pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 161 June 2024

PINFA IN ACTION

pinfa General Assembly

Over forty representatives of pinfa companies discussed flame retardant and plastics chemicals policy, regulation and LCA at pinfa's General Assembly, in Cologne, Germany, and online, on 3rd June 2024.

Anna Ossalinska, CarbonMinds, presented work underway for the European commission to develop coherent LCA (Life Cycle Analysis) data for EU Environmental Footprints for chemicals and for bio-based materials. Some 400 chemicals are initially being considered, including a few PIN FRs. pinfa will make coordinated input, in addition to input from pinfa member companies.

Nina Lazic, European Chemicals Agency (ECHA), presented EU work underway to gather information on alternatives to aromatic brominated flame retardants (BFRs), which are under assessment for possible 'Restriction' under REACH (EU chemicals regulation). Information is being collected on possible alternatives to these BFRs in different applications and polymers (in particular in electronics and automobiles), including possible emissions from articles or hazards of alternative FRs. A report is expected to be finalised and delivered to the European Commission by early 2025, enabling the Commission to then possibly engage the REACH restriction process for these brominated FRs. pinfa is coordinating input on non-halogenated flame retardants and their applications.

The General Assembly discussed the ongoing United Nations discussions of a globally binding treaty on chemicals in plastics (UNEP INC-4), see pinfa Newsletter n°160. Proposals currently on the table could impact many chemicals used to produce performance plastics and composites, with proposed bans or restrictions on various chlorinated and brominated flame retardants, or on all chemicals with certain environmental or health risks, as well as possible bans of all use of certain plastics polymers in packaging. pinfa is following this closely and providing information, via Cefic and the International Council of Chemicals Associations (ICCA), see pinfa Newsletter n°157.

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The General Assembly also updated on pinfa technical work underway, including studies on environmental behaviour of melamine derivative and phosphorus PIN FRs, testing methods for inorganic chemicals (appropriate consideration of particle size), upcycling of secondary FR plastics (performance re-compounding for recycling), as well as communications actions in Europe, North America (pinfa-NA), China (pinfa China) and worldwide.

POLICY

UBA report: environment friendly fire safety

Flame retardants are identified as one route to fire safety in public purchasing and can be without hazards. The German Federal Environment Agency (Umwelt Bundesamt, UBA) report assesses fire safety requirements for public purchasing of PPE (personal protective equipment), work clothing and shoes, textiles, furniture mattresses and floorings. It is noted that fire protection is not a legal requirement in public spaces for all of these. The report notes that public purchasers should verify if fire safety is legally required, and that fire safety can sometimes be achieved by using inherently non-flammable materials. Where this is not possible, flame retardants can ensure fire safety. The report assesses thirty-one flame retardants identified as widely used in the products considered. The report concludes that nine FRs are acceptable for use because they are considered non-toxic, non-persistent, non-bioaccumulative, non-hazardous*.

pinfa questions this approach which ignores low exposure to flame retardants which are integrated into polymers, so have low risk (risk = possible effects on health or the environment, is related to both chemical properties and to exposure). In particular, a number of reactive flame retardants are excluded because of their chemical properties, despite that these FRs are no longer present in the final product and so their initial chemical properties are no longer relevant.

pinfa welcomes the emphasis in the report placed on smoke emission and toxicity. Smoke is often the main cause of fire deaths, incapacitating and preventing escape. Studies show that smoke toxicity is generally not increased by PIN flame retardants**, and smoke emission is mainly linked to the quantities of material burning, which can be reduced by flame retardants.

