PIN FLAME RETARDANTS AND RECYCLING

Non-halogenated Phosphorus, Inorganic and Nitrogen (PIN) flame retardants

pinfa

A sector group of Cefic

Publisher & Editors
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INTRODUCTION TO **PINFA AND RECYCLING**

pinfa is the European industry federation of manufacturers and users of PIN flame retardants (non-halogenated Phosphorus, Inorganic and Nitrogen Flame Retardants), part of the European Chemical Industry Federation (Cefic).

Fire safety is an essential prerequisite for societal use of advanced materials, for example in renewable energy, batteries and information technologies, or for green materials such as wood, natural fibres or recycled cellulose insulation materials.

Flame retardants are designed to durably provide fire safety throughout products' lifetimes, which can be decades for construction materials. They should also be compatible with safe recycling at the end of this lifetime.

PIN flame retardants (not containing halogens) aim to be compatible with safe recycling decades in the future, by offering both durability over time and chemical safety. PIN flame retardants offer the inherent advantage of not contributing to possible dioxin emissions in case of inappropriate disposal. pinfa members are committed to improving the health and environmental safety profile of PIN fire safety solutions, whilst continuing to ensure product durability and performance. pinfa members do not promote SVHC flame retardants, because these are an obstacle to recycling.

All additives used in plastics and in other materials are a potential obstacle to recycling, by increasing complexity of logistics and processing (different materials with different additives), or by possibly interfering with mechanical or chemical recycling processes. PIN flame retardants are one of many additives (alongside e.g. stabilisers, plasticisers, ultra-violet and weathering protection additives, colours and surface treatments) and are often used at higher loadings. Ensuring compatibility of PIN flame retardants with recycling is thus core to the Circular Economy.

This document is developed by pinfa to bring together information on PIN flame retardants and recycling, including both studies funded by pinfa and other reports and publications. The aim is to help researchers, regulators and companies identify where further research, process or product development is needed.

pinfa welcomes additional information, input or dialogue with the aims of better understanding and further promoting compatibility of chemically safe fire safety of modern materials with the Circular Economy.

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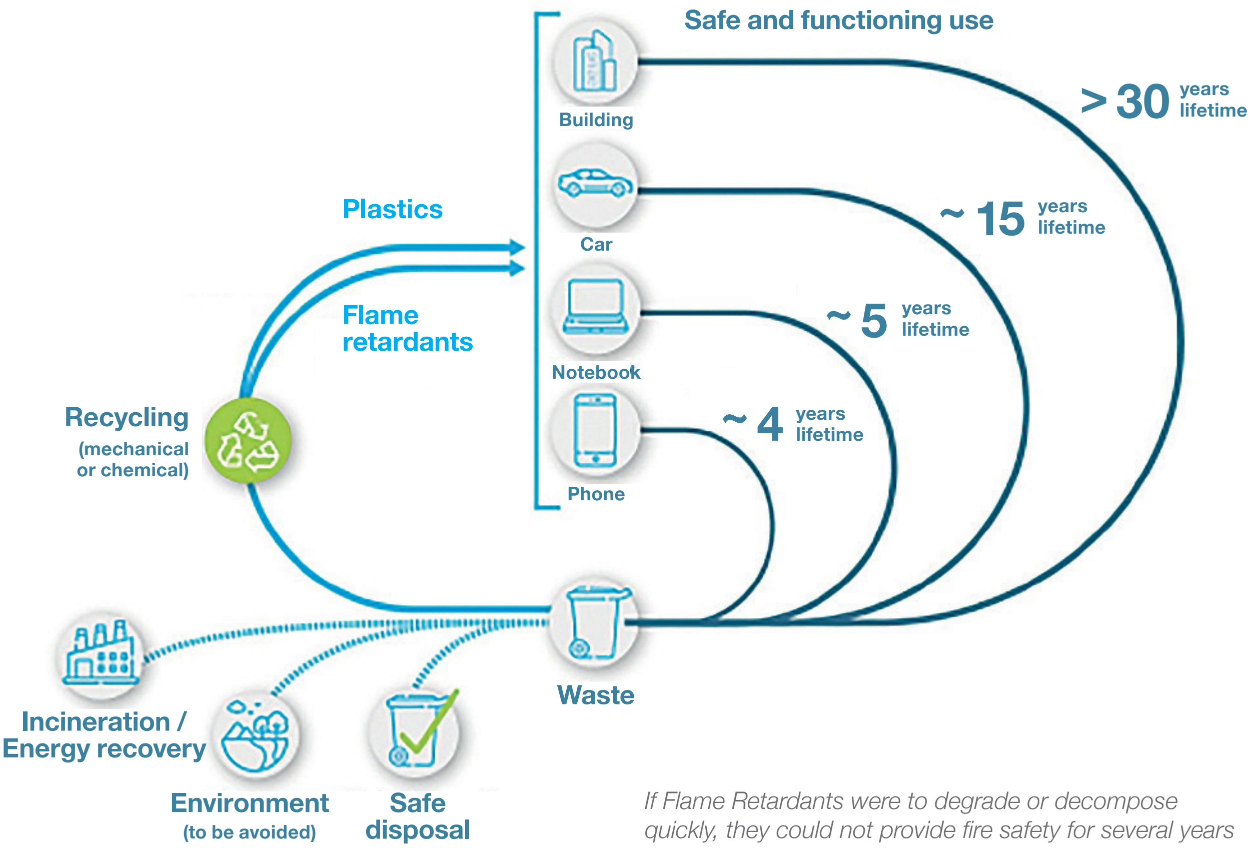
THE PINFA VISION OF **SAFETY BY DURABILITY FOR A LONG PRODUCT LIFETIME**



If Flame Retardants were to degrade or decompose quickly, they could not provide fire safety for several years or decades as required. They are chemically robust and stable to ensure a long product lifetime.

