Flame retardants (FRs): balancing the benefits.

What research is needed on flame retardants' impacts in reducing fires, smoke emission and smoke toxicity ?

Cefic sector group

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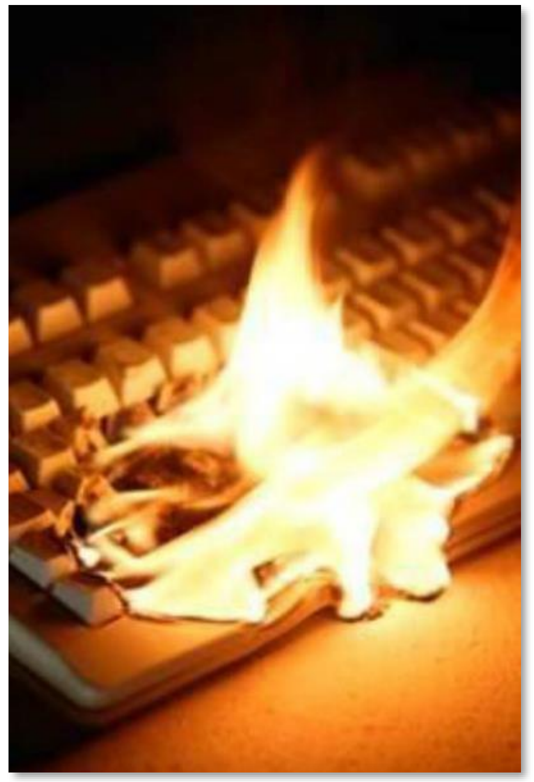

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Presenting *pinfa*

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NFSD Nordic Fire & Safety Days

Nordic Fire Safety Days, 18-19 June 2024

pinfa

pinfa is the Phosphorus, Inorganic and Nitrogen Flame Retardants Association.

pinfa brings together manufacturers and users of non-halogenated phosphorus, inorganic and nitrogen flame retardants (PIN FRs).

pinfa is a Sector Group within Cefic, the European Chemical Industry Council.

pinfa adheres to Responsible Care® - the global chemistry industry's commitment towards safe chemicals management and performance excellence.

***pinfa* sister organisations**:
pinfa North America - www.pinfa-na.org
pinfa China – www.pinfachina.com

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pinfa's mission

"Members of *pinfa* share the common vision of continuously improving the environmental and health profile of their flame retardant products.
This vision is coupled with a commitment to maintain high fire safety standards across the world, standards which minimize the risk of fire to the general public."

pinfa's mission targets:

- Fire safety
- Environment and human health impacts of fire and smoke, and of PIN flame retardants
- Commitment to collaboration with stakeholders, regulators, science and industry

pinfa's mission:
https://www.pinfa.eu/about-pinfa/mission

pinfa Members (EU, China & North America)

ADEKA
AsahiKASEI
AVAKIAN POLYCHEM
AVIENT
BASF We create chemistry
Budenheim
Celanese
CLARIANT
CTF 2000 flame retardants & chemical specialities
domo
DSM BRIGHT SCIENCE. BRIGHTER LIVING.
FR Adviser LLC From Ideation to Commercialization
GC GreenChemicals IMPROVE YOUR PERFORMANCE
Grolman International Distribution
HUBER NON-HALOGEN FIRE RETARDANT ADDITIVES
ICL
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Italmatch Chemicals
java chem 佳華精化
JLS Professional Flame Retardants
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Why do we need flame retardants ?

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Flame retardants are needed for fire safety

We live surrounded by flammable materials

- polymers & composites
- wood & timber
- natural & synthetic fibres/textiles
- cables (electrical, optical)
- batteries

DIGITALEUROPE

Essential for electronics safety

Electronic products are unique because they have potential ignition sources arising from essential components of the product — circuit boards, batteries, and other electrified components. Since 2017, about 500 different types of electronic products have been recalled, withdrawn, or banned from sale in the EU due to fire hazards. One of the most important benefits of flame retardants in product design is they can stop small ignition events from turning into larger fires.

- **Electrical current:** For electronics to operate, the circuit boards and other interior parts like fans, cables, and connectors carry electrical currents. These currents generate heat and can be potential sources of internal ignition, which is why flame retardants are used to mitigate the risk of fire and to help meet flammability standards.
- **Power source:** Batteries are also potential sources of internal ignition. Over-current and over-temperature conditions can be created by external shorts and overcharging and can cause flame ignition within the electronic product. Flame retardants can help fire harden the battery compartment and serve as a critical layer of protection between the battery and the rest of the product.

"DIGITALEUROPE views on upcoming proposal for EU REACH restriction of flame retardants", May 2023 https://cdn.digitaleurope.org/uploads/2023/06/DE-position-on-proposal-for-EU-REACH-restriction-of-flame-retardants.pdf

Fire risks are increasing

pinfa comment:
ubiquitously increasing
fire load:
materials, electronics,
furnishings ...

Challenges identified by IAFSS:

- climate change, wildfires
- new technologies
- globalisation
- population growth, ageing (and so more vulnerable) population
- urbanisation, new construction techniques, tall buildings
- resiliency and sustainability, green buildings

International Association for Fire Safety Science (IAFSS
Agenda 2030 for a Fire Safe World (2019)
https://doi.org/10.1016/j.firesaf.2019.102889

Buses burn, trains don’t

Despite known fire causes (overheating moving parts, electrical systems, batteries) and difficulties of egress (especially in case of accident), fire safety and smoke toxicity requirements for materials used in buses and coaches are much less demanding than for railways - and are widely considered to be inadequate.

Reaction-to-fire testing of bus interior materials: Assessing burning behaviour and smoke gas toxicity”, 2023
https://dx.doi.org/10.1002/fam.3108
Reducing the risk of bus fires”, 2016
https://www.intersecexpo.com/uploads/editor_images/file/fredrik.pdf
Photo: Shutterstock 1791820100

Escape Time in a Modern Domestic Furnished Room Ranges from 1 ½ to 10 Minutes

TIME BEFORE TEMPERATURE REACHES 600–1,000 °C.

These are conclusions of an assessment of > 400 fire tests, including 44 full-scale furnished room tests (2012, 1).

