Your newsletter for non-halogen fire safety solutions n° 170 April 2025

PINFA IN ACTION

Free webinar: the Boston Nightclub fire

May 28th 17h30 CEST: with Stephanie Schorow, lessons from the Cocoanut Grove Nightclub fire, Boston, 1942. This fire tragically killed over 490 people and is the deadliest nightclub fire in history. Stephanie Schorow, journalist and Boston University instructor, is author of The Cocoanut Grove Nightclub Fire: A Boston Tragedy (History Press, 2022). The webinar will look at the causes of the tragedy (which include flammable false palm trees, flammable aircon gas, inappropriate or blocked exits), the social context of the fire (including links to the Mafia and to city and national politics) and lessons learned and consequent changes in fire safety regulations.

Free pinfa-NA webinar: Wednesday, May 28th, 2025, 11h30am – 12h30 EDT (USA) = 17h30-18h30 CEST (Brussels time). Registration: https://us02web.zoom.us/webinar/register/WN_T1MeEHdyTiynQWjEHM8wug

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pinfa General Assembly April 2025

Members exchanged with experts and discussed joint actions on PIN FR environmental data, regulations, applications.

Cefic expert Steven van de Broeck presented updates on expected regulatory developments including the Clean Industrial Deal Chemicals Industry Package (see below), revision of the EU chemicals regulation REACH and ECHA (European Chemicals

Agency) ongoing action on brominated and possibly some PIN flame retardants. pinfa members expressed concern about articles imported into Europe containing chemicals not registered under REACH, posing an unlevel playing field for the EU chemical industry and for EU industrial manufacturing, and possible questions for health and the environment.

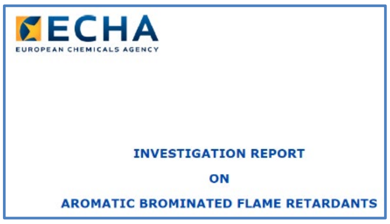
Miguel Angel Prieto Arranz, Cefic, presented the federation's new activities on chemicals used in batteries and in other automotive materials.

Members discussed ongoing pinfa-led studies, possible future studies and information gathering on PIN FRs in recycling, degradation of organo-phosphorus PIN FRs, PIN FR stability in polymers, standards, fire safety of construction materials (Construction Products Regulation), mineral PIN FR particles.

The report of activities from 2024 showed that pinfa organised over 70 internal working and task force meetings, participated in a range of professional and regulatory events and is following 14 different EU policy dossiers.

A communications update noted that pinfa today has over 1 400 subscribers to this Newsletter, nearly 1 000 + 300 followers on LinkedIn (pinfa + pinfa-NA) and 2 300 followers on WeChat (pinfa China) and 20 000 page view per month on our website.

** SVHC = Substance of Very High Concern. PBT= Persistent Bioaccumulative Toxic. vPvB = very Persistent very Bioaccumulative.*


ECHA
EUROPEAN CHEMICALS AGENCY
INVESTIGATION REPORT
ON
AROMATIC BROMINATED FLAME RETARDANTS

Update on EU regulatory action on FRs

Information update for pinfa members on implementation of the ECHA Flame Retardant Strategy and implications for industry. The ECHA report on Aromatic Brominated Flame Retardants (ABFRs) (see pinfa Newsletter n°166) and its annexes were analysed in detail by pinfa member company regulatory experts Adrian Beard, Clariant, Thoralf Küchler, Lanxess and Sander Kroon, ICL. The ECHA report identifies 60 ABFRs, used mainly in electrical and electronic (E&E) and automobile applications. Although only 5/60 are today formally identified as SVHC, PBT or vPvB, ECHA considers that most of the others are likely to also be problematic (based on modelling). Polymeric and reactive ABFRs are not themselves considered problematic, but there is concern about their breakdown products. Alternative FRs are identified, some of which are considered to not be problematic, but many of which do not yet have adequate data. A problem is waste disposal. Only around half of EU E&E waste is collected, so much goes to unknown disposal routes. Losses of ABFRs during waste shredding can be significant and there are concerns about possible breakdown products of ABFRs in the environment. 16 out of 50 brominated FRs indicated as found in the environment are 'not identified', so are either breakdown products of other BFRs or are being imported into Europe (including in articles) without REACH registration. Phosphorus flame retardants are also being found in the environment. pinfa is working on projects to improve information on release of PIN FRs. An important conclusion is the problem of brominated FRs which are not REACH registered coming into Europe in imported articles (finished products or parts): 35 of the 60 ABFRs identified by ECHA are not REACH registered (those which are classed as polymers do not require registration). This reflects the problem that REACH largely fails to address chemicals in imported articles.

