pinfa
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 74 January 2017

Upcoming events

- 23 February, Milan, TMP – pinfa workshop: **fire safety of E&E polymers and PIN flame retardants**
- 25-26 April, Pittsburgh PA, USA , **AMI Fire Retardants in Plastics 2017**
- 25-27 Sept., Ypsilanti, MI, USA, **pinfa NA 5th annual workshop**: Fire Safety Requirements in Automotive Design

For full events listing, see www.pinfa.eu

Health and environmental safety are key objectives for fire safety solutions. PIN flame retardants seek to achieve this by using chemistries based on elements which are widely present in biological systems and are essential for life (phosphorus, nitrogen, magnesium …) and inorganic metals (tin, aluminium …). This is a challenge, as fire safety solutions must be durable (resistant to e.g. washing, ageing) and/or must be mixable with polymers. And of course no chemicals are totally safe, be they naturally occurring or synthesised to fulfil societal needs. Even very innocuous chemicals such as table salt can impact health or the environment depending on the dose. This pinfa Newsletter presents, alongside news on PIN flame retardant applications and innovation, information on a number of studies and initiatives concerning flame retardant health and environmental impacts. This includes assessments underway by regulatory authorities in Europe and North America, new data showing low toxicology and ecotoxicology of DOPO compounds (phosphorus PIN FRs). However, pinfa regrets that some publications present these questions misleadingly, such as the Canadian "Toxic by design" brochure which suggests that all organic phosphorus compounds are dangerous: a generalisation which would lead to ban DNA (genetic material), cell membranes, brain cells and energy metabolism in our bodies.

tmp ASSOCIAZIONE ITALIANA TECNICI MATERIE PLASTICHE

TMP – pinfa workshop fire safety of E&E polymers and PIN FRs

The Italian Technical Plastics Materials industry association (TMP) is organising with pinfa a workshop in Milan, 23rd February bringing together fire fighters, E&E manufacturers, fire safety and regulatory experts and polymer compounders. The objective will be to enable dialogue between technical polymer users and the PIN flame retardant industry, and to discuss trends in industry and regulatory requirements and in PIN fire safety solutions

TMP – pinfa workshop fire safety of E&E polymers and PIN FRs, Milan, 23rd February, 8h30-17h.
To register: pinfa@cefic.be

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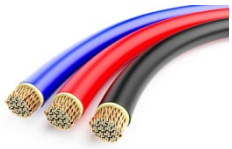
Environment Canada finds no risks for three FRs

Canada's Environment Department has published for consultation draft screening assessments of ten flame retardants, proposing to conclude that three[1] [EBTBP (brominated), TCP (non-halogenated phosphorus ester) and melamine (nitrogen)] do not pose risk and do not require further action. Of the remaining seven substances (brominated or chlorinated), three[2] are recommended for addition to the Canada List of Toxic Substances, or that they may be potential future concerns if exposure increases in the future. The draft screening assessments for the ten flame retardants are open to consultation to 7th December.

1: EBTBP = 1H-isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo CAS 32588-76-4. TCP = Phosphoric acid, tris(methylphenyl) ester CAS 1330-78-5. Melamine = 1,3,5-Triazine-2,4,6-triamine (Melamine), CAS 108-78-1.
2: TCPP = 2-Propanol, 1-chloro-, phosphate (3:1) (TCPP), CAS 13674-84-5. DP = Dodecane Plus = 1,4:7,10-Dimethanodibenzo[a,e]cyclooctene, 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro- CAS 13560-89-9. DBDPE = Decabromodiphenyl ethane = Benzene, 1,1'-(1,2-ethanediyl)bis [2,3,4,5,6-pentabromo- CAS 84852-53-9

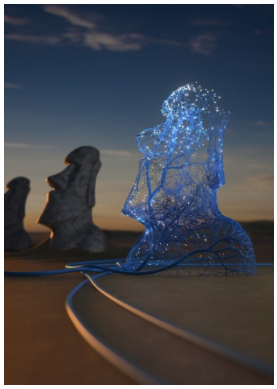
Environment and Climate Change Canada, "Publication of Draft Screening Assessments, Draft State of Science Reports, and Risk Management Scope documents for the Certain Organic Flame Retardant Substances Grouping", covering TCPP, Dechlorane Plas, DBDPE, ATE, TBB, TBPH, TDCPP, EBTBP, TCP, Melamine. Canada Gazette Vol. 150, No. 41, October 8, http://canadagazette.gc.ca/rp-pr/p1/2016/2016-10-08/pdf/g1-15041.pdf



HALBAN™ performance PIN FR cable compounds

New Delhi based global cable thermoplastic specialist Matrix Polytech Pvt has widened its HALBA™ ZHFR (zero halogen flame retardant) range with heat resistant, super floss, enhanced fire safety and UV resistant / outdoor performance grades. ZHFR cables reduce toxic gas emissions and smoke in case of fire, so reducing risks to occupants, and do not emit acid gases, so avoiding deterioration of electrical equipment, safety installations and metallic structural elements. HALBAN ZHFR compounds offer limiting oxygen index (LOI ASTM D2863) 32-45 and smoke density (% absorption ASTM D2843) 8-40, as well as good processability, oil resistance, flexibility and tensile strength.

