pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 111 February 2020

PINFA NEWS

New pinfa member: Grolman

Grolman is a leading international distributor and business development partner in speciality chemicals, present in 40 countries and providing a range of performance materials, additives, fillers, pigments, binders, and flame retardants to Industries including, amongst others: plastics & rubber, wires & cables, paints & coatings, adhesives & sealants, composites, batteries, personal care. Grolman is committed to sustainability, by providing fire safety solutions pursuing health and environmental protection. Grolman delivers integrated and synergistic solutions to customers, and works in long-term partnership with suppliers, especially for PIN flame retardants and their applications, ranging from mineral FRs to expandable graphite. For Grolman, pinfa membership offers an excellent opportunity for networking with most of the leading flame retardant specialist companies, a platform for working together on projects and for information on global developments, including safety and regulations.

https://www.grolman-group.com/ Photo: Grolman's coatings laboratory in France.

Roger Avakian for SPE "Fellow Award"

Roger Avakian, of Avakian Polychem Consulting, will be awarded the prestigious Society of Plastics Engineers (SPE) "Fellow Award" at SPE ANTEC 2020, recognising contributions to the plastics industry. A total of fewer than four hundred plastics professionals have been awarded this honour over some thirty years, so it is a major achievement. pinfa-na (pinfa North America) is proud to have a "Fellow Award" amongst its members, and is grateful for the significant input Roger Avakian has made to pinfa-na since its launch, and continues to make today. Roger is currently coordinating for pinfa the preparation of a first training course in "Non-halogenated Flame Retardant Formulation" at Case Western Reserve University in Cleveland, Ohio USA on 19-20th October 2020.

pinfa-na Non-Halogen Flame Retardant Formulator's Workshop: Two Days of Class and Hands-on Demonstrations, 19-20 October, Cleveland, Ohio: https://www.pinfa-na.org/pinfa-formulator-workshop

ANTEC 2020: https://www.4spe.org/i4a/pages/index.cfm?pageid=3697

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REGULATORY AND COMMUNICATIONS

Washington consultation on "priority products"

Following on from the consultation on defining "priority chemicals" in 2019 (see pinfa Newsletter n°108), the State of Washington has now opened **to 2nd March 2020** a consultation on "priority products". This follows from the State's law RCW 70.365 "Safer Products for Washington" adopted Spring 2019 (Senate Bill 5135) which identifies organo-halogen flame retardants [and other flame retardants identified by the Washington State Department of Ecology] as one of five classes of "priority chemicals". The current consultation somewhat unclearly refers often simply to "flame retardants", but seems to target organ-ohalogen flame retardants. The consultation proposes "Electric and electronic equipment (device casings)" as "priority products" for flame retardants, citing as possible concerns exposure of children, workers in occupations involving electronics and sensitive species. Under "safer alternatives", it is indicated that flame retardants other than organo-halogens can be used (RDP is cited), or "using metal casings or removing the electronic source from the casing".

Washington State public consultation on "Safer products for Washington implementation phase 2", identification of "priority products", open to 2nd march 2020
https://ecology.wa.gov/ToxicsInProducts

PIN FRs maintained on TCO accepted list

TCO, the health, environment and worker protection label for office and home electronics, has updated its list of "alternative safer substances" to now include 14 PIN flame retardants, including mineral FRs (ATH, MDH), nitrogen FRs (melamine polyphosphate) and phosphorus FRs. Five PIN FRs were the object of a TCO request for dossier updates last year, and are now retained on the list following submitted information (TCO list as updated 5th November 2019). TCO inclusion on the "accepted substance list" is based on GreenScreen (recent assessment report, benchmark 2 or higher).

