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Phosphorus, Inorganic & Nitrogen Flame Retardants Association

Your newsletter for non-halogen fire safety solutions
No. 72 November 2016

For events listing, see www.pinfa.eu

Lithium ion batteries are part of the mobile IT revolution that is changing our lives, but they are unfortunately susceptible to overheat and catch fire. The problem is structural: lithium ion batteries consist of cells containing a positively charged lithium cathode and a negative carbon anode, which must be kept separate to avoid arcing. The separation is achieved using permeable polyethylene membranes, across which lithium ions move in a flammable organic liquid, carrying electricity. As batteries are made smaller and more powerful, the separations between cells and the polyethylene membranes are thinner and more fragile and the battery generates more concentrated heat, causing structural stress. Additionally if a battery charges too fast (appliance electronics is intended to prevent this), the lithium forms a coating on the membrane again causing arcing. If this occurs, of if a battery cell is punctured or otherwise damaged, the lithium inside can make contact with air and will then react violently potentially causing a fire or explosion. Flame retardants cannot prevent lithium ion batteries posing such risks, but they can prevent a fire spreading to the plastics and composites which make up the rest of the electronic appliance, so reducing the risk of fire development. PIN FRs can also be integrated into the materials of the battery itself and in the electrolyte liquid to reduce fire risk in case of battery failure.

TCO again criticises Sweden electronics chemicals tax

The international sustainability certification organisation for information technology products, TCO, has again criticised the proposed Sweden chemicals tax (see pinfa Newsletter n°66). TCO states that the proposal "misses environmental target" by focusing on revenue generation, by failing to generate data on which chemicals are used and what are their environmental and health effects, and because it would "penalise the use of substances that have been tested and identified as safer alternatives". In 2015, TCO already took position: "by also including all phosphate-based flame retardants, the

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current proposal does not achieve its desired goal. We believe the current proposal raises the risk that industry will not bother to substitute halogenated substances with safer alternative".

TCO "Chemical tax on products misses the mark", N. Rydell, June 2015 "Proposed chemical tax on electronics misses environmental target" TCO 23 Sept. 2016

Department for Business, Energy & Industrial Strategy

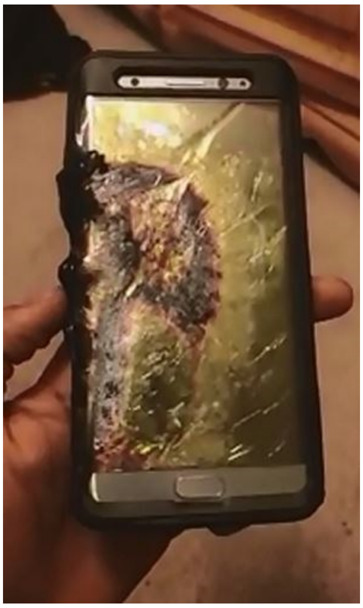
CONSULTATION ON UPDATING THE FURNITURE AND FURNISHINGS (FIRE) (SAFETY) REGULATIONS

SEPTEMBER 2016

UK consultation on furniture fire safety regulations

The UK government has opened a public consultation on the revision of the UK furniture fire safety regulations, **open to 11th November 2016.** The official consultation document states that fires involving furniture were increasing in the UK in the 1980's, but levelled off with the introduction of domestic furniture fire safety standards in 1988 and after twenty years had fallen by nearly 40% and have continued to decline through to 2013/2014 (most recent data). The objective of the proposed regulation revision is to clarify the scope of application (items considered to be domestic indoor furniture), to enable more flexible design to maintain levels of fire safety ("ensure no reduction of safety") whilst enabling industry to innovate new fire protection technologies or reduced flame retardant use, and to facilitate regulation enforcement. Fire testing of furniture is therefore modified to reflect more closely the materials as actually used in complete furniture items: e.g. if a protective barrier or interliner is not used, then all materials close to the covering material must be small flame (match) resistant. At present there are issues with imported furniture not respecting the UK furniture fire safety regulations (see pinfa Newsletter n° 41): this is addressed by new requirements on labelling and traceability (information held by manufacturers) and more flexible conditions for prosecution. Testing costs will be reduced for industry (e.g. cigarette test not required for covers which pass the revised match test). The consultation includes 22 specific questions concerning the proposed regulation changes. Accompanying documents present BSI FW6 comments on these 22 questions.