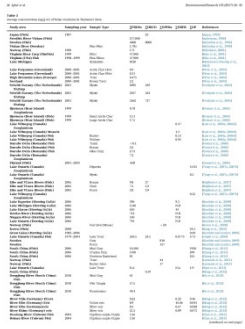
"HALBAN™ Zero Halogen Flame Retardant Compounds", Matrix Polytech Pvt Ltd
http://matrixpolytech.in/halbantm-zhfr-compounds/



Leoni PIN FR X-linked optic fibre cable

Specialist optic fibre cable supplier LEONI's LE.X.CO cross-linked, PIN flame retardant cable jacket material is compatible with almost any cable type and requirement, including offshore, railway, industry and marine applications. This multiple-compatibility enables the use of the same cable design for all requirements across large projects, so reducing project planning and management complexity and costs. The X-linked material is "halogen-free" (acc. to IEC 60754-1), flame retardant (IEC group 60332) and low fire gas acidity (IEC 60754-2). Performance advantages include UV and ozone resistance, abrasion resistance, no deformation after installation, longevity under harsh conditions and mud resistance (NEK606). The material can be used in a wide range of cable and connector design capabilities, with specific protection measures available on request including metal-free, armoured, rodent and water protection)

LEONI press November 2015 "ONE major project – ONE cable solution LEoni X-Linked Compound (LE.X.CO) Saving major projects costs up to 75%" http://www.leoni-fiber-optics.com



Review of flame retardants in the environment

An overview of over 200 published studies summarises currently available data concerning legacy and emerging flame retardants in the environment. The studies provide data on legacy FRs (brominated flame retardants which were widely used in the past: BDEs, PBTs, HBCD, PBPs and TBBPA), recently introduced brominated FRs and organophosphorus FRs, covering water, sediments and biota (living organisms) with data from Asia, North America and Europe. The authors discuss fate and transport of the FRs in the environment. Higher concentrations of FRs are found near manufacturing plants and urban areas. Levels of the legacy FRs are generally falling or stable, following stopping of production and use, even though some of these are bioaccumulative. De-bromination of PBDEs (c.f. BDE-209 DecaBDE) is considered of concern because the metabolism products may be more toxic and more mobile. Data on more recently introduced FRs is considered to be insufficient, requiring more monitoring.

"Legacy and emerging flame retardants (FRs) in the freshwater ecosystem: A review", M. Iqbala et al., Environmental Research 152 (2017) 26–42 http://dx.doi.org/10.1016/j.envres.2016.09.024

Department for Business, Energy & Industrial Strategy

CONSULTATION ON UPDATING THE FURNITURE AND FURNISHINGS (FIRE) (SAFETY) REGULATIONS

SEPTEMBER 2016

pinfa response to UK furniture fire safety consultation

pinfa responded to the UK government consultation on the revision of the UK Furniture Fire Safety Regulations. pinfa indicated agreement with most of the proposed modifications to the Regulations, which aim to clarify the scope, facilitate regulation enforcement and enable more flexible design routes to achieving fire safety. pinfa noted that testing should simulate the real-life situation of furniture in use where fabrics cannot over time be guaranteed to remain always closely held to foams (without air able to feed a possible fire) and barriers may be damaged or pierced. Barriers should also protect the rear and underneath of furniture, which may be exposed to heat sources such as electrical faults. pinfa suggests that in addition to modifying the Furniture Regulations, the UK authorities should seek to identify and ensure the use of flame retardants with better environment and health profiles and to encourage the labelling of furniture using flame retardants conform to independent labels or standards (e.g. OekoTex 100) or approved for e.g. skin contact.

