precipitation techniques are used to separate polymers from additives allowing the recovery of both fractions. Research is looking for alternatives to chemical solvents, such as biobased solvents or supercritical CO_2.
- Solvolysis: specific solvents are used to depolymerise given polymers and obtain the starting monomers. Separation and purification of the dissolved additives and monomers is a challenge.
- Pyrolysis. Polymers are broken down to gas and liquid fractions, which can be used as fuel or to replace crude oil in refining. Some additives can be separated and recovered.

Adrian Beard, pinfa Chairman (Clariant), discussed what is a "sustainable flame retardant", based on the EU Green Deal objective of Safe and Sustainable-by-Design Chemicals (SSbD). This requires looking at many factors, as a priority no or minimal health and environmental hazards and compatibility with safe end-of-life recycling or disposal, and climate impacts, but also life cycle analysis including Critical Raw Materials, smoke toxicity, social benefits and impacts. Clariant is making this analysis for a phosphinate PIN FR used in a USB-C socket. The full analysis implies collection of very much data, including specific studies on possible impacts during processing, collection of exposure data (the PIN FR is not classified hazardous, so no CSR exists to date) and an environmental footprint study. This exercise shows the complexity of the SSbD concept and that it cannot generate a yes/no quantified result, but will enable identification of sustainability "hotspot" challenges.

Aimplas: www.aimplas.es/plasticsacademy

REGULATORY AND POLICY

Polluter Pays consultation to 4th Aug. 2023

Consultation ask questions about Polluter Pays policy implementation, costs and which sectors should be targeted. Several sectors concerned by flame retardants are proposed as possible targets, including plastics and rubber products, electronic and electrical equipment, vehicles, construction, wood products. Other questions address the how Polluter Pays Principle (PPP) should be implemented and integration into and impacts on prices of products. This consultation is open to input from the general public, companies and organisations. At the same time, the recast of the Urban Waste Water Treatment Directive, currently in discussion in European Parliament and Council, raises the question of PPP. The Commission's proposed text would introduce PPP (here called "Extended Producer Responsibility") for costs of removing pharmaceutical and cosmetics residues in sewage works (Recital 13, arts. 9, 10, 30 and Annex 3) and will evaluate for 2030 whether this should be enlarged to other chemicals found in wastewater.

Legislative dossier underway Urban Waste Water Treatment Directive recast
https://oeil.secure.europarl.europa.eu/oeil/popups/ficheprocedure.do?reference=2022/0345(COD)&l=en

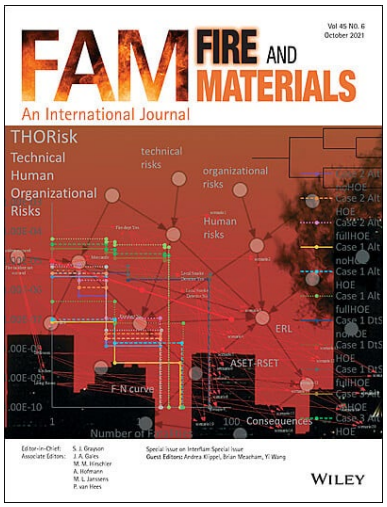
"Polluter Pays Principle – fitness check of its application to the environment", EU public consultation open to 4th August 2023 HERE

Debate on wildfire retardants in US

US regulators are opposing lawsuits attempting to prevent use of fire retardants to fight wildfires. The lawsuits, brought by an NGO of Forest Service employees (FESSS), suggests that a permit would be needed to use fire retardants in wildfire fighting water. It is being opposed by the town of Paradise, California and the California forestry trade association (Calforests). The US Forest Service says that it is now working to obtain permits, but that this will take two or more years. The Forest Service is cited as considering "retardant a critical wildfire-suppression tool … made up of … ammonium phosphate, a salt found in fertilizer." In the legal hearing, the Mayor of Paradise, which saw the deadly 2018 Camp Fire, said "the lawsuit is callous for homeowners and citizens who have experienced a wildfire. They are saying that people's lives are not that important". Calforests CEO said "retardants have played an integral role in stopping some of the most devastating wildfires in recent history - saving lives, businesses, and property. If this important tool is taken away at the federal level, the real-life consequences will be catastrophic".