UK Government open consultation: "Furniture and furnishings fire safety regulations: proposed changes (2016)" – to 11th November: https://www.gov.uk/government/consultations/furniture-and-furnishing-fire-safety-regulations-proposed-changes-2016



Samsung Galaxy Note 7 banned by airlines

The US Federal Aviation Administration (FAA) has issued a warning "strongly" advising passengers not to charge or turn on Samsung Galaxy Note 7 smartphones on board aircraft and not to put them in checked-in luggage. Several airlines, including Lufthansa, have banned the use of the Samsung phone on board. This follows 35 incidents with batteries in this model, leading to the recall of 2.5 million phones by Samsung. The FAA has documented over a hundred incidents of smoke, fire, extreme heat or explosion of different batteries since 1990. Battery fires are considered to have been a contributing factor in three cargo plane crashes since 2006. Recently, a fire started in a Quantas trans-Pacific flight when a passenger's phone was crushed in the business class seat mechanism and the lithium-ion battery ignited. The company's safety video now tells passengers to call the crew if their phone falls down between seat parts, not to try to extract it themselves.

"F.A.A. 'Strongly Advises' Against Using Samsung Galaxy Note 7 Aboard Planes", New York Times 8th September 2016 and "Samsung Urges Consumers to Stop Using Galaxy Note 7s After Battery Fires" New York Times 10th September 2016 YouTube video charred phone.

PlaneGard addresses in-flight battery fires

Tennessee company PlaneGard has developed an emergency containment case for use in case of PED (portable electronic device) battery fires. The case prevents emission of heat and smoke, even in case of thermal runaway (effectively a small explosion) of the battery. The case contains safety gloves and glasses and a metal scoop to safely pick up a burning laptop and put it into the case, and is then designed so water can be added to put out the fire within the case. The company indicates that recent research by General Motors and Tesla has shown significant toxicity of smoke from lithium ion battery fires, related to presence of alkylfluorophosphates.

"As More Devices Board Planes, Travelers Are Playing With Fire", New York Times, 11th September 2016. PlaneGard www.planegard.com

Fire losses in the USA

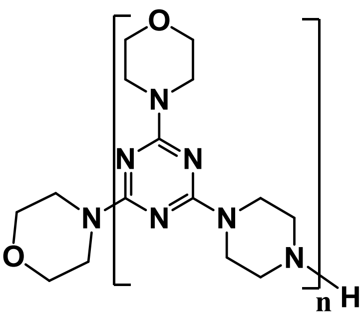
NFPA has published its annual report into national fire losses, showing a significant increase in the number of fires to which public fire services responded (up 3.7% from 2014, to over 1 340 000 fires/year). A US fire department responds to a fire every 23 seconds. In total, some 3 280 civilians were killed by fires in the USA in 2015 and 15 700 were injured in fires. The number of building fires in the USA fell considerably from 1977 (peak high) to 1998, but since then has not fallen (1.5% increase in 2015). Residential structure fires also increased in 2015 (to 388 000) whereas the resulting number of deaths decreased 6.7%. Highway vehicle fires increased 3.9% to 174 000. Property loss caused by fires (to which fire services responded) was estimated at over 14 billion US$ in 2015, of which over 10 billion US$ in non wildland fires (up 4.4% from 2014).

NFPA Journal September 2016 and report "Fire Loss in the United States during 2015", H. Haynes, NFPA, Sept. 2016

Great Fire of London and kitchen fires

UK safety associations are reminding that the Great Fire of London, 350 years ago in 1666, started in a baker's kitchen and destroyed over 13 000 homes. Today, more than a million British people have called emergency services during their life to deal with a kitchen fire, according to Electrical Safety First. A survey by the charity shows that one in six people have cooked when drunk, over a third have been distracted (e.g. by a phone call) when cooking, 2.5 million have fallen asleep whilst cooking and a third have left a hob or oven switched on after use. In 1666, the baker accused of starting the Great Fire of London was executed.

