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Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions n° 122 February 2021

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NEW MEMBER

RioTinto

20 MULE TEAM BORAX™

U.S. Borax joins pinfa North America

U.S. Borax, part of Rio Tinto, is a new member of pinfa-NA (pinfa North America). Borax is a global leader in the supply and science of borates: naturally occurring minerals containing boron and other elements. US Borax supplies 30% of the world's demand for refined borates from its mine in Boron, California, about 100 miles northeast of Los Angeles. Boron-based products are used in a variety of applications in agriculture, glass, ceramics, metals, industrial fluids, oil/gas, nuclear, wood preservation, cleaners/detergents and fire retardancy. U.S. Borax's line of zinc borate products are unique zinc borates that combine beneficial effects of zinc and boron oxides. They are multi-functional fire retardants for polymers and can be used in applications such as construction products, electrical/electronics, transportation (aviation and mass transit), fabrics and industrial coatings. By joining pinfa-NA, Borax will stay up to date on new fire retardant regulations and technological developments and be part of the halogen free FR community.

www.borax.com/firebrake

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FIRE SAFETY

Fatal fire probably started by cell phone

One child died in a house fire probably started by an overheating cell phone igniting a couch in North Carolina. Another child and the mother were injured. The fire occurred early in the morning and extensively damaged the house, which did not have smoke detectors. This incident shows again, tragically, the fire dangers of electronics, lithium ion batteries and upholstered furniture in our homes.

NFPA Journal November-December 2020 "Firewatch"
https://www.nfpa.org/News-and-Research/Publications-and-media/NFPA-Journal/2020/November-December-2020/News-and-Analysis/Firewatch

Review of electric vehicle (EV) battery fires

EV fires show heat release comparable to fossil fuelled vehicles, but with additional risks of toxicity and extinguishing. A review of over 170 publications provides an up-to-date summary on fire risks of batteries in electric vehicles, including photos of EV fires and analysis of several EV fire incidents. The authors suggest that fire safety concerns "stand in the way of the EV becoming the dominating transportation system". Battery fires can start during use, charging or simply whilst a vehicle is parked, due to electric faults, and can be caused by road accidents or by fire starting elsewhere in the vehicle or nearby. The authors note that the combustion energy of plastics in a modern petrol engine car is two to four times higher than that of the petrol. A burning battery can release five to ten times more energy than its stored electrical energy, and maybe over twice the energy from a full fuel tank of petrol in a car with similar milage range. The heat release rate shown in fire tests of EVs is similar to that of diesel or petrol cars, but battery fires can release toxic gases, flame jets (due to pressure build up in the battery case), and are harder to suppress because of the propensity for reignition. They note that extinguishment could be improved by enabling direct application of suppressants into the battery pack, but this is not possible with current EV design. The authors also note the risks of battery fires in end-of-life battery management. A detailed report on battery fires was also published by RiSE in 2019.

"A Review of Battery Fires in Electric Vehicles", P. Sun et al., Fire Technology, 56, 1361–1410, 2020 https://doi.org/10.1007/s10694-019-00944-3

"Fire Safety of Lithium-Ion Batteries in Road Vehicles", R. Bisschop et al., RiSE Report 2019:50 (106 pages)
https://doi.org/10.13140/rg.2.2.18738.15049

Fire risks posed by batteries in WEEE

"Battery fires are one of the most important issue impacting recyclers currently" E. Katrakis, EuRIC (European Recycling Industries Confederation). A report by recycling industry experts and industry federations says that occurrence of fires in electrical waste collection and treatment are increasing, mainly caused by damaged batteries. The WEEE Directive 2012/19/EU (Annex VII) states that batteries have to be removed from separately collected WEEE. Although fires are often small, over a third of participants confirmed having suffered at least one major fire. Costs are estimated at 200 000 to 1.3 million € per fire, with possible costs over long time periods for clean-up and depollution. Over a third of participants reported increased insurance costs for handling WEEE. The report concludes that lithium-ion battery-caused fires in WEEE are an EU-wide issue, which are expected to increase with increasing battery use, and which could be a threat to EU WEEE recycling objectives.

