

Regulatory strategy for flame retardants

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Regulatory strategy for flame retardants

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Glossary

| ARN | Assessment of Regulatory Needs |
|-------------|--|
| ССН | Compliance Check |
| CLH | Harmonised classification and labelling |
| CMR | Carcinogenic, mutagenic and/or toxic to reproduction |
| CSS | Chemical Strategy for Sustainability towards a Toxic Free Environment |
| DEv | Dossier evaluation |
| ED | Endocrine disruptor |
| NONS | Notified new substances |
| OEL | Occupational exposure limit |
| OSII or TII | On-site isolated intermediate or transported isolated intermediate |
| PBT/vPvB | Persistent, bioaccumulative and toxic/very persistent and very bioaccumulative |

| POPs | Persistent Organic Pollutants |
|---------|---|
| RMOA | Regulatory management options analysis |
| RRM | Regulatory risk management |
| SEv | Substance evaluation |
| STOT RE | Specific target organ toxicity, repeated exposure |
| SVHC | Substance of very high concern |

1. Executive summary

There has been a steadily growing demand for flame retardants over the recent decades. Flame retardants consist of a diverse group of chemicals, the main ones being metals, halogenated flame retardants and organophosphorus flame retardants. Of the different chemical classes, organo-bromine compounds have been heavily restricted during the recent decade. Nevertheless, they still have a significant market share.

ECHA has assessed the regulatory needs for halogenated and organophosphorus flame retardants, which make for approximately 70% of the market for organic flame retardants. The regulatory strategy has a particular focus on brominated flame retardants and their prioritisation for restriction, as indicated in the Restrictions Roadmap. Flame-retardant chemistries other than halogen and organophosphorus- based, will be covered in future assessments of regulatory needs (ARNs).

For the **aromatic brominated** flame retardants, a **general concern** has been identified due to their known or potential **PBT/vPvB properties**. Therefore, the release of these kind of flame retardants should be minimised. Viewing the challenges to control release of individual substances (see section 4) and the general availability of alternatives (see section 3.4), **a wide and generic restriction** seems to be the most appropriate regulatory approach (see section 5.2.2.1). Some further preparatory work may be needed before a restriction dossier is developed. This work could include the assessment of the waste stage for flame retardants, including the recycling of material from articles. This is especially relevant in those applications where the release potential during the articles use may be low but where the conditions during or after dismantling, recycling or disposal may lead to release of the flame retardant itself and/or to the break-down into hazardous transformation products.

For the **aliphatic brominated** and the **organophosphorus** flame retardants, the human and environmental health hazards seem more diverse compared to the aromatic brominated flame retardants. The information available to date suggests potential hazardous properties for human health and the environment for a considerable number of substances that may require regulatory risk management. However, for many of these substances data generation is ongoing or planned to verify if these hazards are indeed present. It is proposed that initiating work on potential restriction proposals should await the ongoing data generation (see sections 5.2.2.1 and 5.4). Nevertheless, for two reactive aliphatic brominated flame retardants (BMP and TBNPA) a restriction targeting professional uses could already be considered.

Notably, for several groups of organophosphorus flame retardants, the current information suggests low or unlikely hazards and thus no need for further regulatory action is identified at present (see Section 5.4).

Further data on possible hazardous properties of aliphatic brominated and organophosphorus flame retardants are expected to be submitted from 2024 onwards and thus any potential process for restriction is not expected to be initiated before 2025. It is proposed to **reassess the situation for these groups of flame retardants in 2025 and revise the strategy accordingly**. This revision would then also consider the possible regulatory needs for other flame retardant chemistries to the extent that their ARNs will be available. A time plan of the next steps towards regulatory action is sketched in Figure 1.

The **chlorinated** flame retardants make up for a relatively small market and are either already sufficiently regulated, or regulatory action is already initiated. Based on this, no further action for this group of flame retardants was identified (see section 5.3).

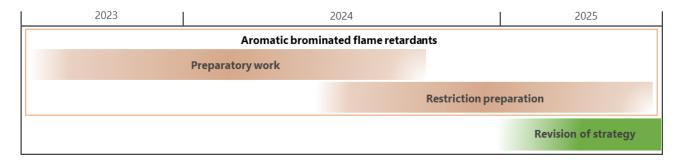


Figure 1 Next steps towards regulatory risk management for flame retardants in time.

In addition to the use of regulatory measures under REACH, the Commission may also introduce **ecodesign requirements** on flame retardants in certain products via the EcoDesign Directive, similar to the restriction on the use of any halogenated flame retardant in the enclosure and stands of electronic displays. Whereas Directive 2009/125/EC already empowers the Commission to set eco-design requirements for energy-related products, the Commission proposed to widen this empowerment to in principle all possible products in the Ecodesign for Sustainable Products Regulation (ESPR)¹. The ESPR foresees the possibility of restricting substances present in products or used in their manufacture that negatively affect their sustainability, including circularity. This route to restrict certain flame retardants may complement, or in certain cases make redundant, the actions proposed to be taken under REACH. During the preparation of restriction proposals on flame retardants, the ongoing or planned activities under the EcoDesign Directive and the future ESPR will need to be considered carefully.

Further, a critical revision of the different national/EU fire safety standards may be carried out by national authorities or at EU level. Potential changes to fire safety standards may influence the use of flame retardant chemicals in certain product groups.

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¹ https://environment.ec.europa.eu/publications/proposal-ecodesign-sustainable-products-regulation_en

2. Introduction

Protecting flammable (polymeric) materials against ignition and fast developing fires has been a steadily growing demand over recent decades, largely driven by the growth of the global economy, in particular by the sectors equipping their products with flame retarded materials: electric and electronic equipment, vehicles and buildings. One of the most efficient chemistries to deliver fire-protection have been organo-bromine compounds still making (together with the synergist antimony trioxide) about 25% of the global flame retardant (FR) market. This is despite the fact that some of the most used brominated compounds have been heavily restricted during the recent decade, due to their persistent, bioaccumulative and toxic properties (see section 2.4). These restrictions focussed on a limited number of brominated flame retardants and frequently have driven the markets to substitutes that are not necessarily always without risk, for example decabromodiphenyl ethane (EC 284-366-9, DBDPE)² being widely marketed as replacement for decabromodiphenyl ether (decaBDE). Therefore, this regulatory strategy aims to assess flame retardants as a market and lay out the steps that are needed to contribute to a future where the flame-retardant functionality in materials and products is delivered with the lowest possible impact to human health and the environment. The strategy builds further on Assessments of Regulatory Needs (ARNs) carried out for groups of substances (see sections 2.3 and 5.1).

2.1 Aim

The aims of this regulatory strategy on flame retardants are to:

- Identify substances used as flame retardants.
- Identify hazard and use patterns that are common at e.g. chemical class, group or subgroup level. This includes identification of substances or groups of substances where based on the assessment of the currently available information, there is no need for (further) EU regulatory risk management. It also includes identification of gaps in our knowledge of the hazardous properties and effective ways to address these gaps.
- Identify the needs for regulatory risk management and strive for consistency of regulatory actions across different groups of flame retardants, and through grouping aim at faster regulatory action. Areas for further assessment and data generation may be identified where no conclusions on the need for regulatory risk management can be drawn at present.
- Support informed substitutions and avoid regrettable substitutions: avoid that when one hazardous flame retardant is regulated it is being replaced by another with hazardous properties leading to concerns that subsequently need to be addressed.
- Contribute to providing long-term predictability to market actors through increased transparency of the regulatory risk management processes envisaged.
- · Where possible, integrate considerations with regard to sustainable product design and

² CAS: 84852-53-9; tradename SAYTEX 4010, SAYTEX 8010, Ecoflame B-971, Firemaster 2100

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circular economy in order to promote sustainable solutions.

While the strategy aims to go beyond substance-by-substance (eco)toxicological assessment, the key concern motivating regulatory action is still the available evidence indicating that certain (groups of) flame retardant substances are likely to cause serious adverse effects to humans and/or the environment.

2.2 Restrictions Roadmap

As one of the actions under the Chemical Strategy for Sustainability towards a Toxic Free Environment (CSS), the European Commission has prepared a Restrictions Roadmap³ to prioritise substances with specific hazards for (group) restrictions under REACH. The roadmap aims to ensure transparent and timely commitments by authorities and allow companies to anticipate (potential) upcoming restrictions. The Restrictions Roadmap sets out a Rolling List in which restrictions are planned, prepared and progressed. Flame retardants are included in Pool 1 'Planned restrictions not yet on the RoI for restriction' of the Rolling List in the following entries:

- Flame retardants: "ECHA, Member States and COM are currently assessing the need for further regulatory management measures on flame retardants. ECHA will prepare an overall strategy on flame retardants by 2022, which will support COM when it decides to request (a) restriction dossier(s). The substances in scope are in principle all flame retardants, and there will be particular focus on brominated flame retardants and their prioritisation for restrictions."
- Organophosphate flame retardants (OPFRs) (tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP).
- CMRs in childcare articles: CMR substances including some organophosphate flame retardants (TCEP, TCPP, TDCP) in childcare articles.

TCEP, TCPP and TDCP were assessed as part of the group 'chlorinated trialkyl phosphates' under the organophosphorus flame retardants (section 5.4).

2.3 Scope of the strategy for flame retardants

The substances in scope of this strategy are in principle all flame retardants. The strategy particularly focusses on halogenated flame retardants and organophosphorus flame retardants, as there is evidence of a considerable number of substances with potentially undesirable properties that may requiring regulatory risk management. Particular attention is given to brominated flame retardants and their prioritisation for restrictions, as indicated in the Restrictions Roadmap.

Any non-FR uses of a substance may be covered by the proposed regulatory actions insofar as the use pattern is similar (e.g. plasticisers in polymeric materials). However, other non-FR uses

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³ https://ec.europa.eu/docsroom/documents/49734

may need regulation as well. Such uses are not specifically addressed in the strategy.

The strategy focusses on registered substances that ECHA has included in groups (see section 5.1). Non-registered substances have been included in such groups as well during group generation but not exhaustively. Substances that are not registered but present in imported articles are consequently also not fully covered by the strategy. The same applies to polymeric flame retardants like brominated polystyrene or butadiene-styrene-copolymer which currently fall under the polymer exemption of REACH. Nevertheless, the current strategy includes some considerations about polymeric flame retardants.

2.4 Regulatory history

Since the 1970s, the primary flame retardant compounds used were polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD). Polybrominated biphenyls (PBB) were used as well. These brominated flame retardants have been replaced by other halogenated and phosphorous-containing flame retardants.

The polybrominated diphenyl ethers (**PBDEs**) pentaBDE and octaBDE (OBDPO or EC 251-087-9) were restricted in 2003, and later also decaBDE followed suit (EC 214-604-9). In 2010, tetra, penta-, hexa- and heptaBDE were banned under the POPs Regulation. ^{4,5} DecaBDE was added later to the POPs Regulation. Commercial octaBDE will de facto be prohibited under POPs as well as it contains BDE-congeners meeting the POP criteria, e.g. heptaBDE.⁶

The brominated cycloalkanes **HBCDD** and its major diastereoisomers (EC 247-148-4, List 603-801-9, List 603-802-4, List 603-804-5 and EC 221-695-9) have been included in Annex XIV^7 of the REACH Regulation in 2011 and were subsequently also banned under the POPs Regulation.

In 1979, tris (2,3 dibromopropyl) phosphate (EC 204-799-9) was restricted in textile articles intended to come into contact with the skin⁸. In 1983, restrictions were introduced on all polybrominated biphenyls (also referred to as **PBB** or polybromobiphenyls) in textile articles intended to come into contact with the skin.⁹

Recently TBBPA (EC 201-236-9) and BTBPE (EC 253-692-3) have been proposed to be identified as SVHC due to their carcinogenicity (CLH cat 1B)¹⁰ and potential vPvB properties,¹¹ respectively.

Although brominated FRs have been especially subject of regulatory scrutiny, also several

⁴ Regulation (EU) 2019/1021, formerly Regulation (EC) No 850/2004, see https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32010R0757

⁵ Entry 45 for diphenylether, octabromo derivative (octaBDE) is still in force. Entries 44 and 67 of Annex XVII regarding pentaBDE (diphenylether, pentabromo derivative) and decaBDE, respectively, were repealed due to the more stringent restrictions under POPs of these substances.

⁶ https://ec.europa.eu/environment/archives/pops/pdf/questions_answers.pdf

⁷ Manufacturing of HBCDD has ceased in the EU and it is no longer used.

⁸ Council Directive 79/663/EEC, currently, restriction in entry 4 of Annex XVII to REACH. The substance is not registered under REACH.

⁹ Currently, restriction in entry 8 of Annex XVII to REACH. Examples of these substances are: decabromo-1,1'-biphenyl (EC 237-137-2); nonabromo-1,1'-biphenyl (EC 248-637-5); tetrabromo(tetrabromophenyl) benzene (EC 248-696-7); 4-bromobiphenyl (EC 202-176-6); 3-bromobiphenyl (EC 218-304-9); hexabromo-1,1'-biphenyl (EC 252-994-2); 4,4'-dibromobiphenyl (EC 202-198-6). None of these example substances are registered under REACH, with the exception of 4-bromobiphenyl (registered for intermediate use only). EC 252-994-2 is also restricted under the POPs Regulation.

¹⁰ https://echa.europa.eu/substances-of-very-high-concern-identification/-/substance-rev/70907/term

¹¹ BTBPE is not registered. The SVHC proposal can be accessed from: https://echa.europa.eu/substances-of-very-high-concern-identification/-/substance-rev/70909/term

chlorinated flame retardants are being regulated.

Alkanes, C10-13, chloro (including 'SCCP') as well as alkanes, C14-17, chloro (including 'MCCP') are SVHC for their PBT and vPvB properties¹². Alkanes, C10-13, chloro were listed in the Stockholm Convention as Persistent Organic Pollutants (POPs) in 2012 and are as a consequence banned in the POPs Regulation.¹³ In addition, Chlorinated paraffins with carbon chain lengths in the range C14-17 and chlorination levels at or exceeding 45 per cent chlorine by weight have been proposed by the UK to be listed in the Stockholm Convention as Persistent Organic Pollutants (POPs).¹⁴ Moreover, ECHA submitted a restriction dossier for medium chain chlorinated paraffins ('MCCP') and other substances that contain chloroalkanes with carbon chain lengths within the range from C14 to C17 in July 2022.¹⁵

Dechlorane Plus is an SVHC based on its vPvB properties. Norway submitted a restriction dossier in April 2021.¹⁶ Norway has also proposed to list Dechlorane Plus and its syn- and anti-isomers in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants (POPs).¹⁷

TCEP is a chlorinated organophosphorus flame retardant that is included in the Authorisation List based on reproductive toxicity. TCEP replaced the historical use of pentaBDE but is currently not used anymore in the EU. TCEP has been replaced with TCPP and to some extent TDCP.

