Your newsletter for non-halogen fire safety solutions

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pinfa — Phosphorus, Inorganic & Nitrogen Flame Retardants Association

AMI Fire Resistance in Plastics 2021

The 2020 AMI Fire Resistance in Plastics Conference, the principal annual industry event in Europe, was postponed and held online 23-25 February 2021. The online event attracted 140 attendees from 24 countries, of whom more than one third were compounders.

North America Fire Retardants in Plastics Virtual Summit, 4th – 5th May 2021 here.

The next European Fire Resistance in Plastics Conference will take place in Düsseldorf, Germany, 30th November 2021 – 2nd December 2021 here.

www.ami.international/conferences

Panel: the future for flame retardants

Addressing the real challenges of fire safety tomorrow and ensuring environment and health safety, including in recycling, showed as priorities in the panel discussion, organised by pinfa at the AMI (online) Fire Resistance in Plastics Conference, 23-25 February 2021. Panellists were from industry (pinfa, Clariant, ICL), science (French National School for Chemistry ENSCL at Lille, Masaryk University) and civil society organisations (ECOS).

Opportunities and challenges

Lein Tange, ICL Europe, underlined the global priority of climate change. For flame retardants, the greenhouse gas emissions related to production are negligible compared to the product use phase, for example energy savings from insulation materials, lightweight materials or e-mobility. Such applications pose new fire safety challenges which must be addressed, whilst ensuring sustainable end-of-life solutions for flame retardant containing materials. He noted that new substances continue to be added to the SVHC (Substances of Very High Concern) list, for example discussion is ongoing on titanium dioxide (a pigment, not an FR) which is widely present in many plastics, meaning that a material which is recyclable today may not be tomorrow.

Sophie Duquesne, ENSCL Lille, France, suggested that key questions for the future of flame retardants are end-of-life and recycling, the demand for fire safety in the global energy transition (especially building energy savings, e-mobility) and the need to develop efficient fire testing which is representative of reality (scaling up of laboratory test results)

Samy Porteron, ECOS (European Environmental Citizens Organisation on Standardisation), emphasised the importance of the Circular Economy, posing a challenge and opportunities for industry. Flame retardants in plastics are difficult to separate from the polymer and so flame retardants included in a material can, through recycling, find their way into other products, not intended to contain them, in the future. Flame retardants now banned can thus still be found in consumer products ("legacy" substances). Fire safety is a real issue requiring solutions, but we need to find solutions which do not create future problems, for health, the environment and the economy. Flame retardants can leach out of products and contribute to cocktails of chemicals with health risks which we do not today understand.

Fire testing standards should be robust and as close to reality as possible. Fire safety solutions which are sustainable for health and the environment are essential and should include basic fire safety principles and safety-by-design.

Franck Poutch, Crepim, France, also emphasised the demand for flame retardant solutions to ensure fire safety in building insulation and e-mobility. The development of bio-based polymers and use of renewable materials (timber, fibres) means more flammable organic materials in buildings and in their contents, requiring flame retardants. The development of flame retardant solutions integrated into the polymer matrix can improve environment and health safety, but can be an obstacle to recycling.

Sebastian Hörold, Clariant, underlined that in addition to fire safety, environment and end-of-life requirements, flame retardants must not deteriorate the mechanical or electrical performance, or the durability, of materials. E-mobility brings new technical demands for flame retardants, in applications such as high-voltage connectors, batteries, vehicle chargers, with demanding requirements such as smoke opacity. Developing state-of-the-art, environmentally safe flame retardants has a cost.

FRs, plastics additives and recycling

The panel discussed how to enable recycling despite the wide range of different additives (of which flame retardants are just one type) in plastics and textiles:

Adrian Beard, for pinfa, indicated the potential interest of chemical markers to enable identification of materials. Further research is needed to address e.g. mixing of markers in recycling. Identification of additives poses questions of formulation confidentiality, but this can be addressed by a non-quantitative list of ingredients (not detailed "recipes"). pinfa is working to develop R&D proposals and dialogue with downstream industry (FR users, compounders, polymers industry …) on possible solutions, but this needs to be taken forward across industry because FRs are only one of many technical additives concerned.

Lisa Melymuk, Masaryk University, Czech Republic, suggested that information on chemicals in product parts can be provided by bar codes and an online data base to enable inclusion on small parts.

Sophie Duquesne, ENSCL, notes that some contaminants in recycled materials may impact the performance of flame retardants and other additives

Lein Tange, ICL Europe, suggested that new recycling technologies can bring solutions, because "legacy" contaminants are eliminated. Full-scale demonstration sites should be developed, like the PolyStyreneLoop industrial pilot. The challenges of logistics and of achieving economically viable quantities must be addressed.

