pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

# Your newsletter for non-halogen fire safety solutions n° 133 January 2022

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# POLICY


## EU public consultation on REACH revision

**To 15th April. Questions on polymers, endocrine disruption, mixture effects, environmental footprint, essential use**. This questionnaire is open to the general public, stakeholders and industry, and aims to shape how the EU's chemical legislation, REACH, will be revised in the context of the Green Deal and the Chemicals Strategy for Sustainability. Specific questions include whether REACH should require more information on carcinogenicity, on MAF (Mixture Assessment Factors), identification of endocrine disruptors, whether certain polymers should be subject to REACH registration, dossier compliance, and whether "essential use" should target consumer or professional products. In addition to these general questions with closed answers, there is a 5 000 character comment field and the possibility to submit documents.

*EU public consultation open to 15th April 2022 "Chemicals legislation – revision of REACH Regulation to help achieve a toxic-free environment"*
*https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12959-Chemicals-legislation-revision-of-REACH-Regulation-to-help-achieve-a-toxic-free-environment/public-consultation_en*

*See also previous consultation on REACH revision Roadmap in pinfa Newsletter n° 126.*

## New York bans halogenated FRs in TVs and non-mineral FRs in furniture

**The New York State "Family and fire fighter protection act" (S. 4630-B/A. 5418-B) was signed into law 2nd January 2022. This law** bans, from 1st January 2024, intentionally added "organohalogen" flame retardants in the enclosure and stand of electronic displays > 100 $cm^2$, and also "halogenated, organophosphorus, organonitrogen or nanoscale chemical" flame retardants and FR synergists in upholstered furniture and mattresses. Mineral PIN flame retardants (if not nano-scale) can continue to be used in furniture and mattresses, and all PIN FRs in TVs and screens. The bill provides some limited exceptions to the bans. Organo- halogen / phosphorus / nitrogen are defined as chemicals containing one or more halogen*/ phosphorus/ nitrogen "elements" and one or more carbon "elements". The Governor's press release refers to "certain dangerous flame retardants" but then seems to suggest that all flame retardants are problematic, including accusing flame retardants of producing hydrogen cyanide in fires.

** halogen is defined as: "including fluorine, chlorine, bromine, or iodine".*

*New York State Family and Fire Fighter Protection Act (S. 4630-B/A. 5418-B) https://www.nysenate.gov/legislation/bills/2021/s4630*

## Roles of US Codes / Standards committees

**Marcello Hirschler's Fire Safety & Technology Bulletin (11/ 2021) outlines roles and functioning of ASTM, NFPA and ICC**. For each, the procedures for representation, proposals and voting are helpfully explained.

ASTM (American Society for Testing and Materials) writes standards not codes. Committees are made up of 'producers', users, consumers and other stakeholders, noting that individuals can significantly impact these.

NFPA (National Fire Protection Association) writes both standards and codes, with strong technical expertise. Committee members are appointed by the NFPA Standards Council, and generally come from representative organisations not individual companies.

ICC (International Code Council) writes codes for the USA, despite its name. Committees are relatively small and most members are officials, resulting in a relative neutrality on proposals.

*Fire Safety & Technology Bulletin (FS&TB) https://www.gbhint.com/fire-safety-and-technology-bulletin/*

# FIRES AND FIRE SAFETY

## 17 die from smoke in Bronx fire, 9th January

**The fire started in a space heater, but smoke spread throughout the building. 17 people died, and over 40 were injured**. The Twin Parks building housed many immigrants, especially from Gambia. Two self-closing doors are said to have failed to function. The fire itself was largely contained in the duplex apartment where it started, but smoke spread throughout the 19 storey building an all the fatalities were caused by smoke inhalation, in particular in the stairwells . A number of the injured were badly burned. The fire alarm system functioned, but was apparently initially ignored by some residents because of frequent false alarms, and fire services arrived within 3 minutes of the fire starting. Following this fire, and the fire in Fairmont, Philadelphia, 5th January 2022, which killed 12 people (probably starting in a Christmas tree), a number of fire safety and firefighter organisations are calling for national fire safety legislation in the USA, in particular for older and high-rise residential buildings.