Electrical and electronic equipment

In 2011, the ROHS Directive¹⁸ introduced restrictions on polybrominated biphenyls (**PBB**) and polybrominated diphenyl ethers (**PBDE**)¹⁹ in electrical and electronic equipment (EEE), alongside restrictions on heavy metals (mercury, cadmium, lead and chromium VI). These restrictions were motivated by the concern that despite the applicable measures for collection, treatment, recycling and disposal of waste EEE under the WEEE Directive, significant parts of waste EEE would not be treated appropriately and would likely pose risks to health or the environment.

Although ROHS restricts some brominated flame retardants in EEE (PBB and PBDE), the presence of halogenated flame retardants was considered to remain a major issue in the recycling of plastics of electronic displays.²⁰ Essentially, it was found not to be cost-effective to monitor the maximum content of non-permitted compounds in recycled plastic. Instead of recycling plastic from electronic displays it has been incinerated.²¹ In response, the Ecodesign Directive restricts from 1 March 2021 onwards the use of any halogenated flame retardant in the enclosure and

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 $[\]frac{12}{\text{https://echa.europa.eu/registry-of-svhc-intentions/-/dislist/details/0b0236e185e9de96}} \text{ and } \frac{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e185e9de96}}{\text{dislist/details/0b0236e1807d8f3f}} \text{ and } \frac{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}}{\text{https://echa.europa.eu/registry-of-svhc-intentions/-/dislist/details/0b0236e185e9de96}} \text{ and } \frac{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e185e9de96}}{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}}} \text{ and } \frac{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}}{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}} \text{ and } \frac{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}}{\text{https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807d8f3f}}$

¹³ https://echa.europa.eu/list-of-substances-subject-to-pops-regulation/-/dislist/details/0b0236e184a318bf

¹⁴ Chlorinated paraffins with carbon chain lengths in the range C14-17 and chlorination levels at or exceeding 45 per cent chlorine by weight: https://echa.europa.eu/list-of-substances-proposed-as-pops/-/dislist/details/0b0236e186a67bfa

¹⁵ https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e18682f8e1

https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e184a168c4
 https://echa.europa.eu/list-of-substances-proposed-as-pops/-/dislist/details/0b0236e1849a7bd7

¹⁸ Directive 2011/65/EU

¹⁹ The POPs Regulation exempts the use in EEE.

²⁰ Halogenated compounds with aromatic rings can degrade into dioxin derivatives, particularly when heated, such as during production, a fire, recycling, or exposure to sun. Recycling can contaminate workers and communities near recycling plants, as well as new materials, with halogenated flame retardants and their breakdown products. Electronic waste is often melted to recycle metal components, and such heating can generate toxic dioxins and furans. Poor-quality incineration similarly generates and releases high quantities of toxic degradation products. Source: SWD(2019) 354 final, see https://ec.europa.eu/transparency/documents-register/detail?ref=SWD(2019)354&lang=en

ontent/EN/TXT/?uri=CELEX%3A62020TN0113&qid=1612858506635

²¹ See Commission Regulation (EU) 2019/2021.

stand of electronic displays because it was preventing recycling.²² The Staff Working Document stated that alternative solutions²³ would exist for the bulk of the plastic part in an electronic display, such as the enclosure and the stand, as they are exposed to lower voltage. Absence of halogenated flame retardants would permit higher yields of recycled plastics. The Bromine Science and Environmental Forum (BSEF) challenged the ban before the ECJ (BSEF v Commission, Case T-113/20),²⁴ the ECJ dismissed the action.²⁵

It is also worth to note that the Swedish Tax Agency and the Swedish Chemicals Agency proposed a tax on hazardous substances used as flame retardants in electronics found in people's homes with the aim of reducing the presence of those hazardous substances. The tax was primarily based on the flame retardants' content of chlorine, bromine or phosphorus and based on whether they are used as additive or reactive flame retardants.²⁶

3. Use and market of flame retardants

3.1 Flame retardancy

The process of fire is a cyclic chain of events that needs the following ingredients: heat, fuel, an oxidising agent (usually oxygen) and an uninhibited chemical chain reaction. The cyclic chain of events consists of:

- Heat produces combustible breakdown products from the pyrolysis of polymer
- Then, an adequate ratio between these gases and oxygen leads to ignition
- The combustion leads to a production of heat that is spread out and fed back
- This heat feedback pyrolyzes the polymer and keeps the combustion going.

Flame retardants are a diverse group of chemicals that are applied to materials to prevent or slow the growth of fire through interfering with one or several stages of the process of fire. It is important to note that the term flame retardant refers to a function and not to a specific family of chemicals. In fact, there are a variety of different chemistries that are used as flame retardants and often these are combined to improve effectiveness. In addition, some substances are

 $\frac{\text{https://curia.europa.eu/juris/document/document.jsf?text=\&docid=256004\&pageIndex=0\&doclang=en\&mode=lst\&dir=\&occ=first\&part=1\\ \frac{\&cid=123667}{26}$

https://www.skatteverket.se/servicelankar/otherlanguages/inenglishengelska/businessesandemployers/startingandrunningaswedishbusiness/payingtaxesbusinesses/taxonchemicalsincertainelectronics.4.5c281c7015abecc2e2019351.html

https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32021R0341&from=EN and https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02019R2021-20210501. The determined value for any homogeneous material should not exceed 0.1% by weight of halogen content. Use is currently restricted in cases and standings for digital screens.

²³ The Staff Working Document indicated that major manufacturers already used alternatives for years for the enclosure, such as: using polycarbonate PC/ABS69 blends and HIPS/PPE blends that can be flame retarded using phosphorus solutions; providing design solutions avoiding any FR such as shields between circuit boards

and the enclosure, or increasing the separating space; or using non-flammable materials. The feasibility is said to be due to a new safety standard EN 62386-1:2014 which removed the requirement for the 'candle' test (which entails an open flame being applied to the back cover of the television over a prolonged period without the back cover actually catching fire). In turn, the standard was changed because modern displays do not involve high voltages. See https://ec.europa.eu/transparency/documents-register/detail?ref=SWD(2019)354&lang=en

²⁴ https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A62020TN0113&qid=1612858506635

designed to have more than one function in the material, e.g. a brominated phthalate can be used both as flame retardant and plasticiser.

Flame retardants are activated in the presence of a flame or an ignition source and the flame retardancy involves several mechanisms occurring in the gas phase of the fire or in the solid phase (material):

- Chemical effect

- Radical quenching by removing H and OH radicals in the flame and thus reducing the propagation of the radical oxidation reaction of combustion.
- <u>Charring</u>: causing the formation of a carbonaceous layer on the polymer's surface via cyclizing and cross-linking processes which acts as a barrier between the flame and the fuel.
- Intumescence: causing the formation of a voluminous insulating protective layer through swelling below the surface layer where charring effect has also taken place.

- Physical effect

- Thermal shielding by creating an insulating barrier between the parts of the combustible that are burning and the unburned ones.
- o <u>Cooling effect</u> by endothermic reactions that remove heat
- Production of inert gases that lowers the partial pressure of oxygen and thus slows the reaction rate.
- <u>Dilution</u> of fuel by the incorporation of inert substances in the polymer, i.e. fillers, like e.g. metal hydroxides.

Some of the substances are used in combination to improve effectiveness through synergistic effects (e.g. antimony has a synergistic effect with halogenated compounds by allowing the formation of volatile antimony species, i.e. antimony halides or antimonyoxyhalide) or combining different mechanisms of action (e.g. halogen-phosphorus systems, phosphorus-nitrogen systems and intumescent systems).

Another type of combination are the intumescent systems. Intumescent systems are systems of substances which act by creating an intumescent char, and causing swelling below the surface layer, covering the polymer surface and insulating the flammable polymer from the source of heat (preventing formation of combustible breakdown products) and insulating the oxygen from the surface of the polymer. They are composed by 3 basic ingredients: a charring agent, a blowing agent (supplying evolving gases) and a "catalyst" (accelerating the process, often ammonium phosphate).

There are polymers that have some inherent fire retardation properties (e.g. nitrogen-containing polymers like polyamides or chloro-containing polymers like PVC) and others that do not (e.g. polyolefines, styrenics, acrylics). For the latter, the concentration of the flame retardant/flame-retardant system needs to be higher or more efficient. But some flame retardants or high

loadings of flame retardants might not be possible to use always with some polymers or materials because they can cause unacceptable loss of mechanical properties and some end uses might require very stringent fire-retardant properties.

3.2 Type of flame retardants

3.2.1 Differentiation by elemental composition

In general flame retardants are normally divided based on whether they contain bromine, chlorine, phosphorus, nitrogen, metals or boron. Nevertheless, there are flame retardants that contain more than one of the elements listed above and even very complex substances for which this simple differentiation by elemental composition does not work.

- Halogenated flame retardants

Halogen-containing flame retardants act in the gas phase by radical quenching, i.e. interrupting the radical chain mechanism that carries the flame in the combustion process.

Brominated and chlorinated flame retardants are the most efficient flame retardants. Fluorine and iodine-based flame retardants are not used because neither of them interferes with the combustion process at the right point (fluorine has low effectiveness due to its strong bond with carbon, and iodine due to its weak bond to carbon and the poor thermal stability).²⁷

Brominated flame retardants are the more effective as bromine can intervene in the course of combustion at a more favourable time than chlorinated flame retardants. It is believed that the effective agent hydrogen bromide, HBr, is set free in a narrow temperature range so that it is present in high concentration in the flame zone. Meanwhile, hydrogen chloride, HCl, that is formed over a wider temperature range, is present in greater dilution and is therefore less effective.

The halogenated substances can be aliphatic or aromatic. Aliphatic halogen compounds are not as temperature resistant as the aromatic ones but are more effective flame retardants because they are easier to break down. Therefore, they can usually not be used in plastics with higher temperature resistance (e.g. engineering plastics), as they would decompose at the processing temperatures used to manufacture these plastics.

Halogen-containing flame retardants are used additively and reactively for the fire protection equipment of practically all plastics due to their excellent effect.²⁸ Flame retardants with aromatically bonded bromine have a significant market share. For certain applications, brominated as well as chlorinated aliphatic and cycloaliphatic flame retardants also play an important role.

Uncontrolled burning and dismantling/recycling of electronic and electric waste that contains brominated or chlorinated FR can result in contamination and formation of brominated and chlorinated dioxins and furans; these substances are highly toxic, thus causing concern both

²⁷ Weil, E. D., et al. (2016). Flame Retardants for Plastics and Textiles.

²⁸ Maier, R.-D., et al. (2016). Handbuch Kunststoff Additive.

for the health of individuals and for the environment.

- Phosphorus-containing flame retardants

Phosphorus-containing flame retardants are particularly effective in oxygen-containing charforming polymers like polyurethanes, epoxies, polyamides and polyester.²⁷ They can also be used in cellulose. Non-halogenated organophosphorus flame retardants promote charring during the pyrolyzation of the substrate. Phosphorus-containing flame retardants may also contain halogens to increase the flame retardancy. A synergistic effect with halogen is suspected, but this has not been definitively shown.²⁸

Phosphorus-containing flame retardants show a considerable diversity and span several phosphorus substance classes. The phosphorous substances found in the mapping of flame retardants are subdivided into inorganic P-based, phosphorous, phosphonates, phosphorous and other phosphorous substances with the respective oxidation state:

- Inorganic phosphates, polyphosphates and their derivatives
- Organic phosphates, phosphites and phosphonates
- Additives having phosphorus and nitrogen like polyphosphazenes and phosphoramines

Oxidation state of the phosphorus-containing substance seems to play a role on the thermal and flame retardant properties. This seems to correlate with the fact that phosphates seem to be the mostly used. However, it seems that there is a difference in reactivity for each polymer and this needs to be considered as well.²⁹

Nitrogen-containing flame retardants

These type of flame retardants are rarely used alone. The mode of action is through cooling and dilution effects (releasing gases containing nitrogen), but they are also used as part of intumescent systems.

Nitrogen-containing flame retardants are used as reactive and additive compounds in plastics. These are mainly isocyanurates, melamine and cyanuric acid derivatives. Certain isocyanurates, such as melamine cyanurate, are also used as additive flame retardants, mainly in polyamide or together with ammonium polyphosphate in intumescent flame-retardant systems for polypropylene. The nitrogen-containing compounds, such as melamine, are converted into cross-linked structures by condensation reactions with gradual loss of ammonia. In addition, the release of molecular nitrogen could dilute the combustible pyrolysis gases. In the presence of phosphorus-containing compounds, nitrogen probably acts by strengthening the phosphorus bond to the polymer.²⁸

In practice, nitrogenous flame retardants are mainly used in polyamide (melamine cyanurate) and polyurethanes (melamine).²⁸

Some polymers containing nitrogen (aromatic polyamides or natural products like wool or

²⁹ Mariappan, T. et al. Influence of oxidation state of phosphorus on the thermal and flammability of polyurea and epoxy resin, European Polymer Journal, 2013, 49, 3171-3180.

silk) have an inherent high fire performance.

Metals

These substances are mainly inorganic substances. As a general rule, the mineral fillers will increase compound density, thermal conductivity and stiffness, and the material becomes more brittle. Moisture uptake will often be increased. The flame retardant efficacy will generally increase with decreased particle size (increased surface area).²⁷ One general downside of the use of metal hydroxides is the high filling level which is required to achieve a basic flame retardancy.

Two of the main metals used as flame retardants are aluminium and antimony.

Aluminium trihydroxide is the most commonly used flame retardant. Aluminium hydroxide begins to decompose in the temperature range between 180 and 200 °C, where the transformation into aluminium oxide occurs in an endothermic reaction with the release of water. This reaction in turn triggers various processes in the combustion zone that affect the burning process. As a result of the endothermic decomposition, the polymer is cooled and fewer pyrolysis products are formed. Furthermore, aluminium oxide is formed on the surface of the substrate which together with the charring products acts as an insulating protective layer. Lastly, the water vapour formed acts as a diluent in the gas phase and is deposited as a protective gas over the condensed phase displacing oxygen. All these processes are of a purely physical nature. Presumptions that aluminium have a cross-linking effect in the condensed phase have not yet been confirmed. Aluminium hydroxide is mostly used in plastics formulations with processing temperatures up to 200 °C. The applications are polyolefins, PVC, polyurethane foams, thermosets and rubber.

Antimony oxide itself renders no flame inhibition properties to polymers, but it is known as a synergist for halogen compounds.³⁰ According to Weil et al., antimony trioxide is typically added in concentrations of 3-6% (based on plastic weight) along with halogenated FR's.²⁷ Antimony oxide is not volatile but antimony oxyhalide (SbOX) and antimony trihalide (SbX3) formed in the condensed phase, by reaction with the halogenated flame retardant, are volatile. They facilitate the transfer of halogen and antimony into the gas phase where they function. Antimony oxide flame retardants are therefore usually used indirectly in the form of antimony trichloride (SbCI3) or antimony tribromide (SbSr3). These forms are very effective retardants at typical flame temperatures.