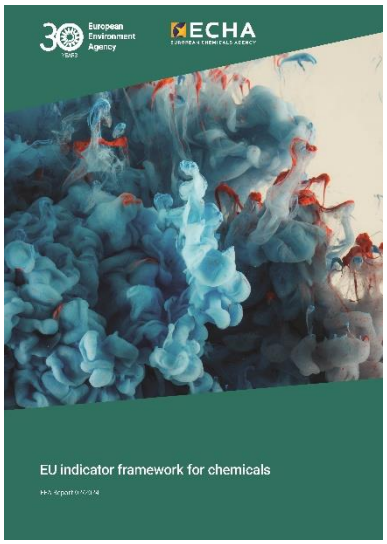
** ammonium polyphosphate, ammonium phosphate, resorcinol bisdiphenyl phosphate, melamine polyphosphate, aluminium hydroxide, expandable graphite, zirconium acetate, ammonium sulphamate, ammonium bromide.*

*** see e.g. Feuchter et al., summarised in pinfa Newsletter n°149.*

"Brandschutzanforderungen für Textilien, Möbel und Matratzen in öffentlichen Einrichtungen: Welche Regelungen bestehen undwie können diese erfüllt werden?" (Fire-safety requirements for textiles, furniture, mattresses in public facilities. What requirements exist, how can they be fulfilled?), 189 pages, in German (one page English summary), UBA 71/2024
https://www.umweltbundesamt.de/publikationen/brandschutzanforderungen-fuer-textilien-moebel

EU recognises fire safety in "Essential Use"

Official guidance cites fire safety as an Essential Use. This concerns harmful chemicals, so PIN FRs are not targetted . The European Commission Communication on Guiding Criteria and Principles for the Essential Use Concept in EU Legislation dealing with Chemicals includes (table 2) "ensure the safety of products, equipment and tools, such as … fire resistance in products anticipated to be heated to a temperature where ignition could occur". This is exactly the purpose of PIN FRs which are used to increase fire resistance (reduce risk of ignition, inhibit burning) of products potentially subject to heat sources (accidental exposure to flames or cigarettes, electrical overheating, arcing or sparks, friction heat …). pinfa has not engaged with the European Commission concerning FRs and Essential Use because this concept, in EU chemicals legislation, concerns only the "most harmful" chemicals (defined in table 1* of this Communication). Essential Use allows exceptional and temporary continuing use of such chemicals in specified ("Essential") uses, until an acceptable alternative is available. Members of pinfa share the common vision of continuously improving the environmental and health profile of their flame retardant products and demonstrating their safety (see pinfa Mission).



This Communication follows publication in February of an ECHA (European Chemical Agency) – EEA (European Environment Agency) joint report which proposes an indicator framework for monitoring progress to safe and sustainable chemicals and summarises current trends. This underlines that hazardous chemicals, not compliant with REACH/CLP are found in 30% of consumer goods tested under enforcement checks, with the proportion increasing in imports. The problem of hazardous chemicals in recycling is also emphasised. Overall, this report suggests that progress is being made in some areas and that overall use of the most harmful chemicals (in particular CMR) is growing more slowly than the overall chemicals market.

"Commission defines principles on limiting most harmful chemicals to essential uses", European Commission press release 22nd April 2024 https://ec.europa.eu/commission/presscorner/detail/en/IP_24_2151 and Commission Communication "Guiding criteria and principles for the essential use concept in EU legislation dealing with chemicals" (C/2024/2894) 26th April 2024 https://environment.ec.europa.eu/publications/communication-essential-uses-chemicals_en

** (simplified) "Most harmful" chemicals are defined as those with the following hazards: Carcinogen – Mutagen or Reprotox 1A 1B, Endocrine disruptor Cat. 1 (health or environment), Respiratory Sensitisorn Cat. 1, Specific Target Organ Toxicity Repeated Exposure (STOT-RE) Cat. 1, Persistent Bioaccumulative and Toxic (PBT), Very Persistent and Very Bioaccumulative (vPvB), Persistent, Mobile and Toxic (PMT), Very Persistent and Mobile (vPvM), Ozone Depletor Cat1.*

"EU indicator framework for chemicals", ECHA – EEA 02/2024 https://www.eea.europa.eu/publications/eu-indicator-framework-for-chemicals/

CALLS FOR INPUT

Call for evidence on alternatives to BFRs

ECHA public call, open to 28th June, looks for information on alternatives to replace aromatic brominated flame retardants. ECHA requests information on uses and applications of aromatic brominated flame retardants (BFRs) which are being assessed for possible Restriction under REACH, information on why FRs are needed, on possible alternative FRs or inherently fire-safe materials, and where possible reformulation or redesign costs and time needed for implementation.