*"Inside a Deadly Bronx Fire: Scenes of Chaos, Desperation and Love", New York Times, 16th January 2022*
*https://www.nytimes.com/2022/01/16/nyregion/bronx-fire-what-happened.html*

## Judgements after nightclub foam fire 2013

**A firework ignited acoustic foam in the Kiss Nightclub Brazil 2013. 242 died. Owners and band members condemned**. Some 1 200 people were in the Kiss Nightclub, Santa Maria, Brazil, 27th January 2013, when the band Gurizada Fandangueira lit pyrotechnic flares on stage. Sparks from one flare ignited sound insulation foam on the ceiling and within seconds the fire spread and rapidly engulfed the club. Court findings indicate that the venue had no functioning fire extinguishers, only two emergency exits and poor emergency signage. 242 people died and over 600 were injured. On 10th December 2021, two owners of the nightclub and two members of the band were condemned to 18 to 22 years in prison, but then released immediately as their lawyers lodged appeals.

*BBC News 11/12/2021 https://www.bbc.com/news/world-latin-america-59617508*

*Photo: By Leandro LV - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=24477308*

## Aviva warning on battery charge fire risks

**One of Europe's largest insurance companies, Aviva, says fires from battery charging are increasing and costing thousands.** The company's Head of Data Science, Sarah Applegate, points to fires with e-scooters, e-bicycles, e-cigarettes and other equipment. Examples of household insurance claims in 2021 believed to be caused by charging batteries are: 150 000 UK£ (e-scooter), 140 000 UK£ (e-cigarette), 150 000 UK£ (electric golf caddy) and 120 000 UK£ (batteries of a model aircraft).

*"Aviva issues warning as battery chargers lead to fires", 7th December 2021 https://www.aviva.com/newsroom/news-releases/2021/12/aviva-issues-warning-as-battery-chargers-lead-to-fires/*

# INNOVATION


## Compounding World innovation overview

**Special articles on flame retardants and cables show leading companies are centring development on PIN technologies**. The articles bring together interviews of FR producers, compounders and production equipment providers, and are accessible online.

Compounding World's review on cables cites **Alphagary, Avient, Benvic, Barouge, Buss, Europiren, Evonik, Hexpol TPE, Innospec Luna, Nabaltec, Pandaplast and Tolsa.** All are concentrating on PIN fire safety solutions, driven by demand for low-smoke "HFFR" (halogen-free flame retardant) cables. Photovoltaic, electric vehicles and optic fibre roll-out are driving new performance formulations. Demand is for PIN fire performance and low-smoke combined with resistance to oil and water, electrical characteristics (for high voltage) and mechanical performance (wear resistance, flexibility, heat resistance) as well as processing qualities. New synergist additives are proposed to combine performance with high mineral PIN FR loadings.

The magazine's review on flame retardant innovation also cites mainly PIN developments from **Adeka, Borax, Byk, Budenheim, Clariant, Evonik, Europiren, FRX Polymers, Hüber, Inovia Materials, Italmatch, Kärtner KMI, Luh, Nabaltec, PAG, Paxymer.** Companies indicate trends towards sustainable materials, driving the move away from halogenated to PIN FRs, towards more demanding fire performance (e.g. for electric vehicles) and continuing push for recycling. Technical developments include improving FR dispersion by using compatibilising synergists or surface treatments, higher FR thermal stability to better target char generation, PIN FR packages with high electrical performance and new mineral FR solutions.