The use of Brominated Flame Retardants (BFRs) together with antimony trioxide (ATO) as synergist is for certain applications indispensable. Some examples:

- Acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) are today
 one of the preferred (technically and economically) polymers for EEE enclosures. The
 BFR-ATO combination is still one the most cost-effective FR system. Alternatives often
 do not fulfil the same combination of functionalities as the BFR-ATO system.
 Replacement by polymer alloys is possible, but this might lead to higher costs and
 still requires up to 0,5% halogen addition (PTFE).
- The BFR-ATO system is also often the material of choice for thermoplastic elastomers used in cabling for E&E.

³⁰ Choudhury, A. K. R. (2020). "Flame Retardants for Textile Materials"

There are other metal salts that are also acting through cooling and dilution physical effects, e.g. Mg, Ca, Sn or Zn.

- Boron-containing flame retardants

The mechanism of action of boron-containing flame retardants are through the formation of glassy residues above the condensed phase and enhancement of char formation and by cooling and dilution physical effects.

3.2.2 Differentiation by type of integration into materials

Another way to categorise flame retardants is considering how they are incorporated into the combustible materials. Here, we can differentiate between:

- Additive flame retardants: the flame retardants are incorporated into the combustible
 materials as additives through mixing and still exist as substances with a certain degree
 of mobility within the material matrix. The flame retarding additive may be also an
 oligomer or polymer on its own.
- Reactive flame retardants: the flame retardants are integrated into the combustible material via covalent bonds (in backbone chain or side chain). The reaction making the flame-retardant part of a polymeric structure can take place at different level in the supply chain.

The way of incorporating the flame-retarding chemistry into the polymeric system has implications in terms of potential release and exposure during the use of the flame retardant, during the service life of materials/articles and when processing these for recycling.

3.3 Market

The worldwide consumption of flame retardants amounts to more than 2.39 Million tons in 2019 (IHS-Consulting 2020) or \$7.4 billion in 2020 (Allied Market Research). The consumption grows with the global economy, in particular with the development of the industry sectors equipping their products with flame retarded materials. Plastic and resin, rubber and textile producers are the main industry sectors purchasing flame-retardants. The most prominent plastic/resin types are in this context unsaturated polyesters, epoxy resins, polyurethane, PVC (mostly soft PVC in which the percentage of chlorine is greatly reduced), polyolefines, Polystyrene and other engineered thermoplastics.

The key sectors using the fire-safe materials are:

- Producers of electric and electronic equipment (EEE), cables and wires (38% of global flame retardant use)³¹
- Building and construction sector (B&C) (28%)
- Producers of transport vehicles: automotive, train, aeroplanes (20%)
- Producers of furnishing/upholstery and others (14%)

³¹ Grandviewresearch 2022

Sector-specific market information is available in 0.

Asia consumed the largest volume of flame retardants in 2019 with a 51% share, with China being the largest single consumer at 27 %. The European market consumed around 25 % (23 % for Western Europe and 2 % for Central and Eastern Europe) (FlameRetardants-Online 2020).

The global distribution of flame-retardant consumption illustrates that product manufacturers located in the EU make choices impacting on about 25% of the global flame retardant market (see Figure 2). These choices may be more related to end-use in construction and automotive rather than electric and electronic equipment where the share of article import is particularly high (about 50% of the goods placed on the EU market is imported, mostly from Asia (based on EEA and EUROSTAT figures for 2012)³². Thus, the relative global shares of the different FR classes depicted in Figure 2 is not representative for the EU market, especially not in sectors with relatively little import of articles.

Among the flame retardant types, aluminium hydroxide is the largest single flame retardant at 38 % share (of total amount). Second are the halogenated flame-retardant systems comprising brominated and chlorinated products which are commonly used together with the synergist antimony trioxide, which in total has a 30 % market share. Organophosphorus and other flame retardants like e.g. inorganic phosphorus compounds, nitrogen and zinc-based flame retardants make up the rest at 32% (see Figure 3).

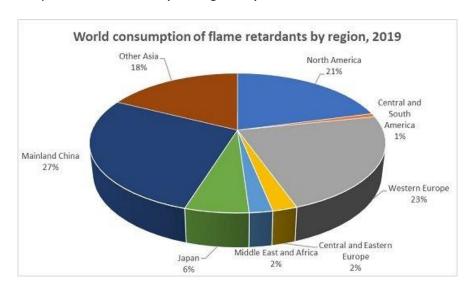


Figure 2. Worldwide consumption of flame retardants by region 2019 (IHS-Consulting 2020).

32 https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Waste statistics - electrical and electronic equipment https://www.eea.europa.eu/data-and-maps/figures/imports-and-exports-of-electrical

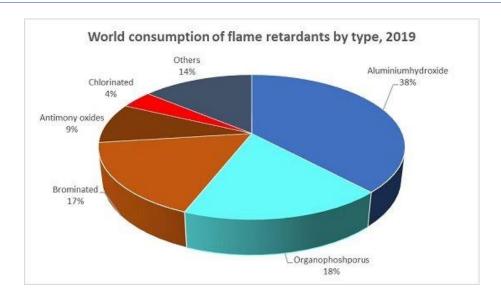


Figure 3. Worldwide consumption of flame retardants by type 2019 (IHS-Consulting 2020)

Government regulations and legal requirements, such as the European Union's RoHS Directive on the restriction of hazardous substances in electrical and electronic equipment, result in significant regional differences: In Western Europe and North America, brominated compounds account for only 5.1% and 11% of the flame retardant market, respectively – while in Asia they account for 28.4%.

In parallel to the trend of replacing brominated flame retardants by other chemistries a trend towards flame-retardants of high molecular weight, polymeric flame retardants or substances chemically bound in the polymer matrix has emerged. This aims to reduce or prevent migration of flame retardants and corresponding occurrence in in-door air (e.g. fogging in cars), environmental media, biota and human tissue.

3.4 Potential for substitution

The information available suggests that there is a large overlap between the different (groups of) flame retardants and the materials or applications in which they are used. Consequently, a significant level of interchangeability is generally expected for additive flame retardants: between the different known or potentially hazardous flame retardants, but also with those of no or low hazard (known or potentially). For several materials or applications, for the most hazardous flame retardants less hazardous alternatives may be available leading to less exposure (e.g. larger oligomers or reactive flame retardants), or alternative materials may be selected that would require less flame retardancy or would allow the use of flame retardants that are non-hazardous or may involve less exposure (reactive uses).

From the above, regulation under REACH and CLP (classification, SVHC identification, restriction and/or authorisation) should incentivise industry to no longer use the most hazardous flame retardants but to substitute them, either by non- or low hazardous alternatives, or by alternative materials or an alternative article design that would no longer require flame retardants or would allow the use of non-hazardous ones. Only when this is not possible, one could consider allowing

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³³ Ceresana Market Research: https://www.ceresana.com/en/market-studies/chemicals/flame-retardants/

in exceptional cases to continue the use of the most hazardous flame retardants and then preferably integrated into the polymer grid in covalently bound form.

4. Exposure considerations

4.1 Drivers of release and exposure

Like for other additives in plastic articles, resins and textiles the release and exposure potential of flame retardants depends on the concentration in the combustible material (loading), the embedding mechanisms into the matrix, the chemical-physical properties of the flame retardant, the diffusivity of the polymer-matrix, the extent to which the use-conditions during service and after service life may increase the mobility or degradation of the flame retardant and the extent to which direct skin, mouth or water contact takes place. While flame retardants with a large molecular size or covalent binding into the material matrix may show negligible migration rates during article service life, significant release potential can be expected from smaller additives, particularly when used in plastic matrices of high diffusivity or textiles in water contact. Also, the shape of the polymeric object in terms of surface/mass ratio plays a role. The larger the surface is compared to the volume, the higher the fraction of flame retardant is that can migrate to the surface. And finally, the migration potential will only result in an actual migration massflow when the migrating molecules are removed from the polymer-surface into the contact medium.

The release of the flame-retardant from the intact material matrix is therefore driven by a number of key drivers intrinsic to the composition/design of the material:

- The concentration of flame retardants in the material is comparably high, typically between 5 to 25% for organic substances and 40-60% for aluminium hydroxide.
- **Reactive and polymeric flame retardants** play a key role in some markets (e.g. epoxyresins for electronic components and PU and PS foams), however the traditional additive flame retardant with a range of exposure potential still dominates the market (see below).
- Additive, non-polymeric flame retardants show a broad variety of molecular weights
 (from a few 100 Dalton for some phosphorous based substances to over 1000 for some
 brominated substances). For substances characterised by a high molecular size and weight
 (>> 1000 Dalton) which is mostly also connected with low solubility in water and very low
 vapour pressure (and no reaction generating smaller molecules) one can assume low or even
 negligible migration from a properly composed material-matrix.
- There are however a few particularities to be considered when relying on high molecular weights to control release and exposure:
 - Brominated flame retardants tend to have a smaller molecular size (higher mobility) than one may expect from the molecular weight, as bromine is heavy. For example, decabromdiphenyl ether (decaBDE) and decabromodiphenyl ethane (EC 284-366-9, DBDPE), both substances with a molecular weight between 900 and 1000 Dalton, are

nevertheless widely present in WWTP sludge, sediments, soil, house-dust and are also accessible to biota (e.g. detected in birds eggs)³⁴. This means a general benchmark of 1000 Dalton to determine molecules with negligible migration potential would not be applicable to brominated substances.

- A flame-retardant, also when polymeric, may break-down into smaller molecules due to hydrolysis, impact of UV radiation or elevated temperature. Particularly where flame-retardants are more sensitive to one of the mentioned mechanisms, dismantling and recycling processes, including a second service life, may lead to use conditions triggering the degradation of the flame-retardant molecules to smaller possibly hazardous degradation products with higher migration potential.
- The diffusivity of the polymer matrix may limit the mobility of the flame retardant. The diffusivity of the various polymer-types significantly differs, but broadly one can distinguish between high-diffusivity matrices (e.g. poly-olefines, soft-PVC and PUR foam) and low diffusivity (e.g. rigid PVC, PA, PET, PS, ABS, PMMA, PC) matrices.³⁵

4.2 Additive and reactive flame retardants

Flame retardants are usually applied in relatively high concentrations to achieve a sufficient loading with the flame retarding element such as bromine or phosphorous. Thus, they do not only deliver their intended technical function but also impact on the performance of the whole polymer system. The flame retarding chemistry can be added to the polymer matrix by mixing or can be integrated into polymer chains or nets through reaction (covalent bounds).

Additives can be small and large molecules, the latter including oligomeric/polymeric forms. These additives are widely used in commodities and engineered thermoplastics. Compounding of the polymer mixture (i.e. adding flame retardants and other additives) and conversion into final physical shape takes place in the middle of the supply chain. It often involves elevated temperatures typically ranging from about 190 °C (e.g. for soft-PVC) over 200 (e.g. for polyolefines or PET) to 340 °C (e.g. for polyamide). The temperatures during foam production processes (PU, PS, PP) are usually lower than 150 °C. Technically, the flame retardant must be "soluble" in the polymer and stable at the foreseen conversion temperature. Also, to prevent losses during conversion the volatility of flame retardant would be expected to be low. Therefore, conversion conditions determine to a certain degree the release potential over service life and during recycling.

There is a trend in the market to use **oligomeric or polymeric substances** to prevent migration of brominated flame retardants from products. This includes substances currently falling under the polymer-exemption from registration under REACH, like for example

³⁴ Summary of the concentration levels of Decabromodiphenyl ethane reported in the lead registrant's Environmental Exposure Assessment Report (2019): < 1 μ g/kg dw up to a few 100s μ g/kg dw in solid media (sludge/soil/sediment/dust) and < 0.1 μ g/kg up to about 1 μ g/kg f.w. in biota (Peter Fisk Associates, 2019).

³⁵https://echa.europa.eu/documents/10162/17228/plastic_additives_supplementary_en.pdf/79bea2d6-8e45-f38c-a318-7d7e812890a1_36https://echa.europa.eu/documents/10162/2777483/use_maps_masterbaching_compounding_converting_processes_v1-0-quidance_en.docx/941e3e9c-4376-24db-50cc-ba6797d4e5db?t=1513782717228

brominated styrene-butadien-co-polymer or brominated polystyrene.

Reactive flame retardants are of particular relevance for polyurethanes and thermosets like epoxy, where polymerisation and physical shaping takes place in one step low in the supply chain. But overall, reactive flame retardants have a comparably small market share, e.g. for phosphorous-based substances it is less than 10% (PINFA meeting 2022).

Table 1: Examples of reactive and polymeric brominated flame retardants

| Substance | EC/CAS | Polymeric or reactive | Area of application |
|---|--------------|-----------------------|--|
| ТВВРА | 201-236-9 | Reactive | Epoxyresins |
| 2,2-dimethylpropan-1-ol, tribromo derivative | 253-057-0 | Reactive | PU foams and unsaturated polyester resins |
| 2,2-bis(bromomethyl) propane- 1,3-diol, | 221-967-7 | Reactive | PU foams and unsaturated polyester resins |
| PHT4 (tetrabromophthalic anhydride) | 211-185-4 | Reactive | Unsaturated polyester |
| PHT4-Diol (reaction product of 3,4,5,6-tetrabromobenzene-1,2-dicarboxylate with 2,2'-oxy-diethanol and 2-epoxypropane | 616-436-5 | Reactive | PU systems |
| Reaction products of tetrabromophthalic anhydride with 2,2'-oxydiethanol and methyloxirane" | 616-436-5 | Reactive | Rigid PU foams Polyurea thermosets |
| Brominated Butadiene-Styrene co-polymer | 1195978-93-8 | Polymeric | PS foams; in future potentially compact PS and HIPS Marketed as alternative to banned HBCDD |
| Brominated polystyrene (BPS) | 88497-56-7 | Polymeric | Polyamid, polyester |

Table 2: Examples of reactive and polymeric Phosphorous based flame retardants

| Substance | EC/CAS | Polymeric or reactive | Area of application |
|---|-------------|-----------------------|--|
| Dibenzo-oxaphosphorine- oxide derivates (DOPO) | 252-813-7 | Reactive | Polyurethane and epoxy resins in a variety of applications |
| 3- (hydroxyphenylphosphinyl) propanoic acid | 411-200-6 | Reactive | Production of polyester products |
| Aluminium tridiethylphosphinate | 428-310-5 | Reactive | Heat transfer fluids, adhesives/sealants |
| Diphenyl phosphonate | 225-202-8 | Reactive | Epoxy resins |
| Methylphosphonic acid | 213-607-2 | Reactive | Flame retardant finishing of textiles |
| Phosphorus rich reactive intermediate | Proprietary | Reactive | Polyurethane applications |
| Polyphosphonate | 68664-06- | Polymeric | Polyesters and |

| Substance | EC/CAS | Polymeric or reactive | Area of application |
|-------------------------------------|-----------------|-----------------------|----------------------------|
| | 2 | | thermoplastic polyurethane |
| Oligomeric ethyl ethylene phosphate | 184538- 58-7 | Polymeric | Flexible polyurethane foam |

Impacts on release potential

While additive flame retardants can potentially be released from the combustible materials (depending on e.g. the molecular size and the diffusivity of combustible material), reactive flame retardants will be immobilised in the material via a covalent bond (except for unreacted residues and unless the covalent bond is broken during use) and thus reducing the potential release from the material. On the other hand, it may be even more difficult or impossible to remove a reacted flame retardant from polymer-materials during recycling (if needed). For the current strategy the substance-specific behaviour of flame retardants during dismantling and recycling has not been further analysed.