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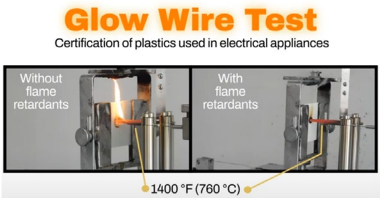
Recording of this online information meeting available on demand for pinfa members only.

See also ECHA presentation to CARACAL on the ABFR report here.

pinfa-NA fire safety scientists of tomorrow

pinfa-NA is partnered with Ecotek Lab to sponsor four high school students' work on flame retardants. Ecotek Lab is a science research organisation for emerging student scientists, creating opportunities for gifted young students, with links to United Nations activities. pinfa-NA is sponsoring four high school students (Alexander Graham, Paul Garrison, Amir Muhammad and Curtis Towns) working on lignin-based flame retardants, red phosphorus, antimony trioxide and aerogel-based coatings.

"Pinfa-NA Partners with Ecotek Lab. Helping Future Technologists & Scientists", March 2025 https://www.pinfa-na.org/education1

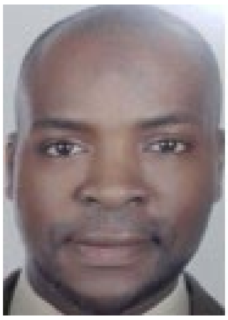


pinfa-NA explainer video : do FRs work?

9th educational video (4 minutes) explains how science shows that flame retardants are effective in improving fire safety. The video shows a logical explanation that FRs do work, based on experience of polymer scientists, fire scientists and materials professionals. A glow wire test video of plastic with and without FRs shows that in these conditions, which are designed to simulate the fire risk of an electrical fault, the FR does improve performance. Examples are cited of experts stating that lives have been saved by FRs. Global companies producing appliances would not pay the additional cost of FRs if they did not work. Because FRs do not prevent all fires does not mean that they do not work. Cases of electrical equipment charring without a fire starting are frequent, as FRs prevent overheating becoming a large fire. To conclude, from a logical perspective, flame retardants play an important role in protecting human life and property from fire.

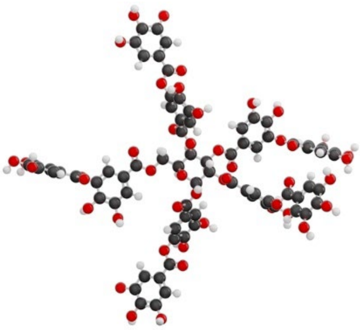
These pinfa-NA educational videos have already been viewed over a thousand times in total on YouTube and are also disseminated on other channels and shown at many trade shows and meetings.

pinfa-NA VOFR-CM (Value of Flame Retardant-Containing Materials) Explainer Video Series (scroll down to video n°9) https://www.pinfa-na.org/learnfrmaterials



pinfa-NA scholarship: intumescent FRs

pinfa-NA will support Taher Hafiz's PhD on biobased PIN intumescents at Case Western Reserve University, including experimental tests and numerical modelling. Taher has research, teaching and work experience at Yanbu University, Saudi Arabia, Becton & Dickinson, Goodyear, Hughes & GE Oil and Gas, in bio-absorbable polymers, cross-linked polyethylene, plastics and rubbers, heat transfer, polymer chemistry and corrosion inhibitors. He has already published a first paper on heat blocking efficiency of intumescent coatings (summarised below). The pinfa-NA scholarship of 2 500 US$ will facilitate the PhD investigation and publication of results. Taher says this work "aims to develop PIN-based fire protective treatments for flammable materials which are safe for health and the environment and more sustainable, because a key component, tannic acid, is derived from natural sources".



PIN FR coatings for fire protection of steel

Intumescent coatings using tannic acid, APP and epoxy showed torch heat resistance up to 20 minutes. The intumescent PIN FR coating was made using tannic acid (derived from gall nuts) @ 43% w/w plus the inorganic salt PIN FR ammonium polyphosphate @ 11% w/w in epoxy (EPON 828 epoxy 28% – Ancamide 503 amine hardener 19%). A coating of 1 mm was applied by brush to a 6.3 mm steel plate. This was subjected to a 130 kW/m^2 methane torch. Detailed COMSOL-based heat transfer modelling closely matched experimental outcomes: the PIN FR coating reduced backside heat by 90%, keeping the steel below 250°C, that is well below the critical temperature for structural failure (550-600°C) after 20 minutes of exposure to the torch flame.