"Characterisation of fires caused by batteries in WEEE. Survey results from the WEEE management chain – part A", 2020 a report by EuRIC and the WEEE Forum with the active contribution of experts from various organisations including ecosystem, a PRO in the WEEE Forum, and the co-signatories namely EERA, EUCOBAT, MWE (Municipal Waste Europe), WEEELABEX. Full report here https://weee-forum.org/wp-content/uploads/2020/05/Report_Characterisation-of-fires-caused-by-batteries-in-WEEE.pdf

WEEE Forum news https://weee-forum.org/ws_news/characterisation-of-fires-caused-by-batteries-in-weee/

EU project on fire safety statistics

Efectis launches EU-funded initiative towards coherence of EU fire safety statistics, terminology and methodologies. This project results from an EU Parliament motion voted in 2018 (see pinfa Newsletter n°95). The aim is to map terminology and fire data collected by EU Member States, including on consequences of fires, and to propose common approaches, in order to develop a meaningful EU data system. The project launch webinar took place on 26th February 2021.

EU Firestat project: https://eufirestat-efectis.com/

Project consortium: Efectis, IFV, CTIF, NFPA, DBI, VFDB, BAM, the European Fire Safety Alliance, The University of Edinburgh and The University of Lund

FLAMMABLE CLADDING

UK taxpayers' cladding bill reaches £ 5 bn

More than UK£ 5 billion to replace flammable building cladding, announced by the UK Government may still not be enough. The UK has promised a further £ 3.5 bn funding to help owners remove non fire safe cladding materials from buildings > 18m high, adding to £ 1.6 bn already allocated (pinfa Newsletter n°116). Many flat-owners face huge bills for fire-safety improvements resulting from inspections launched after the Grenfell fire, 2017. Campaigners say that the £ 5.1 bn funding announced to date is still inadequate, does not help owners in buildings lower than 18m and does not address other fire-safety work needed, such as non fire safe wooden balcony materials (see Barking De Pass fire in pinfa Newsletter n°103) or missing fire breaks. The new funding aims to limit flat owners' payments to "only" UK£50 per month (but for how many years?) and will be funded by a new tax on new high rise buildings and a new tax on all UK residential property. This demonstrates the huge cost of using non-conform and non fire-safe materials in construction.

The UK Government has also announced UK£ 10 million to establish of a new regulatory body, within the OPSS (Office for Product Safety and Standards) to "encourage and enforce" compliance with construction fire safety requirements.

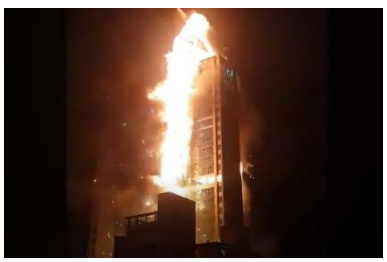
"Cladding: Extra £3.5bn for unsafe buildings 'too little, too late'", BBC, 10 February 2021 https://www.bbc.com/news/uk-56013464

"Grenfell: New body to ban dangerous building materials after inquiry", BBC, 19 January 2021 https://www.bbc.com/news/uk-55722159

More Grenfell Inquiry media questions

The Grenfell fire inquiry is continuing to question information supplied to customers by cladding manufacturers. As indicated in pinfa Newsletter n°121, input to the inquiry has suggested that one product used on Grenfell Tower may have been sold as fire Class 0 based on tests of a different version. Input to the inquiry has now suggested that three different cladding manufacturers did not use fire test results appropriately or did not provide relevant information to the product certification organisation or to customers.

"Grenfell Tower inquiry: Cladding firm 'knew of fire risk'", BBC, 10 February 2021 https://www.bbc.com/news/uk-england-london-56014825



Wikipedia launches cladding fires list

A new list of high-rise building façade fires is launched by Wikipedia, with nearly 60 incidents over the last 30 years. The most recent listed fire is the Samhwan Art Nouveau building façade fire, Ulsan, South Korea, 8th October 2020, in which nearly a hundred people were injured. The fire apparently started on a

balcony and spread rapidly to nearly all of the 33-floors, leaving nearly 200 people homeless.

Wikipedia "List of high-rise façade fires"
https://en.wikipedia.org/wiki/List_of_high-rise_facade_fires

Ulsan Korea cladding fire, 8 October 2020
https://www.youtube.com/watch?v=1sHfn2X5hDQ