For reactive flame retardants, which tend to be smaller molecules, the exposure potential decreases, once the substance has reacted. If the reaction takes place in mixtures with widespread uses (e.g. in-situ foams in construction work) the exposure potential is higher compared to uses in industrial manufacture.

4.3 Exposure potential during use by professionals

Usually, flame retardants as such or in mixtures are used in the industrial production of mixtures or articles. However, there are also flame retardants in wide-spread use of mixtures by professionals (for example in construction, see also section 4.2).

Where the need for restriction has been identified in an assessment of regulatory needs (ARN) typically the need to restrict professional uses has been addressed since such uses are generally expected to be widespread with relatively low levels of operational controls and risk management measures and with often frequent exposures with a long duration.

4.4 Exposure potential during article service life

Apart from the substance properties, the structure of the material matrix and the interaction between the substance and the material matrix, the exposure potential during article service life depends on the conditions of article use. For the regulatory strategy the differentiation of exposure potential may become relevant when a (group of) flame retardant(s) is only suitable (or licensed) for a narrow market segment with clearly defined article types, intrinsically determining the condition of use. For example:

Exposure potential during article service life is generally low where direct contact is limited
(for human skin and for environmental media) and neither large surfaces nor heat or
radiation would promote release. Nonetheless, also for such articles, exposure cannot be
excluded, for example when in-wall construction material is handled during construction or
renovation.

In contrast,

- exposure potential to consumers during article service life is highest from uses of articles such as textiles, household furniture and indoor construction material for which a high frequency of direct contact of consumers (primarily through skin contact or inhalation) can be assumed. Exposure to environment may occur through e.g. washing of textiles and floors.
- Exposure potential to the environment during article service life is highest where the
 use conditions lead to abrasion of the material, intense exposure to radiation and water
 contact, for example in case of tyres, brake-pads or roof-sheets.

4.5 Exposure potential after service life (recycling)

The waste sector consists of a large variety of actors and wastes usually undergo several treatment steps before they are either disposed of or recovered. These steps may be performed at one or several sites, frequently involving separation or mixing of different waste fractions. In this regard, the waste treatment chains are similarly complex to supply chains.

Waste can have several destinations such as landfill and incineration (e.g. municipal wastes); recycling; or hazardous waste treatment (e.g. incineration, recycling). Releases may occur at all relevant waste management steps³⁷. Generally, at the end of service-life of articles the exposure potential, compared to service life, may increase due to milling (increasing the surface, dust formation) and thermal/pyrolytic conversion of the material matrix (exceeding the temperature for conversion and use of the primary material). As result, migration rates may increase or break-down processes may occur, including formation of hazardous transformation products.

In the following, recycling of articles is in focus. Separation and controlled recycling (with minimised exposure) is feasible where large homogenous material streams exist, and some form of EU regulation forces a level playing field covering product design and end-of life (as for example for cars, electronic equipment and buildings).

However, a dedicated recycling infrastructure for the polymeric materials (and the contained flame retardants) is so far under development for a few specific uses only, like for example enclosures and stands for electronic displays. The practical difficulties for separating out materials with hazardous substances have recently been recognised and have led to legal requirements: since substance-specific analytical controls for recycling material were not cost-effective and led to incineration instead of recycling, the Ecodesign Directive restricts the use of any halogenated flame retardant in the enclosure and stand of electronic displays (see section 2.4).

There is an (experimental) example of how a closed-loop waste-stream may be managed under certain conditions. Waste expanded and extruded polystyrene (EPS/XPS) insulation material from demolition work (sheets with HBCCD from the past 40 years) and construction work (cuts with polymeric brominated flame retardants [PolyFR] as used today) is at present mostly incinerated. However, for EPS/XPS waste also some mechanical recycling capacity exists

³⁷ 'waste management' means the collection, transport, recovery (including sorting), and disposal of waste, including the supervision of such operations and the after-care of disposal sites, and including actions taken as a dealer or broker (Directive 2008/98/EC).

basically removing HBCDD from the stream (and keeping polyFR). For the next 2-3 decades a steadily increasing amount of insulation sheets from demolition work containing HBCDD is to be expected. To make these streams of EPS/XPS accessible to recycling, a solvent-based technique has been developed (PSLoop – CreaSolv®) that enables separation of HBCDD (with recycling of bromine) from PS.³⁸ A demonstration plant for EPS exists in Terneuzen (NL) since June 2021. The wave of isolation sheets with PolyFR will come many decades later, when the new or refurbished buildings from today reach the end of their service-life. Differentiation between the two organo-bromine containing waste streams seems analytically possible, based on the difference in extractability with solvents.³⁹

To understand the conditions under which such closed-loop approach (managing waste-stream with brominated flame-retardants) may emerge in practice, the following characteristics are to be highlighted:

- PS-based insulation sheets represent a high-volume and quite homogenous stream of material. The variety of flame-retardants is low.
- The patent-owner of PolyFR (which is the main substitute for HBCDD) limits the market for PolyFR via licensing to EPS/XPS only, to prevent the new bromine-containing FR being used in material and processes where safety issue could arise.
- The use-condition of PolyFR in insulation sheets do not promote formation of brominated breakdown products (no UV access, no intense heating).
- But even when forcing transformation processes via heat and radiation, the transformation rate over time remained low and the transformation products where not persistent.
- There is a simple analytical method available to distinguish different species of bromine containing organic molecules.

4.6 Conclusions on release and exposure

Many factors have an impact on the release potential from the article serve life and during end-of-life, such as the concentration, molecular weight, additive use versus reactive use, and diffusivity of the polymer matrix. High molecular weight or reactive flame retardants have lower release potential compared to smaller additive flame retardants. However, professional uses of reactive flame retardants may still lead to substantial releases. For example, use of *in situ* foams with reactive flame retardant in construction work.

Degradation of the flame-retardant molecules to smaller, possibly hazardous, degradation products with higher migration potential may also need to be considered, especially when the degradation products are to be treated as non-threshold substances in risk assessment. Such degradation is to a large extent substance and material-specific and it is typically very challenging to have sufficient understanding of this aspect in risk assessment.

The above challenges and uncertainties suggest that generally controlling release of, and exposure to, hazardous flame retardants during and after service life must focus on inherently

https://pubmed.ncbi.nlm.nih.gov/26123348/

³⁸ https://webgate.ec.europa.eu/life/publicWebsite/index.cfm?fuseaction=search.dspPage&n_proj_id=6263 and https://www.ivv.fraunhofer.de/en/recycling-environment/recycling-plastics-creasolv.html

safe material design. In other words, hazardous flame retardants may need to be phased out, or there may need to be a demonstrably very low mobility of the flame retardant or degradation products in the material, combined with dedicated end-of-life collection and waste management systems (including recycling and destruction e.g. via incineration), as well as controlled use by industrial or professional users.

5. Strategy to address the regulatory needs

Based on the outcome of the assessments of regulatory needs (ARNs) for groups of substances created around flame retardants (see section 5.1), quite a number of flame retardants are potential candidates for restriction as they are known or suspected reproductive toxicants, neurotoxicants, PBT/vPvB or ED. A few are known or suspected carcinogens, mutagens, respiratory sensitisers. However, the type and extent of suspected hazards differs from subgroup to subgroup, and for most substances further data generation would be needed to conclude on the hazard assessment. However, for a few substances the existing data supports that restriction is required and could be started, and there is also a cluster of substances where the existing data indicate that no regulatory action is needed at present.

One particular challenge for the regulatory strategy lies in the fact that processing, recycling and disposal after article service life may be associated with undesirable impacts, for example releases of hazardous flame retardants or their breakdown products due to conditions during dismantling, reprocessing or second service life. While still focussing on exposure potential during use and service life in articles, the exposure considerations below also take recycling aspects into account to support a path towards sustainable use of chemicals and circular economy.

We note that the Commission may introduce **ecodesign requirements** on flame retardants in certain products via the EcoDesign Directive, similar to the restriction on the use of any halogenated flame retardant in the enclosure and stands of electronic displays. Whereas Directive 2009/125/EC already empowers the Commission to set eco-design requirements for energy-related products, the Commission proposed to widen this empowerment to in principle all possible products in the Ecodesign for Sustainable Products Regulation (ESPR).⁴⁰ The ESPR foresees the possibility of restricting substances present in products or used in their manufacture that negatively affect their sustainability, including circularity. This route to restrict certain flame retardants may complement, or in certain cases make redundant, the actions proposed to be taken under REACH. During the preparation of restriction proposals on flame retardants, the ongoing or planned activities under the EcoDesign Directive will need to be considered carefully.

Further, a critical revision of the different national/EU fire safety standards may be carried out by national authorities or at EU level. Potential changes to fire safety standards may influence the use of flame retardant chemicals in certain product groups. This is not further considered in the strategy below. However, some information on fire safety standards and related legislation is provided in Appendix 2.

⁴⁰ https://environment.ec.europa.eu/publications/proposal-ecodesign-sustainable-products-regulation_en

5.1 Inventory of flame retardants and grouping approach

A list of registered substances (ca. 350) used as flame retardants was developed in ECHA (called "inventory", Appendix 3). Various sources were used in preparing the list:

- ECHA's registration database: registered substances identified as flame retardants in the life cycle description,
- Report commissioned in 2021: in addition to ECHA's registration database the contractor used other sources to collect commercially available flame retardants: PINFA's product selector, SpecialChem database. Nevertheless, only sources containing an identifier (e.g. CAS No.) were considered.
- Information from the PLASI initiative⁴¹
- US EPA list of substances identified as flame retardants⁴²

This is not an exhaustive list of flame-retardants. However, this inventory list was used to create groups of structurally related substances around registered substances used as flame retardants, including substances not explicitly identified as flame retardants. Though not registered for use as flame retardant, those structurally similar substances are relevant for the assessment of regulatory needs and they might, in certain cases, be presumed to be potential alternatives to the identified flame retardants.

Group generation was prioritised for brominated and organophosphorus flame retardants. However, several other flame retardant classes (e.g. chlorinated FRs) have been or will be present in groups of substances that were not specifically created from the flame retardant properties point of view. The table below shows how many substances from the list have been grouped and assessed for their possible regulatory needs (Assessment of Regulatory Needs, ARN) by ECHA up to June 2022.

Table 3: Number of registered substances in the list of flame retardants grouped and assessed (as of 08/06/2022)

| (as or U8/U6/ | 2022) | | | | |
|-----------------------|-------|-------------------|-----------|---------------------|-----------|
| | | | | Assessed | 170 (49%) |
| Registered Substances | 349 | In groups | 233 | Not yet assessed | 63 (18%) |
| | | Not yet in groups | 116 (33%) | | |

The groups created around brominated and organophosphorus flame retardants can be seen in the table below. It is to be noted that not all the substances included in the groups have been necessarily identified as been actually currently used as flame retardants. The groups have been formed based on structural similarity and read-across proposed by the registrants to fulfil the information requirements under REACH.

⁴¹ https://echa.europa.eu/plastic-additives-initiative

⁴² https://comptox.epa.gov/dashboard/chemical-lists/FLAMERETARD

During the assessment of some groups, structural similarity between the substances allowed to draw the conclusion that substances could be potentially used as flame retardants even in the absence of explicit reference as being currently used as such. This is further elaborated in sections 5.2 to 5.5.

| Table 4: Groups created around brominated and organophosphorus flame retardants No. Substances in No. Substances | | | | | | |
|---|--|------------------------------|------------------|--|--|--|
| Flame retardants | Group name | Group name No. Substances in | | | | |
| ridine retardants | Group name | the group | in the inventory | | | |
| Brominated | Brominated cycloalkanes, alcohols, phosphates, triazine triones, diphenyl ethers and diphenyl alkyls (flame retardants related substances) [published] | 32 | 18 | | | |
| | Tetrabromobisphenol A (TBBPA) and its derivatives [published] | 15 | 9 | | | |
| | Brominated phthalates [published] | 12 | 5 | | | |
| | Triphenylphosphate derivatives | 18 | 13 | | | |
| | Organic phosphonic acids, salts and esters | 47 | 8 | | | |
| | Dibenzo oxaphosphorine oxide derivatives | 11 | 10 | | | |
| Organophosphorus | Tetrahydroxymethyl and tetraalkyl phosphonium salts [published] | 17 | 6 | | | |
| | Chlorinated trialkyl phosphates [published] | 10 | 8 | | | |
| | Alkyl aryl and cyclic diaryl esters of phosphoric acid | 14 | 2 | | | |
| | Trialkyl phosphates | 10 | 7 | | | |
| | Ethoxylated alcohol phosphates and phosphinic acid derivatives | 34 | 8 | | | |

5.2 Brominated flame retardants

5.2.1 Summary of the assessments of regulatory needs

59 brominated substances have been assessed for their regulatory needs. Table 5 provides an overview on the subgroups of substances assessed and illustrates the generic structure of the substances per group.

Table 5: Overview on groups of brominated flame retardants assessed

| Group | Sub-group | Generic structure | No. substances |
|--|---|--|-------------------|
| | Bromophenols and related substances | Br B | 5 |
| | Brominated diphenyl ethers (e.g. decaBDE) | j j | 3 |
| Brominated cycloalkanes, alcohols, phosphates, triazine triones, diphenyl ethers and diphenyl alkyls (flame retardants related substances) | Brominated diphenyl ethyls (e.g. decabromodiphenyl ethane) | · } | 2 |
| Substantials | Brominated alcohols and related substances (e.g. BMP) | Br Br Br | 10 |
| | Brominated cycloalkanes (e.g. HBCDD) | Br Br Br | 12 |
| Tetrabromobisphenol A (TBBPA) and its derivatives | | R_1 O CH_3 Br O CH_2 Br | 15 |
| Brominated phthalates | | # T T T T T T T T T T T T T T T T T T T | 12 |

| Group | Sub-group | Generic structure | No. substances |
|-------|-----------|----------------------|-------------------|
| | | | |

Generally, the bromine can be located in an aromatic position and an aliphatic position, and this position has an impact on the hazard profile of the substance, in particular with regard to the stability/lability of the Br-bonds.