TCO "Safer alternatives to hazardous substances listed here", updated 5/11/2019
https://tcocertified.com/accepted-substance-list/

US defines fire standards for mass timber construction

The state of Utah and the city of Denver, Colorado, have taken the lead in introducing mass timber into its Building Code, as of 2020. Mass timber is defined as the use of large, solid wood panels for wall, floor and roof construction. New specifications for mass timber fire safety are included in the 2021 IBC (International Building Code), with different specifications for buildings of over 9, 12 or 18 stories, ranging from gypsum board covering of mass timber up to a two hour fire resistance requirement. The move by Denver was welcomed by the American Wood Council (AWC)

"Denver adopts tall mass timber codes", 7th January 2020
https://www.constructionspecifier.com/denver-adopts-tall-mass-timber-codes/

"AWC Commends Legislation on Tall Mass Timber" (Utah) 27th March 2019
https://news.thomasnet.com/companystory/awc-commends-legislation-on-tall-mass-timber-40022759

AWC summary on "Tall Mass Timber" https://awc.org/tallmasstimber

reThink Wood brochure on "Mass timber in North America"
https://www.awc.org/pdf/education/des/ReThinkMag-DES610A-MassTimberinNorthAmerica-161031.pdf

US heads for minimal national furniture fire standards

The US Congress voted on 17th December 2019 the "Safer Occupancy Furniture Flammability Act" (SOFFA, H.R.2647). This must now pass the US Senate. If the bill is finally adopted, then California Technical Bulletin 117–2013 would become a US federal standard for upholstered furniture. TB-117-2013 is a smoldering cigarette ignition test, which would be a very minimal fire safety requirement. The bill would pre-empt State legislation on fire safety of upholstered furniture. It would apply to furniture, including if intended for children, but not to bedding and mattresses. The bill is supported by the US furniture industry (the American Home Furnishings Alliance) which has consistently opposed stringent fire safety requirements for its products.

US Congress Bill HR2647 https://www.congress.gov/bill/116th-congress/house-bill/2647

MARKETS AND PRODUCTS

PIN FR polyamide for 3D-printing for e-mobility

Clariant has launched a range of glass fibre reinforced polyamides for 3D-printing which use phosphorus-based PIN flame retardants to achieve demanding fire performance and low smoke toxicity. A PA6 + 20% glass fibre formulation achieves a GWIT (glow wire ignition temperature) of 775°C @ 3 mm, and UL 94-V0 @ 0.4 mm and a PA6/66 + 20% glass fibre formulation meets the EU EN 45545-2 and North American NFPA 130 railway norms. Clariant showcased parts produced using these formulations through 3D-printing at Formnext. The 3D printer filaments are compatible with printers using enclosed or heated chambers. The materials are available in a range of colours and offer mechanical performance including low temperature use (-40°C), wear resistance, impact strength and stiffness and long-term stability to weathering.

"Clariant to present fire, smoke and toxicity compliant 3D printing material at Formnext", 14th November 2019 https://www.tctmagazine.com/3d-printing-news/clariant-fire-smoke-toxicity-compliant-3d-printing-material/ and "PA6/66-GF20 FR LS Using Exolit®" https://www.clariant.com/en/Solutions/Products/2019/03/08/15/39/PA666_GF20_FR_LS_3Dprinterfilament

First ever FR photopolymer for SLA 3D-Printing

The Austrian high-tech 2015 start-up Cubicure, a spin-off from TU Wien, has launched the first ever flame-retardant photopolymer for SLA (Stereolithography 3D-Printing process). Cubicure's proprietary 'Hot Lithography' technology enables additive manufacturing with high-molecular weight, high viscosity photopolymers with material properties comparable to injection molding and precision (resolution) up to 10 µm. The new Cubicure Evolution FR is non-halogenated flame-retardant, achieving UL94 V0-classification, opening markets such as spare parts for railway or electronics applications. Its mechanical performance includes high dimensional stability and for example heat resistance >70°C and a tensile strength >30 MPa. "First flame-retardant material for SLA" Cubicure 4 November 2019

http://www.cubicure.com/jart/prj3/cubicure/data/uploads/document/20191030_EvolutionFR_EN_final_cv_2019-11-04_1211392.docx

HEXPOL TPE reliable and durable FR cable compounds

The international polymer compounder HEXPOL TPE, specialised in thermoplastic elastomers, has launched new PIN FR materials for performance cable sheathing, with the objective of ensuring high standards of reliability and durability, customisation and easy processing, as well as low toxicity and smoke levels. The DRYFLEX® cable compounds are based on a range of polymers, including EVA, TPE and TPV (ethylene vinyl acetate, thermoplastic elastomers and thermoplastic vulcanizates). The LSZH (low smoke zero halogen) compounds are halogen-free according to IEC 60754 part 1/2. Compounds are available for low voltage, power, data and with specific requirements such as thermal and fluid resistance, and are adapted for applications such as high-rise buildings, aviation, railway, communication data centres, power generation and offshore. They can be processed with standard extrusion equipment, and post-vulcanisation is not required.