"Experimental and Numerical Approaches to Optimize Heat Blocking Efficiency in Intumescent Coatings", T. Hafiz et al., NAFEMS EMAS vol. 2 issue 1, 2025, https://doi.org/10.59972/xny38fpw

pinfa and members partner EU SSbD project

EU-funded PLANETS project will apply the Safe and Sustainable by Design approach to develop flame retardants, plasticisers and surfactants for coatings, insulation foams and childcare articles. A key target is looking for Safe Sustainable by Design (SSbD) PIN flame retardants for polyurethane foams. The project started in November 2024 and will run for four years. It has an EU funding budget of 14.5 million € and 18 participant organisations (companies, R&D institutes, non-profits), including pinfa members BASF and Budenheim. pinfa is partnering with the PLANETS project for communications and technical input.

Plasticizers, fLame-retardants and surfactANts: new alternatives validating the safE and susTainable by deSign approach (PLANETS), Horizon Europe project https://cordis.europa.eu/project/id/101177608

CONSULTATIONS OPEN

1 May: EU update of certain chemical tests

Consultation on updates to chemical test methods including on measurement of dustiness and respirable particles and on a number of alignments with updated OECD test methods.

EU public consultation, open to 1st May 2025: "Chemicals regulation – update of EU rules for test methods" https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/14501-Chemicals-regulation-update-of-EU-rules-for-test-methods_en

7 May: Canada consultation borate risks

Draft assessment concludes possible environment and health risks from cumulated natural and anthropogenic sources. The draft risk assessment and scope open for consultation is an update of a 2016 screening assessment and risk scope.

The assessment focuses on boric acid, as relevant moiety included in borate salts and potentially released by boron compounds. It is noted that boric acid has both natural and anthropogenic sources. Natural sources include biomass burning, plant aerosols, rock and soil weathering. Background concentrations are c. 10 mg/kg (natural occurrence) in the earth's crust. Boron is an essential micronutrient for most plants and some animals, so uses include in fertilisers. It is also present in cosmetic and natural health care products. Anthropogenic sources include wood processing, mining and minerals extraction, metal processing, fossil fuel burning. Boron compounds are used in, amongst others, adhesives, paints and coatings, water treatment, lithium ion batteries, and flame retardants

Environmental concentrations (PEC) are calculated for local releases for activities such as mining, wastewater releases and several industrial processes which use boron compounds (rubber manufacturing, electroplating, fibreglass, pulp and paper). This concludes "low potential for ecological harm from most sectors and activities that release boric acid".

Boric acid is a metalloid ion so is considered by nature to be "infinitely persistent", but is not generally bioaccumulative and does not biomagnify. Boron can be (eco)toxic at excessive levels of exposure and the draft assessment concludes that it:

- meets the criteria of section 64(a) part 5 of CEPA (Canada Environment Protection Act): "have or may have an immediate or long-term harmful effect on the environment or its biological diversity";
- does not meet the criteria of section 64(b): "constitute or may constitute a danger to the environment on which life depends";
- meets the criteria of section 64(c): "constitute or may constitute a danger in Canada to human life or health"

The draft risk scope proposes actions on boric acid use in flame retardants (in particular in mattresses and futons), cleaning products, swimming pool and spa products and DIY products, arts – crafts, toys, cosmetics, natural health products and non-prescription drugs and one metal ore processing site.

"Updated draft assessment - Boric acid, its salts and its precursors", Health Canada March 2025 LINK.

"Revised risk management scope for boric acid, its salts and its precursors", Health Canada March 2025 LINK.

Canada CEPA "Moiety approach" LINK.

Public consultation on updated draft assessment and scope, ***open to 7th May 2025*** *https://gazette.gc.ca/rp-pr/p1/2025/2025-03-08/html/notice-avis-eng.html#nl1*

21 May: UK construction products

Public consultation on UK "Construction Products Reform Green Paper", part of response to Grenfell report recommendations. The proposed reform addresses accountability, regulatory coverage (gaps in products covered), mandatory compliance for products concerned by designated standards (consistent with the revised EU CPR 3110/2024), enhanced information and transparency, digital traceability, improved enforcement, strengthened third-party testing and certification, coordination and sustainability objectives.

The UK Government has also announced adoption of all 58 recommendations of the Grenfell fire tragedy final report (see pinfa Newsletter n°163) and acceleration of removal of combustible ACM (aluminium composite material) from buildings (over 15 000 buildings, see pinfa Newsletter n°163). The wide range of actions announced include tighter regulatory control, clear definitions of responsibilities and fire-safety training for construction operators, specific actions on "higher-risk buildings", improvement of firefighters' on-site communications equipment, requirement that copies of tests results be supplied with all certificates, increasing training of fire safety engineers, traceability of construction products, development of a cladding materials library.