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PNO STUDY FOR PINFA ON **PERSPECTIVES FOR PIN FRs IN PLASTICS RECYCLING**

Development opportunities and need for more data for PIN flame retardants in plastics recycling.

pinfa commissioned a study from technology perspectives analysts PNO to assess available information on the impacts of PIN FRs on plastics recycling, developments, policy and industry opportunities and research needs.

Nearly 100 publications and patents were analysed, and six research and industry experts interviewed. This showed that there is today very little published information on the impacts and fate of flame retardants in different plastics recycling processes (mechanical, chemical-solvent, chemical-pyrolysis). Most R&D has been concentrated on separation of waste electronics plastics containing brominated flame retardants, because this is a legal obligation in Europe.

PNO expects use of PIN FRs to increase, because of the need to combine fire safety with better environment and health profiles, whilst also end-of-life plastics recycling increases rapidly, driven by EU Circular Economy policy and the Green Deal.

PNO expects mechanical plastics recycling to be developed, with the emphasis on polymer recycling, but with pyrolysis or solvent dissolution recycling as important complementary routes. The main challenges for mechanical recycling are upstream collection and sorting, and degradation of the polymer itself under reprocessing. Chemical recycling technologies are emerging, and will become significant.

The report underlines that there is today little published research on PIN FRs in plastics recycling and recommends to:

- Increase knowledge and mapping of PIN FRs in different end-of-life plastics, through value-chain cooperation and transparency.
- Facilitate access to technical information by developing a database of studies and on PIN FRs in recycling.

The following R&D needs are identified:

- Identification, sorting and separation of plastics containing different PIN FRs, including for specific streams such as end-of-life batteries.
- Separation of PIN FRs in chemical recycling processes, to both recover and recycle the flame retardant and enable recovery of purified feedstock.

"A study of the state-of-the-art and Impact of Phosphorus, Inorganic and Nitrogen Flame Retardants (PIN FRs) on recycling, taking into account the current and upcoming, legislation, policies, technologies and market developments", PNO for pinfa, 2022, (available on request).

Literature Topics Heatmap

Bisphenol A	Electronic Waste	Halogen FR/Brominated FR	High-Density Polyehylene and Polyethylene	Incineration and Combustion
LCA, Environment Pollution	Polymer, Organic and Inorganic Chemistry	Waste Recycling, Waste Management	Ammonium polyphosphate	Catalysis
Cellulose	Chemical engineering	Coating	Composite material	Elastomer
Ethylene	Extraction (Chemistry)	Extrusion	Fiber	Filler (materials)
Fire retardant	Flammability	Glass fiber	Intumescent	Materials Science
Melamine	Nanocomposite	Organophospahte	Phosphate	Phosphorous
Plasticizer	Polyester	Polypropylene	Polyurethane	Solid phase extraction
Solvent	Thermal decomposition	Thermal stability	Thermoplastic polyurethane	Triphenyl phosphate

The darker the green, the more publications identified for a given topic.

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PINFA – FRAUNHOFER LBF
TESTS OF RECYCLING PIN FLAME RETARDANT PLASTICS

This document summarises project IGF 18246N. Funded via AiF within the funding program of Collective Industrial Research (IGF) from the German Federal Ministry for Economic Affairs and Energy on the basis of a resolution of the German Bundestag. With the support of the Forschungsgesellschaft Kunststoffe e.V. and pinfa (Phosphorus Inorganic and Nitrogen Flame Retardants Association, a sector group of Cefic, the European Chemical Industry Council).

Mechanical recycling was tested for ten widely-used polymer / PIN flame retardant compounds, as used commercially including stabilisers and anti-drip agents (including two compounds with glass fibre).

Testing involved five processing cycles (artificial ageing – melting – re-extrusion to film or injection moulding to pellets at 140°C – 290°C depending on the polymer), without any addition of virgin material. Material and fire performance properties of the re-extruded compounds were tested. The neat polymers (or with glass fibre) were also similarly tested for five processing cycles.

In 9 out of ten combinations, flame retardancy was retained after this multiple processing, with changes being related to impacts of reprocessing on the anti-dripping agent not on the flame retardant. For many combinations, material performance properties deteriorated, but this is related to the base polymers and to shortening of glass fibres, not to the PIN flame retardants.