"HEXPOL TPE launch high-performance cable compounds", 12/12/2019
https://www.hexpoltpe.com/en/news.htm?id=440

Fire protecting the world's biggest mall

Over one hundred tonnes of non-halogenated flame retardant coating provided by AUDAX-Keck, Germany, with local partner Padena Hoor, will ensure fire protection of the steel structural elements of the world's biggest mall, the "Iran Mall", currently under construction in North Tehran. The mall, of more than one million square metres surface, will house over 3 000 stores, two hotels, a spa, conference rooms, other facilities and car parking. The spray-on RENITHERM intumescent fire protective coatings used are LEED certified and non-halogenated. They expand 30-50 times in volume with heat, and provide protection against for two hours, conform to demanding building safety regulations. They are non-corrosive, smooth finish and available in a range of colours.

"Fire protective coatings in the world's largest shopping mall", IFP (International Fire Protection) Magazine September 2018 https://ifpmag.mdmpublishing.com/international-fire-protection-issue-75-september-2018/?mc_cid=d130e3c1bf&mc_eid=225f09c9b7

PIN FR for interior wood achieves Greenguard Gold

Koppers, a specialist in wood treatment, wood products and carbon chemicals, has launched FlamePRO, for pressure treatment for fire safety of interior-application wood construction materials, plywood and timber. This market is estimated at 60 – 80 US$ million for the USA alone. The product meets UL Greenguard Gold standard (low VOC emissions) for use in schools, offices and other sensitive environments. FlamePRO achieves a Class A flame spread rating under ASTM E84, with no evidence of significant progression after an additional twenty minutes. Structural performance of FlamePRO plywood has been tested in accordance with ASTM D5516 (D3201) and lumber with D5564 (D6305) and for high temperatures for roof applications. The product contains no halogens.

"Koppers Performance Chemicals Introduces FlamePRO® To Serve Growing Fire Retardant Market", 4 September 2018 http://investors.koppers.com/phoenix.zhtml?c=194019 and http://www.koppersperformancechemicals.com/flamepro/flamepro-architectural.html

Growth predicted for flame retardants

New market studies continue to predict growth for flame retardant demand, particularly for PIN FRs.

Credence Research predicts 6.4% annual growth for the flame retardants globally to 2025, marginally higher than **DataMintIntelligence** (6.2% in pinfa Newsletter n°108), with particular growth in PIN FRs and in electrical & electronics, automotive and construction. Coherent with this, Industry Research predict 7.2% growth for PIN FRs worldwide to 2024, especially in E&E, driven by "rising awareness for eco-friendly FRs" and regulation obliging to move away from halogenated FRs. **Zion** estimated 8% growth (from 3 billion US$ in 2017 to 6.9 billion in 2024) for the global PIN FR market (pinfa Newsletter n°92). **ResearchandMarkets** estimated 6.2% growth from 2018 to 2023 (pinfa Newsletter n°96).

This FR market growth is reflected in **Lucintel's** predictions for the flame retardant plastics market, estimating a 4% growth to US$ 55 billion worldwide by 2024. Lucintel identifies as main growth sectors: E&E, construction, transportation, wire & cable, pipe & tank, aerospace & defence, and marine, with drivers being fire regulations, growing consumption of FR plastics in E&E and increasing demand for halogen free wire and cable. Also, **Transparency** estimates the FR masterbatch market will grow worldwide at 7% to US$ 1.8 billion by 2027, again with especially strong growth in E&E, and driven by fire regulations in construction and industry and electrical vehicles.

ResearchandMarkets estimates the global LSHF (low smoke halogen free) cable market will grow at 10.7% from 2019 to 2027 (from 2.5 to 6.4 billion US$), again driven by regulations on fire safety, especially in construction, in both developed and developing economies.