"pinfa comments on the "Consultation on updating the Furniture and Furnishings (Fire) (Safety) Regulations" by the UK Department for Business, Energy and Industrial Strategy (BIES), 10th November 2016. All responses to this public consultation will be published by BIES at https://www.gov.uk/government/consultations/furniture-and-furnishing-fire-safety-regulations-proposed-changes-2016

polymers MDPI

Article

Structure–Property Studies on a New Family of Halogen Free Flame Retardants Based on Sulfenamide and Related Structures

Sulfenamides as innovative, eco-friendly PIN FRs

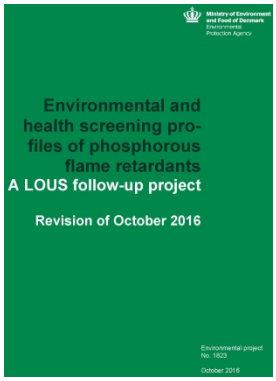
A range of sulfenamide molecules containing sulphur and nitrogen, including oligomers and polymers, were synthesised and tested as flame retardants in polypropylene PP, low density polyethylene (LDPE) and polystyrene. Sulfenamides contain a bond of divalent sulphur and trivalent nitrogen. Their flame retardant effect is thought to result from radicals released by cleavage of S-N or S-N-S bonds which react with polymer pyrolysis products. Sulfenamide polymers have been proposed as biodegradable polymers for medical applications, and have been tested showing very low or no toxicity, suggesting that they would show a positive health and environmental profile as PIN flame retardants. For polypropylene and LDPE films, DIN 4102 B2 (self-extinguishing) was achieved at low sulfenamide loadings (0.5%). For polystyrene, UL94 V-0 was achieved at 5% sulfenamide loading.

"Structure–Property Studies on a New Family of Halogen Free Flame Retardants Based on Sulfenamide and Related Structures", T. Tirri et al. Polymers 2016, 8, 360; http://dx.doi.org/10.3390/polym8100360

Are our genetic and cell materials toxic by design?

A Canadian NGO, funded by SSHRC (Canada Government Research Council) has published a brochure suggesting (p16) that all chemicals containing "*chlorine, bromine* (… or) *phosphorous bonded to carbon*" are "*likely to be: Persistent in the environment … Capable of long-range transport … Bio-accumulative …* (and) *Toxic*". In reality, molecules in our bodies which consist of phosphorus bonded to carbon include our genetic material (DNA), cell membranes (phospholipids), key molecules in cellular energy metabolism (ATP/ADP), nerve cell transmitters, and many others: no known form of life could exist without these. This seems to be part a presentation which suggests that all flame retardants are the same and that all are potentially harmful. For example, the brochure includes chemical symbols of bromine on every page and suggests (p. 3) that all brominated flame retardants are endocrine disruptors. The only non halogenated phosphorus flame retardant cited is (isopropylated) triphenyl phosphate IPTPP/TPP. Despite this biased presentation, the policy recommendations of the document are in line with pinfa's objectives: ban from all consumer products all flame retardants for which there is evidence of harm (pinfa would specify "as used", taking into account whether the FR is fixed in the product), ban those which have no environmental and health safety assessment and "develop a strategy on the use of alternative flame retardant chemicals that meaningfully implements the precautionary principle" (pinfa would specify that this should address fire safety as well as chemical safety).

"Toxic by Design Eliminating harmful flame retardant chemicals from our bodies, homes, & communities", A White Paper by the Endocrine Disruptors Action Group https://endocrinedisruptorsaction.org/ 27 pages, October 2016 https://endocrinedisruptorsaction.org/2016/10/11/toxic-by-design/



Denmark EPA phosphorus FR screening report update

The Danish EPA (Environment Protection Agency) has published an update of its January 2016 screening report on phosphorus flame retardants (see detailed summary in pinfa Newsletter n°66), based on GreenScreen methodology. The report has been updated to adapt to REACH and to GHS /CLP regulations, and to take account of comments from industry and from CPA (Clean Production Action USA, owner of GreenScreen). The update particularly concerns diethylphosphinate, aluminium salt and polyphosphonate and phosphonate oligomers. Three of the twenty-eight phosphorus flame retardants assessed achieve overall hazard scores of 3 or 4 ('Safer' or 'Use but opportunity for improvement'): poly[phosphonate co-carbonate], ammonium polyphosphate, aluminium phosphinite. A further nine* phosphorus FRs are not identified as "high" risk for any health, environment or bioaccumulation endpoint except (in some cases) "persistence", although a number of data gaps are also indicated.

** DOPO, 9,10-Dihydro-9-oxa-10-phosphaphenanthren-10-oxide; N,N-bis-(2-hydroxylethyl) aminomethane phosphonic acid diethyl ester; Oligomeric phosphonate polyol; Bisphenol A bis(diphenyl phosphate); Oligomeric ethyl ethylene phosphate; Melamine pyrophosphate; Melamine phosphate; Red phosphorus; Diethylphosphinate, aluminium. Plus as cited above: Poly[phosphonate co-carbonate]; Ammonium polyphosphate; Aluminium phosphinite*

Denmark EPA "Environmental and health screening profiles of phosphorous flame retardants", LOUS follow-up project, Environmental Project N° 1823, revision of October 2016 http://mst.dk/service/publikationer/publikationsarkiv/2016/nov/environmental-and-health-screening-profiles-of-phosphorous-flame-retardants/ and CPA/Denmark EPA joint statement http://mst.dk/media/177929/mst_joint_statement_regarding_danish_epa_phosphorus_flame_retardant-final.pdf