""Catastrophic": Aerial fire retardant lawsuit could change how California fights wildfires", CBS News 24th April 2023

PIN FRs AND SMOKE



PIN FRs do not increase smoke toxicity

Tests on 72 formulations of 10 polymers show no significant increase in smoke density or toxicity with PIN FRs. The tests, carried out by CREPIM France and funded by 12 pinfa member companies, applied the European railway standard EN 45545-2 as a recognised state-of-the art for smoke hazard testing. Widely used polymers were tested (including polyethylene, polypropylene, polycarbonate, polyamide, PVC, polyurethane, polyisocyanurate): neat, with market-relevant PIN FRs dosed as used, and also with relevant brominated FRs. Other additives and FR synergists, which would be found in commercial formulations, were not included to enable clarity of results. Smoke density (which is critical for escape from fires) and emission of eight toxic smoke gases were measured (CO, CO_2, HBr, HCl, HCN, HF, NO_x, SO_2). There was a wide variation of smoke emission and smoke toxicity between polymers, but the following general overall conclusions could be identified for effects of PIN flame retardants (except for in PVC which showed inherently high smoke toxicity using this test method). Maximum smoke density and indices of toxicity generally showed no significant increase when PIN FRs were added to the polymer (compared to neat polymer). Intumescent PIN FRs and inorganic (hydroxide) FRs reduced smoke density without significant impact on smoke toxicity. Brominated FRs, in most cases, increased measured smoke and/or toxicity.

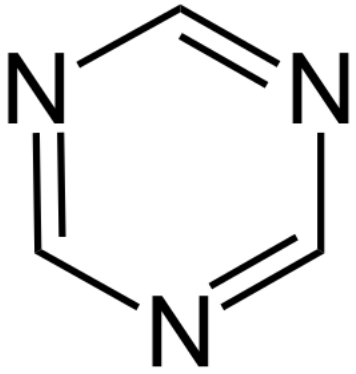
"The impact of halogen free phosphorus, inorganic and nitrogen flame retardants on the toxicity and density of smoke from 10 common polymers", H. Feuchter, F. Poutch, A. Beard, Fire and Materials. 2023;1–21, https://doi.org/10.1002/fam.3145

INNOVATION AND RESEARCH

PIN FR glass fibre polypropylene (GF PP)

Teknor Apex new non-halogen flame retardant GF PP combines mechanical and fire performance for miniaturised components, in applications such as electrical components, electronics housings, structural parts and frames, electrical vehicles, solar power, energy storage. Compared to other polymers available with comparable performance, the new PIN flame retardant GF PP compound offers moisture absorption resistance, acid resistance, adhesion to other thermoplastics and lower density. Fire performance is UL 94 V-0 (1.5 mm), V-2 (0.8mm) and UL 5 VA (3.0 mm) and GWFI 960 °C (0.8 mm). Electrical performance is CTI 600V (PLC=0) and dielectric strength of 26 kV/mm.

"Teknor Apex Introduces New Crealen – an InnovativeGlass Filled Halogen Free Flame Retardant Polypropylene (HFFR PP)", 17 February 2023 https://www.teknorapex.com/teknor-apex-introduces-new-crealen and Crealen Halogen-Free Flame Retardant Polypropylene page https://www.teknorapex.com/crealen-hffr-polypropylene



Perspectives for triazine PIN FRs

Triazines are environment-friendly nitrogen-based PIN flame retardants, generating char, inhibiting fire and reducing smoke. This paper presents different routes for synthesis of triazines, via the chlorinated agent CYC (cyanuric chloride) or from melamine, generating a range of different triazine-based flame retardants, including both additive and reactive, small molecule, linear macromolecular, hyperbranched and polymerised molecules. Examples are given of application of different triazine-based FRs in polypropylene, epoxy, polyamide and melamine resins, including in synergy with phosphorus-based PIN flame retardants.

"Research progress of triazine flame retardants", J. Wang et al., Macromolecular Research (2023) 31:339–357, https://doi.org/10.1007/s13233-023-00157-2 Image Wikimedia.

Recyclable phosphorus ester epoxy

Reaction of P-esters into epoxy generates a thermally recyclable polymer with fire performance and low smoke. The phosphorus ester TDPSD* was synthesised from diphenylphosphite, then reacted with epoxy DGEBA in a one-pot, two-step process without using solvents. This resulted in P-C reactive bonding of the PIN flame retardant into the final polymer, and also P-O bonds in the final polymer which enable thermal recyclability (reprocessability). Inclusion of TDPSD to 2.5% phosphorus loading enabled improved fire performance (-25% peak heat release rate compared to neat epoxy) and inhibition of smoke release (-27.5%) but 6% phosphorus load was necessary to ensure recyclability. The material could be recycled by grinding then by heat pressing at 150-160°C (6MPa, 5 mins).

