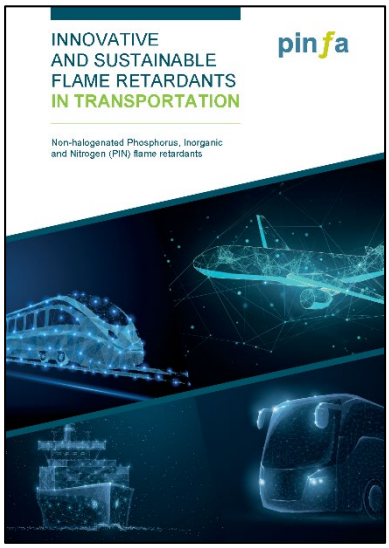
pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 132 December 2021

PINFA



Solutions for new transport fire challenges

pinfa has published a 50-page brochure detailing FR applications for materials in tomorrow's transport vehicles: airplanes, ships, trains, buses, and cars. Designers, manufacturers and transport operators increasingly rely on flammable materials to reduce weight (reduce energy consumption) and improve design. PIN flame retardant solutions, to achieve required fire performance low smoke low toxicity and zero halogen requirements are presented for performance polymers and composites, as well as for textiles and foams necessary for transport vehicle interiors, seats, insulation and soundproofing. PIN FR solutions for new transport energy systems (electric drive, batteries, fuel cells, hydrogen …) are detailed. The brochure provides technical information on fire and smoke regulation, testing and standards and on formulating PIN FR solutions for different materials for transport applications, covering specific materials and requirements for interior parts, textiles, seats, cables, electrics and electronics and e-mobility in the different transport sectors, air, rail, maritime and road.

The new pinfa transport flame retardant applications technical brochure is available free online. pinfa has also online technical brochures on PIN flame retardants in electrical & electronics applications and building & construction.

www.pinfa.eu/media-events/brochures-publications/

CONSULTATIONS AND POLICY

EU consultation on digital chemical labelling

Public and stakeholder questionnaire on how to provide online information, via labels, to consumers for chemical products such as, detergents, fertilisers and "chemical products, such as glues, paints, solvents, lamp oils". Open **to 16th February 2022**. The proposal specifically addresses the Fertilising Products Regulation and the Detergents Regulation, and could also impact the CLP Regulation (Classification, Labelling and Packaging of Substances and Mixtures). The consultation questionnaire collects general information about motivation for looking for information, what IT routes would be preferred for information, demand for more detail or updates, and some questions on specific possible information for different product families. The consultation does not concern chemicals in other consumer products, nor sale of chemicals to professionals. However, conclusions on digital labelling for detergents and fertilising products may possibly be extended to other product types in the future.

EU public consultation open to 16th February 2022 "Chemicals – simplification and digitalisation of labelling requirements"

General Product Safety Directive update

The Commission proposal centres on online sales, enforcement and recalls, and new technologies: fire is not mentioned. The General Product Safety Directive (GPSD 2001/95) will become a "Regulation", making it more directly applicable. The Commission proposal (30th June 2021) particularly targets risks related to "new technologies", such as digital hacking of products, except a few specific listed sectoral exceptions. The regulation covers all manufactured, consumer products, except where other EU legislation already provides safety rules, including covering other aspects of products where existing safety legislation only covers certain points. Safety is defined as "presenting only minimum risks compatible with the product's use, considered acceptable and consistent with a high level of protection of health and safety of consumers". As in the present GPSD text, fire is not mentioned. However, a product can, in theory, be banned from the market if it poses a risk of fire not compatible with this definition of safety. The Commission's proposed text now goes to discussion in the European Parliament and Council in coming months.

European Commission proposal for a Regulation on General Product Safety, COM/2021/346 final, 30th June 2021 and "Factsheet".