Furnished room tests, with non-FR furniture, reached 200°C with significant smoke at open doorway after 4-8 minutes (2020, 2)

These studies confirm a NIST (USA National Institute of Standards and Technology) study (2007, 3) which showed that **escape times have been reduced to around 1/5th since 1975**.

(1) "Der Brand in Räumen Auswertung von Originalbrandversuchen im Vergleich mit analytischen Rechenverfahren- Teil1", in German (Room fires: conclusions from real situation testing compared with analytical modelling), in "vfdb-Zeitschrift für Forschung, Technik und Management im Brandschutz", 6-2, 2012 https://www.baufachinformation.de/Der-Brand-in-R%E4umen-und-seine-Wirkungen/z/2012069003173
(2) "An overview and experimental analysis of furniture fire safety regulations in Europe", E. Guillaume et al., Fire and Materials, 2020, 1-16, https://doi.org/10.1002/fam.2826 Work funded by BSEF and ACFSE
(3) Access to the revised NIST study, including explanations of modifications, etc. Bukowski, R.W. et al.., 2007, "Performance of Home Smoke Alarms, Analysis of the Response of Several Available Technologies in Residential Fire Settings" NIST Technical Note 1455 (396 pages) https://www.nist.gov/publications/performance-home-smoke-alarms-analysis-response-several-available-technologies

Photo from Blais et al. 2019 https://doi.org/10.1007/s10694-019-00888-8. Room with non flame retarded contents 8 ½ minutes after start of fire test.

Flame retardants

are part of the fire safety toolbox

- fire safe design (buildings, products)
- Inherently non-flammable materials
- smoke and fire alarms
- sprinklers
- education & awareness
- fire services
- maintenance, verification

London Fire Brigade and UK consumer magazine 'Which' call for flame retardant backings for fridges and freezers.

London Fire Brigade: https://www.london-fire.gov.uk/news/2015-news/fridge-freezer-delay-putting-lives-at-risk/
WHICH: https://www.which.co.uk/news/2018/02/revealed-the-brands-linked-to-the-most-appliance-fires/
"Grenfell Tower Inquiry Phase 1 report.", October 2019 https://www.grenfelltowerinquiry.org.uk/
Photo Natalie Oxford – WIKI https://twitter.com/Natalie_Oxford/status/874835244989513729/photo/1

Grenfell London 2017

- **fire starts in a fridge-freezer: flammable insulation foam partly not protected around the compressor (1)**
- **failure of uPVC window frame, PC-ABS frame of window ventilation unit (2)**
- **fire spreads over whole building through exterior insulation: PE / PIR / phenolic foam, installed in 2015-2016 refurbishment (2)**
- **issues with sprinklers, gas supply, fire stops, emergency exits**
- **72 people die, more than 70 injured, 127 lose their homes**
- **fire burns for 60 hours before being extinguished**

(1) https://www.gov.uk/government/publications/hotpoint-fridge-freezer-ff175b-independent-investigation
(2) Grenfell Tower Inquiry Phase 1 report https://www.grenfelltowerinquiry.org.uk/

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Role of flame retardants in fire safety

Cefic sector group

NFSD Nordic Fire & Safety Days

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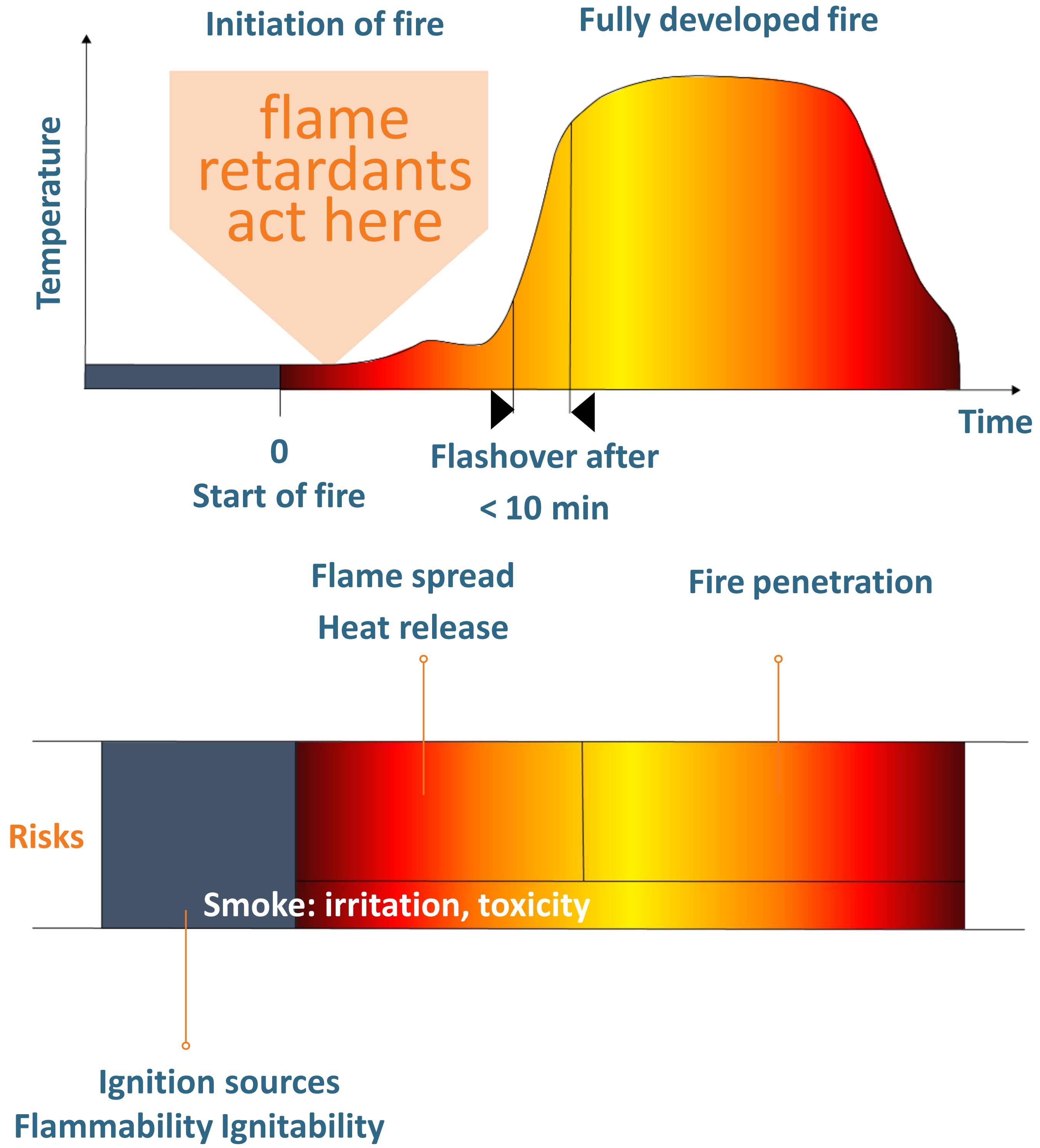
The Fire Curve for a Room Fire