TrendsMarketResearch (TMR) on the other hand predict a 3.7% growth rate in volume for FRs worldwide 2018-2023. TMR however predict the global FR masterbatch market to grow 8% in value 2019-2027 (from US$ 1.8 billion), with E&E and cables, construction and electric vehicles identified as sectors leading growth. For PIN FRs, **DataBridgeMarketResearch** predicts growth of 8.4% for 2019-2026 (from US$ 4.31 billion 2018), driven by increasing regulatory requirements for both fire safety and "environmentally friendly" FRs. For PIN FR cables, **InsightPartners** predicts 10.7% growth for low smoke zero halogen (LSZH) cables 2019-2027 (from US$ 2.5 billion 2018), driven by new testing standards for cables smoke emission and toxicity and corrosion resulting from non-LSZH cables in case of fire. **Acumen** predict 4.9% growth 2019-2026 for intumescent coatings (to reach US$ 1.5 billion 2026), driven especially by passive fire protection of steel structures in the oil and gas industries.

CredenceResearch "Flame Retardant Chemicals Market By Type (Alumina Trihydrate, Antimony Trioxide, Phosphorus Flame Retardants, Brominated Flame Retardants), By End-Use (Automotive, Construction, Textile, Electronics, Aerospace, Paints & Coatings, Packaging) – Growth, Future Prospects And Competitive Analysis, 2017 – 2025"
https://www.credenceresearch.com/report/flame-retardant-chemicals-market

IndustryResearch "Non-Halogenated Flame Retardant Chemicals Market – Growth, Trends, and Forecast (2019-2024)"
https://www.industryresearch.co/non-halogenated-flame-retardant-chemicals-market-14244837

Lucintel "Flame Retardant Plastics Market Report: Trends, Forecast and Competitive Analysis" (2019-2024)
https://www.lucintel.com/flame-retardant-plastics-market.aspx

Transparency Market Research "Flame Retardant Masterbatches Market (Type: Brominated, Chlorinated, Organophosphorus, Antimony Oxides, Alumina Trihydrate [ATH], and Others; Resin: PE, PP, ABS, PS, PC, and Others; and End-use Industry: Automobiles, Building & Construction, Electrical & Electronics, Consumer Products, Packaging, and Others) - Global Industry Analysis, Size, Share, Growth, Trends, and Forecast, 2019 – 2027" https://www.transparencymarketresearch.com/flame-retardant-masterbatches-market.html

Research and Markets "Low Smoke Halogen Free Cable Market to 2027 - Global Analysis and Forecasts by Type; Insulation Material; Application", July 2019 https://www.researchandmarkets.com/reports/4825293/low-smoke-halogen-free-cable-market-to-2027

FIRE SAFETY

Bolton UK student housing cladding fire

A six-storey student residential building, The Cube, housing over 220 students, in Bolton UK, suffered a major fire on 15th November 2019. Fortunately, no major injuries or casualties were incurred. The fire is indicated to have started in a kitchen on the fourth floor, and to have spread rapidly through external cladding materials to the fifth and sixth floors. The cladding is said to be HPL (high pressure laminate). The Manchester Tab stated that the HPL cladding was not fire resistant because the building was just 16 cm short of the 18 metre "tall building" height for which requirements are applicable in the UK. Fire services are pushing for this limit to be reduced to 11 m, compatible with rescue ladders. Inside Housing stated that the cladding "probably" included a non fire retardant version of a polymer film, a product which is also available with fire retardant versions. If correct, this illustrates the problem that fire-protected materials are today available, but that architects or builders are choosing not to use them so putting life and property in danger, in this case because of the absence of applicable fire safety requirements.

"Bolton fire: combustible membrane pictured behind cladding on student halls"
https://www.insidehousing.co.uk/news/news/bolton-fire-combustible-membrane-pictured-behind-cladding-on-student-halls-64247

"Bolton Cube didn't have fire-resistant cladding because it was 16cm too short"
https://thetab.com/uk/manchester/2019/11/28/bolton-cube-cladding-45275

"Fire services to probe cladding role in Bolton blaze"
http://www.constructionmanagermagazine.com/news/fire-services-probe-cladding-role-bolton-student-b/

Fire losses in the USA

The US Fire Administration has published a 100-page report on fire losses in the USA, 2008-2017. Some 1.3 million fire incidents were reported to fire departments in 2017 resulting in 3 400 deaths, 14 700 injuries and 23 billion US$ financial losses. Although fire deaths fell considerably from 12 000 in 1974, they have been rising since their lowest level of 2 900 deaths in 2012. Over the last ten years (2008-2017) fire deaths per capita have increased by +2.4% and dollar losses per capita by +12%, whereas the number of fires -12% and the number of fire injuries -21% have decreased. Nearly 80% of fire deaths occurred in homes. One in seven fires attended by fire services involved vehicles. The report concludes that smoke alarms, sprinklers, strengthened fire codes public education and improved firefighter equipment and training have contributed to reduce the consequences of fires, but that fire deaths are now increasing, with the elderly particularly at risk, as well as certain types of population. Wildland fires are an increasing concern.