All **aromatic** brominated flame retardants have in common that they tend to be persistent. Quite a few are also known or suspected to be bioaccumulative (B/vB) and/or toxic. For some substances, data are available to propose SVHC identification.

However, for most of the substances containing **aromatic** bromine **data generation** to confirm the **PBT/vPvB** properties and in some cases also other hazards is still ongoing or planned:

- For brominated phthalates data generation is ongoing for List 616-436-5 and is planned for EC 242-604-9. The data generation was requested to clarify PBT/vPvB properties and ECHA will assess this information in the beginning of 2023.⁴³
- For decabromodiphenyl ethane (EC 284-366-9, DBDPE) data was requested regarding potential bioaccumulation under substance evaluation⁴⁴ and has been assessed by the PBT expert group⁴⁵. The available data, including field studies, appear to confirm the PBT properties of the substance. The substance evaluation may be finalised in 2023. Furthermore, information is requested regarding reproductive toxicity (data expected by 2024)⁴⁶;
- For a brominated diphenyl ether with confidential EC number, it is planned to initiate CCH to clarify the potential reproductive toxicity and vPvB hazard, and to generate data on repeated dose toxicity. No timing is available yet.
- Substance evaluation for TBBPA (EC 201-236-9) is ongoing based on amongst others potential PBT/vPvB and endocrine disrupting properties. Following testing for persistency on the two transformation products from a first substance evaluation decision in March 2017 a follow-up decision requesting bioaccumulation testing in fish for two transformation products mono- and bismethyl ether TBBPA has been issued⁴⁷. The results

⁴³ All brominated phthalates are suspected vPvB based on structural similarity. However, most of the substances in the group of brominated phthalates are not (yet) registered and consequently no data are available to confirm vPvB properties. For EC 616-436-5 a compliance check decision requested 15 studies to be submitted by June 2022. The deadline set in the adopted decision has passed, and ECHA is assessing whether the information requested in the decision has been provided in the dossier update - This follow-up may also involve the national enforcement authorities. See also https://echa.europa.eu/information-on-chemicals/dossier-evaluation-status/dislist/details/0b0236e18159a3cf

^{44 &}lt;a href="https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/dislist/details/0b0236e1807e3287">https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/dislist/details/0b0236e1807e3287

⁴⁵ https://echa.europa.eu/documents/10162/1459379/summary_report_pbteg-31_en.pdf/9609d0c2-0bb9-c6c4-46ce-4e84a7d7229e?t=1666691773276

⁴⁶ https://echa.europa.eu/information-on-chemicals/dossier-evaluation-status/-/dislist/details/0b0236e18477fab4

^{47 &}lt;u>https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/dislist/details/0b0236e1807e837f</u>

are expected by February 2025. The results may be extrapolated to 8 other members of the group 'Tetrabromobisphenol A (TBBPA) and its derivatives', based on structural similarity.

With increasing **molecular size** (and decreasing water solubility) and if the molecule is not sensitive to forming smaller (and stable) break-down products under use-conditions, bio-accessibility of aromatic brominated flame retardants decreases and may become unlikely. The flame retardant 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (EC 426-040-2) appears to be an example for such trend. The available data (including the ADME study) suggest that the substance does not meet the criteria for being considered B/vB⁴⁸ and hence the general PBT/vPvB concern seems not applicable to this specific substance.

According to the published RAC opinion⁴⁹, TBBPA is also a non-genotoxic **carcinogen** (proposed as cat 1B). It would need to be considered whether its use in unreacted form in mixtures by professionals or incorporation as additive into articles would sufficiently be addressed in any restriction proposal targeting the environmental concern.

For **aliphatic** brominated flame retardants further **data generation** is needed to clarify hazards. Should hazards exist, CLH for reproductive toxicity, carcinogenicity and/or neurotoxicity (STOT RE) or SVHC identification of PBT/vPvB and/or ED properties may be proposed, followed by restriction.

A particular question in this respect is whether and how fast bromide is released in vivo. The release of bromide may cause reproductive and neurological effects (for further explanation refer to the ARN⁵⁰). Reproductive toxicity is already confirmed through harmonised classification for some aliphatic brominated flame retardants: octabromodiphenyl ether (Repro 1B), 2,3 DBPA (Repro 2) and HBCDD and its diastereoisomers (Repro 2). Based on the general chemical knowledge, it is likely that alkyl bromides are generally more labile than aromatic bromides.

Carcinogenicity has been identified for three brominated (non-aromatic) alcohols: 2,3-DBPA (EC 202-480-9), BMP (EC 221-967-7) and TBNPA (EC 253-057-0). These tree substances are already identified as SVHC based on carcinogenicity according to Art. 57(a). According to information received from BSEF, BMP and TBNPA are used as reactive flame retardants in PU foams and unsaturated polyester resins.⁵¹ BMP is a mutagen cat 1B making non-threshold genotoxicity plausible. Further confirmation of the persistency and possible mobility in the environment was concluded not necessary.

2,3-DBPA was not specifically identified as a flame retardant by BSEF (it was identified by US EPA for use as flame retardant and this is why it was included in the assessment). 2,3-DBPA (EC 202-480-9) is registered for intermediate use only. It is concluded that the substance is not likely to be used as flame retardant in the EEA and is therefore not discussed further.

5.2.2 Regulatory strategy

Table 6 summarises the outcome of ECHA's assessment of regulatory needs for 59 brominated

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⁴⁸ Conclusions of the PBT expert group; updating of PBT factsheet and drafting of Hazard Assessment Outcome Document in progress.

⁴⁹ https://echa.europa.eu/registry-of-clh-intentions-until-outcome/-/dislist/details/0b0236e184330ec8

 $^{^{50} \, \}underline{\text{https://echa.europa.eu/assessment-regulatory-needs/-/dislist/details/0b0236e186309713}}$

https://www.icl-ip.com/product/fr-513/; https://www.icl-ip.com/product/fr-522/

substances (potentially) used as flame retardants. All grouped substances (registered/non-registered, intermediates, low tonnages) have been considered. However non-registered substances in (imported) articles are not fully covered yet.

Table 6: Overview of regulatory status and data availability

| Proposed next action | Number of substances | Comments | |
|---|----------------------|--|--|
| No action needed (already sufficiently regulated) | 7 | Listed as POPs under the Stockholm Convention | |
| Substances ready for starting restriction with focus on professional use (sufficient information is expected to be available) | 2 | Brominated alcohols BMP and TBNPA (2,3-DBPA not considered further ⁵²) | |
| Substances ready for SVHC identification or CLH and subsequently restriction | 1 | Brominated phthalate EC 247-426-5 | |
| Action pending, data generation | >40 | | |

Two registered brominated diphenyl ethers, DecaBDE and OBDPO, and five brominated cycloalkanes (HBCDD and its major diastereoisomers) are listed as POP under the Stockholm Convention (many more polybrominated diphenyl ethers under the POPs Regulation as discussed in section 1.4, but these substances are not registered). These seven brominated flame retardants are considered to be **sufficiently regulated** and not further addressed below.

The current regulatory strategy was developed based on 12 **brominated** substances that have been identified as being fully registered (not intermediates) and marketed as flame retardants in the EU in amounts larger than 10 tonnes per year⁵³. The eventual regulatory action is considered equally applicable to not (yet) fully registered substances with similar hazards and uses.

Table 7: Aromatic brominated flame retardants in focus of the strategy

| | No. FR ⁵⁴ | Additive /reactive | MW > 1000 | Examples for uses | Immediate next action |
|---------------|----------------------|--------------------------|----------------------|---|-------------------------------------|
| TBBPA and its | | 3 reactive | | EPS/XPS/HIPs, PPFlexible foam, | TBBPA: Carc.1B; pending SEv |
| derivates | 7 | 5 additive ⁵⁵ | 0 | Dispersion for | for ED, PBT |
| | | | textile back-coating | • Pending SEv (6) for C, | |

52 As concluded above, this substance is not likely to be used as flame retardant in the EEA and is therefore not discussed further

⁵³ The exception is the brominate phthalate EC 428-050-2. This substance was previously registered under the REACH Regulation but the registration is no longer valid. It was nevertheless included because the substance contains EC 247-426-5 as a constituent largely above the regulatory limit of 0.1% w/w, it can also be considered to have vPvB properties.

⁵⁴ TBBPA and its derivates in focus: EC/List 201-236-9 (TBBPA); 221-346-0; 244-617-5; 306-832-3; 500-107-7; 926-564-6; and 944-461-4. Brominated phthalates in focus EC/List 247-426-5; 428-050-2; 616-436-5; and 242-604-9. Brominated diphenyl ethyls: decabromodiphenyl ethane (EC 284-366-9, DBDPE).

⁵⁵ TBBPA is used as both reactive and additive flame retardant.

| | No. FR ⁵⁴ | Additive /reactive | MW > 1000 | Examples for uses | Immediate next action |
|----------------------------------|----------------------|--------------------------|------------------|--|--|
| | | | | Coatings and adhesives | ED, PBT CCH for (4) |
| Brominated phthalates | 4 | 1 reactive 3 additive | 2 | Engineered plasticsSoft foam,Textile treatment | SVHC for PBT (1)⁵⁶ CCH pending PBT (2) |
| Brominated diphenyl ethyls | 1 (DBDPE) | additive | 0 (971 g/mol) | Various thermoplastic, elastomeric, thermoset polymers Textile back-coating | SEV repr, PBTCCH Repr, neuro, ED, PBT |

5.2.2.1 Strategy for substances with bromine bound in aromatic rings

From the information available, it appears that flame retardants with **aromatic bromine** are of a **general concern** due to their known or potential **PBT/vPvB properties**. Therefore, the exposure potential to these kind of flame retardants needs to be minimised. With a view to the challenges to control exposure to individual substances (see section 4) and the availability of alternatives (see section 3.4), **a wide and generic** restriction seems to be the most appropriate regulatory approach. A broad restriction would also send a clear signal to manufacturers to move away from brominated flame retardants and all aromatic brominated flame retardants with PBT/vPvB properties would be addressed in one restriction (with a mechanism for future addition of substances). Reacted and/or polymeric flame retardants seem to be less likely to be identified as PBT/vPvB. As already anticipated in the Restrictions Roadmap (see section 2.2), restriction is preferred over authorisation as it is considered to be more efficient and effective to introduce controls at the level of placing on the market rather than at the level of uses, especially considering the fact that imported articles could not be addressed through the authorisation system, as well as the challenges to achieve the aim to minimise release through other means than restriction (see 'Considerations on recycling and disposal' below and section 4).

Consequently, for the **aromatic brominated** flame retardants, it is proposed that the restriction scope could cover all aromatic brominated flame retardants that are confirmed or will be confirmed to be persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) through harmonised classification or identification as substances of very high concern. Therefore, a restriction dossier could already be initiated with a core set of substances including two brominated phthalates and one brominated biphenyl. The core set of substances could be:

⁵⁶ The brominate phthalate EC 428-050-2 was previously registered under the REACH Regulation but the registration is no longer valid. The substance contains EC 247-426-5 as a constituent largely above the regulatory limit of 0.1% w/w, it can also be considered to have vPvB properties. Thus, a potential restriction may be formulated that it directly or indirectly covers also this substance.

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- Decabromodiphenyl ethane (EC 284-366-9, DBDPE) is an additive flame retardant being widely marketed in the EU as replacement for the very similar molecule decabromodiphenyl ether (decaBDE). It is manufactured in and / or imported to the EEA at 10,000-100,000 tpa and is present in important articles in quantities yet to be estimated. The assessment of bioaccumulation under substance evaluation is ongoing. The conclusion may be available in 2023. Of note is that many of the polybrominated diphenyl ethers are already restricted under POPs (see section 2.4).
- The brominated phthalates EC 247-426-5 (manufactured in and / or imported to the EEA at 100-1000 tpa) and 428-050-2 (registration no longer valid). Data generation is ongoing or planned for EC/List 616-436-5 and 242-604-9 (both are manufactured in and / or imported to the EEA at 100-1000 tpa). Most other brominated phthalates are not registered.

Data generation is still on going for tetrabromobisphenol A derivatives (testing results for TBBPA are expected by the end of 2024 and the substance evaluation conclusions may then be available early 2026, see also above). In case it is concluded that TBBPA has PBT/vPvB properties it would fall under the restriction as well⁵⁷.

Considerations on recycling and disposal

Ensuring the absence of specific brominated substances from the material streams and specifically controlling use conditions throughout the different markets seems practically challenging to say the least (as illustrated with the example of brominated flame retardants in electrical and electronic equipment), see sections 2.4 and 4.

Moreover, although high molecular weight or reactive flame retardants may have lower release potential compared to smaller additive flame retardants during the article service life as (see section 4), during waste processing, recycling, re-use and/or disposal the exposure potential to the flame retardant or its degradation products may increase.

Therefore, one of the key questions for the regulatory strategy is whether bromine as an effective flame retardant can be further used if covalently bound in high molecular weight structures (including polymeric forms), or whether polymers should be free of bromine in future, as (i) the release/exposure potential to hazardous brominated substances during dismantling, recycling and disposal operations may not be sufficiently controlled (or excluded), and (ii) the presence of brominated flame retardants may encumber the move towards toxic-free material cycles, to achieve the objectives of Circular Economy.

The following questions need to be clarified:

 If wide-spread use of organo-bromine flame-retardants in polymeric or reacted form would be exempted from a generic restriction on brominated FR with aromatic bromine binding,

and European Commission (2021), Directorate-General for Environment, Köhler, A., Baron, Y., Gensch, C., et al., Study to support the review of the list of restricted substances and to assess a new exemption request under RoHS 2 (Pack 15): final report, Publications Office, 2021, https://data.europa.eu/doi/10.2779/47125

⁵⁷ TBBPA is manufactured in and / or imported to the European Economic Area, at ≥ 10 000 to < 100 000 tonnes per annum. Under ROHS, a Commission initiative proposes adding tetrabromobisphenol A (TBBPA) to the list of restricted substances https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/13469-Hazardous-substances-in-electrical-and-electronic-equipment-list-of-restricted-substances-update-en

does such exemption need to be limited to material or articles for which dedicated collection systems and adequate re-processing can be expected? How are such collection infrastructure and recycling techniques expected to develop? Will such collection in the foreseeable future be regulated? Is it likely to establish dedicated material-cycles with bromine being present, but not leading to the release of hazardous organo-bromine compounds?