This follows the European Commission mandate to ECHA for further work on flame retardants (December 2023, pinfa Newsletter n°159), in particular to assess whether aromatic brominated flame retardants (BFRs) should be 'Restricted', and the ECHA call for information on aromatic brominated FRs (April 2024, pinfa Newsletter n°158).

The survey lists fifty BFRs under assessment for possible restriction, including BDEs, brominated phthalates, bromophenols, TBBPA and their derivatives. Comments are request on a table of some 200 identified BFR/use combinations and on a table of around 150 possible substitute FRs (all of which are organophosphates, and some of which are chlorinated), with the possibility to indicate additional possible substitute FRs.

pinfa has met ECHA and clarified that the aim is to identify: uses for which alternatives are available on the market and already implemented by EU actors, uses for which alternatives appear to be generally available but more time is needed to substitution, uses for which alternatives may not be readily available to implement, and for each identified use information on alternative FRs, alternative materials, technical feasibility and economic considerations.

pinfa is coordinating an industry input to ECHA with information from pinfa members (subject to anti-trust and confidentiality). Compounders, OEMs and PIN FR users, PIN FR manufacturers and other companies are invited to also submit information directly to ECHA using the excel file provided on the survey website.

ECHA call for information and evidence "Aromatic brominated substances", open to 28th June 2024 https://echa.europa.eu/calls-for-comments-and-evidence/-/substance-rev/76701/term

EU survey on computer Ecodesign

Public questionnaire open to 18th July on user wishes for computer energy performance, repairability and durability. The EU Ecodesign Regulation defines mandatory product specification on energy efficiency, repairability (design, parts supply) and use of materials (Critical Raw Materials) and chemicals. Criteria for computers include batteries for laptops and power supplies. The current computer Ecodesign Regulation criteria (2014) are

considered as needing updating to reflect developments in computer power, design and uses. The EU survey questionnaire addresses user purchase choices, ecodesign priorities, repair and end-of-life disposal. In addition to the questionnaire, position papers can be submitted. pinfa will submit a position underlining the impact of fire on the environment, and so the need to ensure fire resistance, the role of flame retardants in ensuring this, and the availability of PIN FRs with safe health and environment profiles.

EU public and stakeholder survey, open to 18th July 2024 "Ecodesign requirements for computers – review" https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/1581-Ecodesign-requirements-for-computers-review/F_en

US NFPA consultation on battery standard

Call for public comment, open to 12th July, on proposed NFPA 800 Battery Safety Code covering fire, electrical, other safety. NFPA 855 (first issued 2019) covers stationary battery energy storage systems. The proposed new NFPA 800 will cover all batteries, from portable consumer products to electric vehicles, over the whole battery life cycle. The proposal is to cover battery fire and explosion risks, electrical safety, impacts on life and property, including raw materials for batteries, production, storage, use and end-of-life. The consultation is looking for input on whether there is support for development of such a standard. NFPA is also looking for candidates for a Technical Committee should the project be taken forward.

"New Standards Development on Battery Safety", US National Fire Protection Association (NFPA), deadline for input 12th July 2024 https://www.nfpa.org/For-Professionals/Codes-and-Standards/Standards-Development/New-projects-and-draft-documents/New-Standards-Development-on-Battery-Safety

CONFERENCE SUMMARIES

AMI | Events
Plastics in Electric Vehicles

AMI Plastics in Electric Vehicles conference

Presentations underlined the value of PIN flame retardants in enabling lightweight, fire-safe component performance, in particular protection in case of battery thermal runaway.

The AMI conference "Plastics in Electric Vehicles", Cologne 4-5 June 2024, sponsored by pinfa, with nearly 100 participants, showed the high level of innovation in polymer materials to meet demanding requirements of EVs, in particular electrical performance, lightweighting, fire and battery thermal runaway protection. Several presentations showed the essential role of PIN FRs in achieving this whilst meeting sustainability objectives.