Leglislative train https://www.europarl.europa.eu/legislative-train/theme-a-new-push-for-european-democracy/file-revision-of-the-general-product-safety-directive

EU proposal on POPs in recycling

Proposed "POP" Regulation update will reduce limits for certain chlorinated and certain FRs in recycled wastes. Consultation was open to 23rd December 2021. The objective is to improve protection for human health and the environment from 'POP' (persistent organic pollutants) listed in the Stockholm Convention, including a number of chlorinated and brominated flame retardants, whilst at the same time enabling the circular economy by tolerating low levels of these substances in recycled materials. The proposed amendments to the existing POP Regulation (2019/1021) lower the limits of POP substances which define whether wastes can go to recycling, or whether they must be disposed of in such a way as to eliminate the POP. Amongst other substances concerned by the amendments, limits are introduced for PFOAS (art. 7 annex IV) and limits for SCCPs (short chain chlorinated paraffins) are reduced from 10 000 to 1 500 mg/kg, PBDEs (sum including Deca-) from 1 000 to 500 then after 5 years to 200 mg/kg, and HBCD from 1 000 to 500 mg/kg. Additionally, in the limit values for wastes for pre-treatment DecaBDE is now included in the sum of PBDEs (was not previously included, the limit for sum of PBDEs is unchanged at 10 000 mg/kg).

POPs Regulation 2019/1021, consolidated: https://echa.europa.eu/fr/pops-legislation

EU consultation on proposed Regulation amendment COM(2021)656 final, 28th October 2021, open to 23rd December 2021 "Hazardous waste - updated concentration limits for chemical pollutants" https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12411-Dechets-dangereux-mise-a-jour-des-limites-de-concentration-pour-les-polluants-chimiques_fr

Canada proposal on P-ester FRs

Screening risk assessment proposes regulatory action on TEP and IPP (aryl organophosphate FRs) in foams. The draft screening assessment was open for comment and for input of information to 5th January 2022. It covers nine aryl organophosphate (phosphate ester) PIN FRs and one brominated FRs, concluding that five of the P-esters are toxic (under Canada CEPA $64(a), and that of these five, two are persistent and two bioaccumulative. None are PBT. The other four FRs are considered to not meet CEPA $64a criteria. Possible environmental concerns are identified for the aryl P-FRs identified as toxic, in particular in water and soil, and possible health concerns are identified for skin contact with polyurethane foams containing the aryl P-ester FRs IPPP and TEP. Proposed regulatory actions are to minimise releases of aryl P-FRs from industrial processing, to minimise release from consumer products to wastewater and so to the environment and to reduce human exposure from use in foams.

Substances assessed: TPHP (triphenyl phosphate), BPDP (tert-butylphenyl diphenyl phosphate), BDMEPPP (bis(tert- butylphenyl)phenyl phosphate), IDDP (isodecyl diphenyl phosphate), IPPP (isopropylated triphenyl phosphate), TEP (triethylphosphate; Triethyl Phosphate), TBOEP

(tris(2- butoxyethyl) phosphate), TEHP (tris(2- ethylhexyl) phosphate), BEHP (bis (2-ethylhexyl phosphate; bis (2- ethylhexyl) hydrogen phosphate), TDBDPB (tetradecabromo- 1,2- diphenoxybenzene; perbromo- 1,4 diphenoxybenzene)

Summary: "Risk management scope for TPHP, BPDP, BDMEPPP, IDDP, IPPP and TEP", Canada Government, November 2021, consultation open to 5th January 2022 https://www.canada.ca/en/environment-climate-change/services/evaluating-existing-substances/risk-management-scope-tphp-bpdp-bdmeppp-iddp-ippp-tep.html

"Publication after screening assessment of 10 substances of the Flame Retardants Group specified on the Domestic Substances List" https://canadagazette.gc.ca/rp-pr/p1/2021/2021-11-06/html/notice-avis-eng.html

Full screening assessment (200 pages) https://www.canada.ca/en/environment-climate-change/services/evaluating-existing-substances/draft-screening-assessment-flame-retardants-group.html

FIRE RISKS

UL points to increasing home fire risks

Underwriters Laboratories expert says US fire deaths are increasing with changing design and content of homes. Steve Kerber, VP Research at UL and Director of the UL's Fire Safety Research Institute, shares research that shows that fire remains an important problem with US fire services responding to nearly 1.3 million fires (2019), 3 700 fire deaths, 16 600 injuries and nearly 15 billion US$ property damage. The number of home structure fires has not decreased significantly since 2000 and the number of home fire deaths is trending upwards over the last decade. Home fire dangers are increasing with factors such as home design (bigger homes, open floor plan and open staircases, high ceilings) and with increasing fire load and synthetic materials (leading to faster flashover). He concludes that fire is an evolving challenge demanding evolving interventions.