*"What's new in flame retardants", Compounding World, December 2021.*
*"Formulating for performance cables", Compounding World, May 2021.*
*http://www.compoundingworld.com/*

## PIN FR polyamide 6 meets Glow Wire Test

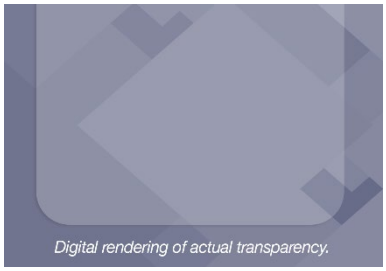
**Lanxess' new PIN FR compound offers high flame retardancy and tracking resistance for demanding applications**. The 30% glass-fibre reinforced compound uses short glass fibres. It also offers high elongation at break, enabling mechanical stability of e.g. snap fits. The compound has GWIT (Glow Wire Ignition Test IEC 60695-2-13) value of 775°C for 0.75 – 3 mm, achieved with PIN flame retardants, and CTI A (Comparative Tracking Index, IEC 60112) of 600V, allowing compact design of electronic modules. The high level of flame retardancy meets the demands for applications such as electric vehicles and battery charging systems, consumer electrical equipment and electronics.

*Photo: charging station – Lanxess. Lanxess is a pinfa member. "Designing fireproof household appliances", Lanxess press release 29/9/2021*
*https://lanxess.com/en/Media/Press-Releases/2021/09/Designing-fireproof-household-appliances*

## EV battery housing in PIN FR polyamide

**Korean auto parts specialist INFAC and Lanxess' new PIN FR housing satisfies stringent mechanical and chemical demands**. The housing uses a non-halogenated FR, 30% glass fibre reinforced polyamide 6, which offers the specific necessary properties. High processability enables production of a complex housing with few parts, simplified assembly and lightweight. The compound is mechanically robust, ensures shock absorption and electrical insulating is resistant to battery electrolyte or cooling media and uses PIN flame retardants to achieve required fire performance.

*Photo: battery housing for electric vehicles – INFAC. Lanxess is a pinfa member. "LANXESS: High performance plastics grade for production of battery housings", Lanxess press release 24/8/2021*
*https://lanxess.com/en/Media/Press-Releases/2021/08/LANXESS-High-performance-plastics-grade-for-production-of-battery-housings*




## PIN FR transparent polyethylene film

**Techmer PM offers non-halogenated flame-retardant additives for polyethylene films and extrusion coatings with high clarity**. Techmer, specialised in technical polymers, offers non-halogenated flame retardant solutions for low density and linear low-density polyethylene for blown film and extrusion applications with processing temperatures of up to 200°C or 315°C. PIN FR solutions for transparent film are increasingly demanded in applications such as building and construction and signage, where fire performance standards are required, as well as in certain packaging and agricultural applications.

*"Techmer PM's halogen-free, flame-retardant additives can produce high-clarity PE films and extrusion coatings", 19th July 2021*
*https://www.techmerpm.com/2021/07/19/techmer-pms-halogen-free-flame-retardant-additives-can-produce-high-clarity-pe-films-and-extrusion-coatings/*

## PIN FRs for high performance insulation

**Evonik has launched a new PIN FR polyamide 12 for e-vehicle busbars with electrical and fire safety, fast extrusion, adhesion**. Busbars are metallic strips (e.g. copper or aluminium) which locally transmit high current power and are needed in electric vehicle batteries. The new Evonik compound ensures electrical insulation up to 1000 V and UL 94 V-0 (0.4 mm) fire safety. A 0.5 – 0.7 mm coating meets e-mobility insulation requirements. The compound can be used at operating temperatures up to 125°C and is available in RAL 2003 signal orange. High extrusion speeds, adhesion to metal (without adhesion promoters) facilitate processing, and high elasticity means that the busbars can be bent to small radii after extrusion without losing insulation protection.

*"New VESTAMID® polyamide 12 compound with highest fire protection for busbars", 12th September 2021 https://www.vestamid.com/en/new-vestamid-polyamide-12-compound-with-highest-fire-protection-for-busbars-162733.html See also pinfa Newsletter n°84.*

## Floreon non-halogenated FR bioplastic

**Innovative PIN flame retardant compound from bio-based PLA offers performance to replace ABS with UL 94 V2 (3mm).** Floreon is a specialist innovation company, set up in 2011 who, with Sheffield University UK, develop plant-based plastics using specific compounds from PLA (polylactic acid), derived from corn and sugar cane. The company's new PIN flame retardant compound offers properties comparable to ABS for injection moulding of consumer electronics, electronic toys, home furnishings. Fire performance is UL 94 V2 (@ 3mm), achieved using non-halogenated PIN flame retardants. The material is compatible with mechanical recycling, and claims up to seven times lower carbon footprint than oil-based plastics.