- Is it easily possible to analytically differentiate bromine bound in polymers from restricted organo-bromine compounds that may migrate during or after recycling? And if it is not feasible to differentiate easily, would this mean that it is not possible to target the restriction to exempt polymeric or reacted bromine?
- What kind of evidence would be required to demonstrate that under the foreseeable conditions of recycling or disposal (e.g. exposure to heat or sun) no degradation of the polymeric structures containing bromine is to be expected, or that the possible degradation products would not have PBT/vPvB properties?

Based on current knowledge, ECHA cannot propose answers to these questions and recommends further investigating the expected developments in the recycling business before starting the restriction process.

5.2.2.2 Strategy for substances with bromine bound to aliphatic structures

For the substances with pure **aliphatic bromine** the hazard profile is more diverse. Setting aside the brominated cycloalkanes as being already regulated, action on 2 brominated alcohols (confirmed genotoxic carcinogens) and one brominated phosphate (CMR, neurotox and PMT suspicion) would have the highest regulatory impact.

Table 8: Aliphatic brominated flame retardants in focus of the strategy

| Substance | Additive/reactive | Examples for uses | Immediate next action |
|---|-------------------|---|--|
| 2,2 bis(bromomethyl) propane-1,3-diol (EC 221-967-7, BMP) ⁵⁸ | Reactive | PU foams and unsaturated polyester resins | Restriction for professional use in unreacted form |
| 2,2- dimethylpropan-1- ol, tribromo derivative (EC 253- 057-0, TBNPA) ⁵⁹ | Reactive | PU foams and unsaturated polyester resins | Restriction for professional use in unreacted form |
| (tribromoneopentyl) phosphate (EC 413-060-1) ⁶⁰ | Additive | PP and HIPs | CCH to confirm CMR, neurotox and PMT suspicion |

For the two reactive alcohols (BMP and TBNPA) restriction could be initiated based on their

⁵⁸ Also referred to as FR-522 or Dinol.

⁵⁹ Also referred to as FR 513 or trinol.

⁶⁰ Also referred to as FR 370.

carcinogenic properties. They are used in PU foams and unsaturated polyester resins. The concern is probably more related to widespread use of the unreacted substance by professionals (e.g. in chemicals for construction work), rather than the exposure potential from article service life (where the substance has been covalently bound into the polymer matrix). BMP is manufactured in and / or imported to the EEA at 1 - 10 tonnes per annum (at the time of the ARN the registered tonnage was 100-1000 tonnes per annum) and TBNPA is registered by one registrant for intermediate use only (in the ARN a full registration was available at 100-1000 tonnes per annum). Although initiating a restriction targeting professional use may already be considered, it seems advisable to consider also the release potential from reactive flame retardants during the (article) service life and waste stage, see section 4.

For the brominated alkyl phosphate (EC 413-060-1), once the CMR concern would have been confirmed, CLH and restriction probably targeting article service life may be the next actions.

5.3 Chlorinated flame retardants

The market for chlorinated FRs is relatively small and covers relatively few substances. No specific groups were formed for chlorinated flame retardants (see section 5.1). However, several chlorinated FRs were present in groups of substances that were not specifically created from the flame retardant properties point of view.

For some chlorinated flame retardants, regulatory action is already in place or ongoing based on their PBT and/or vPvB properties, e.g. alkanes, C10-13, chloro; alkanes, C14-17, chloro and Dechlorane Plus (see section 2.4).

Paraffin waxes and hydrocarbon waxes, chloro (also referred to as 'LCCP') may contain alkanes, C14-17, chloro congeners identified with PBT/vPvB properties (constituents). These are expected to be addressed in the restriction proposal for medium-chain chlorinated paraffins (MCCP) and other substances that contain chloroalkanes with carbon chain lengths within the range from C14 to C17. In addition, data generation (CCH, possibly followed by SEv) is suggested to further clarify human health hazards and PBT properties of paraffin waxes and hydrocarbon waxes, chloro.

TCPA (EC 204-171-4, tetrachlorophthalic anhydride) and chlorendic anhydride (EC 204-077-3) are part of the Assessment of Regulatory Needs for phthalic anhydrides and hydrogenated phthalic anhydrides (as is the flame retardant tetrabromophthalic anhydride (TBPA), see section 5.2)⁶¹. The Assessment of Regulatory Needs concludes that all substances in this group (including also TBPA) have known or potential skin and respiratory sensitising properties. Most of the substances in the group have a harmonised classification as respiratory sensitiser. As a first step, it is proposed that CLH proposals are initiated and submitted jointly for respiratory and skin sensitisation for all substances in the group that do not yet have CLH covering these hazards (such as chlorendic anhydride). The Assessment of Regulatory Needs proposes a restriction for all substances. A restriction would target primarily 6 substances in mixtures handled by professional users and some consumer uses (e.g. bi-component adhesives, hardener for epoxy resins). Tetrachlorophthalic and chlorendic anhydride are currently only used in formulation and industrial uses as intermediate, in polymer preparations and compounds or in

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⁶¹ https://echa.europa.eu/documents/10162/8806792e-2eeb-8bf2-b811-f0fa21e91be0

coatings and paints, thinners, paint removers. As the substances are likely substitutes for each other, all substances may be included in a restriction and a proposal may consider to restrict targeted industrial uses.

5.4 Organophosphorus flame retardants

5.4.1 Summary of the assessments of regulatory needs

Organophosphorus flame retardants can be divided in four general main groups: phosphates, phosphonates, phosphonates and phosphonium salts. Nevertheless, 8 groups of substances were created around organophosphorus flame retardants identified in our inventory (see section 5.1 above) according to structural similarities. 130 organophosphorus substances have been assessed in those groups. Table 9 provides an overview on the groups and subgroups (if relevant) of the substances assessed and illustrates the generic structure of the substances per group and sub-group.

Table 9: Overview on groups of organophosphorus retardants assessed

| Group | Sub-group | Generic structure | No. substances in the sub- group |
|---|--|---|---|
| Triphenyl phosphate derivatives | N/A | R: alkyl, phenyl | 18 |
| Trialkyl phosphates | N/A | R—OOR R R R: alkyl | 10 |
| Chlorinated trialkyl phosphates | N/A | R—O R R R: chlorinated alkyl | 10 |
| Alkyl aryl and cyclic esters of phosphoric acid | Non-cyclic alkyl aryl ester | R: alkyl R1 \neq R2: alkyl or aryl | 8 |
| Organic phosphonic acids, salts and esters | Alkyl (<c8) alkyl(<c8)phosphonates<="" and="" diesters="" hydrogenphosphonates="" of="" th=""><th>R1: H, alkyl (<c8) (<c8),="" alkyl="" phenyl<="" r2,="" r3:="" th=""><th>13</th></c8)></th></c8)> | R1: H, alkyl (<c8) (<c8),="" alkyl="" phenyl<="" r2,="" r3:="" th=""><th>13</th></c8)> | 13 |

| Group | Sub-group | Generic structure | No. substances in the sub- group |
|--|--|--|---|
| | Alkyl esters of alkyl(≥C8)phosphonates | 0 R ₂ 0 | 5 |
| | Other hydrogenphosphonates and alkyl phosphonates, their salts and esters with alkyl chains <c8< th=""><th>R1: H R2, R3: H, alkyl + polyphosphonates</th><th>29</th></c8<> | R1: H R2, R3: H, alkyl + polyphosphonates | 29 |
| Dibenzo oxaphosphorine oxide derivatives | N/A | P R | 11 |
| Tetrahydroxymethyl and tetraalkyl phosphonium salts | Tetrakishydroxymethyl phosphonium salts and their condensation products with amines | OH HO H | 7 |
| Ethoxylated alcohol phosphates and phosphinic acid derivatives | Hydrocarbyl phosphinic acids, salts and esters | Tris(2-butoxyethyl) phosphate (TBEP) $ \begin{array}{cccccccccccccccccccccccccccccccccc$ | 1 18* |

*From the 18 phosphinate substances in the sub-group only 8 are used as flame retardants (reactive). No extrapolation to the rest of the group was possible considering structural dissimilarities.

The **triphenyl phosphates mono-phosphate derivatives** are all potential reproductive toxicants with a potential for ED hazard for human health and the environment. One of them, TXP (EC 246-677-8), has a harmonised classification as Repr.1B and is already included in Annex XIV (entry number 47, sunset date: 27 May 2023). Nevertheless, it is proposed to first clarify the potential ED properties as this will have an important role in the regulatory needs of the substance considering it is a non-threshold hazard. For one other, TPP (EC 204-112-2), data on

reproductive toxicity and ED hazard is being generated though SEv. For two others (List 809-930-9 and 945-730-9), further data will be generated through CCH, which may be followed-up by SEV for List 809-930-9 and 939-505-4 when the potential hazards would require further clarification. Should hazards exist, it is proposed to consider extrapolating hazards to all monophosphate derivatives and to confirm reproductive toxicity through CLH and/or ED hazards through SVHC identification and followed-up by restriction. EC 273-066-3 is also potentially PBT/vPvB and under scrutiny for this endpoint. Should this hazard clarify, SVHC identification should be considered for this substance also for this endpoint. None of the other mono-phosphate derivatives screen for PBT/vPvB. For the **polyphosphate derivatives**, reproductive toxicity, ED and neurotoxicity are inconclusive requiring further clarification through CCH. Pending those results, data may need to be further generated on List 807-250-7 to clarify its hazards through SEv.

Triphenyl phosphates are used as flame retardant plasticisers in different plastics, thermoplastics, rubber and rigid and flexible foams in building and construction work, furniture and electric and electronic devices. They are also applied as plasticisers and flame retardants in products like paints, lacquers and varnishes. In addition, they are also used as flame-retardant hydraulic fluids, heat transfer fluids, metal working fluids and lubricants.

The **trialkyl phosphates** have all a potential for ED hazard for human health and the environment that is independent of the chain length based on the information available in the registration dossiers. Data generation is on-going to confirm this conclusion (EC 201-114-5 and EC 201-116-6) and SEV is foreseen if further clarification is needed. Should hazards exist, SVHC identification followed-up by restriction is proposed. In addition, a CLH proposal for trimethyl phosphate (EC 208-144-8) has been submitted for Repr. 1B/F, Muta 1B, Carc 1B, STOT RE 2 (neurotoxicity). These hazards have been tentatively extrapolated to triethyl phosphate (EC 201-114-5) in the group assessment since short-chain trialkyl phosphates may function as alkylating agents. Nevertheless, the available information does not support this mechanism for longer chain trialkyl phosphates. A potential hazard for carcinogenicity category 2 was also identified for the substances in this group, other than trimethyl phosphate, which is unlikely driven via genotoxicity.

Trialkyl phosphates are used as flame retardant plasticisers in a variety of polymers and applications. They are also applied as plasticisers and flame retardants in products like paints, lacquers and varnishes. In addition, they are also used as flame retardant lubricants.

All the substances in the group **chlorinated trialkyl phosphates** have all been assessed with carcinogenicity as the common potential hazard. Other hazards were also identified but not common to all the substances in the group. The ECHA Screening report⁶² on TCEP, TCPP and TDCP (EC 204-118-5, 237-158-7, 807-935-0, 911-815-4, and 237-159-2) "identified a risk for children from exposure to TCEP, TCPP and TDCP in flexible polyurethane (PUR) foams in childcare articles and residential upholstered furniture, ECHA recommends an Annex XV restriction dossier is prepared.(...) If a restriction report is prepared, exposure from other uses, article groups and exposure populations will need consideration". Carcinogenicity was considered to be the leading effect in the ECHA Screening report. The Commission requested ECHA to prepare a restriction dossier. The preparation of the proposal was put on hold (19/7/2019), pending the availability

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^{62 &}lt;u>https://echa.europa.eu/documents/10162/17233/screening_report_tcep_tcpp_td-cp_en.pdf/e0960aa7-f703-499c-24ff-fba6270606987t=1523014289559</u>

of new critical data (US NTP studies on the carcinogenicity of TCPP, technical report still not available). The report proposes to extend the assessment of exposure from articles also to adults and additional groups of articles, such as automotive applications and furniture, electrical/electronic equipment and additional uses (for example, spraying of insulation foams). After assessment of the group, it is proposed to include all the substances in the group in a restriction provided the new data highlighted above confirms the hazard.

As for the previous groups, chlorinated trialkyl phosphates are used as flame retardants also in a variety of polymers and applications including plastics, foams, coatings, paper and textiles potentially ending up in a number of different article types.

The **non-cyclic alkyl aryl esters of phosphoric acid** are of unlikely or low concern for hazards for humans and the environment. Although a hazard for potential Carcinogenicity Cat. 2 was highlighted the relevance for humans is unclear. In addition, this hazard was related to one of the constituents of substance List No. 907-672-2, i.e. tributyl phosphate. No other potential hazard was identified for human health based on the available information in the registration dossiers.

Non-cyclic alkyl aryl esters of phosphoric acids are plasticiser flame retardants. Although, there is only explicit evidence for a few substances, the chemical structure similarity with the rest of the substances in the group suggests that all the substances are able to provide flame retardant properties for the same applications. These substances are used in the production of plastics, adhesives/sealants, fillers, coatings and paints and leather treatment products.

The organic phosphonic acids, salts and esters contain Alkyl(<C8)diesters of hydrogenphosphonates and alkyl(<C8)phosphonates, Alkyl esters of alkyl(≥C8)phosphonates and Other hydrogenphosphonates and alkyl phosphonates, their salts and esters. The alkyl(<C8)diesters of hydrogenphosphonates and alkyl(<C8)phosphonates are potentially reproductive toxic, mutagenic and neurotoxic (STOT RE). Further data generation though CCH is needed on EC 217-316-1, 225-202-8, 231-388-1 and 242-555-3 to clarify these hazards as well as their persistency and mobility in the environment. Should hazards exist, extrapolating hazards to the other short-chain phosphonates should be considered and confirmed through CLH and followed-up by restriction. These substances seem to be used as reactive flame retardants and it should be considered against the assumed additive use of the other short-chain phosphonates as reactive uses lead to comparatively lower exposure potentials during use. The **Alkyl esters of alkyl(≥C8)phosphonates** are potentially PBT/vPvB based on the information currently available in the registration dossier. Further data are to be generated on EC/List 246-904-0, 417-170-0 and 939-595-5 through CCH to clarify this, and for EC 246-905-6 and 268-740-9 for which no further data generation is proposed for the moment. Should hazards exist, SVHC identification of PBT/vPvB properties followed by restriction is proposed. Based on the available information from the registration dossiers, the longer chain phosphonates are of no or unlikely hazard to human health.

The **Other hydrogenphosphonates and alkyl phosphonates, their salts and esters** are all of no/unlikely or low concern for hazard for humans and the environment based on the currently available information from the registration dossiers with the exception of EC 443-520-7 which is self-classified as Skin Sensitiser Cat. 1A and is potentially P/vP and EC/List 275-063-2 and 944-574-9 that are Self-classified as Skin Sensitiser Cat. 1B. In addition, several of these substances seem to be used as reactive flame retardants, which is expected to lead to comparatively lower exposure potentials during use to additive uses.