"Construction Products Reform Green Paper 2025", UK Government public consultation open to 21st May 2025
https://www.gov.uk/government/consultations/construction-products-reform-green-paper/construction-products-reform-green-paper-2025-html#chapter-4-interaction-with-the-united-kingdom-internal-market-and-the-european-union

"Grenfell Tower Inquiry Phase 2 Report: Government response", UK Government, 26th February 2025
https://www.gov.uk/government/publications/grenfell-tower-inquiry-phase-2-report-government-response/grenfell-tower-inquiry-phase-2-report-government-response-html#chapter-11-our-next-steps

2 June: ISO Flame Retardant codes

Consultation open to modify ISO 1043 with more precise code definitions of nitrogen and organo-phosphorus FRs. The proposed amendment will modify ISO 1043-4:2021 "Plastics - Symbols and abbreviated terms - Part 4: Flame retardants" concerning only the codes for "Nitrogen" and "Organo-phosphorus" flame retardant compounds.

For Nitrogen compounds, the current two codes become six: melamine, urea, monomeric melamine-based compounds (melamine salts), polymeric melamine-based compounds, N-alkoxy hindered amine-based compounds, other nitrogen-based compounds.
For Organo-phosphorus, the current three codes become five: aryl phosphates, chlorinated organic phosphorus compounds, brominated organic phosphorus compounds, methyl esters of phosphoric or phosphonic acid, other halogen-free organic phosphorus compounds.

Input to the consultation is only via national standards organisations (ISO members).

Current most up-to-date standard: ISO 1043-4:2021 "Plastics - Symbols and abbreviated terms - Part 4: Flame retardants" available for 10€ from the EESTI Estonia standards organisation (or different prices from other national organisations) https://www.evs.ee/en/evs-en-iso-1043-4-2021

ISO website: https://www.iso.org/standard/91076.html

Proposed amendments can be read here (but not downloaded): https://komport.evs.ee/Default.aspx?s=standardCommenting&doc=18765

Policy and Regulation

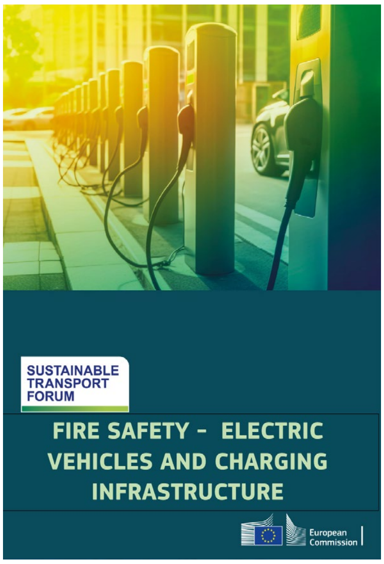
EU Clean Industrial Deal

Business welcomes Commission proposals, calls for rapid implementation. Chemicals Industry Package for late 2025. The European Commission published the Clean Industrial Deal (CID) on 26th February, a year after the Antwerp Declaration of business leaders calling for such a Deal, including the European Chemical Industry Council (Cefic), of which pinfa is a Sector Group. The Commission's CID aims to make decarbonisation a driver for economic growth, quality jobs and business resilience, by removing dependency on energy prices and imported resources. It will particularly target energy-intensive industries (including chemicals), the clean-tech sector and circularity. A Chemicals Industry Package, announced for late 2025, will recognise the sector's strategic role as "industry of industries" and will aim to enhance the EU chemical industry's competitiveness, supporting modernisation, production and innovation in Europe. Cefic says: The Antwerp Declaration remains an urgent call to revitalise Europe's industrial landscape. Europe's industries stand ready to do their part and continue supporting policymakers in building a competitive, resilient and sustainable future in Europe amid shifting geopolitics.

Cefic statement 26th February 2025: https://cefic.org/media-corner/newsroom/cleanindustrialdealantwerp/

Amsterdam Declaration, 20th February 2024, see pinfa Newsletter n°158.