"Fire in the United States 2008-2017", US Fire Administration – FEMA National Fire Data Center (NFDC); November 2019 https://www.usfa.fema.gov/data/statistics/reports/fius_2008-2017.html

RESEARCH

Database shows variability of cladding fire performance

Data from 252 commercial fire tests in Poland (KRESNIK) was analysed (tests of 90 façade materials, some were tested three times, some fewer if failed). Façade

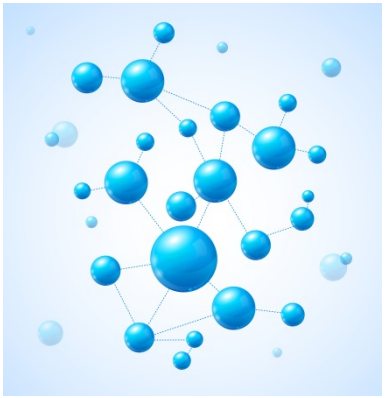
materials were tested to the standardised Polish PN-B-02867 test, in which a 20 kg wood crib is the fire source, 50 mm from the façade, with a 2 m/s airflow towards the façade. The material is mounted vertically, as it would be on a building, approx. 2m x 2m, depending on panel size. The authors classified the façade materials as 24 ETICs (external thermal insulating composite materials: a layer of insulation fixed to a substrate with a thin layer of external render), 21 sandwich panels (insulation between two substrates, usually metal), 38 rainscreen facades (multiple layers of insulation, vapour and weather control layers, usually with a cavity) and 7 other. None of the ETICs or sandwich panels failed the test, whereas 45% of rainscreens failed (pinfa comment: probably companies only presented materials expected to pass). The authors conclude that a cavity in the panels significantly impacts fire performance, as can different material layers. General categories of materials correlated to pass/fail, with (predictably) non-combustible (Euroclass A2) materials not failing. Flame retardant ACP (aluminium composite panel) and HPL (high pressure laminates) showed significant fail rates, but this could not be predicted by total fuel content nor by conductive resistance.

"KRESNIK: A top-down, statistical approach to understand the fire performance of building facades using standard test data", M. Bonner et al., Building and Environment 169 (2020) 106540 https://doi.org/10.1016/j.buildenv.2019.106540

Recycling FR boron from insulation to fertiliser

A R&D trial tested biochar, produced by pyrolysis at 600°C of boric acid flame retardant treated cellulosic insulation material (produced from recycled paper, Isocell Austria), as a boron fertiliser in pot trials with rape and sunflower. Such boron-treated flame retardant cellulose can be recycled as building insulation material only a few times because of deterioration in fibre length. The pyrolysis reduces the solubility of the boric acid, which is important because boron is a necessary micronutrient for plants, but is toxic if released too rapidly. Challenges to possible industrial implementation include collection of spent insulation material without contamination, PAH (naphthalene) levels in the biochar and regulatory status of the product (end-of-waste, fertiliser authorisation).

"Functional recycling of biobased, borate-stabilized insulation materials as B fertilizer", O. Duboc, J. Santner et al., Environ. Sci. Technol 2019, 53, 24, 14620-14629, https://doi.org/10.1021/acs.est.9b04234