The use profile of organic phosphonic acids, salts and esters seem to be linked to the size of the alkyl chains in the structure. Thus, when alkyl chains are >C8 they are mainly used in hydraulic fluids, heat transfer fluids, metal working fluids and lubricants and, although not always explicitly mentioned in the registration dossiers, they might provide flame retardancy in those uses as well. When the alkyl chains are <C8 they are mainly used as reactive substances that can be incorporated in a polymer providing flame retardant properties.

Based on the information available in the registration dossiers the **Dibenzo oxaphosphorine oxide (DOPO) derivatives** are of no/unlikely or low concern for hazards for humans and the environment. EC 252-813-7 and 426-480-5 are classified as Skin Sensitiser 1B and 1 respectively and four others, i.e. EC/List 264-313-6, 619-409-6, 823-458-0 and 827-182-1, screen as inconclusive for Skin Sensitisation. Data will be generated through CCH to clarify low hazard potential for EC/List 252-813-7, 619-409-6, 700-929-8, 815-096-7, 823-458-0 and 947-340-4. In addition, all DOPO derivatives are used as reactive flame retardants, which is expected to lead to comparatively lower exposure potentials during use to additive uses.

DOPO substances are mostly used as reactive flame retardants in polyurethane and epoxy resins in a variety of applications. ⁶³ Those include electrical and electronic applications, and automotive and aviation.

From the group Tetrahydroxymethyl and tetraalkyl phosphonium salts, only the substances in sub-group Tetrakishydroxymethyl phosphonium salts and their condensation products with amines were identified as flame retardants. Tetrahydroxymethyl phosphonium salts are known or potential reproductive toxicants based on information on EC 204-707-7 and 259-709-0 (both self-classified) and possible extrapolation of this hazard based on structural similarity to the rest of the substances in the sub-group. All substances are selfclassified as Skin Sens 1A, except for EC 204-707-7 and 422-720-8 (self-classified as Skin Sens. 1) and all are toxic to the aquatic environment. In addition, carcinogenicity cannot be excluded for these substances due to either the presence of formaldehyde as a constituent or impurity, or the formation of formaldehyde as principal metabolite, but there is very limited information available from the registration dossiers to substantiate this concern for hazard. Further data generation through CCH on EC/List 259-709-0, 436-230-7, 613-239-6 and Substance X will further clarify the potential hazards. Should these exist, confirming these through CLH, including Skin Sensitisation, is thought sufficient to manage possible risks for workers, consumers and the environment due to the polymeric nature of the use, the fact that these seem to be primarily used for textile and leather treatment and the regulatory measures already in place for such uses.64

The group containing **Ethoxylated alcohol phosphates and phosphinic acid derivatives** is structurally highly heterogeneous. Tris(2-butoxyethyl) phosphate (TBEP) (EC 201-122-9) is the only **ethoxylated alcohol phosphate** with explicit evidence of being used as a plasticising flame retardant in the production of plastic and rubber products. Potential endocrine disrupting properties for human health and the environment have been identified for this substance that need to be clarified through data generation. The **Hydrocarbyl phosphinates** in this group have been identified as generally of low hazard potential. Nevertheless, for diethylphophinates

⁶³ https://doi.org/10.1016/j.polymdegradstab.2014.12.014

⁶⁴ E.g. restriction under REACH on CMR in textile and footwear articles (entry 72), the restriction under development on Skin Sensitisers in Textile, leather and fur articles, and Regulation (EU) 2016/425, regulating the safety of personal protective equipment and the use of flame retarded textiles.

(EC 700-732-7, 428-310-5, 457-580-7, 434-510-3, 609-080-7) potential vPvM properties have been identified that need to be clarified with data generation. Hydrocarbyl phosphinates are used as reactive flame retardants in the production of textiles and plastic products.

A summary of the information available from the assessments of regulatory needs done at ECHA can be seen in the Table 10 below.

Table 10: Summary of from the assessments of regulatory needs for organophosphorus flame retardants

| retardants | | | | |
|--|-----------|---|---|--|
| Group/sub-group | No. FR | Examples for uses | Immediate next action and hazard endpoints | |
| Triphenylphosphate derivatives | 18 | Plastics, thermoplastics, rubber and rigid and flexible foams in construction, furniture and electrical and electronic devices. Paints, lacquers and varnishes. Flame retardant hydraulic fluids, heat transfer fluids and lubricants | CCH and SEV Repro. and ED | |
| Trialkyl phosphates | 10 | Plastics, thermoplastics, rubber and rigid and flexible foams in construction, furniture and electrical and electronic devices. Paints, lacquers and varnishes. Flame retardant lubricants | CCH and potentially SEV for ED | |
| Chlorinated trialkyl phosphates | 11 | PU foams and coatings, plastic and textile articles in e.g. vehicles and furniture | Pending data for Carc. | |
| Non-cyclic alkyl aryl esters of phosphoric acid | 8 | Leather treatment, coatings/paints, plastic products | No action, Carc. 2 and unlikely hazard for mutagenicity and skin sensitisation | |
| Alkyl (<c8) alkyl(<c8)phosphonates<="" and="" diesters="" hydrogenphosphonates="" of="" th=""><th>13</th><th>Textile treatment, coatings/paints, plastic products</th><th>CLH proposal (IE) for CCH Repro., Muta. And neurotox</th></c8)> | 13 | Textile treatment, coatings/paints, plastic products | CLH proposal (IE) for CCH Repro., Muta. And neurotox | |
| Alkyl esters of alkyl(C≥C8)phosphonates | 5 | Flame retardant hydraulic fluids, heat transfer fluids, metal working fluids and lubricants | CCH for PBT/vPvB | |
| Other hydrogenphosphonates and alkyl phosphonates, their salts and esters | 29 | Textile and leather treatment, paper treatment, electrical and electronic equipment, plastic products | CCH unlikely hazard | |
| Dibenzo oxaphosphorine oxide derivatives | 11 | Textile treatment | Skin sensitisers No further action | |
| Tetrakishydroxymethyl phosphonium salts and their condensation products with amines | 7 | Textile and leather treatment | Skin sensitisers CCH Carc. Repro. STOT RE (liver) Then CLH, Restriction entry 72 (REACH Annex XVII) | |

| Group/sub-group | No. FR | Examples for uses | Immediate next action and hazard endpoints |
|--------------------------------|-----------|-------------------------------|---|
| | | | and restriction proposal on skin sensitisers in textiles, leather, and fur and hide articles |
| Ethoxylated alcohol phosphates | 1 | Plastic and rubber products | CCH and potentially SEV for ED |
| Hydrocarbyl phosphinates | 8 | Textiles and plastic products | Generally of low hazard potential. CCH for Diethylphophinates to clarify potential vPvM properties |

5.4.2 Regulatory strategy

The organophosphorus flame retardants appear to be different from the halogenated ones since not all of them seem to be of immediate concern and their (eco)toxicological profile seems to be diverse across the different groups of substances. In addition, substantial data generation is still needed to clarify the hazards. Considering the data generation needed, precise timelines cannot be proposed. However, the results are not expected before 2025/2026 in most of the cases and it is proposed to assess the situation in 2025 and revise the strategy accordingly.

Thus, based on the current information, groups of low or unlikely hazards can be identified such as:

- Non-cyclic alkyl aryl esters of phosphoric acid,
- Other hydrogenphosphonates and alkyl phosphonates, their salts and esters, and
- Dibenzo oxaphosphorine oxide derivatives (DOPO derivatives)
- Hydrocarbyl phosphinates

At the same time, the concerns identified for the substances in the group tetrakishydroxymethyl phosphonium salts and their condensation products with amines could also be addressed by restriction entry 72 (REACH Annex XVII) and restriction proposal on skin sensitisers.

However, similar to halogenated flame retardants, many other organophosphorus flame retardants are suspected as human toxicants, e.g. reproductive toxicants, ED, neurotoxicants, and some may also be suspected PBT. Nevertheless, the results from data generation or data that are being generated are needed to confirm the potential hazards. Thus, although trixylyl phosphate (EC 246-677-8) is classified as Repro. 1B in the assessment of regulatory needs for the triphenylphosphate derivatives both Repro. 1B and endocrine disrupting properties have been identified and proposed to be followed in parallel. Also, the potential carcinogenic properties (Cat 2) of chlorinated trialkyl phosphates are expected to be confirmed by pending toxicological studies under the US NTP (finished but technical report still not available).

All in all, the hazardous properties of organophosphorus flame retardants seem to be more group specific. Sub-grouping based on structural characteristics and a confirmed hazard/non hazard within such groups may be better to incentivise the substitution.

5.5 Other flame retardants

5.5.1 Summary of the assessments of regulatory needs

Substances identified with a use as flame retardants have also been identified in other chemistries that do not belong to the halogenated or the organophosphorus flame retardants. The regulatory needs for some of these substances have also been assessed in groups that were not generated based on their flame retardancy.

Those substances are normally used in combination to achieve the desired flame retardancy and they are also used with other technical functions.

Inorganic phosphates, polyphosphates, phosphinates, phosphonates and phosphorous and its inorganic salts have been assessed with low hazard and no further EU regulatory risk management need.

With regard to **nitrogen-containing flame retardants** the regulatory needs for several groups containing substances identified as flame retardants have been assessed:

- The ARN for **triazinetrione and triazinetriamine derivatives** did not identify a need for further EU regulatory risk management. Substances in this group were identified as Carc. 2 and STOT RE 1 but harmonised classification has been considered sufficient to address these substances. However, the German Competent Authority prepared an RMOA and has submitted a proposal to identify melamine as a SVHC due to PMT properties. The MSC unanimously agreed on the proposal and added melamine to the REACH Candidate List.⁶⁵
- For guanidine-based substances, both in the Guanidylureas, cyanoguanidines and biguanidines group and the non-aromatic guanidines group, no need for further EU regulatory risk management was identified for the substances identified as flame retardants. Nevertheless, data generation was foreseen and the assessment of regulatory needs may be revisited in light of the data.
- For polyamine substances in the groups piperazine-functonalised polyamines and primary aliphatic diamines and their salts, no need for further EU regulatory risk management has been identified for the substances identified as flame retardants.
- For urea-based substances, although no need for further EU regulatory risk management was identified for the aliphatic and benzylic ureas group, a potential hazard for reproductive toxicity and ED was identified for thioureas that needs to be confirmed by further data generation. For thioureas, authorisation was initially identified as the likely EU regulatory risk management. Nevertheless, restriction may also be considered.

With regard to inorganic substances, for molybdenum and its simple compounds, zirconium and its simple inorganic compounds, and Sulfur, its oxides, halides, sulfides, sulfites, thiosulfates, sulfamides and salts of sulfuric acid with counterions of low hazard no further EU regulatory risk management was identified due to the low or inconclusive hazard during the assessment of regulatory needs (to be confirmed with data generation as relevant).

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⁶⁵ https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e187e71e46

For **simple inorganic silicon compounds**, an OEL setting and targeted restriction considering potential silicosis (expressed via Carc. Or STOT RE) was foreseen for substances 231-130-8, 215-710-8, 231-545-4, 945-327-8 and 238-877-9 which are identified with the technical function of flame retardants.

Antimony inorganic compounds were assessed by DE CA and it was concluded that carcinogenicity should be further assessed for the substances using SEV considering Antimony trioxide (EC No. 215-175-0) is already classified as Carc. 2 and indications suggesting genotoxicity is a possible mechanism for the carcinogenic effects. Data is expected during the second half of 2022.

Inorganic borates have also been assessed by SE CA. Some substances were already classified as Repro. 1B and included in the candidate list. The conclusion from the assessment was a proposal for harmonised classification as Repro. 1B for the substances not yet classified and it has recently been submitted by SE. An RMOA assessing borates in consumer products was performed by the DE CA⁶⁶ for the substances already classified as Repro. 1B. The RMOA was triggered by alerts regarding toy slimes with high boron migration rates and resulting in possible health hazards. Nevertheless, the RMOA covered other uses of boric acid and borates in mixtures and articles intended for consumer use. Overall, the RMOA concluded that no further regulatory actions of the substances were required if the revision of the concentration limits for boric acid and borates are enforced.

Further groups under generation/assessment also contain substances in the list of identified flame retardants.

5.5.2 Regulatory strategy

The strategy for flame retardants does not yet expand on those other than halogenated or organophosphorus. The main reason is that the applied chemistries are very diverse and that no overarching hazard profiles have been identified from the perspective of their use as flame retardants. Nevertheless, these substances are/will be covered in the continuous group assessment where hazards of concern have been identified for one or more substances.

When restrictions are being developed, it should be considered to what extent similar restrictions would apply for other flame retardants with similar toxic properties and potential for exposure.

6. Conclusions and next steps

We conclude that for the **aromatic brominated** flame retardants, **a wide and generic** restriction seems to be the most appropriate regulatory approach for which preparatory work may be needed. This work could start and may include the assessment of the **waste stage**, and in particular the recycling of material from articles.

For the **aliphatic brominated** and the **organophosphorus** flame retardants, we conclude the scoping of a further restriction should await the ongoing data generation. These data are expected to come in from 2024 onwards and thus any potential process for restriction is not

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⁶⁶ https://www.echa.europa.eu/documents/10162/1ff23fa1-9c94-c5f9-b4c5-d16f6f55fd14

expected to be initiated before 2025. It is proposed to **reassess the situation for these groups of flame retardants in 2025 and revise the strategy accordingly**. Nevertheless, for two reactive aliphatic brominated flame retardants (BMP and TBNPA) a restriction targeting professional uses could already be considered.

We conclude there is currently no further need for regulatory action for several subgroups of the **organophosphorus** flame retardants due to no or likely low hazard properties, and for **chlorinated** flame retardants due to regulatory measures being already in place or initiated.