Protective role of flame retardants in different phases of a fire :

Ignition
- Prevent ignition
- Possibly self-extinguish

Flame spread
- Slow down flame spread
- Reduce heat release
- Delay flash-over

Fire penetration
- Prevent the collapse of structures, e.g. steel columns protected by intumescent coatings
- Prevent fire moving to adjacent room or building compartment



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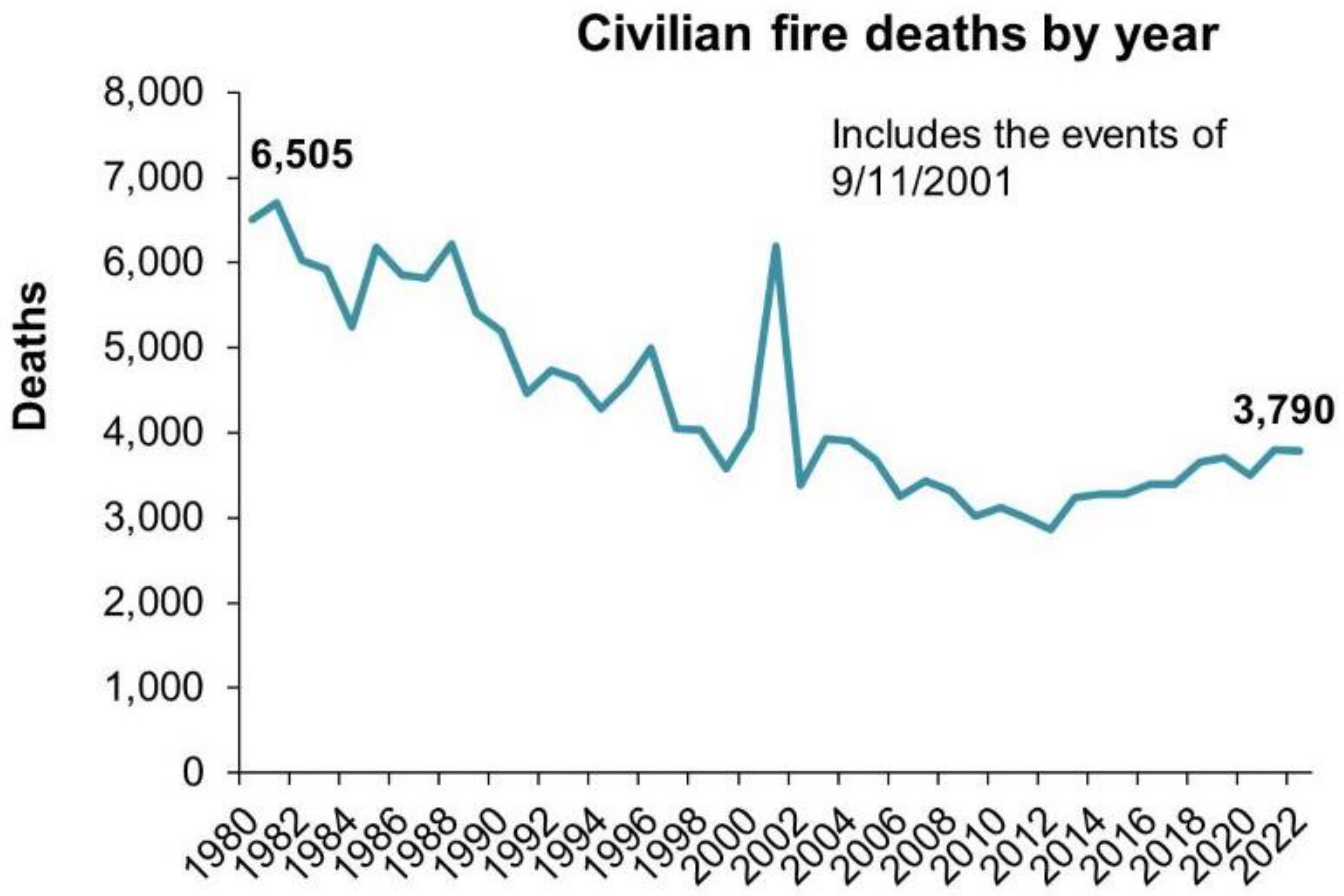
The fire which didn't happen



Fire Loss in the United States, US National Fire Protection Association (NFPA) https://www.nfpa.org/education-and-research/research/nfpa-research/fire-statistical-reports/fire-loss-in-the-united-states

International standards require materials used in electrical and electronic equipment to resist ignition from a local heat source (wire @ 650-800°C : "glow wire" test).

In this case, flame retardants probably prevented a fire starting and spreading to the whole electrical box, surrounding items and beyond.

Photo: pinfa

The variety of Flame Retardants

Phosphorus based

- Inorganic, e.g. red phosphorus, ammonium polyphosphate (APP), aluminium phosphite (AlPi), etc
- Non-halogenated phosphorus esters, e.g. TCP, TPP, TBEP, etc.
- Organic P compounds, e.g. DOPO, aluminium alkylphosphinates (AlPi), phytate (bio-based), etc.

Inorganic:

- Metal hydroxides, oxides, etc, e.g. MDH (magnesium), ATH aluminium), copper, zinc, boron, molybdenum, iron, etc.
- Expanded graphite
- Natural and synthetic clays and organo-clays

Nitrogen based:

e.g. melamine polyphosphate and other melamine-based compounds, ammonium compounds, N-alkoxy hindered amines.