Steve Kerber, UL's Fire Safety Research Institute https://fsri.org/steve-kerber

Video comparison, fire behaviour of natural and synthetic home furnishings (FSRI) https://vimeo.com/463653907

Video "Close Before You Doze - See the Dramatic Difference a Door Can Make" (FSRI) https://vimeo.com/293952932 (photo)

"Turning to science for life-safety solutions", S. Kerber, Life Safety Digest, Fall 2021 (page 22) https://lsc-pagepro.mydigitalpublication.com/publication/?i=723042&ver=html5&p=24

"Analysis of Changing Residential Fire Dynamics and Its Implications on Firefighter Operational Timeframes", S. Kerber, Fire Technology, 48, 865–891, 2012 https://dx.doi.org/10.1007/s10694-011-0249-2

NFPA US Fire Loss Report 2020

Numbers of fires and of fire casualties in the USA are approximately stable since around 2010, with some 1.4 million fires, 3 500 civilian fire deaths, 5 200 reported civilian fire injuries and nearly US$22 billion fire damage in 2020. Compared to 1980, numbers of fires and deaths were both around 50% lower, but the death rate per 1 000 fires was nearly unchanged. Three quarters of civilian fire deaths and injuries occurred in home fires. 18% of deaths and 11% of injuries occurred in vehicle fires.

"Fire Loss in the United States During 2020", M. Ahrens & B. Evarts, 9/2021 https://www.nfpa.org/fireloss

Insurers cautious on building cladding

One third of UK underwriters are willing to cover fire safety risks in building works to replace defective cladding, and nearly all of the remaining two thirds offer only partial coverage. Three quarters considered that the UK construction industry has not yet learnt the lessons of the Grenfell fire tragedy. Questions remain about accountability, supply chain management and "lowest cost culture". The International Underwriting Association of London surveyed 26 insurance underwriters active in the sector. The association hopes that the new UK Building Safety Bill will help resolve issues of accountability for fire safety and encourage investment in building quality.

"IUA survey shows cautious support for building recladding but urges construction sector to do more", 16th September 2021 https://staff.iua.co.uk/IUA_Member/Press/Press_Releases_2021/IUA_survey_shows_support_for_building_recladding_but_urges_construction_sector_to_do_more.aspx

New UK tax to fund cladding fire safety

A new 4% yearly tax on property developers' profits will fund building fire safety remediation for the coming decade. The tax, announced in the Government's budget, aims to raise UK£ 2 to 5 billion to remove and replace dangerous building cladding materials, following the Grenfell Tower fire in 2017. The tax will apply to trading profits above UK£ 25 million on residential property development activities and interests in development land. The total remediation costs are expected to reach UK£15 billion (report to UK Parliament in 2020).

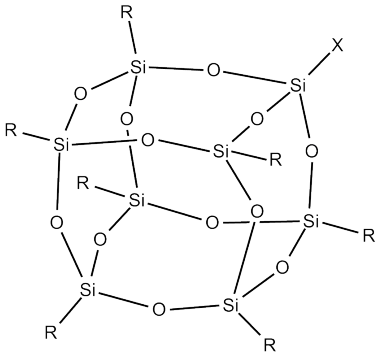
"Developers will pay £5,000,000,000 tax to fix homes with dangerous cladding", Metro UK, 27/10/2021 https://metro.co.uk/2021/10/27/budget-2021-sunak-confirms-property-tax-to-remove-grenfell-cladding-15496255/