*"Floreon launches halogen-free flame retardant bioplastic", 11th November 2021 https://www.floreon.com/post/floreon-launches-halogen-free-flame-retardant-bioplastic and https://www.floreon.com/*

# RESEARCH AND PUBLICATIONS

## PIN FR combination for PA 3D-printing

**APP with aluminium phosphate provided fire performance compatible with PA6 3-D printing**. 20% APP (ammonium polyphosphate) and 10% aluminium phosphate ($AlPO_4$) was compounded/extruded at 235°C into polyamide-6 for 3D-printing filaments (FFF additive manufacturing: Fused Filament Fabrication). T-shaped parts, c. 4 cm, were then printed, with an internal lattice structure (not solid filled). Such hollow-structure 3D-printed items

are potentially highly flammable. The PIN FR PA6 filaments could be printed identically to neat PA6. Compared to neat PA6, the PIN FR PA6 showed much higher char yield, 47% and 31% lower peak and total heat release, and reduced melt dripping. The authors conclude that this PIN FR combination can significantly improve the fire safety of 3D-printed materials.

*"Environmentally Benign Flame Retardant Polyamide-6 Filament for Additive Manufacturing", T. Kolibaba et al., Macromol. Mater. Eng. 2021, 2100245 https://doi.org/10.1002/mame.202100245*

## PIN FR combination for ABS 3D-printing

**Red phosphorus and ATH proved provided fire performance compatible with ABS 3D-Printing**. A total load of c. 21% of the PIN FR combination microencapsulated red phosphorus and ATH (aluminium trihydroxide), 2:1 ratio redP:ATP, was compounded into ABS at 185°C – 215°C, then dried, then extruded at 190°C – 225°C to a standard spline. This was then printed on a Tiertime UP-BOX+ MEM (Melted Extrusion Modeling) printer. Fire performance was tested on the spline (solid plastic) not after 3D printing. LOI was increased from 24.5 (neat ABS) to nearly 30, achieving UL 94 V0 (3 mm). Mechanical properties of the ABS deteriorate with addition of the PIN FR (c. 1/3 loss in tensile strength and elongation at break), but the material remains compatible with 3D-printing on the Tiertime machine, printing smoothly, without clogging or warpage, resulting in a high-quality surface finish.

*"Study on Additive Manufacturing of ABS Flame Retardant Wire", Y. Zhong et al., Journal of Physics: Conference Series 2021 (2021) 012012 https://doi.org/10.1088/1742-6596/2021/1/012012*

## Reactive PIN FR for bio-based fibre

**A phosphoric acid and urea-based PIN compound provided an effective PIN FR for the cellulose-derived fibre lyocell**. Lyocell is a lightweight, soft, wrinkle-resistant fibre produced by processing cellulose fibres from wood or bamboo, but it is highly flammable. A novel PIN FR was synthesised by combining in water ethanolamine, glyoxal, phosphoric acid and urea at c. 170°C. This PIN FR was then reacted onto lyocell by soaking in aqueous solution with dicyandiamide as a catalyst, resulting in P-O-C covalent bonding, in this study to a weight gain of c. 15 % dry matter. This resulted in an increase in LOI from 18 (untreated lyocell) to 44, which fell back to 34 after 30 laundering cycles. The treated lyocell could not be ignited in cone calorimeter tests. The treated lyocell showed only slightly deteriorated mechanical properties (c. 15% loss in tensile strength and elongation at break). The authors conclude that this novel PIN FR provides a durable and effective PIN flam retardancy solution for lyocell.