DOPO – nitrogen – silicon FR for cotton

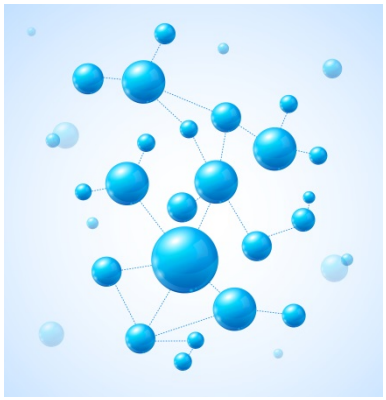
DOPO was reacted (in solvents) with piperazine (an organic compound containing nitrogen) and then with a chloro-silane compound, to produce a DOPO-N-Si molecule (not containing the chlorine): 1-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-4-(trimethoxysilylmethyl) piperazine (DOPO-PiP-Si). This was applied to cotton fabric (122 g/m^2) by dissolving the FR in solvent, adjusting pH to hydrolyse and then soaking the cotton (two dips), drying and then curing at 110°C, with 25 – 40% weight gain FR loading. LOI (limiting oxygen index) was increased from 18% to 25 – 28%, peak heat release rate was reduced by 30% and the treated cotton passed the vertical flammability test (GB/T 5455-2014). Analysis showed that this P-N-Si FR acted by both char formation and in the gas phase: in particular, ammonia release in "bubbles" both directly acts as a fire quenching gas and also carries phosphorus – silicon particles into the gas phase, where they act as radical inhibitors. The silicon also generates SiO_2 reinforcing char.

"Preparation of a synergistic reactive flame retardant based on silicon, phosphorus and nitrogen and its application to cotton fabrics", Z. Zhang et al., Cellulose, 2019 https://doi.org/10.1007/s10570-019-02900-4

Bio-based (vitamin B5) P - N FR for cotton

D-Panthenol (vitamin B5) is widely present in plants and animals, including in e.g. milk and soybean, and naturally contains both nitrogen and reactive OH groups. D-Panthenol was here reacted with phosphoric acid, without using solvents, to produce a phosphorus and nitrogen containing molecule: D-Panthenol-tri (methylphosphonic acid) (ADPTMPA). This was applied to 127 g/m^2 cotton fabric in water, with dicyandiamide as a catalyst to accelerate grafting, then cured at 180°C, to reach 20 – 40% FR by weight. Wash durability was tested by 50 laundering cycles (at 50°C, 45 minutes). Limiting oxygen index was increased from 19 (untreated cotton) to 47 (before laundry cycles) and 36 (after washing) and peak heat release rate was reduced by over 90% (before washing). Carbon monoxide release rate was also significantly reduced. Whiteness and gas permeability of the treated cotton were maintained, but the breaking strength was reduced by 31 – 34%, probably as a consequence of the curing temperature, but this is considered not significant for fabric applications. The authors conclude that this bio-based N-P FR acts by releasing non-combustible gases and by char generation and offers good performance and wash durability.

"Renewable vitamin B5 reactive N–P flame retardant endows cotton with excellent fire resistance and durability", C. Wan et al., Cellulose 2019 https://doi.org/10.1007/s10570-019-02886-z



Phytic acid - zirconium bio-based FR for epoxy

The zirconium-containing MOF metal organic framework UiO66 (University of Oslo Zirconium 1,4-dicarboxybenzene, a MOF known for its exceptional stability) was functionalised with an amine and with phytic acid (PA, which can be bio-sourced and contains 60% phosphorus), in a one-step synthesis. Both UiO66-NH_4 and PA-UiO66-NH_2 were tested as PIN flame retardants at 2, 5 and 10% w/w in epoxy resin (Epoxyhedraz C). 5% loading of the phytic acid + ammonia UiO66 achieved UL94-V1 (3.2 mm), whereas pure epooxy and even 10% ammonia (only) UiO66 in epoxy did not. 5% of the phytic acid + ammonia UiO66 also reduced both peak heat release and total smoke production by over 40% compared to neat epoxy. Emission of carbonyls and styrenes in burning were reduced compared to neat epoxy. The PA-UiO66-NH_2 also showed to increase cross-linking in the epoxy structure, resulting in a small increase in storage modulus.