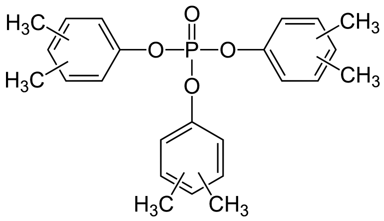
European Commission "Clean Industrial Deal. A plan for EU competitiveness and decarbonisation", 26th February 2025 https://commission.europa.eu/topics/eu-competitiveness/clean-industrial-deal_en



Fire safety in EVs and charging in car parks

pinfa input to the European Commission guidance on electric vehicles and charging infrastructure in covered parking. The now-published EU Sustainable Transport Forum "Guidance" document (80 pages) underlines that electric vehicles (EVs) do not present a higher fire risk than internal combustion engine cars (ICEVs): statistics suggest that ICEVs are more than twenty times more likely to catch fire, and spread of fire from EVs to adjacent vehicles is no faster than for ICEVs. However, but lithium ion battery fires do pose specific dangers and challenges for firefighting. Also, EV charging installations may pose fire safety issues. The Guidance summarises relevant legislation in EU Member States, specific challenges of EV fires, fire prevention, detection, evacuation, propagation control and extinction and provides recommendations for car park operators, EV users, firefighters and public authorities. The report notes that speed of battery thermal runaway is related to materials in the battery (use of flame retardants) and to cooling, control and shutdown systems, and is strongly influenced by state of charge (energy present in the battery).

"Guidance on fire safety for electric vehicles parked and charging infrastructure in covered parking spaces", European Commission / Sustainable Transport Forum, 80 pages, 2025 ISBN 978-92-68-25223-9, https://doi.org/10.2832/6681178



Canada – new uses rule trixylyl phosphate

SNAc (Significant New Activity) order for trixylyl phosphate, requiring information and assessment of new uses. Canada concluded in 2020 that trixylyl phosphate (an aryl phosphate PIN FR*) did not meet the CEPA section 64 criteria (not harmful to health or the environment, Canadian Environment Protection Act), see pinfa Newsletter n°122. However, Canada considers that the substance "is recognized as having potential human health effects of concern. The SNAc Order means that any new uses must be declared 90 days before starting, with information to assess possible risks to human health and the environment. New uses include manufacture or import of products containing > 0.1% w/w trixylyl phosphate. In Europe, trixylyl phosphate is already largely phased out with only a few very restricted uses authorised for a limited further time.

Trixylyl phosphate = phenol, dimethyl-, phosphate (3:1)

Diagram: Wikipedia https://gazette.gc.ca/rp-pr/p2/2025/2025-03-26/html/sor-dors81-eng.html

Canada Government SNAc (Significant New Activity) Order for trixylyl phosphate, 26th March 2025 https://gazette.gc.ca/rp-pr/p2/2025/2025-03-26/html/sor-dors81-eng.html

Construction Products Regulation updated

The recast EU CPR is now published, including new rules on traceability, product LCA and end-of-life information. The CPR defines harmonised rules for all construction products placed on the European market, defining how to express not only technical and safety performance, but also now environmental performance, LCA, carbon footprint, traceability and end-of-life (recyclability and reusability). pinfa made input to the preparation of this revised text in 2021 (pinfa Newsletter n°121) and via contacts with professional organisations in the construction industry. A key development in the recast Regulation is the construction product "digital passport" including Declaration of Performance and Conformity (DoPC) and other information. The revision also aims to facilitate certification of prefabricated and modular systems, including façade systems. Fire safety is reinforced, with more detail in para. 2 of Annex I (Basic requirements for construction works).

pinfa has launched work to update our [Technical Brochure](#) "Innovative & Sustainable Flame Retardants in Building and Construction" (56 pages, 2017). **Input is welcome**.

European Commission "New EU rules on the safety and sustainability of construction products mark a new step for the sector's competitiveness", 7th January 2025 https://www.pinfa.eu/resource/innovative-sustainable-flame-retardants-in-building-and-construction/ https://single-market-economy.ec.europa.eu/news/new-eu-rules-safety-and-sustainability-construction-products-mark-new-step-sectors-competitiveness-2025-01-07_en

EU Regulation 2024/3110, 27th November 2024,recast of the EU Construction Products Regulation https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:L_202403110

FIRE SAFETY

59 dead: another nightclub fire tragedy

Flammable materials contributed to the 59 fire deaths and 196 injured at the Pulse Club, Kocani, North Macedonia, 16th March. The country's Interior Minister said the fire may have been caused by pyrotechnic devices, with sparks igniting the ceiling "made of easily flammable materials", and with fire spreading rapidly across the whole discotheque with thick smoke. The venue, in a former warehouse, is said to have lacked fire extinguishers, sprinklers and emergency exits, with access difficulties for firefighters, and to have been illegally licensed. Media suggest that these failures correspond to systemic government failures. Sadly, history repeats, and the lessons of the 1942 Boston Cocoanut Gove fire (see pinfa-NA webinar, above) are not yet learned everywhere.