ECOS has questions about the life cycle analysis of chemical recycling: more information is needed on the energy balance and so climate emissions, and on the level of sorting needed for the input waste streams.

Adrian Beard, pinfa, notes that 40% of WEE plastics are "small volume" speciality polymers. Work engaged by pinfa with Fraunhofer LBF (see pinfa Newsletter n°105) show that the principal obstacle to material recycling, after logistics (separation, collection), is deterioration of the polymer in re-extrusion, not the flame retardant. New formulations and corrective additives are needed to address this.

Environmental safety of flame retardants

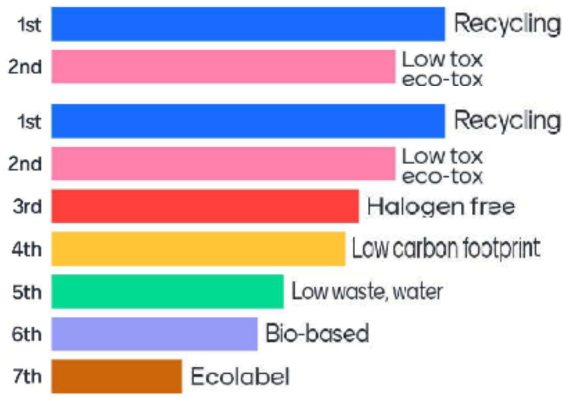
Lisa Melymuk, Masaryk University, Czech Republic, notes that currently three families of chemicals stick out looking at toxicology indicators: PFAS (perfluorinated chemicals), phthalates and the older brominated flame retardants such as PBDEs, HBCD. Phosphorus-based and other non-halogenated flame retardants have received less attention so far. The toxicological and environmental science is behind today's market and is still working on the brominated flame retardants used in the past because they are very persistent in the environment whereas there is a need for more environmental research into new flame retardants.

Samy Porteron, ECOS considers that, today, information on chemicals present in products (articles) is inadequate and does not allow traceability along the value chain, resulting in problems for recycling. This will be partly addressed by the ECHA SCIP database (Chemicals of Concern in Products, see pinfa Newsletter n°119), where companies must declare all products containing >0.1% w/w of any chemical on the REACH Candidate List of SVHCs, as required by the revised Waste Framework Directive.

Adrian Beard, pinfa, recognises that it is a challenge to release confidential toxicity data held by companies concerning their products because the data was generated at high cost and so companies are reluctant to share e.g. with competitors.

Needs and trends for tomorrow's FRs

Mentimeter input from Conference delegates during the pinfa panel discussion



Which needs or trends do you see for FRs?

Sustainability and recycling potential.
Environmentally friendly.
Biodegradable.
Halogen-free, to avoid future legacy chemicals.
Address toxic emissions during burning.
Low smoke Life cycle analysis.
Char promoters and low hazard FR synergists.
Bio-based FR additives.
Zero hazard statements on MSDS is goal.

Recycling.
Cost acceptability for Circular Economy.
Recovery of FR additive in recycling.
Recycling of mineral filled materials.
Need for funding of recycling.
Better information on additives in materials.

Cost and performance.
Cost - performance ratio, with recyclability.
Cost-competitive halogen-free.
Effective without compromising mechanical properties.
Efficient at lower loadings.
CTI levels higher than 600V.
Good easy processing, heat stability.
Heat stability.
Low acid, non-corrosive.

Standards.
Unify fire standards between different regions.

Round robin testing at small and application scales. *Mentimeter input from Conference delegates during the pinfa panel discussion*

New chemistries and applications.
Polymeric FRs, intrinsically FR polymers, FRs reacted or integrated into polymer: not additive, to avoid offgassing and leaching.
Halogen free solutions, e.g. for styrenics.
R&D on synergies between FR combinations.
Thermal conductivity.
Hydrolic stability.
New technologies: electric vehicles, 3D-printing.

Information.
Risk assessment of FR use versus non-use.
More complete data time of product life cycle.
More complete MSDS risk information.

What should the FR industry do ?

to demonstrate safety of their products? and fitness for circular economy?.