Other components:

Blowing agents for intumescents (e.g. pentaerythritol), carbon char sources (e.g. lignin, cellulose)

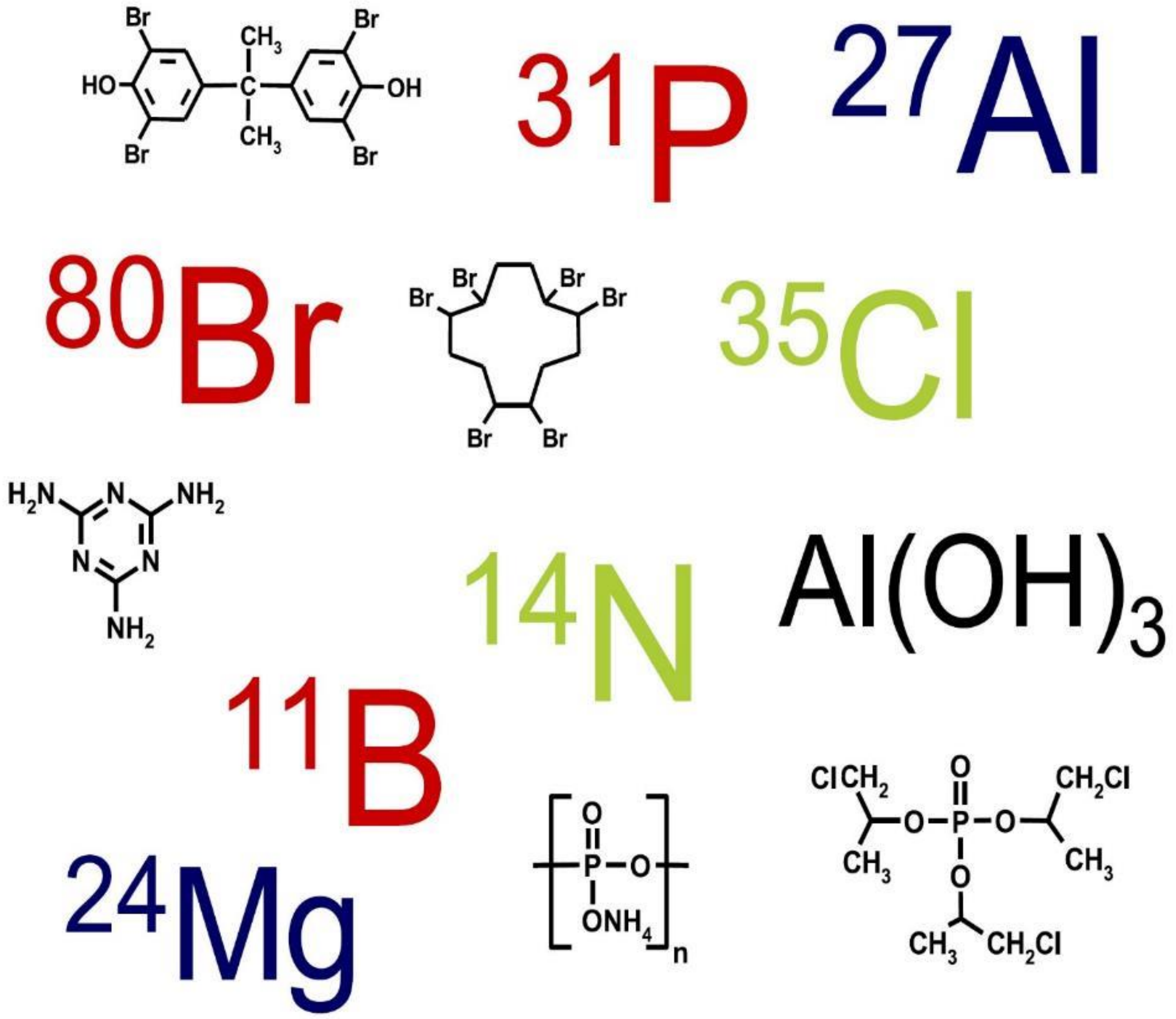
Halogenated flame retardants (brominated or chlorinated): (not covered by *pinfa*)

e.g. PBDEs (such as DecaBDE)*, DBDPE (Decabromodiphenyl ethane), HBCD*, TBBPA, brominated polymers, chlorinated paraffins, chlorinated alkyl phosphates (TCPP), etc.

[= no longer in use in Europe]*

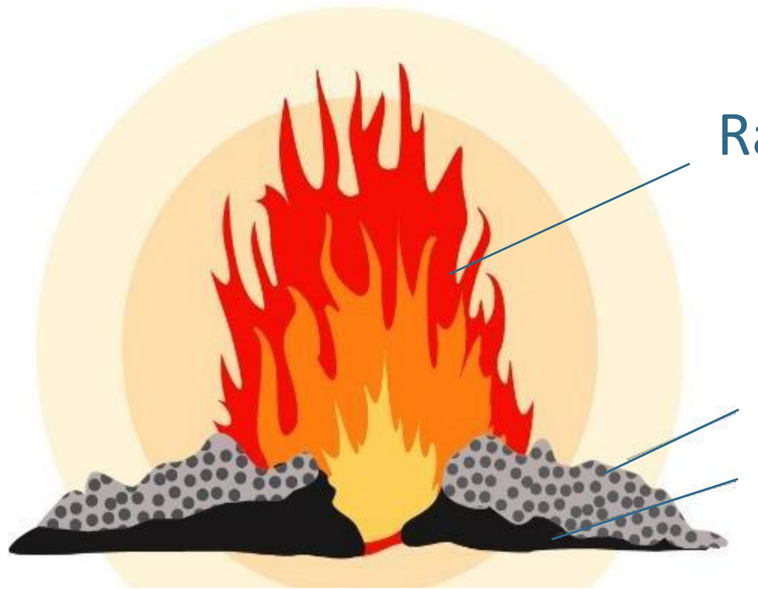
These are often used with antimony trioxide (ATO)

Many very different chemicals are used as "flame retardants" (FRs) and/or as "smoke suppressants"