Compounds tested and processing conditions

POLYMER	PIN FLAME RETARDANT(S)	PROCESSING	PROCESSING TEMPERATURE
PP (polypropylene)	30% APP (ammonium polyphosphate)	Injection moulding (pellets)	230°C
	27.5% piperazine pyrophosphate	Injection moulding (pellets)	200°C
	0.5% Triazine derivative	Extrusion (film)	210°C
	1% N-alkoxy hindered amine	Extrusion (film)	210°C
LLDPE (low density polyethylene) + 5% coupling agent	60% ATH (aluminium trihydroxide)	Injection moulding (pellets)	140 -165°C
	62% ATH + 3% sepiolite	Injection moulding (pellets)	140 -165°C
Polyamide PA66 with 30% glass fibre	20% DEPAL (aluminum diethyl phosphinate)	Injection moulding (pellets)	290°C
Polyamide PA6 with 30% glass fibre	20% DEPAL (aluminum diethyl phosphinate)	Injection moulding (pellets)	270°C
	10% melamine cyanurate	Injection moulding (pellets)	230°C
PC/ABS (80/20)	12% phosphate ester	Injection moulding (pellets)	260°C

In all cases, compounds also included standard commercial stabiliser and/or anti-drip additives at 0.1 – 0.3%.
LLDPE included a coupling agent at 5%

Selection of polymer – PIN FR combinations

Five of the most widely used thermoplastic polymers were tested, with in each case 1 – 3 non-halogenated (PIN) flame retardant solutions selected to be representative of typical commercial compounds. Phosphorus, mineral and nitrogen-based PIN flame retardants are covered. In all cases, standard additives were also included as in commercial plastic formulations: stabilisers, anti-drip and/or coupling agents. The ten resulting formulations are typical of thermoplastics used in electronics and construction, in injection moulding or film extrusion.

Repeated ageing – recycling

Each PIN FR material was tested over five processing passes, without any addition of virgin material, to simulate repeated recycling, that is: virgin material processing, and four ageing-reprocessing cycles. Each of the four reprocessing passes included several stages: extrusion to produce granules, degassing to remove low molecular weight breakdown products, artificial ageing and injection moulding / film extrusion. Ageing before or after granulation were tested. Artificial ageing was by dry oven heating at 100°C – 135°C for up to 1900 hours (temperatures adapted to polymer resilience).

Accelerated oven ageing of specimens, reprocessed granules, as subsequently extruded into films or injection molded into specimens

Materials testing

1.6 mm (and in some cases 0.8 mm) samples were fire performance tested using UL 94 vertical and horizontal burn tests, or for films DIN 4102-1 B2 (building materials).

Mechanical properties of samples (DIN EN IS0 527-2) were tested to tensile strength, elongation at break and Young's modulus (elastic deformation).

Mechanical testing was carried out on both freshly processed samples and aged samples.

Effects of recycling on properties

Analysis of molecular weights show, depending on the polymer, that these are slightly reduced by recycling, but that this is not impacted by the presence of the PIN FRs.

First tests showed around twenty-fold reductions in glass fibre length after just one extrusion pass for PA66. The extrusion screw initially used, which was equipped with mixing and kneading, was replaced by a pure feed screw, thus reducing this impact.

These impacts of recycling on polymer molecular weight (breaking of some polymer chains) and on glass fibres (breaking of fibres resulting in shorter fibres), explain why mechanical properties deteriorate with recycling. However, these effects are in nearly all cases not modified by the presence of PIN flame retardants. In some cases, the deterioration of mechanical properties due to polymer degradation in reprocessing can be mitigated by using chain-extender additives.

Fire performance was in most cases not impacted by recycling, showing that the PIN FRs were resilient to ageing and reprocessing (subject to respecting the recommended processing temperatures).

In some cases, however, UL 94 vertical burn test performance was reduced to V2 because of flaming dripping. This was considered to be probably due to deterioration in the polymer and fibres, not to the PIN FR. Tests showed that this problem could be addressed by addition of a chain-extender additive during recycling (e.g. maleic anhydride, in order to retain zero-halogen quality), in which case UL 94 V-0 fire performance could be maintained (example of PA6 – melamine cyanurate).

Fire performance testing: DIN 4102-1 and UL 94

Summary of results by polymer / PIN FR combination

Polypropylene + different PIN FRs:
(APP = ammonium polyphosphate, piperazine-pyrophosphate, triazine derivative, N-alkoxy hindered amine): PIN FRs do not significantly modify consequences of reprocessing on mechanical properties nor on fire performance, but can accentuate discoloration resulting from reprocessing.

Polyamide:
+ melamine cyanurate: significant deterioration of properties with polyamide only, and similar with polyamide plus PIN FR. This can be remedied using a chain-extender additive.
+ glass fibres + aluminium diethyl phosphinate: shortening of the glass fibres deteriorated mechanical performance, unaffected by the PIN FR. Fire performance did not decrease. The PIN FR tended to reduce discoloration.

Polyethylene + ATH (aluminium trihydroxide): no significant negative impacts.

PC/ABS + phosphate ester: deterioration of fire behaviour, probably due to loss of effectiveness of anti-drip agent.

General conclusions: fire performance is retained after multiple reprocessing and ageing for nearly all tested PIN FR formulations. Damage to the polymer matrix is generally not accentuated by the PIN FR. Also, except in polypropylene, the PIN FRs do not accentuate discoloration.

References & links

Fraunhofer IGF (Institute for Structural Durability and System Reliability; Plastics Division), project n° 18246N "Recycling of halogen-free flame retardant plastics", Forschungsgesellschaft Kunststoffe e. V. (FGK), 18.02.2019 (available on request).