Develop R&D projects, collaborate.
Define joint industry policies.
Green Screen benchmark.
Eco labels.
Make hazard and toxicity data available.
Include long-term toxicity data in REACH dossiers (beyond minimum requirements).
Recycling studies and demonstration.
R&D into recovery of FR additives from wastes.
Chemical recycling tests with non-halogen FRs.
Collaborate with downstream users, R&D, on recycling.
Promote use of recyclates.
Research FR leaching and losses from products.
Transparency and patenting of FR chemicals (molecular formulae) .
Improve information on plastic material composition and additives.
Traceability of FRs in articles.
Communication to the public on benefits of FRs and environmental impacts

FLAME RETARDANT TRENDS

Flame retardant trends

R&D trends show performance synergies from combining PIN FRs, and new PIN FR systems for performance HFFR cables.

Günter Beyer, Fire and Polymer, presented his view of key new flame retardant research in 2019 and 2020. He summarised three papers (below, Seidi, Yan, Li) and other research concluding several trends:

- Development of the "Flame Retardancy Index", providing an indication of fire performance based on several different parameters (see Vahabi et al. in pinfa Newsletter n°111).
- Synergies between several PIN FRs increase fire protection, so enabling lower FR loading and so reduced impact on mechanical performance
- Development of nano-composite PIN FRs to for HFFR (Halogen Free Flame Retardant) cables achieving CPR B2 fire classification
- Combinations of modified intumescent PIN FRs, modified clays, nano silica compounds (e.g. Yan et al.)
- Ceramifiable polymer composites, combining PIN FR, synergists, silicate and fluxing agent, enabling high-temperature, high performance materials.

https://gbeyer.tripod.com/

Synergy of PIN FRs in polypropylene

Research review shows that synergies between PIN FRs in polypropylene can combine fire safety and material performance.

Seidi, Vahabi et al. assessed data on fire performance of flame retardant propylene formulations from some 150 publications, considering PIN FRs only. For each data point (formulation), the FR or FR combination, and loading are specified, and test results are indicated (as available) for time to ignition (TTI), peak heat release rate (pHRR), total heat release -THR), irradiance, LOI, sample thickness and UL-94 result. Where sufficient data is available, the dimensionless "Flame Retardancy Index" (FRI) is derived (as defined in Vahabi et al. 2019, see pinfa Newsletter n°111, combing TTI, THR, pHRR).

The authors conclude that phosphorus PIN FRs generally achieve Good FRI, and some specific phosphorus compounds achieve Excellent. Two nitrogen-phosphorus PIN FRs also achieve Excellent. Mineral and bio-based PIN FRs can also achieve Good FRI, depending on particle size and dispersion for minerals.

Combinations of PIN FRs show the best FRI, with many combinations achieving Excellent at intermediate loadings (25-30% w/w). PIN FRs generally also achieve UL94-V0.

Analysis of data showed that combining PIN FRs increased effectiveness for the same dose, compared to use of a single FR, showing the interest of synergy effects in enabling fire performance whilst limiting impact on material mechanical performance.

"Flame Retardant Polypropylenes: A Review", F. Seidi, H. Vahabi et al., Polymers 2020, 12, 1701; https://dx.doi.org/10.3390/polym12081701

PIN FR synergy for epoxy

PIN FR solutions with phosphorus, nitrogen organo-clay and nano-silica enables UL94-V0 in epoxy at 30% loading.

The authors tested a PIN combination of organically modified sodium montmorillonite (OMMT), amino-functionalised nano silica (nano-silica) and intumescent PIN FR (IFR: ammonium polyphosphate, melamine and pentaerythritol) in epoxy resin. In all cases, total PIN FR loading was 30% w/w. Optimal LOI (28% compared to 19% for neat epoxy), as well as IL94-V0 (4 mm) was achieved with a combination of all three PIN FR components: 27% IFR, 1.5% OMMT, 1.5% nano-silica. The authors conclude that well dispersed OMMT and nano-silica act in synergy to improve the performance of standard PIN intumescent flame retardant in epoxy, by facilitating formation of more compact and continuous char.

"Combination effect of organically modified montmorillonite and nano-silica on reducing the fire hazards of intumescent flame-retarded epoxy resins", L. Yan et al., J Vinyl Addit Technol. 2020;26:490–501, https://dx.doi.org/10.1002/vnl.21764

Ceramifiable FR polymers for fire safety

PIN FRs enable high fire performance HFFR cables which retain structure and water resistance in fire.

The authors review research and patents into PIN FR ceramifiable polymer-based compounds, in silicone-rubbers (cross-linked), styrene-butadiene rubber, ethylene, polyvinyl acetate, ethylene vinyl acetate, ethylene propylene diene, epoxy and wood materials. Formation of a ceramified surface layer in fire results in fire protection of the polymer substrate by a self-supporting ceramic char layer which is resistant to fire-fighting water spraying, and also inhibits melt dripping. Ceramisation is optimised by a combination of silicate compounds, which form ceramic matrices (both as additives or from the polymer in silicone rubbers), ammonium polyphosphate and magnesium hydroxide which react to form crystalline phases in fire, fluxing agents and synergists to facilitate reactions.