E-scooters banned because of fire risks

Transport for London (TfL) has banned electric scooters on buses and the underground because of fire risks for batteries. This follows a fire on a tube train (Parsons Green, 1/11/21), which caused the train to be evacuated and where the scooter continued to burn after removing it onto the platform, and a fire in a scooter in lost property. The ban was called for by the trade union TSSA who said that e-scooter fires "pose a significant threat to the traveling public, our members and all workers at TfL". E-scooters are now banned on all London Transport buses and trains from 13th December 2021. London Transport referred to "intense fires and considerable smoke and damage" related to the scooters' lithium-ion batteries. The scooters are also banned on all UK roads and pavements, for road safety reasons, except for public rental service e-scooters where deployed.

"TfL bans e-scooters on transport network amid safety concerns"
https://internationalfireandsafetyjournal.com/tfl-bans-e-scooters-on-transport-network-amid-safety-concerns/

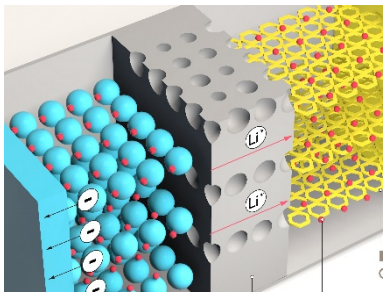
RESEARCH AND INNOVATION



Silsesquioxane synergist for PIN FR

1% POSS significantly improved fire performance achieved by a phosphorus – nitrogen intumescent FR in polypropylene. Nano- octavinyl POSS (polyhedral oligomeric silsesquioxane) was supplied by Zhengzhou Alfa. The intumescent PIN FR was produced by thermal reaction of APP (from Clariant), melamine and PER (pentaerythritol), to produce a single-component PIN FR (RMAPP). This was tested at 25% loading in polypropylene, improving UL 94 (1.6 mm) from unrated to V2 and LOI from 18 to 28. Replacing 1% RMAPP by POSS considerably improved fire performance, to UL 94 V0 (with no dripping), LOI 31, and also reduced peak heat release rate (1023 kW/m^3 for pure PP, 89 with 25% RMAPP and 66 with 1% POSS). Increasing POSS to 2% or 5% (replacing RMAPP) resulted in fire performance poorer than with 1% POSS. Similarly, mechanical performance was best with 1% POSS. The POSS was well mixed with the PP and the RMAPP before injection molding of the samples, and the authors suggest that the improved fire performance and mechanical properties with 1% POSS results from improved dispersion and compatibility between the PIN FR and the polymer and from silicon oxide reinforcement of the char layer.

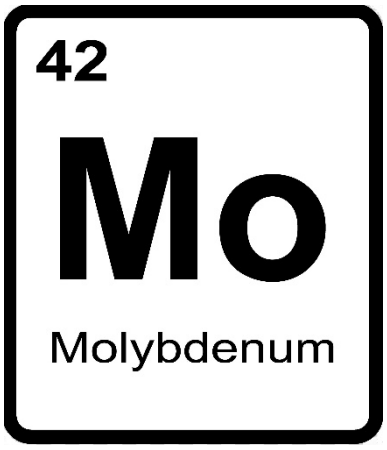
"Synergistic and compatibilizing effect of octavinyl polyhedral oligomeric silsesquioxane nanoparticles in polypropylene/intumescent flame retardant composite system", B. Yang et al., Composites Part A 123 (2019) 46–58
https://doi.org/10.1016/j.compositesa.2019.04.032 Image: Wikipedia.



Flame retardants for battery electrolytes

Flame retardants can reduce the fire risk of the liquid carbonate-based electrolytes in lithium-ion batteries. Two PIN flame retardants (phenoxycylophosphazene, melamine phosphate) and tris (2-chloropropyl) phosphate were tested in a battery electrolyte consisting of 1M $LiPF_6$ dissolved in 1:1:1 ethylene carbonate – dimethyl carbonate – diethyl carbonate. Both of the PIN FRs, at 5 – 15% loading, reduce the combustion rate of the electrolyte and the flame height, but do not reduce the flame temperature. The chlorinated phosphorus FR reduces both the combustion rate and the flame temperature. Higher FR loadings offer greater reductions in fire risk. The lithium salt in the electrolyte accentuates fire risk. The authors conclude that "composite" flame retardants combining several different elements, and so different action mechanisms, are more effective.