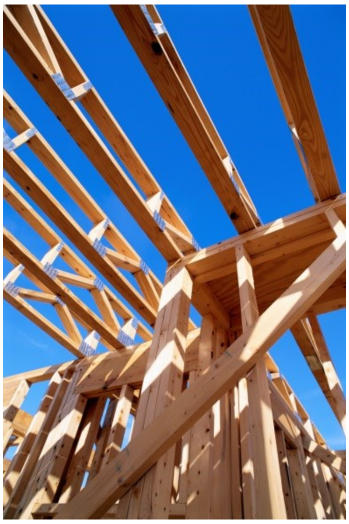
"Worshipful Company of Firefighters Releases "Cold-Case Investigation of The Great Fire of London" 8/9/2016 "More than a million call 999 because of kitchen fires" International Fire Protection Magazine 9/9/2016



Polymeric nitrogen fire retardancy synergists

MCA Technologies (see pinfa Newsletter n° 61) have developed polymeric PPM Triazines (PPMT) for use as nitrogen-containing synergists with a range of flame retardants. The PPMT are non halogenated poly(piperazinyl,morpholinyl,triazines) and are produced by processes without solvents. They show to be effective synergists for both inorganic and phosphorus flame retardants, e.g. ATH, MDH, metal carbonates (such as the magnesium carbonates huntite and hydromagnesite), ammonium poly phosphates (APP), phosphinates. The PPMT synergy mechanisms are shown to be the generation of a resistant, ceramic residue layer (with inorganic FRs) and the formation of high-temperature resistant phosphorus oxynitrides (PON) as fire barriers. The non-ionic nature of PPMT contributes to durability and can improve polymer characteristics such as electrical insulation capacity. This can be further improved by siloxane coating of the PPMT-FR blends. Applications include EVA, polypropylene, polyesters & polyamides.

"PPM Triazines. Lightweight organo-polymeric universal fire and flame retardant synergists", B. Kaul, Rubber Fibres Plastics (RFP) 3/2016



D-BLAZE fire retardant wood is GREENGUARD Gold

D-Blaze® from Viance LLC (a Huntsman Corporation and Dow Chemical Company joint venture) is the first pressure-impregnated Fire Retardant Treated Wood (FRTW) to obtain the GREENGUARD Gold Certification, part of UL Environment. This Certification is recognised by more than 450 US purchasers, green building rating tools (including is referenced by CHPS and LEED) and building codes worldwide. The Certification particularly requires very low volatile organic carbon (VOC) emissions. D-Blaze is a fire retardant wood treatment that is impregnated into framing lumber and plywood products by a pressure process to reduce combustibility and smoke development, and offers a 50-year limited warranty. D-Blaze is a water-based formulation that does not produce harmful off-gassing. Lumber and plywood treated with D-Blaze is UL® Classified with an FR-S Rating for low smoke development and low flame spread index. D-Blaze is suitable for weather protected applications but can be used in relative humidity up to 95%. It meets AWPA Standards C-20 and C-27 for an Interior Type A fire retardant.

"D-Blaze® Fire Retardant Treated Wood (FRTW) Earns GREENGUARD Gold Certification", 21 July 2016

Polyonics PIN FR labels achieve FMVSS 302

Polyonics XF-603 and XF-611 non-halogenated flame retardant label materials have been certified to FMVSS 302, the US Federal Motor Vehicles Safety Standard specifying burn resistance for materials used in the passenger compartments of cars, trucks and buses. The Polyonics labels use Flameguard™ technology, combining PIN-based chemical and physical mechanisms to control heat, flammable gases and fire propagation. XF-611 is a low-cost polyester (PET) and XF-603 a high temperature polyimide (operating 260°C) with low smoke emission and low smoke toxicity. Both include acrylic PSAs (pressure sensitive adhesives), are thermal transfer and flexo printable, REACH and RoHS compliant and UL94-VTM0 and UL969 rated.

"Polyonics material gets FMVSS 302 certification" 4th July 2016 and www.polyonics.com

OEKO-TEX®
CONFIDENCE IN TEXTILES

FRX Polymers® phosphonate FRs Oeko-Tex accredited

FRX Polymers' Nofia® OL1001, OL3001, OL5000, OL9000 and HM1100 phosphonate-based PIN flame retardants have achieved accreditation by the Oeko-Tex Ecolabel. Oeko-Tex is an international association of 16 independent research and testing institutes active in more than 60 countries, focused on product safety and sustainable production in the textile industry. The Oeko–Tex label means that these Nofia flame retardants have been independently assessed as harmless to health in a range of uses and applications. Jan-Pleun Lens, Vice-President Research and Applications at FRX Polymers indicates that the Oeko-Tex accreditation recognises Nofia's high performance and sustainability advantages. The Nofia chemistry enables tailor-made phosphorus products to be produced with a wide range of compositions and molecular weights, including oligomers and polymers. Nofia PIN FRs are being used in commercial textiles for building and construction as well as transportation applications and also in some non-woven applications.