DOPO and EDA-DOPO show low toxicity / ecotoxicity

The organophosphorus PIN FR DOPO*, and three derivatives (ETA-, EG- and EDA-DOPO) were tested in vitro (i.e. screening test, not with living organisms) for neurotoxicity, cytotoxicity and in vivo for algae and daphnia ecotoxicity, comparing to "PBDE-99". Both ETA-DOPO and DOPO showed no neurotoxicity, no effects on neural crest cells or human skin cells, and no effect (down to 400 µM) on algae or daphnia. These results relevant to inhalation, skin exposure, sensitisation and neurotoxicity, and the flame retardant properties of ETA-DOPO and its compatibility with polyurethane foams lead the authors to suggest it as a possible candidate flame retardant, with preferable environmental properties, for such applications.

** DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. "Multiparameter toxicity assessment of novel DOPO-derived organophosphorus flame retardants", C. Hirsch et al., Arch Toxicol 2016*
http://dx.doi.org/10.1007/s00204-016-1680-4

Other News

ECHA (European Chemical Agency) has proposed nine additional chemicals for "authorisation" under REACH Annex XIV (SVHC Substances of Very High Concern) because considered toxic for reproduction. These include the plastic additive Trixylyl phosphate, used in the past as a flame retardant.

"ECHA proposes 9 substances for authorisation - PR/16/14" 10th November 2016 https://echa.europa.eu/-/echa-proposes-nine-substances-for-authorisation

ECHA CoRAP: REACH chemicals plan. The European Chemicals Agency (ECHA) has updated its draft CoRAP list (Community Rolling Action Plan, update 2017-2019), which "contains substances suspected of posing a risk to human health or the environment" and which are proposed for evaluation. The new proposed list now contains 117 chemicals (22 are newly added), of which a number are flame retardants/synergists.

The flame retardants /synergists on the CoRAP list are:
New entries:
- 2,2-dimethylpropan-1-ol, tribromo derivative EC# 253-057-0
- 1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy)benzene] EC# 306-832-3
- Tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDPP) EC# 237-159-2
Already in CoRAP list:
- Zinc oxide EC# 215-222-5
- 1,1'-(isopropylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)benzene] EC# 244-617-5
- Dipotassium tetraborate EC# 215-575-5
- N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide EC# 251-118-6
- Triphenyl phosphate TPP EC# 204-112-2
- Tris(2-chloro-1-methylethyl) phosphate (TCPP) EC# 911-815-4
- Diantimony trioxide EC# 215-175-0
- bis(2-ethylhexyl) tetrabromophthalate EC# 247-426-5

ECHA Draft Community Rolling Action Plan (CoRAP) update for years 2017-2019, 27th October 2016
https://echa.europa.eu/fr/information-on-chemicals/evaluation/community-rolling-action-plan/draft-corap

US EPA selects two flame retardants under new TCSA. The US Environmental Protection Agency has announced five types of chemical for fast tracking under the newly updated TCSA (Toxic Substances Control Act), see pinfa Newsletter n°69. Of these, two are flame retardants. Under the new TCSA provisions, EPA must now take "expedited action" on these chemicals, to identify where they are used and to "move directly to propose limitations on their use" (at the latest by June 2019).

The two flame retardants on the EPA TCSA list are:
- DecaBDE (Decabromodiphenyl ether)
- Tris (4-isopropylphenyl) phosphate.

"EPA Acts on New Chemical Law to Fast-Track Five Chemicals", 11th October 2016
https://www.epa.gov/newsreleases/epa-acts-new-chemical-law-fast-track-five-chemicals-0

Flame retardant market reports: Value Market Research have published a report on global "low smoke halogen-free (LSZH)" cables. This market is indicated to be developing strongly because of advantages of fire safety, as such cables emit limited smoke and reduced toxic or corrosive gases in case of fire, in particular for polyethylene and thermoplastic polyurethane cable sheaths. A further report by QY Research covers the European flame retardants market, through to 2011.

"Global Low Smoke Halogen-Free Cable Materials Market Research Report - Industry Analysis, Size, Share, Growth, Trends and Forecast, 2014 – 2021", Value Market Research, Dec. 2016
http://www.decisiondatabases.com/ip/53-low-smoke-halogen-free-cable-materials-market-research-report

"Europe Flame Retardant Chemicals Market Report 2016", QY Research, Nov. 2016
http://www.decisiondatabases.com/ip/4961-europe-flame-retardant-chemicals-industry-market-report

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For abbreviations see: www.pinfa.org