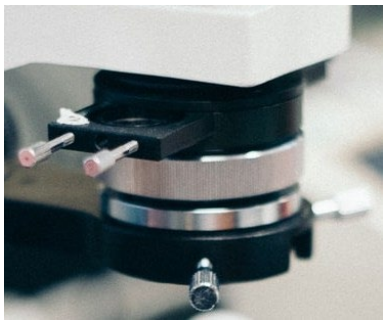
"Comparative studies on the combustion characters of the lithium-ion battery electrolytes with composite flame-retardant additives", M. Chen et al., J. Energy Storage 2021 https://doi.org/10.1016/j.est.2021.103642



Novel PIN additives reduce smoke toxicity

Carbon microspheres modified with molybdenum reduced smoke and carbon monoxide emission from TPU polyurethane. Hollow carbon microspheres were synthesised using polyacrylic acid, ethyl orthosilicate and phenolic resin, then carbonised and acidified with phosphoric acid and then reacted with ammonium molybdate. The resulting molybdenum carbon microspheres were then blended into thermoplastic polyurethane elastomer (TPU) at 4% loading. Peak heat release was reduced by 63% compared to neat TPU, peak smoke production rate by 52% and peak carbon monoxide production by 72%.

"Fabrication of hollow carbon spheres modified by molybdenum compounds towards toxicity reduction and flame retardancy of thermoplastic polyurethane", T. Feng et al., Polym Adv Technol. 2021;1–15 https://doi.org/10.1002/pat.5550



PIN FRs showed effective in particle board

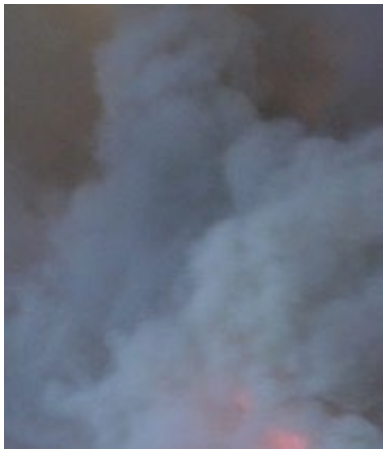
An ATH – APP based PIN FR system reduced heat loss and smoke emission from wood – polyester particleboard. The particleboard was produced by compression molding of sawdust with polyester resin, after treating the sawdust with sodium hydroxide to improve compatibility. A PIN FR system consisting of ATH (aluminium trihydroxide), APP (ammonium polyphosphate), gum Arabic powder and carbon black (1:1.5:3:3) was tested at 0 – 18% loading in horizontal burn tests of 100 x 000 x 10 mm samples. At 18% loading the PIN FR reduced heat release (FIGRA) from 388 to 37 kW/s (no FR), and smoke release from 39 to 3 m^2/s^2. The Construction Products Regulation classification was thus improved from D-S_2 to B-S_1. The authors conclude that PIN FR treated particleboard contributes very little to fire.

"Development and Prediction of Flame Retarded Particleboard Fire Behaviour in Real Scale", T. Suoware et al., NIJOTECH, Vol. 40, No. 4 July, 2021, pp.558 – 563 http://dx.doi.org/10.4314/njt.v40i4.10