REGULATORY

US federal furniture fire safety standard

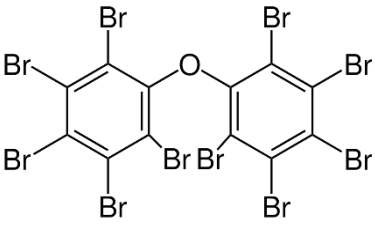
Cigarette ignition resistance will be legally required for all furniture sold in the USA. The provision is included in the 1.4 billion US$ US Covid relief package, finally signed by Donald Trump at the end of December. Six months from enactment of the bill, the California furniture fire safety standard (CA TB 117-2013) will become mandatory for all furniture and bedding products sold in the USA. This takes up the proposed "Safer Occupancy Furniture Flammability Act" 2020 (see pinfa Newsletter n°111). Most large furniture manufacturers in the USA already respect this standard, but the new regulation will render standards consistent for all companies in all States of the USA. This standard is considered to provide inadequate fire safety by many experts. For example, the US Consumer Product Safety Commission (CPSC) itself concluded in 2019 that the California standard does not relate to furniture in the real world, does not give consistent results and does not offer improved safety because 90% of the furniture on the market would pass the test (see pinfa Newsletter n°108).

US "Consolidated Appropriations Act, 2021', Title XXI – Covid 19 Regulatory Relief and Work from Home Safety Act (Sec. 2101)
https://www.govinfo.gov/content/pkg/BILLS-116hr133enr/pdf/BILLS-116hr133enr.pdf

Massachusetts bans ten halogenated FRs

The State has enacted legislation banning ten brominated and chlorinated FRs and ATO in a range of applications: residential upholstered furniture, bedding, carpets, curtains and blinds, children's products. The ban applies to sale, distribution and manufacture of products from 1st January 2020. The FRs banned are: TDCPP, TCPP, TCEP, HBCD, TBPH, TBB, TBBPA, Penta- and Octa-BDE, chlorinated paraffins and ATO (antimony trioxide). The State will update the list of banned FRs every three years.

"An act to protect children, families, and firefighters from harmful flame retardants", Massachusetts legislation chapter 261
https://malegislature.gov/Laws/SessionLaws/Acts/2020/Chapter261



US bans nearly all uses of Deca-BDE

The US EPA has effectively banned five PBT chemicals including the brominated FR DecaBDE. Under TSCA (Toxic Substances Control Act) section 6(h), the US EPA has effectively banned five Persistent Bioaccumulative Toxic (PBT) chemicals, including decabromodiphenyl ether DecaBDE, from February 2021, and covering manufacture, import, sale or distribution of the chemical or of any product containing it. Temporary exceptions to the ban are made for some specific uses such as hospitality industry curtains, nuclear power installation cables, aerospace, replacement automotive parts, recycled plastics.

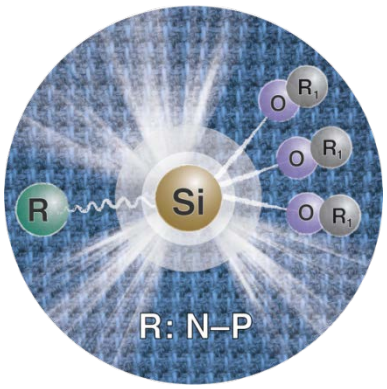
"EPA Issues Final TSCA Section 6(h) Rules for Five PBT Chemicals", 6 January 2021 https://www.natlawreview.com/article/epa-issues-final-tsca-section-6h-rules-five-pbt-chemicals and EPA official website https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/persistent-bioaccumulative-and-toxic-pbt-chemicals-under

RESEARCH

Smoke propagation from furniture fires

Full-scale building tests by IFV Netherlands show dangers from upholstered furniture fires. IFV carried out 19 full-scale fire and smoke propagation tests in a 4-storey disused residential building dating from 1973, comparing fires involving only a standard 2-place sofa to fires burning only wood (set up give a similar heat release rate to the sofa) with a range of scenarios for doors open or closed, exterior ventilation, smoke resistant partitions, fire service deployment and mobile water mist. Smoke density, irritant and asphyxiant gases and heat were measured. The sofas used were all the same: the best-selling model in the Netherlands where upholstered furniture is not subject to fire safety requirements (non flame retardant). The tests conclude that the upholstered sofa fires generate considerably more smoke than fires burning only wood. The room containing the sofa (only) became unsurvivable 4 -7 minutes after igniting the sofa (using propane source). If the fire room door is opened, then the situation in the corridor becomes very rapidly life-threatening or lethal and residents in other flats can no longer escape. It is concluded that both reducing fire and smoke from upholstered furniture and actions to contain the fire and smoke (closed doors, fire breaks) are necessary to improve escape and survival for other flat occupants.