"Investigation underway into Macedonian nightclub fire that killed 59", UK Fire Protection Association news 23rd March 2024 https://www.thefpa.co.uk/news/investigation-underway-into-macedonian-nightclub-fire-that-killed-59 Photo Wikipedia, Toshe Ognjanov https://commons.wikimedia.org/wiki/File:Remains_of_night_club_in_Kochani_after_the_fire_VOA-full.jpg

Climate change will mean more city fires

Scientists say statistics show that warming climate will result not only in more vegetation fires but also more urban fires. Fire incidence data was collected from 20 countries, categorised into fire type, then statistically correlated to climatic conditions (monthly air temperatures from 2 800 cities) and to climate change models. The authors note with regret that, despite efforts, no data was obtained from Africa or South America so that results are only directly representative of the rest of the world. Conclusions are that urban fire frequencies increase by over +3% for +1°C global warming with a disproportionately higher increase in fire deaths and injuries (+ 1/3 million fire deaths and +1.1 million injuries with global warming of +4°C). These numbers are surprising given that increasing temperature is correlated (in some cases) to more outdoor fires and vehicle fires but fewer building fires.

"City fires likely to increase with climate change – Expert Reaction", New Zealand Science Media Centre SMC, 4th March 2025 https://www.sciencemediacentre.co.nz/2025/03/04/city-fires-likely-to-increase-with-climate-change-expert-reaction/

"Increasing fire risks in cities worldwide under warming climate", L. Shi et al., Nature Cities, vol. 2, March 2025, 254-264 https://doi.org/10.1038/s44284-025-00204-2

Research and Innovation

PIN FRs for unsaturated polyester resins

Various experimental phosphorus PIN FRs were tested in UPR, looking at solid and gas phase action and P oxidation state. In Chu, 2022, three polymeric glycerol-DOPO-based phosphorus compounds were tested in UPR (unsaturated polyester resin), with one achieving, with 15% loading (2.5% P loading), UL-94 V-0 (3 mm) and 29% LOI (limiting oxygen index, compared to 23.5% for neat UPR). The better fire performance between the three molecules was considered to result from better gas phase action, with all three molecules acting effectively in the sold phase (char formation). These molecules included phosphorus with oxidation state +5 (same oxidation state as in phosphoric acid and natural P molecules such as DNA) – see article on P oxidation states below.

"An insight into the effects of the low oxidation states of phosphorous on the combustion behavior of intrinsically flame-retardant unsaturated polyester resins", Y-D Hu et al., Polymer Degradation and Stability 232 (2025), 111156 https://doi.org/10.1016/j.polymdegradstab.2024.111156

PIN FRs for recycled polyethylene

PIN FRs zirconium phosphate and ATH improved mechanical and fire performance of post-consumer recycled rHDPE. The recycled high-density polyethylene (rHDPE) was supplied from a Brazil recycler. Layered zirconium phosphate (ZrP) was synthesised in the laboratory and aluminium hydroxide (ATH) was purchased as such. To optimise dispersion, specimens (125 x 12 x 3 mm) containing 10% PIN FR were extruded after first extruding masterbatches of rHDPE with 20% FR., Tests compared neat rHDPE with 10% ZrP, 10% ATH and 5% ZrP+5% ATH. Analysis showed that the reprocessing of the rHDPE led to some oxidative degradation. The PIN FRs showed some molecular reaction with the rHDPE, increased rHDPE stiffness and tensile strength was maintained. ASTM D635 fire testing showed increased burning rates with the PIN FR addition but much longer times to dripping (nearly 7x longer) and with ZrP+ATH burning drips extinguished. The authors conclude that the PIN FRs increased flame retardancy, with synergy between zirconium phosphate and the ATH shown by increased char formation.

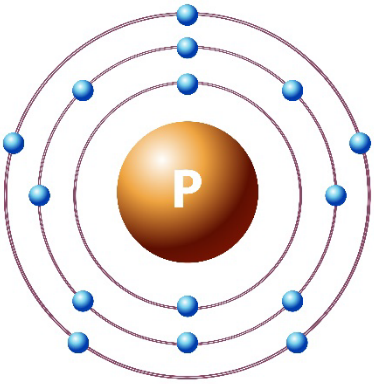
"Post-consumer high density polyethylene / zirconium phosphate and aluminum hydroxide composites: Assessment of physico-mechanical and flame retardancy properties", G. Albitres et al., J. Composite Materials 2024, Vol. 58(4) 489–503, https://doi.org/10.1177/00219983231226278

Polymeric Si-N PIN FR for polycarbonate

Functionalised polysiloxane 2% loading in polycarbonate (PC) achieved UL 94 V-0 (3.2 mm), PHRR -64% and total smoke -18%. Siloxane (4Si-4O-8H ring) was reacted with a silane (3-aminopropylmethyldiethoxysilane) and different benzaldehydes to give a silicon-nitrogen polymer with annexed benzene rings functionalised with 0 to 3 OCH_2 groups. This polymer was compounded into polycarbonate at 2% w/w. Results showed that more OCH_2 groups were present resulted in improved fire performance and also improved notched impact strength. The PC with Si-N polymer with benzene - 3 OCH_2 groups achieved UL 94 V-0 (3.2 mm) and peak heat release -64% and total smoke production -18% lower than neat PC, and also +190% notched impact strength at room temperature and + 72% at -25°C.