Summary table of results

Impacts of multiple ageing – reprocessing cycles

POLYMER	PIN FLAME RETARDANT(S)	Young's Module	Tensile Strength	Elongation at break	Gloss or discoloration	Fire performance
PP (polypropylene)	APP (ammonium polyphosphate)	N	N		•	
	Piperazine pyrophosphate	N	N	S	•	S
	Triazine derivative	N	N		•	
	N-alkoxy hindered amine	N	N	N	(2)	
LLDPE (low density polyethylene)	ATH (aluminium trihydroxide)	N	N	N	(1)	N
Polyamide PA6 or PA66 with glass fibre	DEPAL (aluminum diethyl phosphinate)	S	S	S	S	S
	Melamine cyanurate					
PC/ABS	Phosphate ester	N	N	N	Gloss N Gloss S	S

S = similar deterioration of properties with polymer-only and with polymer-plus-PIN FR
N = no significant deterioration with polymer plus PIN FR
• = deterioration only with PIN FR or significantly greater for PIN FR compound compared to polymer only
(1) Polymer only not tested so comparison not possible
(2) Not measured

Fraunhofer LBF
iGF Industrielle Gemeinschaftsforschung
Bundesministerium für Wirtschaft und Energie

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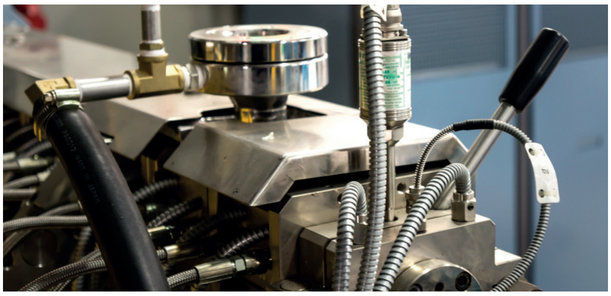
OTHER TRIALS OF **MECHANICAL RECYCLING OF PIN FR PLASTICS**



Mechanical recycling of PIN FR polymers

A TU Darmstadt thesis suggests that PIN FRs are not an obstacle to mechanical recycling of thermoplastics.

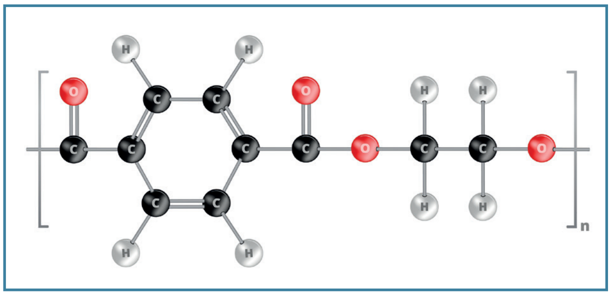
Mineral, nitrogen and phosphorus based PIN flame retardants (ATH, sepiolite, aluminium diethylphosphinate, piperazine pyrophosphate, phosphate ester, APP, melamine cyanurate) were tested in various thermoplastics: polypropylene, polyethylene, polyester, polycarbonate/ABS blend, including with glass fibres and stabilisers. Material deterioration with multiple recycling (five extrusion cycles) showed to be principally related to the base polymer properties, and to shortening of glass fibres, rather than to the PIN FR used, and deterioration of fire performance to damage of anti-drip agents. In PA6 with melamine cyanurate, it was shown that use of a chain-extension additive (maleic anhydride) during re-extrusion significantly reduced polymer property deterioration.

"Recycling von halogenfrei flammgeschützten Kunststoffen" (Recycling of halogen-free flame retardant plastics), Technische Universität Darm stadt thesis, Christoph Schultheis, 2021 ***https://tuprints.ulb.tu-darmstadt.de/18626/1/Dissertation_ChristophSchultheis.pdf***
See also summary of pinfa - Fraunhofer LBF project above.

Phosphorus PIN FR improves PET recycling

Two phosphorus PIN FRs show to protect polymer properties in recycling (multiple re-extrusion cycles) of PET.

Poly(ethylene terephthalate) (PET), a polymer widely used for films and textiles, was tested pure and flame retarded with DOPO-PEPA (5%) or with a phosphate ester (3%). Three re-extrusion cycles were carried out. The DOPO-PEPA containing PET showed less deterioration of material properties than pure PET after mechanical recycling, attributed to DOPO-PEPA improving lubrification and melt properties (stabilisation). The phosphate ester however led to embrittlement of the PET after mechanical recycling, probably by boosting polymer chain branching and extension.



"Investigating thermomechanical recycling of poly(ethylene terephthalate) containing phosphorus flame retardants", C. Bascucci et al., Polymer Degradation and Stability, vol. 195, January 2022, 109783
https://doi.org/10.1016/j.polymdegradstab.2021.109783

"Enhanced PET processing with organophosphorus additive: Flame retardant products with added-value for recycling", A. Gooneie et al., Polymer Degradation and Stability 160 (2019) 218e228
https://doi.org/10.1016/j.polymdegradstab.2018.12.028

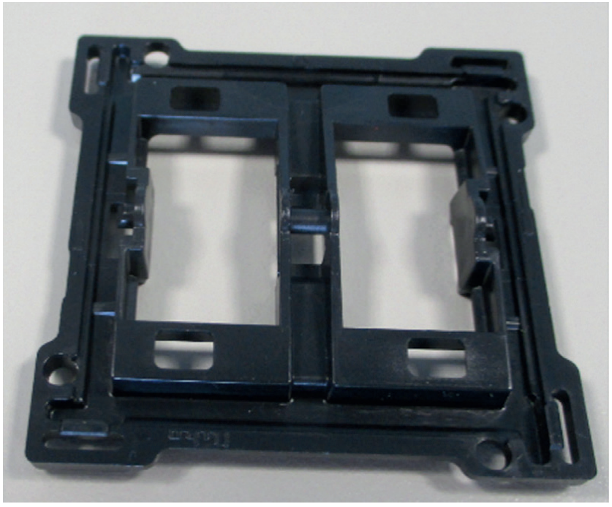
DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
PEPA = 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2]octane

FRs compatible with TV plastics recycling

A study (two papers) from Belgium[1], shows that phosphorus flame retardants in LCD TV back covers are compatible with an optimal recycling strategy, identified as dismantling, take-back of the covers and reprocessing to new E&E parts.