"Smoke propagation in residential buildings. The main report on the field experiments conducted in a residential building with internal corridors", IFV Brandweer Brandweeracademie 2021 https://www.ifv.nl/kennisplein/brandpreventie-fire-safety-engineering/publicaties/smoke-propagation-in-residential-buildings and annexes https://www.ifv.nl/onderzoek/Paginas/Praktijkonderzoek-rookverspreiding-in-woongebouwen.aspx#tab2

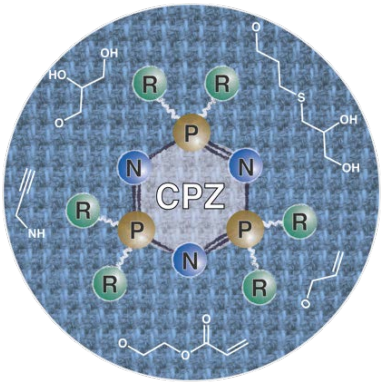


Silanes-based P & N FRs for textiles

New wash-resistant Si - N – P flame retardants developed by DTNW in German government innovation project. The AiF-IGF project No. 19617 N has developed new silane-based PIN FRs, containing silicon, phosphorus and nitrogen, using industrially available amino silanes. The FRs were synthesised according to different strategies with either one or two reaction steps. Lab-scale production was then scaled up to 250g. Depending on the FR chemistry, fire tests including DIN EN 15025 protective clothes, FMVSS 302 automotive, DIN 4102-B2 fire performance are passed for cotton, wool, cotton/polyester and cotton/polyamid fabrics with loadings of 3-10 % (w/w) for textile finishing. Fire resistance is maintained after six home laundry wash cycles at 60 °C. Industrial production is now planned with abcr GmbH.

"Neue stickstoff- und phosphormodifizierte Verbindungen für den permanenten Flammschutz von Textilien via Sol-Gel-Applikation", W. Ali et al., DTNW (Deutsches Textilforschungszentrum Nord-West), 2020
http://dx.doi.org/10.13140/RG.2.2.23821.36326

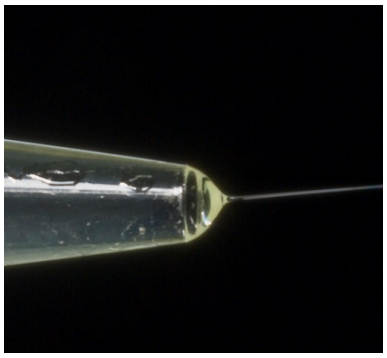
"N-P-Silane" http://www.dtnw.de/forschungsvorhaben/abgeschlossene-forschungsvorhaben/n-p-silane/



Cyclotriphosphazene durable textile FRs

New phosphorus-based PIN FRs developed by DTNW for textiles show wash resistance. Cyclophosphazenes and their derivatives (CPZs) are heterocycle 6-atom rings with alternating P and N atoms with six attached reactive groups. They are versatile chemical building blocks for multifunctional materials. The German Government innovation project AiF-IGF No. 19739 N developed new water-soluble and durable cyclophosphazene PIN flame retardants. Textiles (cotton, wool, cotton/polyester and cotton/polyamide) finished with the new FR (at 15-20 % (w/w)) showed LOI values between 27 and 40 %, depending on the reactive groups used. Fire testing showed results compatible with use in building applications (DIN 4102-B2) and in fire-protective clothes (DIN EN 15025). Fire performance was maintained after 10 home laundry cycles @ 80 °C.

"Cyclophosphazene als umweltfreundliche halogenfreie permanente Flammschutzausrüstung textiler Materialien" DTNW 2021
http://www.dtnw.de/forschungsvorhaben/abgeschlossene-forschungsvorhaben/cyclophosphazene/ and report
http://dx.doi.org/10.13140/RG.2.2.24593.66407/1

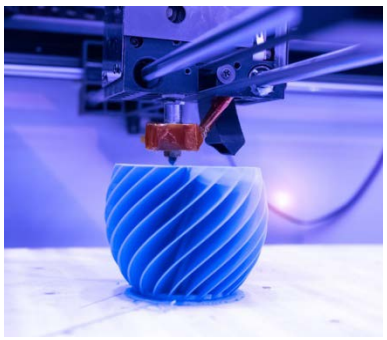


Review: electrospinning for FR polymers

Electrospinning offers routes to develop new FR fibre solutions with improved mechanical properties, e.g. with multiple materials. Electrospinning is a known process for producing continuous polymer fibres, with diameters from 100 nm to 10 µm, or fibre mats. Injection under high voltage induces polymer polarity resulting in highly stretched flow. FRs can be effectively dispersed into the fibres as micro- or nano-particles, either in the bulk polymer or in the surface layer. Some 25 examples from literature are shown, covering a range of polymers (polyamide, polyimide, cellulose and others). Applications include membranes, filters, protective clothing and fabrics. All the FRs in the identified applications are PIN, including minerals, nano-carbons and P-based PIN FRs, for example for safer membranes for lithium-ion batteries. The authors suggest significant development possibilities for miniaturisation, nano fibre integration, improved FR dispersion, polymer surface heat-shielding.