Philipp Genders and Julian Haspel, Envalior, presented PIN FR polymer-composite material solutions for battery enclosures, with fire tests showing that these offer high resistance to thermal runaway (considerably better than aluminium), whilst offering design

flexibility, physical toughness and recyclability. Resistance to battery and cooling fluids is also essential. Envialor also offers bio-based and recycled polymer composites.

Guillaume Blancard, Renault Group, explained the company's classification of polymer materials to fire performance requirements specifically defined for electric vehicles, based on UL 94 V-0 and Glow Wire Ignition Test (both @ 1.6 mm). Additional requirements are that FRs are resistant to and not leached by battery immersive cooling fluids. PIN FRs offer the benefits of not deteriorating material electrical properties (CTI) and not emitting toxic fumes, but can impact material properties or cause degradation. PFAS restrictions are likely to impact the anti-drip agent PTFE, requiring to find other solutions.

Corina Neumeister, Nabaltec, presented inorganic PIN FRs used within battery cells and battery packs, for electrodes, cell separators, adhesives and tapes, fillers, … Nabaltec now offers a ceramifying PIN FR for battery casings which can enable polyamide plates to resist temperatures up to 1650°C (burn through time > 20 minutes,), whilst retaining bending strength.

Sebastian Harms, Budenheim, presented development of materials with high electrical performance (Comparative Tracking Index), which is important in high-voltage EV applications, by combining two PIN FRs (phosphinate and melamine polyphosphate) in PBT polymer. PIN flame retardants can achieve mechanical performance including electrical characteristics, whilst offering positive environmental profiles, such as no hazard labelling, GreenScreen Benchmark 3 and recyclability.

AMI "Plastics in Electric Vehicles", Cologne 4-5 June 2024, sponsored by pinfa, https://www.ami-events.com/event/1dd8f1ff-1dbd-4c36-8b6b-3646026cc494/summary

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Developments in EV materials testing

Ken Vessey, UL Solutions, summarised challenges and perspectives for EV polymer materials and battery fire testing. Weight reduction is important to the critical objective of EV innovation today, which is to extend vehicle range. Polymer-based composites enable lightweighting, but must contain battery hazards, in particular thermal runaway. This requires resistance to fire and temperature, but also to mechanical impacts, pressure, particle abrasion during offgasing. The webinar presentation covered existing UL tests and new developments underway, including test methods recognised by the automotive industry, and screening tests for material development. These include UL 2580 comprehensive evaluation of EV batteries, UL 746C for batteries for portable and fixed equipment, UL 2596 battery enclosure material screening.

pinfa-NA's 9th Lunch and Learn webinar, Wed. 29th May. pinfa-NA webinars are available for free replay at https://www.pinfa-na.org/presented-webinars

California SAFER consultation

California State call for input, to 1st July, on draft Priority Product Work Plan for "SAFER Consumer Products" (SCP). The work plan defines the product categories to be addressed. Product classes already underway (with materials fire safety relevance) are building products and childrens products*, with proposed addition of paints, and proposed as a second stage motor vehicle parts, electronics and sports equipment* (* = mostly not materials fire safety relevant). The consultation presents for comment work completed and ongoing on the product classes already covered, and the rationale and scope for proposed future product classes.

California DTSC (Department of Toxic Substances Control) SAFER Consumer Products, Priority Product Work Plan https://dtsc.ca.gov/scp/priority-product-work-plan/ and call for comments https://calsafer.dtsc.ca.gov/cms/commentpackage/?rid=12771 open to 15th July 2024.