"Excellent flame-retardant polycarbonate composites with improved notched impact toughness via introducing imine-functionalized polysiloxane", Y. Zhu et al., Composites: Part A 186 (2024) 108416, https://doi.org/10.1016/j.compositesa.2024.108416

THEMATIC RESEARCH UPDATE SUMMARY:



Phosphorus oxidation states and FR effects

pinfa research mini-review on how valency of phosphorus in PIN FRs impacts flame retardancy effectiveness. With continuingly increasing interest in phosphorus-containing PIN flame retardants as a key solution for fire safety in many applications (electronics, batteries, textiles …), researchers are looking at how P oxidation state (valency) impacts fire retardancy effects, in order to support design of future PIN phosphorus FRs. This may also support development of PIN FRs which can be produced without relying on P_4 derivates (today, phosphorus chemicals with oxidation state other than +5 are only produced via P_4 derivates).

Overall conclusions are that PIN FRs with higher P oxidation state tend to act in the solid phase (char formation) whereas lower P oxidation state FRs act both in the gas phase (PO radicals which engage in complex reactions continuously consuming H and OH flame radicals) and the solid phase. This confirms the conclusion of presentations at FRPM 2023 (pinfa Newsletter n°151) and Zou et al. 2024 (pinfa Newsletter n°161). However, all studies are based on only a few more-or-less similar phosphorus PIN FR compounds, and it seems clear that the effects of differing P valency are less important than effects of interactions with the polymer, and of the PIN FRs degradation temperature (gas phase action only if degradation before polymer decomposition).

In phosphorus compounds (including PIN flame retardants), the phosphorus atom can have different oxidation states (valency), for example:

- phosphines -3
- phosphine oxides -1
- elemental phosphorus 0
- phosphinates +1
- phosphites +3
- phosphonates +3
- inorganic phosphorus compounds, including phosphoric acid, phosphates, and biological organo-phosphorus compounds (DNA, phospholipids, phytate …) +5

For detail see W. Schipper in ESPP [SCOPE Newsletter n°136.]()

Qin et al. 2024 make detailed chemical modelling of five structurally similar phosphorus flame retardants (all consisting of three benzene rings joined via a phosphorus atom) with different P oxidation states:

- R1 = triphenylphosphine = PPh3, P-bonds: 3xP-C
- R2 = triphenyl phosphate oxide = TPPPO, P-bonds: 3xP-C + P=O
- R3 = phenyl diphenylphosphinate = PDPP, P-bonds: 2xP-C + P-P + P=O
- R4 = diphenyl phosphate = DPPO, P-bonds: P-C + 2xP-O + P=O
- R5 = triphenyl phosphate = TPP, P-bonds: 3xP-O + P=O

It is not specified in what oxidation state is the phosphorus in each of these molecules, but it is indicated that the oxidation state is higher as the R-numbers increase.

The decomposition of these different P bonds in the five chemicals constitute 27 different main reaction pathways. In general, the P-C bond in the FRs was more resistant to disassociation than P-O bonds and phenoxy (benzine-O^+) was more selective in the flam retardancy process than phenyl (benzine-carbon containing group). However, this general rule show significant variations between the different tested compounds and their different degradation compounds.

The authors conclude that as P oxidation state increases, the FRs act increasingly in the solid phase - char formation) whereas lower P oxidation state act rather in the gas phase (PO radicals which engage in complex reactions continuously consuming H and OH flame radicals). This confirms the conclusion of presentations at FRPM 2023 (pinfa Newsletter n°151) and Zou et al. 2024 (pinfa Newsletter n°161).