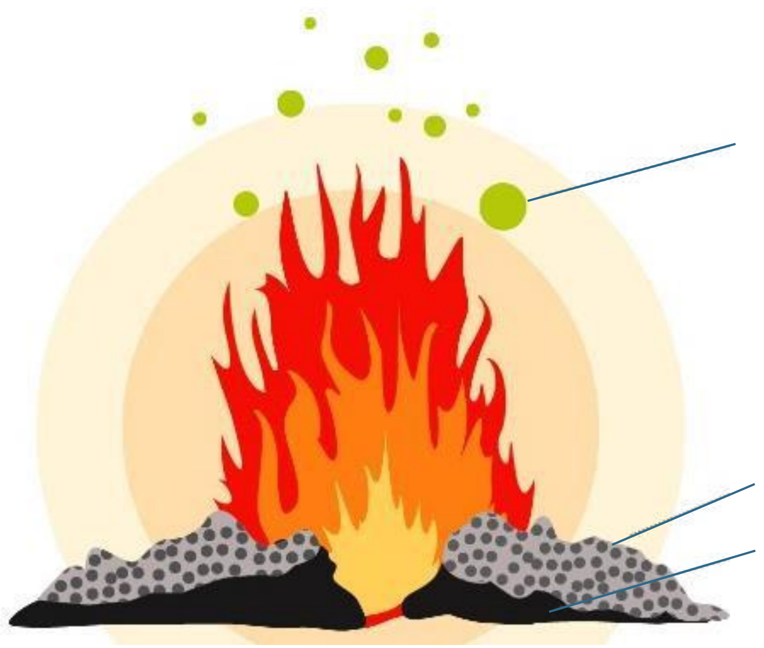
The Different Mechanisms of PIN Flame Retardants

Phosphorus-based



*Some phosphorus FRs release radicals which quench the combustion reactions

Nitrogen-based



Inorganic flame retardants
- quench and cool -

Question:
Do Flame Retardants impact smoke toxicity ?

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Smoke and Toxicity

- All fires generate toxic smoke
- Inhalation of smoke is the main cause of death for fire fatalities (> 70%)
- The total toxicity of gases emitted in fires is principally related to the quantities of materials burned
- Dense smoke can make orientation impossible, and so prevent escape
- Acutely toxic components prevent escape, can cause injury and death
  - narcotic: CO, HCN - deadly within minutes; but also CO_2, O_2-deficiency
  - irritants for eyes and breathing: HCl, SO_2, NO_x, aldehydes
- Compounds with long term effects pose significant concerns for firefighters and other professionals repeatedly exposed to smoke or soot:
  - polycyclic aromatic hydrocarbons (PAHs)
  - halogenated dioxins + furans (PCDD/F)
  - mostly adsorbed to soot, so inhaled in smoke particles or resorbed by skin contact

Fire and smoke demonstration at firefighter training centre PIVO, Brussels, *pinfa* Advisory Board meeting 2019. Screenshot from video https://www.pinfa.eu/media-events/photo-video/

PIN smoke suppressants can significantly reduce emitted smoke & also act as flame retardant synergists

Mode of action:

- Catalysis of cross-linking of carbon compounds in fire, so stabilising char and preventing the release of smoke and of soot particles
- In gas phase, vaporised metal compounds react with hydrogen radicals
- Release of water from hydroxides at high temperatures or release of ammonia which acts in the gas phase
- In halogenated polymers (e.g. PVC), volatilisation of metal halides, which act as flame retardant catalysts in the gas phase

Examples:

- Molybdenum minerals, e.g. ammonium octamolybdate
- Zinc minerals, e.g. zinc oxide, zinc phosphate, zinc stannates, zinc borate
- Calcium, copper, iron, nickel, silicon, tin minerals

Smoke chamber ISO 5659.
Photo © courtesy of Crepim

Do PIN Flame Retardants Make Smoke More Toxic?

In 2019, the French institute CREPIM completed a study testing 94 polymer samples from 12 companies, with and without flame retardants.

Results highlight that phosphorus, inorganic or nitrogen-based flame retardants have no significant negative impact on the evaluated smoke parameters of the study (CIT_{NLP}, $CIT_{4\ min}$, $CIT_{8\ min}$ and Ds values) under the testing conditions. Several PIN flame retardants can have a positive impact on the evaluated parameters when used judiciously.

CREPIM evaluated the smoke toxicity and the smoke density according to two well-recognized protocols: the norm NF X 70-100 at 600°C (tubular furnace) and the ISO 5659-2 with Annexe C of EN 45545-2 method (smoke chamber) at 50 kW/m2. Evaluated parameters were the Conventional Index of Toxicity for non-listed products and toxicity index at 4 or 8 minutes (CITNLP, CIT4 min, CIT8 min as per EN 45545-2) as well as smoke density values at various time intervals (DsMAX, Ds10, Ds4, Ds1.5 and calculated VOF4 values).

Study funded by *pinfa*. Summary of results in *pinfa Newsletter* n° 109 at www.pinfa.eu "The impact of halogen free phosphorus, inorganic and nitrogen flame retardants on the toxicity and density of smoke from 10 common polymers", H. Feuchter, F. Poutch, A. Beard, Fire and Materials. 2023;1–21, https://doi.org/10.1002/fam.3145

Effect compared to neat polymer

- Much worse
- Slightly worse
- Neutral
- Neutral to Better
- Better

Polymer	Toxicity Concern	PIN FR Effect Toxicity	Smoke Density	Halogen / Br-FR Effect Toxicity	Smoke density
Polyolefins (PE, PP)	CO, CO_2	Slightly worse	Better	Much worse	Much worse
Polystyrene (PS)	CO	Slightly worse	Neutral to Better	Slightly worse	Neutral to Better
Polycarbonates (PC)	CO, CO_2	Neutral	Slightly worse	Neutral	Neutral
Polyesters (PBT)	CO, HCN, NO_x	Neutral	Neutral	Not evaluated	Not evaluated
Epoxy resins	CO, HCN	Neutral to Better	Neutral to Better	Neutral	Slightly worse
Polyamides (PA6, PA66)	CO, HCN, NO_x	Slightly worse	Slightly worse	Slightly worse	Much worse
Polyurethanes (PUR, PIR)	CO, HCN, NO_x	Neutral	Neutral	Slightly worse	Slightly worse
Polyvinylchloride (u-/p-PVC)	HCl	(1)	(1)	(1)	(1)

(1) Minor impact of flame retardants on toxicity and smoke. In all cases huge contribution from HCl far exceeding threshold values

Different messages

Studies funded by industry suggest that in lab scale tests [previous slide] and in full-scale room tests [1]: FRs do not significantly impact smoke toxicity.