"FRX Polymers' Nofia® Flame Retardants Obtain Accreditation from Oeko-Tex® Association", Textile World 29 August 2016

N-P flame retardant best solution for shelter furniture

Corrugated cardboard is widely used in Japan in shelters and medical facilities for earthquake response, because of low price, strength and recyclability. Fire retardancy is considered important for safety. Six flame retardants (FRs) were tested including ammonium sulphate, TOP, TBP and three commercial FRs from Marubishi Oil Chemical Co. Ammonium sulphate gave the best fire performance (lowest peak heat release rate PHRR) but was considered potentially toxic at the application levels needed. A commercial nitrogen-phosphorus (N-P) FR gave significantly reduced PHRR at <20% loading, better than the halogenated FR tested. The authors conclude that P and N are both required for corrugated cardboard flame retardancy and that halogen is not needed.

"The Flame retardancy study of the furniture made from corrugated cardboard", Mochizuki et al., Energy Procedia 89 (2016) 93 – 97 http://dx.doi.org/10.1016/j.egypro.2016.05.013

ECHA
EUROPEAN CHEMICALS AGENCY

Restriction on ammonium salts in insulation materials

ECHA has published the expected Restriction (see pinfa Newsletter n°55) of the use of "inorganic ammonium salts" in cellulose insulation materials. The objective is to avoid risks of ammonia gas release in certain conditions (high humidity and temperature, pH) which could cause irritation to the respiratory tract and eyes (e.g. building workers installing insulation in enclosed spaces). pinfa emphasises that ammonium salts are recognized to be non-toxic: this operational issue is the only risk with their use, and they have no long-term or chronic toxic effects, are not carcinogenic, mutagenic, teratogenic or impacting on the immune system. The published Restriction does not apply if ammonia emissions are shown to be low (specified concentrations and CEN/S 16516 adapted conditions), so enabling continuing use of ammonia phosphates for fire safety, subject to processing or application which prevents ammonia emissions.

Commission Regulation 2016/2017 of 23 June 2016, amending REACH http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2016.166.01.0001.01.ENG&toc=OJ:L:2016:166:TOC

PIN FR infusion epoxy for composites

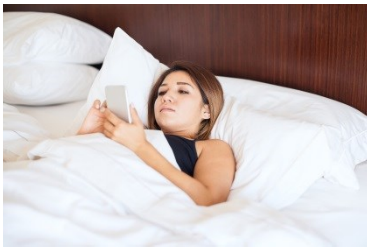
Sicomin, a leading formulator and producer of advanced epoxy systems, has launched a new PIN flame retardant epoxy formulation, SR 1125, for infusion technologies for composite production. The non-halogenated system offers low smoke opacity and low smoke toxicity and meets fire protection standards for construction, automotive and railway applications, including ASTM E84 Class A when used with epoxy gel-coat SGi 128. Very low viscosity ensures a steady and consistent resin flow, enabling to pass through reinforcement fabrics or other obstacles in composites. This facilitates the production of composite parts with high quality, fire resistance and performance mechanical properties. Sicomin has also launched SR 1124 which offers similar properties but with excellent wet-out, adapted also for handlaminating and filament winding applications.

www.sicomin.com "Sicomin presents unique fire retardant infusion epoxy at Composites Europe 2015" 16/9/2015 and SR 1124 / SD 893x and SR1125 / SD 3303 technical data sheets

Low formaldehyde phosphorus FR for textiles

A combination of citric acid and sodium hypophosphite (CA and SHP, two inorganic chemicals) was tested as an alternative cross-linker for application of Pyrovatex CP New (an organophosphorus PIN flame retardant for textiles), for lyocell fabric. Lyocell is a cellulose microfibre with environmental, moisture transport, aesthetic and comfort properties, but which is readily flammable. The CA-SHP effectively replaced the standard cross-linker used with Pyrovatex (methylated melamine), in both cases also with phosphoric acid, showing in most cases good fire performance even after ten washes, with a 75% reduction in formaldehyde release. Low formaldehyde is required by regulation in some countries and by ecolabels such as OEKO-TEX 100.