FIRE SAFETY

Buildings Directive recognises fire safety

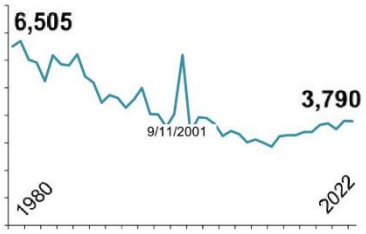
Revised EU Energy Performance in Buildings (EPBD) recognises the importance of fire safety:

- Energy performance improvements should not affect fire safety (recitals 11)
- Electrification (heat pumps, solar, batteries and recharging) modifies fire risks in buildings and car parks (recital 36)
- Major renovations can be the opportunity to address fire safety issues (recital 45)
- The European Commission shall issue guidance, share evidence and offer technical support to Member States on request in relation to fire safety of new buildings (art.7.6)
- For buildings undergoing major renovation, Member States shall address issues of fire safety (art. 8.3)
- The European Commission shall publish guidelines for fire safety in car parks by 31/12/2025 (art. 14.10)
- Member States shall ensure guidance and training … (which may address) fire safety (art. 29.3)
- Fire safety is an indicated optional indicator in National Building Renovation Plans (Annex II)

A number of associations published a call to include fire safety and new energy systems into the EPBD in early 2023 (see pinfa Newsletter n°153).

"Energy Performance of Buildings Directive adopted to bring down energy bills and reduce emissions", European Commission, 12th April 2024 https://ec.europa.eu/commission/presscorner/api/files/document/print/vi/ip_24_1965/IP_24_1965_EN.pdf

Directive 2024/1275 on the Energy Performance of Buildings (recast), EU Official Journal 8th May 2024 https://eur-lex.europa.eu/eli/dir/2024/1275/oj



Fire safety no longer progressing

1.5 million fires in the USA in 2022 caused nearly 3 800 deaths, over 13 000 injuries and US$ 18 billion property loss. This covers only fires to which fire services responded. The US NFPA (National Association for Fire Protection) "Fire Loss" 2022 report notes that this is one fire every 21 seconds, and a home fire death nearly every three hours. The total number of fires was half that in 1980 and inflation adjusted property damage was 20% lower, despite increases in population. However, the death rate per reported home fire was higher in 2022 than in 1980. NFPA state that most of the reduction in the number of fires and in fire losses occurred more than a decade ago and the data suggest that since around 2012 – 2014 the number of fires and the number of fire deaths per million population have not decreased and the absolute numbers have begun to rise. NFPA underline that there is still much to do to reduce fire incidence and improve life safety, especially for home fires.

Graph: Civilian fire deaths 1980-2022 from NFPA report cited.

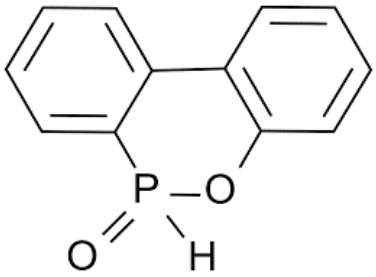
"Fire Loss in the United States During 2022", S. Hall, NFPA, November 2023 https://www.nfpa.org/education-and-research/research/nfpa-research/fire-statistical-reports/fire-loss-in-the-united-states

INNOVATION

Lotte's PIN FR PP achieves ASTM A-grade

PIN flame retardant enables A-grade fire safety for building interiors with large volume, highly adaptable polymer (polypropylene). The non-halogenated (PIN) flame retardant used by Lotte Chemicals is non-toxic (no GHS toxicity label) and the PIN FR polypropylene compound is recyclable. ASTME E84 Class-A was achieved in fire testing, that is limited flame spread and smoke indeed, meaning that a fire starting is unlikely to spread and the smoke emission is reduced. The new compound will be used in building interior finishes, in particular in North America and the Middle East (where ASTME is the reference test method) and also in applications such as automobile and home electrical equipment.

"LOTTE Chemical develops recycled flame-retardant PP material for building interior materials acquired Grade A in the ASTM flame retardant test", 20th December 2023
https://www.lottechem.com/en/media/news/869/view.do



Phosphorus PIN FR acts as antioxidant

Research shows that DOPO-derivate coated APP can provide both fire resistance and anti-ageing in EVA (Ethylene Vinyl Acetate), a performance polymer used in e.g. cables, transport, construction, sealants. The widely available PIN FR DOPO* was reacted with glutaraldehyde, then used to coat APP**. At 25% loading the resulting PIN FR achieved UL94 V-0 (3 mm) and LOI*** increased from 17% (neat EVA) to 27%, reduced peak heat release by -52% and maximum smoke density by -54%. The PIN FR increased the oxidation induction time of EVA by nearly 4x and very considerably improves the elongation at break of the EVA after 4 – 14 days @ 165 or 180°C, that is shows an anti-ageing effect.