UK study, based on fire tests of four mock-furniture items, suggested higher smoke toxicity but lower fire growth rate with FRs [2]. This led to dissent and rebuttal [3], [4].

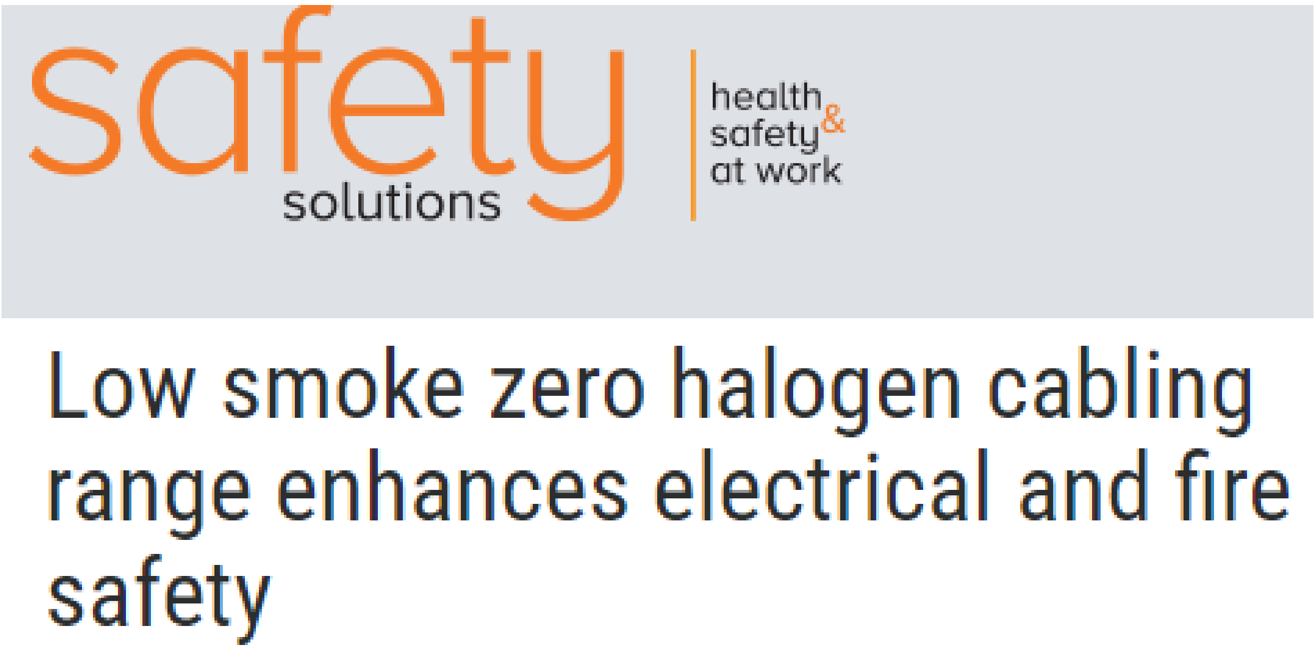
Some studies suggest that different FRs impact smoke toxicity differently [5]:

- gas phase FRs potentially increase incomplete combustion products
- char-forming FRs reduce toxicity [6], [7].

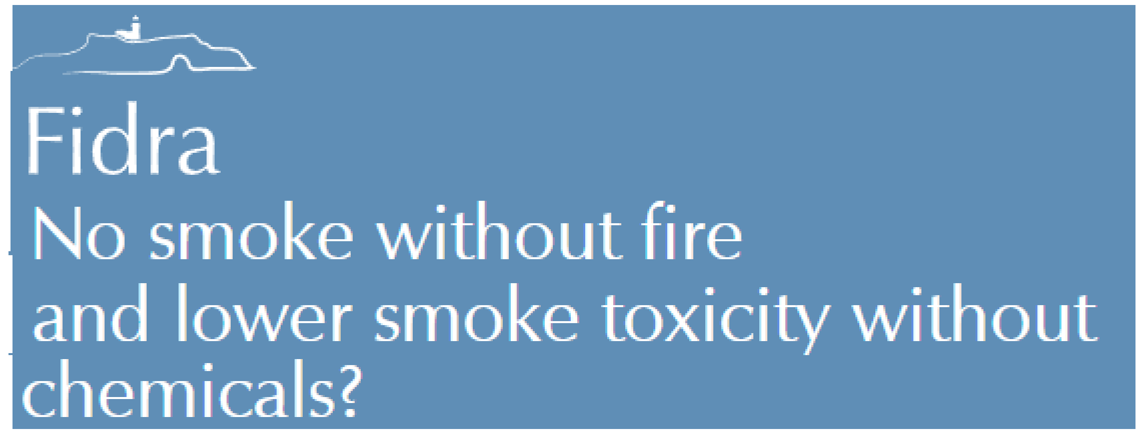
Other studies suggest that FRs do not increase overall smoke toxicity in real fires [8].

LSZH (Low Smoke Zero Halogen) FR cables reduce smoke and corrosivity [9].

What research is needed to identify and develop FRs which reduce smoke emission and toxicity in real fire conditions in different materials?



https://www.safetysolutions.net.au/content/electrical/case-study/low-smoke-zero-halogen-cabling-range-enhances-electrical-and-fire-safety-1243520876



https://www.fidra.org.uk/sustainable-fire-safety/no-smoke-without-fire-and-lower-smoke-toxicity-without-chemicals/

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6 = "Fire toxicity – The elephant in the room?", A. Stec, Fire Safety Journal, 2017 http://dx.doi.org/10.1016/j.firesaf.2017.05.003

7= "The Decomposition of Polyurethane and Fire Retardants: A Review", G. Peck, pre-print https://doi.org/10.20944/preprints202311.1646.v1

8 = "The fire toxicity of polyurethane foams", A Review, S. McKenna & T. Hull, Fire Science Reviews, 2016 (5:3), open access https://dx.doi.org/10.1186/s40038-016-0012-3

9 = "Evaluation of flammability and smoke corrosivity of data/power cables used in data centers", D. Zeng et al., Fire Safety Journal 2020 https://doi.org/10.1016/j.firesaf.2020.103094

Question:
What impacts do Flame Retardants have on Fire Fighters ?