Hu, Chu et al. 2022 and 2025 studied different polymeric and reactive phosphorus PIN FRs in unsaturated polyester resins (see above). In the 2025 study, two reactive phosphorus PIN FRs were synthesised by combining itaconic acid (ITA) with DOPO or diphenylphosphine oxide (DPPO), then polymerised with 1-2-propanediol, maleic anhydride and phthalic anhydride to produce phosphorus FR-containing unsaturated polyester (with final 3%P content). The DOPO-ITA had P oxidation state +1 whereas the DPP-ITA had P oxidation state -1. The authors consider that there was little difference in flame inhibition (gas phase action). Fire performance was very similar between the two PIN FRs (both reduce peak heat release by over 40%). The DOPO-ITA (higher oxidation state) however produces more stable char and achieves UL 94 V-1 (3.2 mm). In the 2022 study, five reactive PIN FRs containing phosphorus and sulphur were reacted to unsaturated polyester resins with 8 – 11 %P and 0 – 10 %S. PIN FRs with P oxidation state +3 and sulphur (as sulfone) achieved UL 94 V-0 (3.2 mm), despite again higher P oxidation state of +5 resulting in more charring. The authors conclude that in this case, in unsaturated polyester resin, the gas phase action is most important in improving fire performance and they underline the synergy between phosphorus and sulphur (as sulfone).

Yin et al. 2025 tested PIN FRs derived from DPP (diphenyl phosphate, P-bonds: 2xP-C, P=O, P-OH) and DHP (diphenyl hydrogen phosphate, P-bonds: 2xO, P=O, P-OH) in vinyl ester resins. Both were combined 1:1 with 1- vinylimidazole salts. The resulting ViDPP (low oxidation state +1) and ViDHP (high oxidation state +5) both showed good curing compatibility, thermal stability and flame retardancy effects at 20% loading in vinyl ester, with >50% increase in LOI (limiting oxygen index) and decrease in smoke production. ViDPP (low P oxidation state) showed the best fire performance reducing peak heat release by half and achieving UL 94 V-0 (3.2 mm) at 20% loading, despite significantly lower char residues than for ViDHP.

This again show low P-oxidation state acting in the gas phase and high P-oxidation state acting in the solid phase (char formation).

Denis, Sonnier et al. 2023 tested four phosphorus – carbonate PIN FRs (based on MBDA 4,40-methylenebis(N,N-diglycidylaniline) reacted to polyhydroxyurethanes. These were based on:

- DOPO (a phosphonate), P oxidation state +3
- diethyl phosphite DEP, P oxidation state +3
- diphenyl phosphite DPP, P oxidation state +3
- dibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide BPPO, P oxidation state -1

This study also concluded that the higher P oxidation state compounds resulted in more char generation. DEP offered the best fire performance, with over 75% reduction in peak heat release rate (2% P loading in final polymer).

Mariappan et al. 2013 tested, in polyurea and in epoxy resin, three PIN phosphorus FRs, as above each with three benzene rings linked by one phosphorus atom: TPPi = triphenylphosphite (P bonds: 3xP-O, oxidation state +3), TPP = triphenyl phosphate (P bonds: 3xP-O + P=O, oxidation state +5 and TPPO = triphenylphosphine oxide (P-bonds: 3xP-C + P=O, oxidation state -1).

The TPP (oxidation state +5) was much more effective at reducing heat release rate in polyurethane, the TPPi (oxidation state +3) was much more effective in epoxy. The effectiveness of TPPi in epoxy was considered to result from generation of non-conventional intumescent char, generated by a tans-esterification between the phosphite group and the epoxy, whereas the TPPi gave poor results in polyurethane because of a plasticisation effect.

This study confirms that P oxidation state is one factor influencing FR effectiveness, it is principally driven by interactions avec the polymer.

Luo et al. 2023 summarise links between P oxidation state and flame retardancy effects in polyurethane elastomers (PUE), noting that for similar molecular structures, the P-content (%P by weight) of molecules tends to decrease with increasing oxidation state. This is within a detailed review of reactive phosphorus PIN FRs in PUE, covering different chemical structures, phosphorus – nitrogen synergies, P-containing chain extenders, P-containing polyols, impacts on PUE mechanical performance, toxicity and environmental safety, burning behaviour.

Modesti et al. 2011, cited by Luo, tested phosphorus PIN FRs with different P oxidation states in rigid polyurethane (PUR) foam:

- aluminium phosphinate (AlPi), P oxidation state +1
- dimethylpropanphosphonate (DMPP), P oxidation state +3
- triethylphosphate (TEP), P oxidation state +5
- ammonium polyphosphate (APP), P oxidation state +5

This study concluded that when the PIN FR degraded at temperatures below the onset decomposition temperature of PUR (c. 300°C) – as do TMPP and TEP, they acted only in the gas phase irrespective of P oxidation state (because no longer present to cause charring). For TEP and APP, which decompose at c. 350°C, AlPi (lower P oxidation state +1) had both gas and solid phase effects, whereas APP (P oxidation state +5) acted only in the solid phase.

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