"Citric acid based durable and sustainable flame retardant treatment for lyocell fabric", Mengal et al., Carbohydrate polymers 153 (2016) 78–88 http://dx.doi.org/10.1016/j.carbpol.2016.07.074



Heat release from bed mattresses in case of fire

At Interflam 2016, Jeong et al presented five full scale fire tests carried out on 97 x 196 cm spring-coil bed mattresses manufactured in Japan. The mattresses were 23 cm deep, of which around 3 cm of foam (total top and bottom) and 17 cm of polyester cloth sheathed springs. The mattresses were fire tested placed on the floor and on steel frames of heights 12 – 52 cms. Peak Heat Release and speed of fire growth increased with the height above the floor. The mattresses at 32 and 52 cm height reached heat release of 1 700 kW, with flames spreading >1 m over the mattress, within 5 – 6 minutes after ignition. These results confirm the danger of non fire-safety treated mattresses including those based on metal springs.

"Analysis of heat release rate of bed mattress installed at different heights", J-J. Jeong et al., Interflam 2016, Windsor UK, 4-6 July 2016, proceedings page 269 http://www.intersciencecomms.co.uk/html/conferences/Interflam/If16/if16%20Table%20of%20Contents.pdf

Phosphorus, nitrogen and silicon FR action in cotton

Cotton fabrics were modified to take up 1-4% phosphorus (P) plus 0-0.8% nitrogen by phosphorylation (application of phosphoric acid, urea, potassium hydroxide, sodium xylenesulphonate and heat treatment) and 0-1% silicon by a sol-gel process. These processes showed good durability (resistance to textile washing). Increased P content generally resulted in better fire performance. Si and N addition improved fire performance (LOI) for the same P content. Addition of only N did not do so at low P content. The authors suggest that urea (N source) acts by improving accessibility of hydroxyl groups in the cotton fibre and silicon by forming stable silicates in char. These PIN flame retardant treatments reduced smoke density very considerably (75% lower specific smoke density with 2% P).

"Synergistic effects in the pyrolysis of phosphorus-based flame retardants: the role of Si- and N-based compounds", S. Deh et al., Polymer Degradation and Stability 130 (2016) 155e164 http://dx.doi.org/10.1016/j.polymdegradstab.2016.06.009

ECHA proposals on safer chemicals substitution

ECHA has published a study commissioned from University of Massachusetts Lowell on how to improve implementation (from identification to adoption) of safer chemicals alternatives. ECHA considers the designation of SVHCs (Substances of Very High Concern) under REACH to drive substitution in Europe. The flame retardants HBCDD, SCCPs, TCEP and TXP are today on the SVHC "Candidate List". Nearly 90% of industry respondents (N=79) to a survey carried out for the study indicated already to have implemented chemical substitution, but important challenges are identified concerning access to data on possible substitute chemicals and evaluation of technical feasibility. The report recommendations to facilitate effective substitution include investment support to develop and roll out substitutes, technical support to SMEs for adoption and extending GPP (green public procurement – the US EPA Safer Choice Program is cited). The report recommends to develop networks of experts and R&D institutes to support industry and governments in assessment and adoption of substitutes.

"Improving the Identification, Evaluation, Adoption and Development of Safer Alternatives: Needs and Opportunities to Enhance Substitution Efforts within the Context of REACH. An evaluation and report commissioned by the European Chemicals Agency", J. Tickner and M. Jacobs, University of Massachusetts Lowell, Lowell Center for Sustainable Production, August 2016

Demand for PIN flame retardants continues to grow

A market report by Zion Research predicts accelerating growth in the world flame retardant market, from US$ 6 billion in 2014 to US$10 billion in 2020, with an annual growth rate increasing progressively each year and averaging +10%/year over the 6 years. This growth will be particularly driven by safety regulations in buildings and in automobiles. "Toxicity issues related to halogenated FRs" will result in organic molecule, phosphorus-based FRs being one of the fastest growing segments. A second report by 360 looks at the non-halogenated FR market to 2021. A third report by QY Research predicts growth of PIN flame retardants in the specific market of PBT (polybutylene terephthalate), a technical engineering thermoplastic polymer, from 2011 to 2020. PBT offer performance mechanical properties and resistance to wear and is increasingly used in electronics, automobile construction and in technical fibres. A fourth report (WGR) on all flame retardants estimates that the global FR will more than double from 6.7 billion US$ in 2016 to over 14 billion US$ in 2022, driven by increasing fire safety requirements and new end-user industries. Construction and infrastructure applications will grow particularly, and the development of synergists will contribute to market diversification.