Tests carried out showed that PC/ABS containing phosphorus FRs could be recycled (melt filtration compounding and injection moulding), showing quality compatible with industrial use in existing E&E parts production (without process redesign), and achieving UL 94 V-0 at 3.2 mm and V2 at 1.7 mm without addition of FRs.

It is concluded "that when a dismantling based recycling for direct reapplication is applied for PC/ABS with phosphorus FRs a high quality recyclate can be produced which is characterized by good processing, mechanical, flammability and aesthetical properties". The authors indicate that nearly 400 000 t/y of LCD TVs will reach end-of-life in Europe in 2020, of which 14% by weight is plastic back covers. The paper summarises sorting technologies available today: Fourier Transform InfraRed (FTIR), Raman spectroscopy, X-ray transmission, X-ray fluorescence, sliding spark spectroscopy and laser induced breakdown spectroscopy.



© light switch internal part injection molded from recycled PIN flame retardant PC/ABS. From Wagner et al. 2014.

Other recycling strategies compared included recycling of the back covers to masterbatch production (tested and shown operational for HIPS containing brominated FRs). This may offer logistic benefits because low recyclate quantities can be handled by masterbatchers. Both the above strategies were considered preferable to sorting after shredding of mixed WEEE because higher quality sorting is achieved by dismantling, so enabling economic recovery of "high value of additives, such as FRs".

A key conclusion is the importance of collaboration between WEEE recyclers and customers for recycled materials, as well as the need for E&E equipment to be designed for dismantling. The Life Cycle Assessments (LCA) of the different recycling scenarios are compared in a third paper[2] indicating that in this case, WEEE plastics recycling has lower environmental impact than incineration with energy recovery and virgin plastic production. The LCA is above all driven by quantities of plastic recycled, rather than the recyclate quality. Recycling of FRs has no significant impact on the LCA, because the impact of their production (per kg) is considered similar to that of polymers.

1 = "Towards a more circular economy for WEEE plastics – Part A: Development of innovative recycling strategies" and "Towards a more circular economy for WEEE plastics – Part B: Assessment of the technical feasibility of recycling strategies", F. Wagner et al., Waste Management 100 (2019) 269–277 ***https://doi.org/10.1016/j.wasman.2019.09.026*** *and Waste Management 96 (2019) 206–214,* ***https://doi.org/10.1016/j.wasman.2019.07.035*** *funded by the Flemish Environmental Technology Platform (MIP) and the Flanders Innovation & Entrepreneurship (VLAIO) in the Next Level Plastics Recycling project and with Bertin Technologies, Belgium.*

2 = "Diversified recycling strategies for high-end plastics: Technical feasibility and impact assessment", W. Dewulf et al., CIRP Annals - Manufacturing Technology 68 (2019) 29–32 ***https://doi.org/10.1016/j.cirp.2019.04.004***

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RECYCLING **CABLE POLYMERS**

Diaz et al. (2018) tested recycling of post-consumer cable polymers back to cables by milling and rotational molding to produce 200 mm test polymer cubes, after blending 10-50% with virgin polyethylene (PE).

The recovered cable materials came from a waste management company in the Canary Islands, Spain, after metal recovery from cables, and contained a mixture of PE, cross-linked PE co-polymers, PIN flame retardants, PVC and rubber. Up to 35% of recovered material that is, 65% virgin polymer could be used without significant deterioration of mechanical properties.

Use of multiple layers in the moldings, with lower recycled content in external layers, improved appearance. In previous cited work (Boss, Swerea, 2014) cable production scrap, cables recycling (ABB, Draka, Eriksson, Nexans) and End-of-Life cable wastes (Stena recycling) were tested, concluding that recycling was feasible, but that recycling of HFFR (halogen free flame retardant) cable was challenging because of high filler content and filler decomposition.

Additionally, contamination by even small amounts of PVC (from non HFFR cables) drastically reduced the mechanical performance of recycled HFFR materials, although use of an EVA compatibiliser may mitigate this problem.

Diaz, S., et al., Waste Management, Volume 76, June 2018, Pages 199-206, Recycling of polymeric fraction of cable waste by rotational moulding. ***https://doi.org/10.1016/j.wasman.2018.03.020***

Boss A. 2014, Swerea IVF-Report 21813, Recycling of electrical cables. With focus on mechanical recycling of polymers, (35pp) ***http://cable.extranet.swereaivf.se/documents/2014/06/recycling-of-electrical-cables-with-focus-on-mechanical-recycling-of-polymers.pdf***

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PIN FR PLASTICS AND SOLVENT RECYCLING

FRs and solvent-based recycling

Different solvents were tested for dissolution - purification recycling of mixed E&E waste showing recovery of polymers and removal of FRs.