"Polymer-based ceramifiable composites for flame retardant applications: A review", Y-M. Li & S-L. Hu (Chongqing, China) and D-Y. Wang (IMDEA Materials Institute in Madrid), Composites Communications 21 (2020) 100405 https://doi.org/10.1016/j.coco.2020.100405

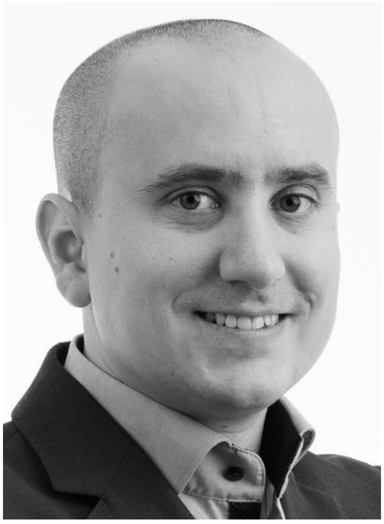
Lightweight PIN FR composites

Vacuum infusion composites with PIN flame retardants enable lightweight, performance components for transport systems.

Peter Kornas, Büfa, summarised innovation in laminate composites for transport. A combination of PIN FRs, in particular mineral intumescents and phosphorus PIN FRs, can be used in paint, gelcoat, sandwich bond, resins and fire-stop backing to achieve the most demanding railway fire and smoke specifications EN45545 R1, R7, R17, HL3, without halogens or antimony. Train parts, large and small, can be molded, such as bodywork, bumpers, interior and seat parts, with high strength, lightweight and rapid production. Production costs and emissions are lower than for HLU laminates (hand lay up), and more reliable. Büfa is also opening the market for fire-safe laminates for bus and coach parts, despite the current absence of fire safety requirements: laminates currently used can reach heat release of 500 kw/M^2 in tens of seconds and are completely burnt in minutes. Other future tendencies include water-based paints (posing challenges for intumescent FRs), conductive mods and electrostatic spraying of gelcoats and recycled materials.

See interview of Peter Kornas at FRiP2018 in pinfa Newsletter n°98.

https://www.buefa.de/en/composites/

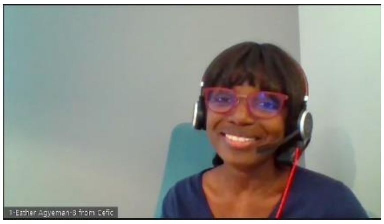


Bespoke performance organo-mineral FRs

Ivan Kotek, Funzionano, presented the company's range of silicon-containing POSS (polyhedral oligomeric silsesquioxane) PIN FRs, developed with Norwegian research centre SINTEF. These are highly-branched nano-polymers in which the organic group can be modified to design specific compounds adapted to different polymer matrices and for different customer applications. These organo-mineral FRs are free of any hazard labelling and can replace halogenated FRs and ATO (antimony tri oxide), in synergy with other PIN FRs, particularly in polyethylene, polypropylene, polyurethane, rubbers. Examples of applications shown, with fire test results, included in polyurethane (peak heat release halved with POSS, pass for EN-ISO 11925-2 30s flame), in glass fibre unsaturated polyester, with ATH and peroxide, again passing EN-ISO 11925-2, in vinyls and epoxies, offering self-extinguishment and reduced flame spread.

https://funzionano.com/

FLAME RETARDANTS AND PLASTICS RECYCLING



PIN FRs are the future for plastics recycliFlame ng as they avoid halogens or antimony in tomorrow's waste and recycling

Esther Agyeman-Budu, pinfa Manager at Cefic, and Adrian Beard, pinfa Chairperson (Clariant), outlined EU policies and challenges for plastics recycling, and implications for flame retardants. The EU Plastics Strategy (2018) states that 250 million tonnes per year of plastics are produced in Europe, but only one fifth are today recycled. The EU has fixed a recycling objective of 65% of plastic in municipal waste by 2030, but the objective for WEEE recycling (waste electronic and electrical equipment) is higher: 65% of equipment placed on the market and 85% of end-of-life WEEE. An important obstacle to recycling is cost, of collection logistics and reprocessing, often more expensive than virgin plastic.