*"Synthesis of an effective halogen-free flame retardant rich in phosphorus and nitrogen for lyocell fabric", Y. Guo et al., Cellulose (2021) 28:7355–7372 https://doi.org/10.1007/s10570-021-03975-8*

## Effective PIN FR backcoating for cotton

**A silicone elastomer with modified ATH provides fire safety for furniture and retains aesthetic and mechanical performance**. The backcoating was prepared by mixing 35% silicone elastomer base (Dow) and Pt-catalyst (for cross-linking) with 65% vinyl-silane modified ATH (aluminium tri hydroxide), then applying manually to the back side of the velvet cotton fabric and curing at 80°C. Untreated cotton and PIN FR back-coated cotton were tested for fire performance, touch and mechanical properties, and also fire tested in full-scale chairs with four cushions of polyurethane foam covered with the fabrics. In microscale combustion calorimetry, the PIN backcoated cotton showed nearly no heat release, whereas the untreated cotton showed peak heat release of c. 150 W/g and the polyurethane foam nearly 600 W/g. The mock-up chairs showed peak heat release rate around six times lower with PIN backcoated cotton, when ignited by an open flame (18 kW burner). With a smouldering cigarette, the PIN backcoated chair did not smoulder nor ignite, whereas the untreated chair smouldered for over an hour and then transitioned to a flaming fire. The backcoating reduced air permeability of the cotton to zero, multiplied flexural rigidity by ten times and considerably increased abrasion resistance, without modifying the feel of the fabric.

*"Demonstration of an all-in-one solution for fire safe upholstery furniture: A benign backcoating for smoldering and flame-resistant cover fabrics", I. Kim et al., Fire and Materials. 2021;1– https://doi.org/17.10.1002/fam.3015*

## Casein-based PIN FRs for cotton

**Caseins are natural phosphorus-rich proteins, making up around 80% of milk protein**. Casein was hydrolysed using acid, to give free amino groups, then reacted with phosphonic acid, formaldehyde and urea, to give a phosphorus – nitrogen bio-based PIN FR. Cotton fabric was then treated by reacting with this PIN FR in aqueous solution with dicyandiamide catalyst, curing at 180°C, then washing and drying, to achieve up to 16% w/w loading. At this loading, LOI of the cotton fabric was increased by nearly 100%, remaining increased by c. 40% after 40 wash cycles. Tensile strength and whiteness of the cotton were substantially retained. Analysis suggests that the casein-based PIN FR grafts onto the cellulose in cotton by P(=O)-O-C and C(=O)-O-C bonds and acts mainly by increasing char generation, with phosphorus preventing formation of levoglucosan by cellulose and by catalysis of dehydration of cellulose.

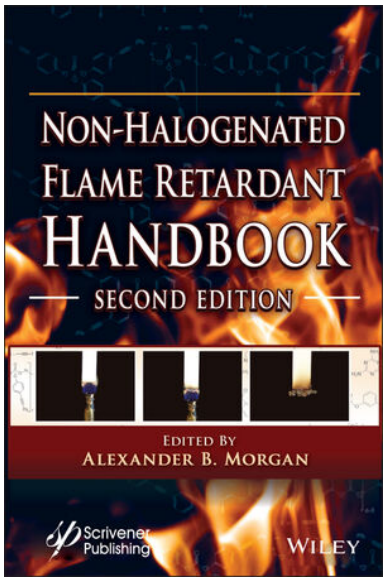
*"Novel High-Efficiency Casein-Based P−N-Containing Flame Retardants with Multiple Reactive Groups for Cotton Fabrics", F. Xu et al., ACS Sustainable Chem. Eng. 2019, 7, 13999−14008 http://dx.doi.org/10.1021/acssuschemeng.9b02474*

## Phosphorus-modified coffee waste

**Coffee wastes showed some fire performance effect in epoxy, and better effect if loaded with phosphorus**. Coffee wastes are proposed as the base for renewable PIN flame retardants as they contain in particular lignin, cellulose and hemicellulose. Used ground coffee, from a coffee machine, was mixed with dimethyl phosphite then dried to give a material with 20% P loading. 30% loading of dried coffee wastes into epoxy resulted in only a 20% reduction in peak heat release rate, whereas 30% loading of the phosphorus-coffee-waste led to a nearly 40% reduction and to significant char formation. Further work is needed to assess whether the coffee waste brings significant flame retardancy (beyond simply "diluting" the epoxy) or whether the flame retardancy is due only to the phosphorus, and to assess impacts on the mechanical and other properties of the epoxy.