Mixed, shredded E&E plastic waste was provided by a commercial waste recycler in the USA, after mill beating and metal separation. This waste contained 6 – 12% phosphorus (P) and 1 – 6% bromine (Br), presumed to be in flame retardants. Eleven different solvents were tested for polymer dissolution, then dichloromethane (DCM), tetrahydrofuran (THF), methanol (MeOH) and ethylene glycol (EG) selected for further testing. Various anti-solvents were tested to precipitate and recover the polymers from solution.

Depending on polymer and on the solvents/anti-solvent combinations, up to 99% of polymer was recovered from the wastes. The optimum solvent/antisolvent combination (methanol / ethylene glycol) removed up to 94% of phosphorus flame retardants (based on measurement of phosphorus contents), resulting in low levels in the recovered polymer, whereas removal of brominated FRs was ineffective, leaving 3 – 4% bromine in the recovered polymer.

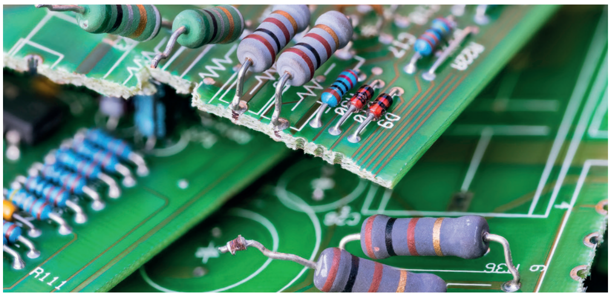
pinfa comment: other trials show that different solvents can remove bromine in polystyrene recycling down to ppm levels.

"Chemical Recycling of Mixed Plastics in Electronic Waste Using Solvent-Based Processing", L. Anderson et al., Processes 2022, 10, 66. ***https://doi.org/10.3390/pr10010066***

Recovery of PIN FR from waste printed circuit boards

Solvent extraction was tested to recover the organophosphorus PIN flame retardant TPP from waste printed circuit boards.

TPP (triphenyl ether phosphate) is used as a flame retardant in CEM types of printed circuit boards based on phenol formaldehyde resins. After removing components such as capacitors and relays, the circuit boards were ground then placed in methanol solvent for different times and temperatures. Two hours at 90°C in the solvent showed to be optimal, enabling recovery of nearly 85% of the flame retardant. The flame retardant was then recovered by evaporating the solvent, which was recovered for reuse, using a vacuum rotary evaporator. The recovered flame retardant was over 90% pure.



"Recovery of triphenyl phosphate from waste printed circuit boards by solvothermal process", C-C. Zhang, F-S. Zhang, Chemical Engineering Journal, 2013, DOI: ***http://dx.doi.org/10.1016/j.cej.2013.11.048***

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PIN FRs ENABLE RECYCLING OF PLASTICS