Recycled PIN FRs from flue gas cleaning

Magnesium and aluminium minerals from coal power plant flue gas scrubbing can be recycled as PIN flame retardants. The 1 400 MW coal power plant, Nantong, Jiangsu, China, operates lime/gypsum flue gas desulphurisation (FGD), with an objective of zero liquid discharge. In this study, the FGD wastewater was treated in five stages with lime, sodium hydroxide, $NaAlO_2$ and $NaHCO_3$ to stepwise remove and separate heavy metals, calcium sulphate (gypsum), calcium carbonate, magnesium dihydrate (MDH) and ettringite (a calcium aluminium sulphate mineral $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$). Gypsum can be recycled to the construction industry and calcium carbonate reused in desulphurisation. MDH and ettringite were soak-washed and analysed, and showed to have purity and particle size compatible with use as PIN flame retardants (particle size mostly 1 – 10 µm). Tests in EVA showed that 10% recovered MDH + 20% ettringite increased LOI from around 15 (neat EVA) to around 25.

"Recovering chemical sludge from the zero liquid discharge system of flue gas desulfurization wastewater as flame retardants by a stepwise precipitation process", J. Guo et al., J. Hazardous Materials 417 (2021) 126054 https://doi.org/10.1016/j.jhazmat.2021.126054



PIN FRs reduce smoke and toxicity

APP with bio-based cobalt phytate reduce heat release, smoke production, density and toxicity from polyurethane foam. The recognised workhorse PIN flame retardant, ammonium polyphosphate (APP), was dosed at 33% loading in polyurethane rigid foam during foaming reaction, and at 27% with 6% cobalt phytate (a commercially available metal salt of bio-sourced phytate, a phosphorus-rich molecule found in plant seeds). The phytate improved compatibility of APP with the foam and improved foaming, possibly by reacting with isocyanate. APP showed peak heat release 34% lower than neat polyurethane, and APP + cobalt phytate 43% lower. APP alone had little impact on smoke, whereas APP + cobalt phytate reduced total smoke production by 42%.and maximum smoke density by 27%, as well as significantly reducing emissions of the toxic gases carbon monoxide and hydrogen cyanide. Analysis showed that the cobalt phytate improved the density and graphitisation of the char layer.

"Effect of ammonium polyphosphate/cobalt phytate system on flame retardancy and smoke & toxicity suppression of rigid polyurethane foam composites", B. Zhang et al., J. Polymer Research (2021) 28:407 https://doi.org/10.1007/s10965-021-02763-z

OTHER NEWS

Study suggests PBDEs fed to mother mice can cause brain modifications in offspring. Penta-BDE was fed to mother mice at 0.4 mg/kg body weight per day (orders of magnitude higher than general human population exposure). PBDEs were transferred to offspring both in utero and in lactation and resulted in modifications in brain chemistry and in behaviour of offspring, including modifying social recognition and object memory, but not impacting anxiety or depressive behaviour. Media coverage suggests that such changes are comparable to symptoms of ASD (autism spectrum disorder).

"Persistent autism-relevant behavioral phenotype and social neuropeptide alterations in female mice offspring induced by maternal transfer of PBDE congeners in the commercial mixture DE-71", E. Kozlova et al., Archives of Toxicology, 2021 https://doi.org/10.1007/s00204-021-03163-4

"Study shows flame retardants cause brain changes in mice offspring", California News Times, 5th November 2021 https://californianewstimes.com/study-shows-flame-retardants-cause-brain-changes-in-mice-offspring/582884/

Leaching of FRs from recycled ABS plastic in birds' digestive fluids. Recycled ABS was obtained from a plastic producer in China. Levels of individual FRs analysed in the ABS were highest for BTBPE at 1.8 mg/kg, with DecaBDE (BDE 209), several other brominated FRs and TPHP and EHDPP also around 1 mg/kg. Results showed that lipophilic FRs had a higher tendency to migrate out of the plastic, in particular BDEs, BTBPE and DBDPE. This could be related to affinity to bile salts and enzymes in birds' digestive fluids.

"The leaching of additive-derived flame retardants (FRs) from plastics in avian digestive fluids: The significant risk of highly lipophilic FRs", H. Guo et al., J. Env. Sciences 85 (2049) 200-207 https://doi.org/10.1016/j.jes.2019.06.013

PUBLISHER INFORMATION

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For abbreviations see: www.pinfa.org