*"Coffee Wastes as Sustainable Flame Retardants for Polymer Materials", H. Vahabi et al., Coatings 2021, 11, 1021.*
*https://doi.org/10.3390/coatings11091021*

# PIN FR REFERENCE BOOK UPDATE




## Non-Halogenated FR Handbook

**The 2nd Edition, editor Alex Morgan, updated from 2014, with 600 pages, details different PIN FR technologies and trends**. The Handbook includes 335 references and a 35-page detailed index. The 1st Edition, 419 pages, was summarised in pinfa Newsletter n° 45. The editorial notes that since 2014 there has been increasing regulation and deselection of halogenated FRs, and diversification of PIN FRs. The book chapters in detail on phosphorus-based, minerals (including clays), intumescent, nitrogen-, silicon- and boron-based PIN FRs are updated. The chapter on other PIN technologies is significantly extended, covering metal oxides and complexes, sulphur-, carbon-, tin-based PIN FRs, engineered PIN FR solutions (coatings, barriers), polymer nanomaterials and bio-based materials. New chapters are added on regulation, conformal PIN FR coatings and on multicomponent FRs.

The first chapter notes that a volume of data shows small-molecule, halogenated FRs to be persistent – bioaccumulative – toxic (PBT), and suggests that even if bans on whole classes of FRs may not be scientifically justified, this is pushing tendencies to move away from all halogenated FRs. Thus, this updated, comprehensive book on non-halogenated FR solutions.

The chapter on Future Directions underlines concerns about halogenated flame retardants in environment, but notes that some PIN flame retardants are also now being detected. Routes towards sustainability are discussed including polymeric and reactive flame retardants, noting that polymeric phosphorus, nitrogen, born and silicon FRs are emerging, and that a range of reactive PIN FRs are

available. Recycling is discussed, proposing different approaches: use of bio-sourced or recycled inputs to PIN FR production, compatibility of PIN FRs with multiple polymer recycle – regrind – reprocess – reuse cycles, compatibility with waste-to-heat disposal and compatibility with composting and/or environmental decomposition. Growing fire risk scenarios are also discussed: wildfire WUI (wildland – urban interface) and electric vehicles / batteries.

*Non-halogenated Flame Retardant Handbook, 2nd Edition, 608 Pages, Alexander B. Morgan (Editor), Wiley, ISBN: 978-1-119-75056-7 December 2021 available printed and e-book https://www.wiley.com/en-ie/Non+halogenated+Flame+Retardant+Handbook,+2nd+Edition-p-9781119750567 Chapter authors: Alexander Morgan, Sergei Levchik, Reiner Sauerwein, Serge Bourbigot, Martin Klatt, Mert Kilinc, Kelvin Shen, Frederic Carasio, Bernhard Schartel, Parul Cusack, Charles Wilkie.*

# OTHER NEWS

**US lists ATO as "reasonably anticipated to be a human carcinogen"**. The 15th Report on Carcinogens of the US Department of Health and Human Services adds antimony trioxide, as one of eight further substances to the 248 already known or anticipated to cause cancer. The published report on ATO indicates that in addition to occupational exposure, the "Members of the general population potentially are exposed to antimony trioxide from consumer products containing the compound as a flame-retardant synergist, and more specifically from the dust generated through wear and tear of these products.".

*"Eight Substances Added to 15th Report on Carcinogens", NIH press release, 23rd December 2021 https://www.niehs.nih.gov/news/newsroom/releases/2021/december21/index.cfm and report on ATO (antimony trioxide) https://ntp.niehs.nih.gov/ntp/roc/content/profiles/antimony.pdf*

# PUBLISHER INFORMATION

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

For abbreviations see: www.pinfa.org