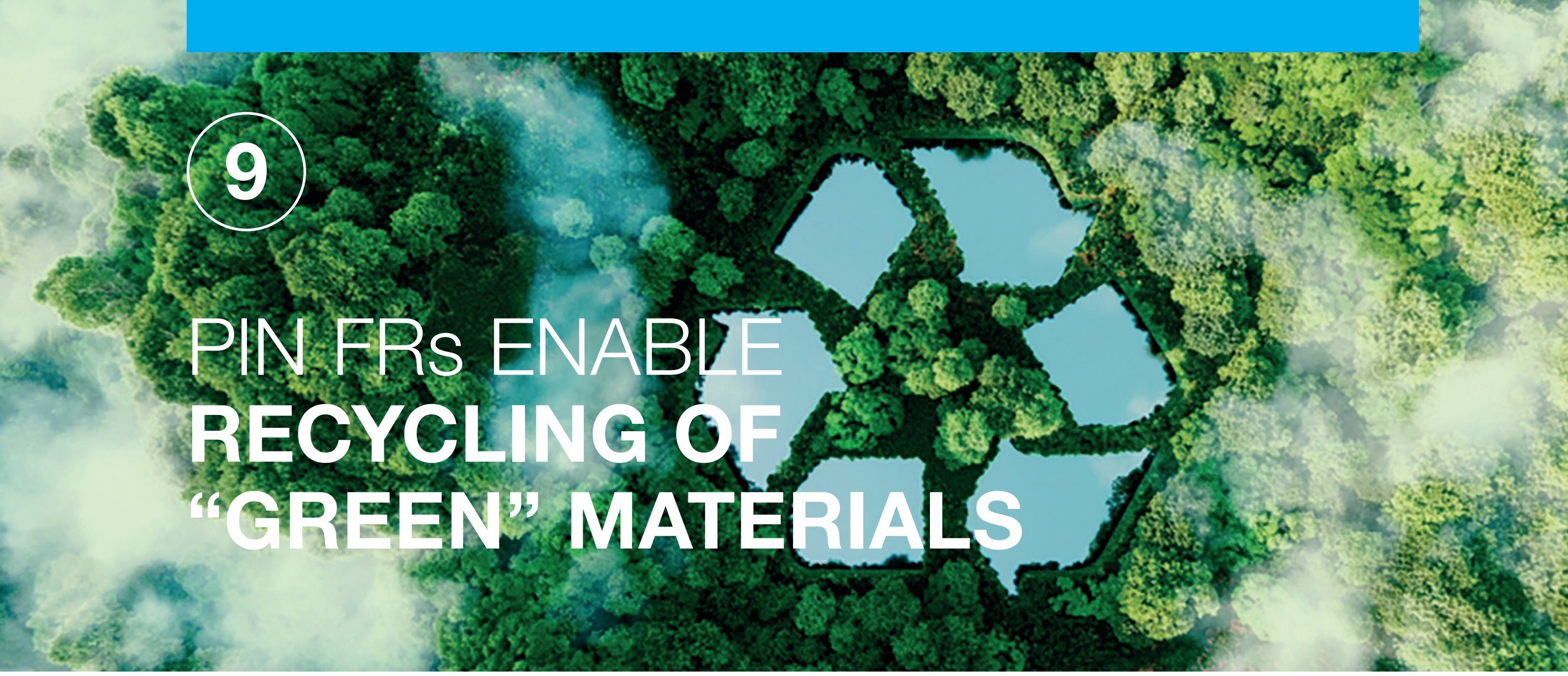
PIN compounds to recycle polyurethanes

Phosphorus, nitrogen and inorganics used in polyurethane chemical recycling produce PIN flame retardant recycled PUR.

Glycolysis is the most widespread route for chemical recycling of polyurethanes (PUR). Glycols or glycerol (which can be bio-derived), with catalysts, are used as depolymerising agents (usually at around 180 to 240°C). This breaks chemical bonds, converting PUR polymers to oligomers (ended by hydroxyl and amine moieties) and breaking crosslinking.

Seven studies are summarised which show that PIN compounds, phosphate esters or nitrogen-mineral (urea-boron) containing polyol, can be used for glycolysis of PUR then production of a PIN FR recycled PUR. Other studies show that glycolyzed PET poly(ethylene terephthalate) plastic waste can also be recycled to PIN flame retardant polyurethane (PUR).

"Materials and Chemistry of Flame-Retardant Polyurethanes", Volume 1: A Fundamental Approach, 2021, ed. K. Gupta
https://pubs.acs.org/doi/10.1021/bk-2021-1399
chapter 12, pages 265-284, "Recycling of Polyurethanes Containing Flame-Retardants and Polymer Waste Transformed into Flame-Retarded Polyurethanes", M. Włoch
https://doi.org/10.1021/bk-2021-1399.ch012



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PIN FRs ENABLE **RECYCLING OF “GREEN” MATERIALS**

PIN FR recycled denim fire blocks

Denim cotton fabric can be recycled using PIN flame retardants to produce composite boards for fire compartmentation.

The world produces some 150 million t/y of textile waste. This review suggests that end-of-life denim cotton fibres treated with PIN flame retardants (such phosphorus-based compounds, nano-coatings or borates) can be used to produce structural boards suitable for use as fire-resistant barriers (fire compartmentation). pinfa notes FRs are important to ensure fire safety of recycled organic materials used in construction. See e.g. pinfa Newsletter n°38: recycled denim based material used for insulation caused fire spread, resulting in 6 million US$ damage to an industrial building in Wisconsin in 2014.

“Development of fire retarding composite board for fire compartmentation application using waste denim: A review”, Aman et al., Materials Today Proceedings 2022 ***https://doi.org/10.1016/j.matpr.2021.12.513***

PIN FRs for recycled Tetra Pak

PIN flame retardants show to be effective in PEAL, a composite material resulting from recycling of Tetra Pak packaging.

PEAL is produced in Italy by collecting used Tetra Paks 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 UL94-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***

PIN FR polyester from waste plastic

© Clariant

Clariant and Lavergne have launched a PIN flame retardant polyester produced from ocean-bound plastic (OBP).

This is plastic waste, collected in Haiti, which would have reached the ocean if it had not been recovered. Some 8 million tonnes of plastic are estimated to enter the world's seas each year. The new OBP-based compound, Lavergne VYPET OBP-FR is 30% glass fibre reinforced PET (polyethylene terephthalate). It offers UL94-V0 (0.8 mm) fire performance, achieved using PIN flame retardants from Clariant, in particular phosphinates which offer GreenScreen Benchmark 3 and have been demonstrated to be compatible with plastics recycling.

The PIN FR and synergists used ensure that the compound is adapted for E&E applications, requiring structural and aesthetic qualities, and is compatible with reprocessing of post-consumer plastics. pinfa member Clariant is a phosphorus FR specialist. Lavergne is a Canada-based world leader in engineering resins from recycled plastics.

"A new high-performance life for plastic waste: Lavergne and Clariant develop halogen-free flame-retardant compounds for electronics based on recycled ocean-bound plastics (OBP)", 27 February 2020
https://www.pressreleasefinder.com/Clariant/CLAPR1660/en/

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RECYCLING THE **ELEMENTS OF PIN FRs**

PIN FRs and circular chemistry

Different elements in PIN flame retardants can be potentially derived from end-of-life PIN FR treated materials and from other secondary materials:

- **Phosphorus** used in PIN flame retardants, currently coming from mined phosphate rock, could be recovered as P4 from wastes such as sewage sludge incineration ashes. This was piloted full-scale at the Thermphos P4 production site, The Netherlands[1], but this company is now closed. An experimental pilot was demonstrated in Austria[2], and the technology has been purchased by pinfa member company Italmatch and is being developed in the EU-funded FlashPhos project[3].
- Phosphorus and nitrogen in spent fire extinguishers (which can no longer be reconditioned) can be recycled as fertilisers[4].
- **Boron** can potentially be recovered from boric acid treated cellulosic insulation material, when this can no longer be recycled, then valorised as a fertiliser[5].
- **Magnesium** for PIN flame retardants can be recovered from ferronickel slag[6].
- **Bio-based flame retardants** can be produced from a range of waste materials or by-products, including fish waste (DNA[7]), crop by-products (phytate[8], lignin, etc).