"Demand Globally for Flame Retardant Chemicals to Grow", 9 June 2016 Zion Research report Dec. 2015 "Halogen-Free Flame Retardant Market Analysis and Forecast by Applications and Competitors to 2021", 360 Market Updates, October 2016. "Flame Retardant Chemicals (Aluminum Trihydrate (ATH), Antimony Oxides, Bromine, Chlorine, Organophosphorus and Others) Market for Building & Construction, Electronics, Automotive & Transportation, Wires & Cables, Textiles, and Other End-users: Global Industry Perspective, Comprehensive Analysis, and Forecast, 2014 – 2020"

"Global Halogen Free Flame Retardant PBT Market Professional Survey Report 2016", QY Research July 2016

"Flame Retardant Chemicals - Global Market Outlook (2016-2022)", WGR649638, 1 August, 2016

EU Ecolabel criteria updates

The European Commission has published revised EU "Flower" Ecolabel criteria for computers and for furniture. Furniture must not contain chemicals are on the Candidate List for Substances of Very High Concern nor adhesives, varnishes, paints or flame retardants which are classified for certain environmental or health hazards. Flame retardants may nonetheless be classified as H317, H373, H411, H412, H413 if the fire protection for the product is required by regulation, public procurement or standards. Additionally, in polyurethane foam ten designated flame retardants are specifically excluded. For computers, plasticisers, additives, coatings, salts and flame retardants are similarly required not to be classified for the specified health and environmental hazards, but in this case with exemptions for certain parts under certain conditions: for example in external power cables and printed circuit boards if halogen acid gas emissions or dioxin/PCDD/DF emissions are low in case of fire. Also, for parts such as casings the flame retardant must be recycling compatible as specified in the criteria.

Revised EU Ecolabel criteria for furniture, Commission Decision C(2016)4778 of 28 July 2016

Revised EU Ecolabel criteria for personal, notebook and tablet computers, Commission Decision (EU) 2016/1371 of 10 August 2016

International concerns about external foam insulation

The US NFPA (National Fire Protection Association) Vice-President, Donald Bliss, underlines the risks to life and property of non fire-safety treated external façade cladding on buildings across the world. Polyurethane foam or extruded polystyrene, for example, with a covering, provides weather protection and thermal insulation. Fire standards such as NFPA 285 (Standard Fire Test Method for Evaluation of Fire Propagation Characteristics of Exterior Non-Load-Bearing Wall Assemblies Containing Combustible Components) define fire testing for such components. But in many countries, there are no fire safety regulations or no enforcement to enable implementation of such standards. The result in such situations is that many buildings are clad in foam materials which are not fire-safety treated, and as high-rise building accelerates in developing nations without appropriate standards being put into place, the extent of risk is increasing. Donald Bliss concludes: "The stark reality is that jurisdictions without modern building codes and effective regulatory systems have a high potential to experience large-loss-of-life fires if nothing is done to address the problem." A reader response to the NFPA article indicates that a building cladding fire in China in 2000 caused 58 deaths and injured over 70 people.

"Skin Deep. Exterior facade fires become an increasingly worrisome international problem", D. Bliss, NFPA Journal July – August 2016

Correction – PIN FRs in poly lactic acid (PLA)

In pinfa Newsletter n°63, page 5, summarising Wang et al. 2016 we indicated that with 5% PIN flame retardant loading (a combination of phosphorus and nitrogen FR and graphene) UL9-V0 (3mm thickness) fire performance was achieved. It should be clarified that this was achieved for the solid PLA (polylactic acid). For PLA foams, UL-94 V0 was not tested, but linear burning rate was reduced by around 25% at 15% FR plus 1.5% graphene loading. We would like to thank Daniel Vadas for bringing this error to our attention

Publisher information:

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For abbreviations see: www.pinfa.org