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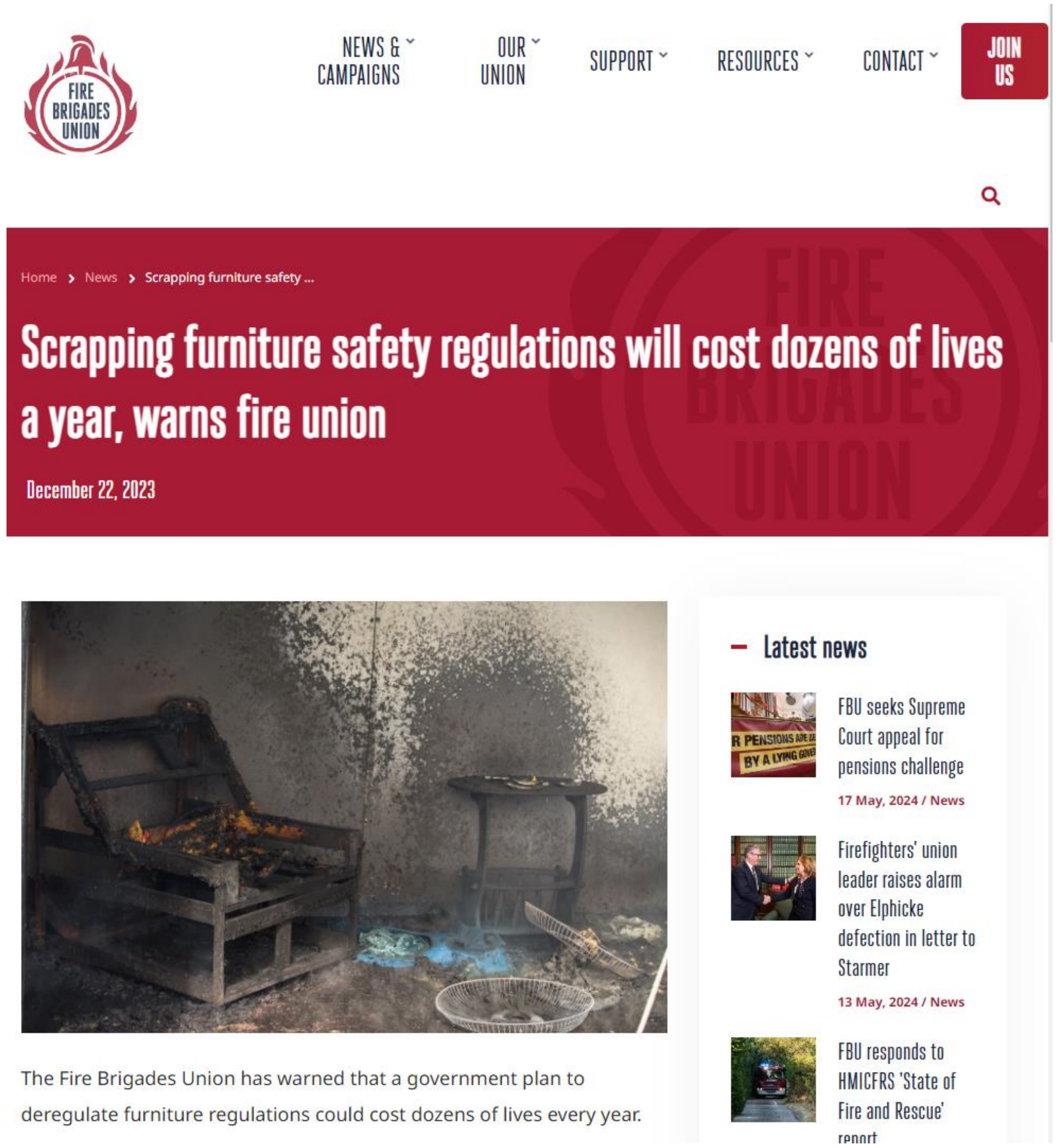
Nordic Fire Safety Days, 18-19 June 2024

Different messages

- Firefighters say fire safety standards are essential to save lives [10] [11].
- But, respecting fire safety specifications is not possible in many flammable materials without flame retardants
- Including non-flammable fire safety barriers is often not feasible or incompatible with consumer design requirements, cost or light-weighting.
- Occupational exposure to fires and smoke is recognized as a cancer risk for firefighters [12].
- Some firefighters reported in media suggest that FRs are a cause of this risk [13].

What research is needed to clarify whether or not FRs, or which types of FR in which applications, might impact chronic cancer risks of smoke for firefighters?



https://www.fbu.org.uk/news/2023/12/22/scrapping-furniture-safety-regulations-will-cost-dozens-lives-year-warns-fire-union