** DOPO = 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (diagram)*

*** APP = ammonium polyphosphate, inorganic phosphorus PIN FR*

**** LOI = Limiting Oxygen Index*

"Unlocking anti-aging potential: Flame retardants thrive without added antioxidants", P. Sun et al., Composites Part B 279 (2024) 111450, https://doi.org/10.1016/j.compositesb.2024.111450

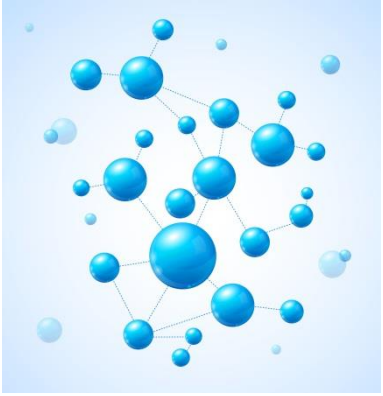
Polymer DOPO FR for polyamide (PA6)

Polymeric DOPO-based phosphorus PIN FR achieved UL94 v-0 (3.2 mm) in polyamide at 0.3% total phosphorus content. The phosphorus-nitrogen polymeric PIN FR was synthesised by melt polymerisation of a DOPO-derivative (DDP*) with DMDA** and caprolactam (a nitrogen-containing chemical used in polyamide production). In polyamide-6 – PIN FR compounds with phosphorus content of 0.3%, UL 94 V-0 (3.2 mm) was achieved (V2 for neat PA6) and LOI of 25.8% (21.7% for PA6). With 0.5%P, LOI reached nearly 29% and peak heat release rate was more than 35% lower than for neat PA6. The mechanical properties of the polyamide were however considerably deteriorated by compounding with the polymeric PIN FR.

** DDP = 9,10-dihydro-10-(2,3-dicarboxypropyl)-9-oxa-10-phosphaphenanthrene 10-oxide (a DOPO derivative)*

*** DMDA = decamethylene diamine*

"Polymer-type flame retardants based on a DOPO derivative for improving the flame retardancy of polyamide 6: Preparation, properties and flame retardancy mode of action", B. Liang et al., Polymer Degradation and Stability 225 (2024) 110807, https://doi.org/10.1016/j.polymdegradstab.2024.110807



Effects of P-FRs on material fire hazard

Theoretical analysis of how phosphorus PIN FRs effect aircraft carbon fibre – epoxy composites shows divergent conclusions. Two phosphorus PIN FRs were tested in carbon fibre high-temperature TGDDM epoxy (c. 33% fibre): a DOPO derivative* (16% loading) and a lab-synthesised organic P-N macromolecule DPO (7% loading). Loadings of the FRs were defined to achieve UL 94 V-0 (3 mm). Heat release was decreased lower with both PIN FRs (compared to neat carbon fibre epoxy), but smoke and carbon monoxide production were increased, in particular with DOPO-HQ. Analysing the different effects, using weightings based on subjective and objective factors, the authors conclude that DOP-HQ, in this case, increases the overall fire hazard of the carbon fibre composite, whereas the DPO P-N FR overall reduces the fire hazard. They suggest that this is related to the phosphorus oxidation state (+1 in DOPO-HQ, +3 in DPO) leading to a gas-phase effect (causing pyrolysis) with DOPO-HQ and solid-phase (charring) with DPO.

** DOPO-HQ = 10-(2,5-dihydroxyphenyl)-10-H-9-oxa-10-phosphaphenanthrene-10-oxide*

"Quantitative assessment of whether phosphorus-based flame retardants are optimizing or degrading the fire hazard of aircraft carbon fiber/epoxy composites", B. Zou et al., Composites Part B 279 (2024) 111413, https://doi.org/10.1016/j.compositesb.2024.111413

PUBLISHER INFORMATION

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