** = 2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5] undecane, 3, 9-dioxide*

"Recyclable flame retardant phosphonated epoxy based thermosets enabled via a reactive approach", W.W. Klingler et al., Chem. Eng. J. 466 (2023) 143051 https://doi.org/10.1016/j.cej.2023.143051

PIN FR synergy in polypropylene

Expandable graphite (EG) enhanced fire performance and reduced smoke with magnesium hydroxide in polypropylene. Polypropylene was tested with 0 – 63% magnesium hydroxide (MH), 9 – 30% EG and a combination of 4 – 17% EG with MH to a total of 57% PIN FR. Replacing c. 9% MH by EG enabled total PIN FR load needed to achieve UL 94 V-0 (3 mm) in polypropylene to be reduced from 63% to 57% with the same LOI as with 63% MH. The authors note that there is no chemical reaction between EG and MH and that the improved fire performance and smoke suppression was because EG on the polymer surface hinders acid erosion of MH.

"Role of expandable graphite on flame retardancy, smoke suppression, and acid resistance of polypropylene/magnesium hydroxide composites", S. Liang et al., Polym. Eng. Sci. 2022;1–12, https://doi.org/10.1002/pen.26093

Review on FR metabolites in fauna

Despite extensive studies available, further data is needed on breakdown products of novel brominated and organo-P FRs in fauna. This review of 150 publications concludes that metabolism pathways of organo-phosphorus flame retardants are similar in different animals (O-dealkylation, hydroxylation and phase II conjunction) and that di-alkyl phosphates (DAPs) and hydroxylated OPFRs (OH-OPFRs) are the metabolites most present in fauna. Information on metabolic pathways of recent ("novel") brominated flame retardants is considered lacking. Some studies suggest that certain flame retardant metabolites may cause negative effects and therefore further studies on exposure, effects and risks are considered to be needed, in particular concerning biotransformation and transmission of metabolites between species in food webs.

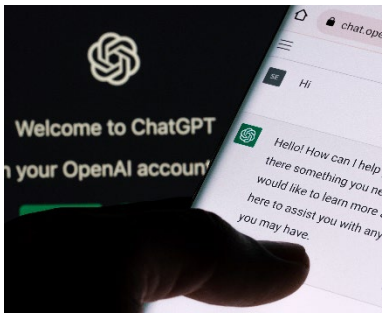
"The metabolism of novel flame retardants and the internal exposure and toxicity of their major metabolites in fauna - a review", R. Hou et al., J Environ Expo Assess 2023;2:10, https://dx.doi.org/10.20517/jeea.2023.08

OTHER NEWS

18 000 cows die in Texas fire

Some 18 000 cows died and a worker was seriously injured in a fire on a Texas dairy farm, 10th April 2023. The fire may have started in a slurry pumping machine, possibly leading to an explosion of methane gas released from manure. This is the deadliest "barn fire" since US data collection started in 2013. Nearly a million farm animals per year die in fires in the USA, but these are mostly chickens. Safe regulatory disposal of the bovine remains will be a significant problem. Fire Safety & Technical Bulletin (April 2023) suggests that fire risks in US farms could be mitigated if states were to adopt the NFPA 150 Fire and Life Safety in Animal Housing Facilities Code,

"Texas dairy farm explosion kills 18,000 cows", BBC 13 April 2023 https://www.bbc.com/news/world-us-canada-65258108



ChatGPT rather likes flame retardants

If asked about flame retardants, ChatGPT says they "can be effective in reducing the risk of fires". The artificial intelligence large-language motor says that "phosphorus-based flame retardants are generally considered to be safer and less toxic than other types of flame retardant … less hazardous to human health … may have low toxicity and be less likely to accumulate in the environment". Nitrogen-based FRs are also considered "less toxic … do not produce harmful by-products when exposed to heat or flames". Melamine phosphate is also considered to be "safe and non-toxic" with no evidence of cancer risk. However, the AI seems somewhat confused or wrong when asked "What is a PIN FR", indicating that all PIN FRs are nitrogen-based, that PIN stands for "polymerization induced by nitrogen", and that PIN FRs act by a "polymerization reaction produces a protective layer of char". The AI considers that "an effective and safe flame retardant technology, as they do not produce toxic or corrosive by-products when exposed to heat or flames. They are also considered to be environmentally friendly, as they do not contain halogens or heavy metals". pinfa suggests to prefer other sources of information, such as the pinfa Academy slide set, which tries to be more accurate.

ChatGPT *(OpenAI): https://openai.com/blog/chatgp*

PUBLISHER INFORMATION

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