"Electrospinning for developing flame retardant polymer materials: Current status and future perspectives", H. Vahabi et al., Polymer 217 (2021) 123466, https://doi.org/10.1016/j.polymer.2021.123466

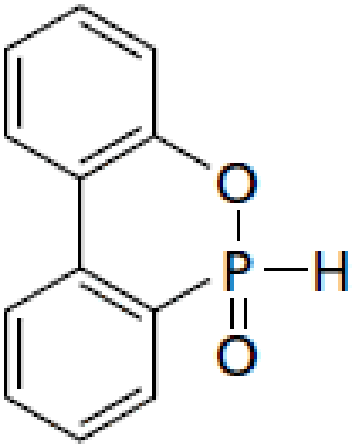
Photograph by Robert Lamberts at The New Zealand Institute for Plant and Food Research Ltd



Review: FR polymers for 3D printing

3D printing enables new approaches to flame retardancy, such as surface layers or enclosure of FRs in structural voids. This review summarises different current FR solutions for different polymers and outlines AM (additive manufacturing) technologies: stereolithography (SLA), digital light processing, multijet/polyjet, selective laser sintering (SLS), selective heat sintering (SHS), fused deposition or filament fabrication, laminated object manufacturing. A range of polymer FR formulations are today available for 3D printing: 14 different companies' products are cited (all non-halogenated except one), covering polyamides, ABS, PLA and specialist polymers. Instead of including FRs in the bulk polymer, 3D printing enables other fire retardancy approaches, in particular including the FR only or at higher loadings in the article surface, or building the article with structural micro-voids containing concentrated FRs. These strategies can avoid impacts of FRs on printed polymer properties. These new approaches may require new fire standards and testing methods.

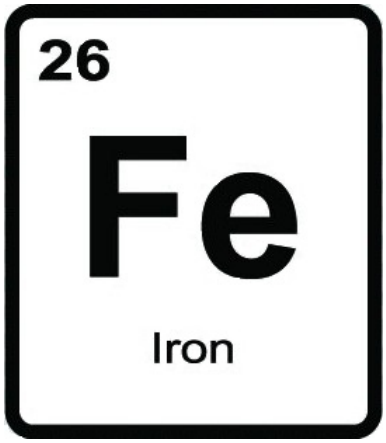
"Flame retardant polymer materials: An update and the future for 3D printing developments", H. Vahabi et al., Materials Science & Engineering R 144 (2021) 100604, https://doi.org/10.1016/j.mser.2020.100604



Developments in DOPO derivatives as FRs

A review paper summarises recent progress in phosphorus PIN FRs derived from DOPO, replacing halogenated FRs. DOPO, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, offers thermal and chemical stability, oxidation resistance, and its O=P-H bond enables reaction with various chemicals enabling development of a wide range of derivatives, for different applications or bringing other functional properties to the polymer, or reaction with the polymer matrix. DOPO derivate FRs for epoxies, cellulose, PET, PBT, polyamides, polyurethane, PLA, polycarbonates, polystyrene and polypropylene are indicated.

"Recent Progress of DOPO-Containing Compounds as Flame Retardants for Versatile Polymeric Materials: Review", Q. Wu et al., World Journal of Textile Engineering and Technology, 2020, 6, 89-103
https://doi.org/10.31437/2415-5489.2020.06.7



Phosphorus – iron synergy for cotton FR

PIN FRs, 3D DOPO (P-based) and ferrocene (Fe-based), reacted onto cotton provided durable fire resistance and waterproofing. Cotton fabric was first grafted with PEI (polyethyleneimine) then reacted in alcohol solution at 60°C with first ferrocene then DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), achieving a 21% w/w loading of ferrocene/DOPO. Peak and total heat release rates were reduced by 50% and 19% and LOI increased from 18 to 28.5. After 12 laundry cycles (GB/T17595) the LOI remained higher than pristine cotton at 24, showing durability of the reacted ferrocene – DOPO treatment. The treatment also significantly improved waterproofing of the cotton.