To ensure that flame retardants, and other plastic additives, do not become obstacles to recycling, FRs should be compatible with recycling processes, and importantly must be safe for health and the environment, in order to ensure that their presence in future generations of recycled materials is accepted. Sustainability assessments can support such design for recycling, including independent labels such as TCO, which has a "white list" of accepted (all PIN) flame retardants (see pinfa Newsletter n°123).

Plastics recycling will necessitate collaboration throughout the value chain and a range of solutions including mechanical recycling, innovative sorting supported by design-for-dismantling and material identification and tracking, new additives and formulations to improve performance of recyclates, and chemical recycling for difficult-to-separate mixed materials. Flame retardants are only one factor impacting plastics recycling, along with polymer selection and other plastics additives. pinfa has carried out intensive testing of mechanical recycling of PIN FR plastics (see pinfa Newsletter n°105) and will cooperate with the value chain to support plastics recycling.

In discussion with conference delegates online, the challenge of information on additives in plastics was raised. pinfa suggested that transparency and tracking of additives in plastic parts should be ensured, but without revealing precise formulations which is commercially confidential information.

PIN FRs TO MAKE TOMORROW'S TRANSPORT SAFE

Flame retardants in e-mobility

Rapid growth of e-mobility requires specific flame retardant materials to ensure safety with batteries and high voltages.

Sebastian Hörold, Clariant, outlined potentials and challenges for PIN flame retardant plastics in electric vehicles. Power battery prices are falling continuously, and are now ten times lower than ten years ago, offering e-vehicle ranges of around 600 km. However, this stored electrical energy and high-voltage charging and drive transmission pose fire safety challenges.

Properties such as UL94-V0 (increasingly down to 0.4 mm and after ageing), laser marking and welding, low blooming and no mould deposits are required in e-vehicle materials as in current vehicle performance applications. PIN FR polymers can already achieve this. New requirements for e-vehicles include however electrical performance (CTI 600V and higher), low hydrolysis and no acid / halogen leaching.

Phosphorus PIN FRs in polyamides demonstrate high performance, good colour (e.g. e-vehicle high voltage safety orange), and new tests show that fire performance UL94, afterburn and CTI are maintained after heat and humidity ageing. Trials also show that PFR polyamide can offer better laser transparency than bromine – antimony polyamide.

https://www.clariant.com/en/Business-Units/Additives/Flame-Retardants

New phosphorus PIN FR for e-mobility

Adeka new liquid phosphorus ester to combine fire resistance and mechanical performance for e-vehicle materials.

Yohei Inagaki, Adeka, explained how PIN FRs can respond to new, demanding requirements for electric vehicles. Vehicle manufacturers are looking for lightweight combined with strength, and are demanding UL94-V0 fire performance at low thickness (0.4 mm). Increasing FR load can deteriorate mechanical performance and heat deflection temperature. Adeka have developed a new, bis-phenol free phosphorus ester to respond to these demands. It is a viscous liquid with high thermal stability, facilitating processing at higher temperatures, offering well balance flame retardancy and heat deflection temperature. Another demand is to have no loss of fire safety when recycling. Five times multiple re-extrusion of PC/ABS was tested comparing this Adeka PIN FR to bisphenol-A bis(diphenyl phosphate), in both cases with PTFE as anti-dripping agent. This showed that UL94-V0 dropped to V2 as flaming dripping increased. This was probably related to deterioration of the polymer and/or the anti-dripping agent in recycling and could be resolved by adding c. 0.1% of anti-dripping agent when re-extruding..

https://www.adeka-pa.eu/specialty-additives/flame-retardants

Fire safety in public transport

Eurotec see non-halogenated FRs as necessary for low toxicity - low smoke public transport and for sustainability.

Buket Turan, Eurotec Engineering Plastics, explained that plastics enable weight reduction (so energy efficiency) in transport applications, as well as noise reduction and design flexibility. However, their flammability means that fire risk must be addressed using flame retardants.

The leading cause of death in public transport fires is smoke toxicity, in particular because of carbon monoxide. Fire standards limit smoke toxicity and smoke density, e.g. the European railway standard EN45545, UK underground BS6853, aviation FAR 25.853. Non-halogenated flame retardants enable to achieve these

Eurotec has developed specific HFFR (halogen-free flame retardant) formulations, in e.g. polyamide or polycarbonate, to meet public transport fire performance standards (including UL94, horizonal and vertical burning, burning dripping), low weight, mechanical performance and stress resistance, aesthetic quality, as well as low smoke density, low smoke toxicity standards.

For Eurotec Engineering Plastics, the sustainability advantages of non-halogenated flame retardants also make them tomorrow's solution in e-mobility and consumer applications.

PUBLISHER INFORMATION

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