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 (***www.matrixpolymers.com***). 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***

1 *W. Schipper 2001* ***https://www.researchgate.net/publication/11555468_Phosphate_Recycling_in_the_Phosphorus_Industry***
2 *Recophos, Leoben, Austria, see* ***www.phosphorusplatform.eu/Scope112***
3 *FlashPhos* ***https://cordis.europa.eu/project/id/958267***
4 ***http://phosave.com/***
5 *O. Duboc et al., 2019* ***https://doi.org/10.1021/acs.est.9b04234***
6 *N. Sun et al., 2012* ***http://onlinelibrary.wiley.com/doi/10.1002/9781118359341.ch49/summary*** *X. Zang et al., 2019* ***https://dx.doi.org/10.1021%2Facsomega.9b02262***
7 ***http://www.dafia-project.eu/***
8 ***https://polymerandfire.files.wordpress.com/2012/02/polyflame-nc2b06.pdf***

Recycling boron from cellulose insulation

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Field trials show effectiveness of a fertiliser made by pyrolysis of cellulose fibre insulation containing boron flame retardant.

Boron is on the EU Critical Raw Materials list since 2014, with 70% being used in glass and ceramics, 12% in fertilisers (18% other). Borate is used as a PIN FR in bio-sourced insulation materials, with annual use in the application estimated by the authors as around a quarter of EU use in fertilisers. For this study, boric acid treated cellulose insulation material (produced from recycled paper, Isocell, Austria) was pyrolysed at 600°C to generate a biochar, tested in field trials with maize and sunflower.

The pyrolysis partly converts the boron to low-solubility forms, which is important to avoid losses from soil or possible toxicity to plants, and to reflect plants' slow need and uptake over time. Plant uptake of boron using the insulation material biochar was double that of control (boron content in shoots) and similar to that with a soluble synthetic sodium tetraborate. Lysimeter tests were also carried out, showing that boron losses to ground water using the insulation material biochar did not exceed EU drinking water boron limits.

"Field evaluation of a boron recycling fertiliser", O. Duboc et al., Plant Soil & Environment, 67, 2021 (2): 110–119
https://doi.org/10.17221/567/2020-PSE

Recycled PIN FRs from flue gas cleaning

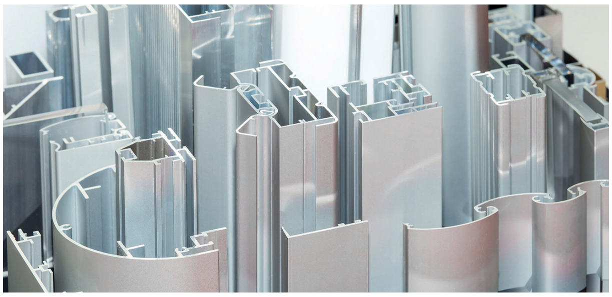
Magnesium and aluminium minerals from coal power plant flue gas scrubbing can be recycled as PIN flame retardants.

The 1 400 MW coal power plant, Nantong, Jiangsu, China, operates lime/gypsum flue gas desulphurisation (FGD), with an objective of zero liquid discharge. In this study, the FGD wastewater was treated in five stages with lime, sodium hydroxide, NaAlO2 and NaHCO3 to stepwise remove and separate heavy metals, calcium sulphate (gypsum), calcium carbonate, magnesium dihydroxide (MDH) and ettringite (a calcium aluminium sulphate mineral Ca6Al2(SO4)3(OH)12·26H2O).

Gypsum can be recycled to the construction industry and calcium carbonate reused in desulphurisation. MDH and ettringite were soak-washed and analysed, and showed to have purity and particle size compatible with use as PIN flame retardants (particle size mostly 1 – 10 µm). Tests in EVA showed that 10% recovered MDH + 20% ettringite increased LOI from around 15 (neat EVA) to around 25.

"Recovering chemical sludge from the zero liquid discharge system of flue gas desulfurization wastewater as flame retardants by a stepwise precipitation process", J. Guo et al., J. Hazardous Materials 417 (2021) 126054
https://doi.org/10.1016/j.jhazmat.2021.126054

ATH from secondary materials



Aluminium trihydroxide was produced from anodisation residues and demonstrated as a PIN flame retardant in polyethylene.

Anodisation of aluminium items uses an acid bath to generate a corrosion resistant surface. Waste from a Brazil aluminium plant was a humid solid. This was dissolved in sodium hydroxide, then aluminium trihydroxide was precipitated by dosing hydrochloric acid. This generated ATH nanoparticles (< 50 nm) with c. 45% crystallinity and a filamentous morphology. 0 to 6% of this ATH was tested as a PIN flame retardant in LLDPE (low linear density polyethylene). 6% ATH reduced the horizontal burning rate of LLDPE from 46 mm/s (neat) to 27 mm/s. The authors conclude that this process could potentially recover aluminium from this industrial waste stream as a useable PIN flame retardant.

"Synthesis of aluminum hydroxide nanoparticles from the residue of aluminum anodization for application in polymer materials as antiflame agents", F. Kuball Silva et al., J. Mater. Res. Technol. 2020 ; 9(4): 8937–8952
https://doi.org/10.1016/j.jmrt.2020.05.108

pinfa

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