"Durable flame retardant and water repellent cotton fabric based on synergistic effect of ferrocene and DOPO", Y. Luo et al., Cellulose 2021
https://doi.org/10.1007/s10570-020-03636-2

PIN FRs for recycled Tetra-Pak

PIN flame retardants show to be effective in PEAL, a composite material resulting from recycling of TetraPak packaging. PEAL is produced in Italy by collecting used TetraPaks with paper, processing to remove paper (which is recycled), then separation of impurities and foreign polymers to give a material which is mainly around 85% low density polyethylene (LDPE) and 15% aluminium, which can be injected, extruded or compounded. PIN FRs tested were magnesium hydroxide (MH, 50-60% loading), ammonium polyphosphate (APP, 30% loading) and APP + pentaerythritol (intumescent, 3:1 ratio, 30-40% loading). Peak heat release rate was reduced by over 60% by the PIN FRs and the 40% APP (intumescent) formulation achieved UL+4-V2 @ 2mm (neat PEAL is not classified).

"Improving Fire Performances of PEAL: More Second-Life Options for Recycled Tetra Pak®", F. Cravero, A. Frache, Polymers 2020, 12, 2357;
https://doi.org/10.3390/polym12102357

Recycling fire-extinguishers to PIN FRs

Ammonium phosphate from end-of-life ABC dry-powder fire extinguishers is an effective PIN FR in polyethylene. Fire-extinguishers must be refilled or completely replaced after specified periods. The resulting spent mono ammonium phosphate (MAP) powder can be recycled as a fertiliser, but this requires purification, e.g. to remove silicones included to improve dispersion and prevent caking. This may not be feasible in some regions, because of logistics costs for transport to reprocessing sites. In this study, the spent MAP was tested directly as a PIN FR at 0 to 60% loading in polyethylene (Matrix Polymers). At 40% loading, the aircraft interior vertical fire test CS25.853 (group 1) was passed (1 mm sheets) but with some deterioration of mechanical properties.

pinfa note: MAP is not generally used as a flame retardant, with ammonium polyphosphate being preferred, because of the sensitivity to water of MAP.

"Mechanical and fire characterization of composite material made of polyethylene matrix and dry chemical powder obtained from end-of-life extinguishers", Z. Ortega et al., Fire and Materials. 2020;1–10, https://doi.org/10.1002/fam.2926

OTHER NEWS

Developmental toxicity of brominated FR (BDE) but not PIN FR (AlPi). Lethality and teratogenicity were tested using the standard fish species, zebrafish, for up to 96 hours after fertilisation of eggs. No significant mortality was observed at the concentrations tested, but the brominated diphenyl ether cogeners BDE-47 and BDE-99 showed developmental effects at 48 hours at tested 14 – 16 mg/l for the BDEs. AlPi (aluminium diethylphosphinate) showed no developmental toxicity, inducing no morphological changes after 96 hours at the highest concentration tested (30 mg/l). The authors conclude that the PIN FR AlPi may be considered a suitable alternative.

"A comparison of developmental toxicity of brominated and halogen-free flame retardant on zebrafish", F.R. Abe et al., Ecotoxicology and Environmental Safety 208 (2021) 111745
https://doi.org/10.1016/j.ecoenv.2020.111745

A Canada Government screening concludes trixylyl phosphate has low environment risk and adequate health safety margins. In Europe, however, trixylyl phosphate is on the REACH SVHC Candidate List (Substance of Very High Concern). The Canada "screening assessment" covers the PIN FR trixylyl phosphate and two other organo-phosphate chemicals. Trixylyl phosphate is used as a PIN flame retardant, and also in food packaging, hydraulic fluids, as a plasticiser, and in wire and cable insulation. The other

two chemicals assessed are used in cosmetics and in plastics, rubbers and food packaging. Trixylyl phosphate is considered not to meet the Canada CEPA para. 64(a) or (b) criteria, because it does not enter the environment in concentrations susceptible to have intermediate or long-term harmful effects. Population exposure to trixylyl phosphate, in products and dust, is considered low enough to address uncertainties in exposure and health effects.

"Screening assessment - Phosphoric Acid Derivatives Group", Government of Canada, ISBN 978-0-660-36664-7, December 2020, https://www.canada.ca/en/environment-climate-change/services/evaluating-existing-substances/screening-assessment-phosphoric-acid-derivatives-group.html

PUBLISHER INFORMATION

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