"Green Synthesis of Biomass Phytic Acid-Functionalized UiO-66-NH2 Hierarchical Hybrids toward Fire Safety of Epoxy Resin", J. Zhang et al., ACS Sustainable Chem. Eng 2019 http://dx.doi.org/10.1021/acssuschemeng.9b05658

ATH effective as FR and smoke suppressant in epoxy

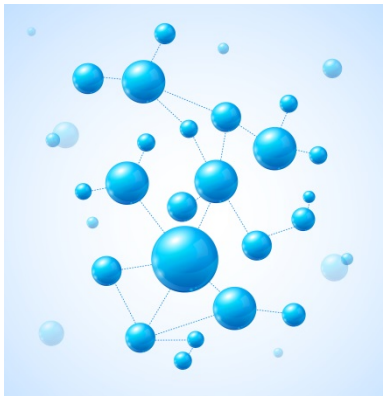
Aluminium tri-hydroxide (ATH) powder was tested at 0 – 15% loading in epoxy resin (E51) in 4 mm sheets. Peak heat release rate was reduced by nearly 30% by 15% ATH compared to neat epoxy, total smoke release was reduced by nearly 18% and carbon monoxide production rate reduced by over 30%. The FR and smoke suppressant effects of ATH are the result of release of water, which decreases flammable gases and inhibits combustion, and of the production of an Al_2O_3 film on the epoxy surface, improving charring, so reducing combustion and reducing smoke release. However, the 15% ATH loading caused a significant loss of mechanical performance of the epoxy (>50% reduction in tensile strength).

"On improving flame retardant and smoke suppression efficiency of epoxy resin doped with aluminum tri-hydroxide", G. Chai et al., Advanced Composites Letters, Volume 28: 1–12, 2019 https://doi.org/10.1177/2633366X19894597

Comparing smoke suppressants for APP – vinyl ester

Vinyl ester resins (VER) are polymers offering mechanical performance, temperature resistance, good processing and chemical resistance, used in applications including pipelines, electrical insulation, automobile and aviation. However, VER are highly flammable and generate problematic smoke and gases in combustion. Here different PIN smoke suppressants for the PIN flame retardant APP (ammonium polyphosphate) were tested at 80% VER / 20% APP and 75% VER / 20% APP / 5% suppressant, and were compared to 100% VER. The smoke suppressants tested were calcium carbonate ($CaCO_3$), zinc molybdate ($ZnMoO_4$), ferric oxide (iron III oxide Fe_2O_3) and cuprous oxide (copper I oxide Cu_2O). All of the APP or APP + suppressant formulations showed LOI (limiting oxygen index) improved by around one third and achieved UL94-V0 (3.2 mm). Peak heat release rate with APP only was <55% of neat VER, and was further reduced by the different suppressants, but to different extents, with the most effective being $CaCO_3$ (<31% of PHRR of neat VER), then $ZnMoO_4$, Cu_2O and Fe_2O_3 (51% of neat VER). $CaCO_3$ also gave the biggest reduction in smoke release (c. 10% lower than neat VER with APP only, around one third lower than neat VER with APP + $CaCO_3$. APP or APP + suppressants also reduced emissions of hydrocarbons, carbonyl compounds, esters/ethers and olefins. The authors conclude that, in VER with APP, calcium carbonate is the most effective of the four smoke suppressant synergists tested, and that it acts mainly by promoting dense, stable, anti-oxidation char.

"The Effect of Different Smoke Suppressants with APP for Enhancing the Flame Retardancy and Smoke Suppression on Vinyl Ester Resin", X. Zhang et al., Polymer Engineering and Science 2019 https://doi.org/10.1002/pen.25286



Hyphosphite PIN FRs for cotton

A research paper tests calcium hypophosphite (CaPi) and magnesium hypophosphite (MgPi) as PIN FRs for cotton fabrics, also with nano-particles of a clay and a silsesquioxane as synergists (sodium montmorillonite, octa-ammonium polyhedral oligomeric silsesquioxane POSS). CaPi showed slightly better flame retardant effectiveness (LOI 23 at 15% weight loading CaPi on cotton, compared to 21 with 14% MgPi and 18 for untreated cotton fabric). FR effectiveness was only very slightly further improved by replacing 10% of the CaPi by clay or POSS. The lowest heat release was 43% that of untreated cotton with 15% loading of 95% calcium hypophosphite / 5% POSS. FR effect is identified as resulting from char formation. The different PIN products used are water soluble, so wash durability would need to be addressed for these treatments to be useful.