References

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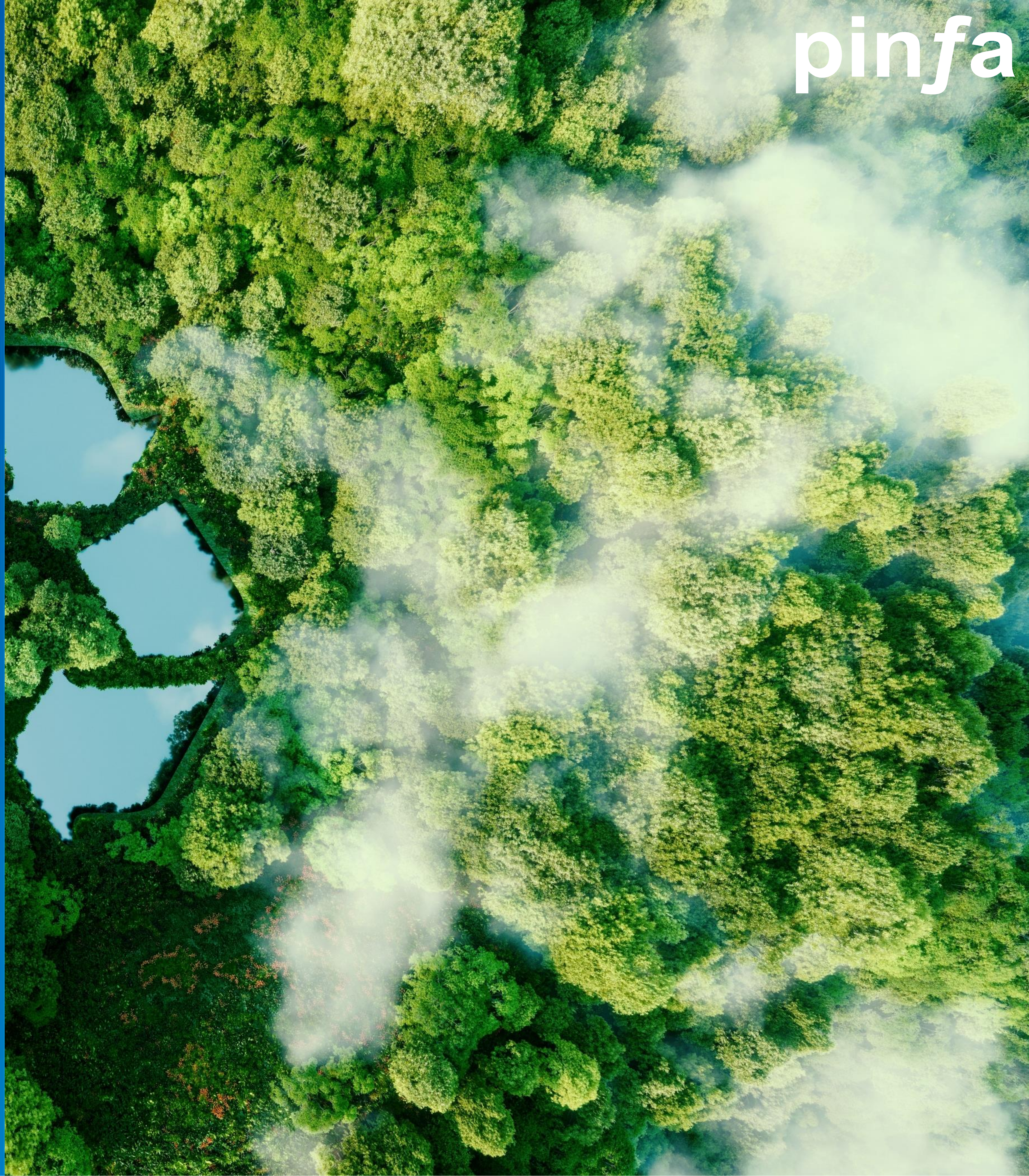
12 = WHO International Agency for Research on Cancer, IARC Monographs - vol. 132 “Carcinogenicity of occupational exposure as a firefighter”, in The Lancet – Oncology, vol. 23, August 2022 https://doi.org/10.1016/S1470-2045(22)00390-4

13 = The Guardian 24th May 2019 https://www.theguardian.com/us-news/2019/may/24/massachusetts-flame-retardants-firefighters-safety-cancer

Question:
Flame Retardants –
risks versus benefits ?



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Public acceptance of chemicals for fire safety ?

- Citizen survey, 1500 respondents, 7 EU countries
- Question posed:
  Does society "need to have" possibly persistent chemicals for different uses?
- 57 different uses were proposed
  Of these, the following **six uses** had > 60% positive replies:
  - cancer drugs,
  - rescue worker protective clothing
  - four* fire safety uses
    - firefighters protective clothing
    - firefighting foams
    - non-flammable cable insulation
    - fire resistance in aircraft passenger compartment
  ** that is, all four of the proposed fire safety uses*

***pinfa comments**: vox populi is not science,*
answers are orientated by questions (selection / presentation of "uses").

"Citizens' opinions on (non-)essential uses of persistent chemicals: A survey in seven European countries", A. Karinen et al., Environmental Science and Policy 153 (2024) 103666, https://doi.org/10.1016/j.envsci.2023.103666

Photo © Shutterstock 635438435

See the *pinfa* Mission

Science controversy over effectiveness of flame retardants

- There is confusion over what flame retardants can and cannot do
- Babrauskas 1998 [14]:
  "in these [large-scale] tests, the fire retardant additives did decrease the overall fire hazard of their host products."
  "none of the [small-scale] test specimens produced smoke of extreme toxicity. The smoke from both the FR and the NFR products was similar in potency …"
- Babrauskas 2011 [15]:
  "extensive use of chemical flame retardants to meet the California Furniture Flammability Standard Technical Bulletin 117 … has not been shown to have a measurable fire safety benefit."

JOURNAL OF FIRE SCIENCES

Forum/Discussion Articles

Journal of Fire Sciences
1–5

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DOI: 10.1177/07349041221096609
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The well-meaning but misguided rollback of fire safety in the United States

Alexander B Morgan

Photo © udayton.edu

"It is a blatant falsehood that flame retardants do not work, and it is something that all fire safety scientists should speak up about. … It is possible to have fire safety AND environmental safety".

https://doi.org/10.1177/07349041221096609 [16]

Balancing risks and benefits of flame retardants

Page et al. 2023 [17]
"There is significant uncertainty about whether and to what extent flame retardants contribute to fire safety"

Reports for revision of UK Furniture Fire Safety Regulations. 2023 [18, 19]
"The starkly contrasting conclusions of these studies exemplifies the difficulty in evaluating the relative risks and benefits of FR use in furniture."

To reconcile FRs and fire risk in furniture, one proposal suggests to lower fire safety standards in a few specific article types (e.g. small items, items for infants) [20]

- ❑ ***How to show to what extent FRs contribute to fire safety ?***
- ❑ ***How to ensure that "risks" address today's FRs and not 'legacy' FRs ?***
- ❑ ***Use EU chemicals regulation REACH to ensure that only safe FRs are on the market, including in imported articles.***
- ❑ ***What approaches are needed for risk-benefit analysis of FR use (use of different FRs, use in certain applications or conditions ...) ?***

Photo © Shutterstock

References

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https://nvlpubs.nist.gov/nistpubs/Legacy/SP/nbsspecialpublication749.pdf

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