"Thermal stability and flame retardant properties of calcium and magnesium-hypophosphite-finished cotton fabrics and the evaluation of interaction with clay and POSS nanoparticles", S. Furtana et al., Journal of Thermal Analysis and Calorimetry https://doi.org/10.1007/s10973-019-08751-2

Researchers propose "Flame Retardancy Index"

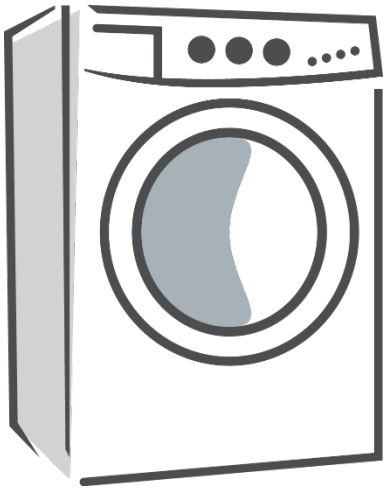
Several leading materials fire scientists have proposed a dimensionless "Flame Retardance Index" for flame retarded (compounds), based on cone calorimetry data: pHRR (peak heat release rate), THR (total heat release) and TTI (time to ignition). Each of these reflects a different aspect of fire performance. This is an extension of the "Fire Performance Index" proposed by M. Hirschler in 2017. The key paper (1) defining the index is based on over 100 data points from around 20 publications, covering four thermoplastic polymers (PP, PMMA, EVA, PLA) either neat or with

known and specified loadings of different PIN flame retardants. A second paper (2) assess nearly 900 data points from over 100 publications, covering these and other polymers, including epoxies, again neat or with flame retardants (in all cases PIN FRs). The "Flame Retardancy Index" proposed is calculated as THR x PHRR / TTI for [neat polymer / polymer with FR]. This Index, on a logarithmic scale, show to effectively differentiate compounds into three groups defined as Poor, Good and Excellent. The Index was then used (3) to model, then test, optimal combinations of phosphorus and mineral PIN FRs for EVA after compression molding (APP ammonium polyphosphate, CC calcium carbonate and ethylene vinyl acetate copolymer, respectively). The best Flame Retardancy Index was achieved with 15% APP + 5% CC, with limited reduction in mechanical properties, considered to be the result of synergy between the two PIN FRs in char formation, and optimisation of reduction of TTI by APP and reduction in total heat release by the mineral FR.

(1) "Flame Retardancy Index for Thermoplastic Composites", H. Vahabi B. Kandola M. Reza Saeb, Polymers 2019, 11, 407; https://doi.org/10.3390/polym11030407

(2) "Flame Retardant Epoxy Composites on the Road of Innovation: An Analysis with Flame Retardancy Index for Future Development", E. Movahedifar et al., Molecules 2019, 24, 3964; https://doi.org/10.3390/molecules24213964

(3) "Description of complementary actions of mineral and organic additives in thermoplastic polymer composites by Flame Retardancy Index", H. Vahabi, F. Laoutid et al., Flame Retardancy Index. Polym Adv Technol. 2019; 30: 2056– 2066 https://doi.org/10.1002/pat.4638



Wash-resistant P-N flame retardant for cotton

A phosphorus-nitrogen flame retardant for cotton was synthesised and tested, showing good washability without formaldehyde release, maintaining self-extinguishing (125 g/m^2 fabric) after 50 laundering cycles. Ammonium salt of tris-(hydroxymethyl)-aminomethane-penta(methylphosphonic acid) (ATPMPA) was synthesised in three steps, from the biological buffering agent tris-(hydroxymethyl)-aminomethane (THAM), urea, formaldehyde, phosphorus acid and phosphoric acid, then purified. Dicyandiamide was used as a catalyst to graft ATPMPA from aqueous solution onto the cotton at 14 – 26% by weight (3 hours at 70°C followed by 180°C for 6 minutes). The higher loading of ATPMPA increased LOI of cotton fabric from 18 to 44, and still 32 after 50 laundering cycles. The higher loading of ATPMPA reduced the breaking strength of the cotton by around 24%, possibly partly due to the baking at 180°C, but did not significantly deteriorate whiteness (12% decrease) and increased elasticity of the fabric.

"Synthesis of a phosphorus-nitrogen flame retardant endowing cotton with high whiteness and washability", C. Wan, Industrial Crops & Products 141 (2019) 111738 https://doi.org/10.1016/j.indcrop.2019.111738

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