Appendix 1. Market sectors

1. Electric and electronic devices

In the electric and electronic devices market in 2014 about 12% of all used flame retardants in Europe where for electronic and appliances and another 20% for wires and cables.⁶⁷

The following table gives a general overview of the different flame retardants used in HFFR (Halogen Free Flame Retardant) cable compounds. Aluminium hydroxide (ATH), aluminium-oxide-hydroxide (AOH), magnesium hydroxide (MDH) and nanocomposites are by far the most important ones in regard to HFFR cable compounds by volume and variety of application within the cable industry.⁶⁷

Table 11: Overview of the different flame retardants used in HFFR cable compounds.

| Flame retardant | Polymers |
|---|--|
| Aluminium-tri-hydroxide (ATH) | Low density polyethylene |
| Magnesium-dihydroxide (MDH) | Poly-ethyl-co-vinyl acetate |
| Boehmite (AOH) (aluminium-oxide-hydroxide | Polyolefin elastomers |
| Phosphorus flame retardants | Used in fire resistant coatings for cables |
| Zinc borate | Synergist with ATH |
| Red phosphorus | Polyolefins |
| Phosphate esters (eg. Tricresyl Phosphate TCP) | Rubber |
| Melamine cyanurate, melamine phosphate | Polyamides |
| | Polypropylene |
| Ammonium polyphosphates | Polyolefins |

Electronic enclosures are a market segment which includes primarily the enclosures of consumer and information technology equipment such as televisions, desktop or notebook computers, monitors, printers, copiers, household appliances, etc. These housings are made of different types of polymer resins. Common polymer resins are

- High impact polystyrene (HIPS)
- Acrylonitrile butadiene styrene copolymers (ABS)
- Polycarbonate / ABS blends (PC/ABS)

⁶⁷ PINFA. (2017) "Flame Retardants in Electric and Electronic Applications." from https://www.pinfa.eu/wp-content/uploads/2018/05/PINFA_EE_brochure_Edition_2017-11.pdf.

- Polyphenylene ether / HIPS blends (PPE/HIPS)
- Polycarbonate (PC).

Based on data by PINFA⁶⁸, in electronic enclosures, mainly phosphorus compounds that are based on aromatic phosphate esters are used. This includes mainly four individual substances and one phosphorous based polymer:

- Triphenyl phosphate (TPP)
- Resorcinol bis (diphenyl phosphate) (RDP)
- Bisphenol A bis (diphenyl phosphate) (NDP)
- Resorcinol bis (2.6-dixylenyl phosphate)
- Polyphosphonate co-carbonate

All four phosphorus compounds can be used in PC/ABS blends as well as in PPE/HIPS blends. TPP, RDP, BDP, Resorcinol 2,6 and Polyphosphonate co-carbonate are suitable halogen-free flame retardants for PC/ABS blends. The required loadings depend on the ratio of PC and ABS in the blend. In commercial PC/ABS blends where the ABS content normally does not exceed 25% it is possible to achieve a UL 94 V 0 rating (see Appendix 2 for more info on the tests) with these products at 8 – 15wt% loading in combination with a co-additive (Table 12). The co-additive usually retards the dripping. Fluoropolymers, especially high molecular weight (HMW) PTFE, provide flame retardancy to polymers used in various industrial applications. PTFE, when incorporated into the polymer compound, reduces the dripping of the polymer upon burning and thereby retards the spread of flames.⁶⁹ PTFE is added with loadings up to 0,5 wt%. Polyphosphonate co carbonate is added at levels of 15-20% with a co-additive and enhance the performances to fire.

Table 12: UL-94 flammability in FR-PC/ABS (4/1).

| PC/ABS 4/1 | % FR Additive | UL94* (1.6mm) |
|------------------------------|---------------|---------------|
| RDP | 9 | V-0 (1.5) |
| BDP | 12.3 | V-0 (1.5) |
| PX-200 | 11.5 | V-0 (1.5) |
| TPP | 14 | V-0 (1.7) |
| Polyphosphonate Co-carbonate | 15-20 | V-0 (1.5) |

PPE/HIPS blends can be flame retarded with the aromatic phosphates TPP, RDP and BDP. Typical levels of PPE used to achieve a UL 94 V 0 rating are 30-70%; these blends also contain 10-20% of TPP, RDP, BDP and Resorcinol 2,6.

According to EFRA, ABS and HIPS are today one of the preferred (technically and economically) polymers for E&E enclosures. The BFR-ATO combination is still one the most cost-effective FR

⁶⁸ https://www.pinfa.eu/wp-content/uploads/2018/05/PINFA_EE_brochure_Edition_2017-11.pdf

⁶⁹ https://www.inolub.com/INOLUB-I-SAN.php

system. Alternatives often do not fulfil the same combination of functionalities as the BFR-ATO system. Replacement by polymer alloys is possible, but this might lead to higher costs and still requires up to 0.5% halogen addition (PTFE).

Electronic installations and components like connectors and switches play an essential role in every electrical component. According to PINFA, often used polymers are polyamides and PBT, Polyamides for example are often chosen because of their good toughness and rigidity. Polyamides typically also perform well regarding heat ageing, which is important because of the increasing temperatures due to miniaturization of electrical components. PBT on the other hand offers the benefit of good dimensional and hydrolytic stability.

In electronic installations and components a variety of FR is used. This covers:

- 1. Metal phosphinates: These are well suited for glass fibre reinforced polyamides and polyesters and are added at levels of about 20% often combined with N-synergists. Key aspects are a high phosphorus content (> 23%), no affinity to water and a good thermal stability (up to 320°C) which make them compatible with lead-free soldering operations.
- 2. Inorganic Metal phosphinates have been recently introduced as active FR component in different proprietary synergistic blends under the Phoslite® trade name. Used in different polymers, especially Polypropylene homo and copolymer for UL-94 V2 applications at some percent loading, gives very high GWIT (Glow Wire Ignition Temperature) on thin items. Possible to use in PC, PC/ABS, PS, TPU and some engineering polymers like PBT and PA6 thanks to its very high phosphorus content in the range 20% 40%, thermal stability, and non-blooming characteristics
- 3. Melamine Polyphosphate (MPP) is especially suited for glass fibre reinforced polyamide 6,6, where it is added at ca. 25% for UL V0 performance. It has a good thermal stability (ca. 300 °C). Melamine cyanurate (MC) is equally well suited for unfilled and mineral filled polyamides. UL V0 can be achieved with 10 to 15% in unfilled PA and up to 20% for UL V2 in low glass fibre filled PA 6. MC and MPP are often used as synergist in combination with other phosphorus based FRs
- 4. Ammonium polyphosphate in combination with nitrogen synergists can be used in polyolefins at addition levels of ca. 20% to 30%
- 5. Aryl phosphates and phosphonates: their main use is styrenic blends at 10 to 20% addition level for UL 94 V0. They are often used as co-components in FR-formulation. Their limitations are possible plasticizing effect and a certain volatility at high processing temperatures. Blooming may have a negative influence on electrical properties.
- 6. Red phosphorus is a polymeric form of elemental phosphorus. It is used mainly in glass fibre reinforced PA 6,6 at 5 to 8% addition level where its high efficiency at low loading guarantee to maintain the excellent mechanical and electrical properties of the polymer while obtaining the highest flame proofing characteristics. Due to its inherent colour, compounds are limited to red or black colours. In addition, precautionary measures against degradation have to be taken.
- 7. Magnesium hydroxide (MDH): high filler levels of about 45 to 50% are necessary to reach UL 94 V0. Because of its limited temperature stability, it is mainly used in low glass fibre PA 6

The following table presents an overview of typical technical properties which can be achieved

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⁷⁰ EFRA (2014). "Subject: Feedback to the Öko-Institute "Questionnaire for Substance Prioritisation" under RoHS"

with nonhalogenated flame retardants in different polymers and with different glass fibre contents. The values are meant for orientation only, because the exact properties depend on the specific polymer used, additive packages and processing conditions.

Table 13: Overview of typical technical properties which can be achieved with non-halogenated

flame retardants in different polymers and with different glass fibre contents

| Polymer | Glass fibre (%) | Halogen free FR | UL 94 |
|---------------|--------------------|---|-------|
| | 0 | melamine cyanurate | V-0 |
| Polyamide 6 | 30 | metal phosphinate + melamine polyphosphate | V-0 |
| | 30 | metal phosphinate + melamine polyphosphate | V-0 |
| Polyamide 6,6 | 30 | red phosphorus | V-0 |
| | 30 | melamine polyphosphate | V-0 |
| HTN | 30 | metal phosphinate | V-0 |
| | 0 | metal phosphinate + melamine polyphosphate | V-0 |
| РВТ | 30 | metal phosphinate + melamine polyphosphate | V-0 |
| | 30 | V-0 | |
| PET | 0 | metal phosphinate (+melamine polyphosphate) | V-0 |
| 7.21 | 30 | metal phosphinate (+melamine polyphosphate) | V-0 |
| Polyolefins | 0 | intumescent system | V-0 |
| rolyolelilis | 30 | intumescent system | V-0 |

Nearly all electronic items contain a **printed wiring boards** (PWB also used printed circuit board PCB)⁷¹. Epoxy resins are widely used as resin backbone for PWB base materials.

The brominated TBBPA is used as reactive flame retardant (FR) in printed circuit boards for EEE products and as additive FR in housings (mainly ABS) of E&E products.⁷⁰

⁷¹ PCB refers to a board with the whole circuitry and PWB means a board without further components see here https://absolutepcbassembly.com/pwb-vs-pcb/ last accessed 30.06.2021.

Based on data by EFRA from 2014, TBBPA in combination with FR4 Epoxies were the current industry standard and thus the most common type of printed circuit boards. This information is also verified by the report "Justification for the selection of a substance for CoRAP inclusion"⁷² from ECHA (submitting MS has been DK).

Typically, PCBs have to meet the flammability requirement UL 94 V-1 or V-0. Around 80-90% of these printed circuit boards are based on brominated epoxy resins, i.e. on TBBPA, because brominated epoxy-based FR-4 boards provide the best combination of mechanical properties, thermal stability, moisture uptake, electrical performance and cost-effectiveness. Brominated epoxies also have low levels of failure during drilling and assembly operations, especially for multi-layer laminates. TBBPA is chemically reacted to form a TBBPA-epoxy resin. This resin is then used to make a pre-impregnated composite, which is then fully cured to make a laminate. The laminates are then used to make circuit boards. The reaction is close to 100% which means that TBBPA as such is not identifiable any more in the final printed circuit boards.

2. Textiles

According to Grand View Research, the **global textile flame retardants** market size was valued at USD 504.6 million in 2019 and is projected to register a compound annual growth rate (CAGR) of 3.9% from 2020 to 2027. The market is driven by the increasing demand for fire retardant fabrics from various end-use industries, such as defence, transportation, and industrial manufacturing.

The polyester application held the largest revenue share of 39.5% in 2019 and is anticipated to maintain its dominance over the forecast period (Figure 4). Polyester can be used for the finishing of flame retardants on textile fibers as polyester cannot ignite easily. However, once the fabric is ignited, it melts and can potentially cause severe burns. Further, the inherent non-flammability offered by polyester coupled with its easy availability is expected to drive the product demand in this segment.

Cotton is expected to be the second-largest application of the textile FR market. Cotton is one of the prominent fabrics used in household textiles owing to its physical properties, such as absorbency, breathability, and exceptional softness. However, cotton textiles are more combustible compared to their synthetic counterparts. This necessitates the application of flame retardants on cotton fabrics, thereby, offering potential growth opportunities for the overall market.

Polyurethane (PU) is likely to witness the fastest growth over the forecast period. It is an essential polymer used in several applications, such as textile coatings, fibers, and foams. Polyurethane dispersions are predominantly used in textile coatings for further application in medical, sports, fashion articles, clothing, general protective equipment, and technical articles. The rising demand for these types of textile fibers from several end-use industries is expected to fuel market growth.

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⁷² See here https://echa.europa.eu/documents/10162/8ac6a2d5-4749-14f2-e7e0-214d7b235ce3 accessed 02.07.2021

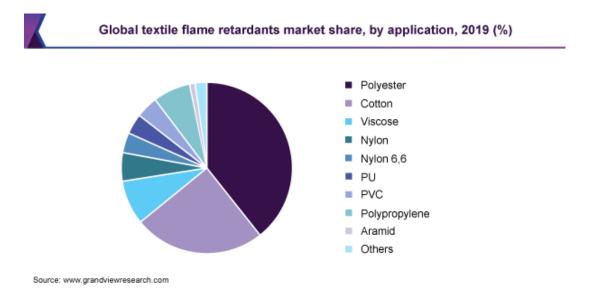


Figure 4. Global textile flame retardants market share, by application. Source: Grandview Research

Nearly 80% of textile floor coverings in the private sector do not have additional flame retardants added, whilst within the commercial sector, with its higher statutory requirements, approximately 43% have no additional flame retardants (Figure 5). This proves that textile floor coverings can be produced safely and without the need for additional chemicals to be used in order to achieve the required National and European fire regulations, providing the correct materials are selected for the correct construction in manufacture.

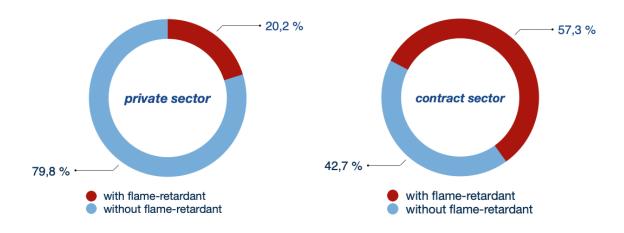


Figure 5. Use of flame retardants in textile floor coverings in the European Union.⁷³

According to ECRA (European Carpet and Rug Association), Carpets produced by ECRA member companies, do not contain any brominated or chlorinated flame-retardants. The commonly used flame retardant is ATH (aluminium trihydroxide).

The demand for textile flame retardancy is mainly in work clothing, firefighter apparel, institutional draperies, institutional upholstery, institutional and commercial carpet,

⁷³ ECRA (2021) "Safety at Home - Flame retardant chemicals." from https://www.ecra.eu/carpets/safety/flame-retardants/

transportation (especially aircrafts where blankets and seat covers must pass Federal requirements), military garments, professional racers garments, and bedding.²⁷

Generally, halogen and halogen-antimony systems tend to be flame inhibitors, the phosphorus and boron systems tend to enhance charring and formation of surface barrier layers, and the metal hydroxides tend to be endothermic water-releasing systems. In thermoplastic textiles, such as PET, some of the additives also aid extinguishment by melt flow enhancement. Otherwise, many inherently flame retardant fibers and fabrics are those which form a char on fire exposure.²⁷

Flame retardancy of textile fabrics can be achieved by use of inherently flame resistant fibers, use of chemical after-treatments or both.⁷⁴ Inherent flame retardancy may arise from a chemical composition, which is thermally stable or transforms to one (e.g., the polyaramids or other aromatic structures). It can also be achieved by incorporation of flame-retardant additives during the production of man-made fibers (e.g., FR viscose) or by the synthesis of conventional fiber-forming polymers which include flame retardant comonomers (e.g., FR polyester). Chemical after-treatments include surface or topical treatments, coatings and functional finishes which become a part of the final fiber structure.

Table 14 below lists maximum FR application levels assuming a range of fabric weights between 150 and 300 g and that lighter fabrics generally require higher treatment levels than heavier fabrics. Wholly thermoplastic fiber (e.g. polyester, polyamide)-containing fabrics require higher resin levels because of the need to provide a charring scaffold sufficient to maintain a barrier in spite of the melting fiber characteristics (see below).

According to NRC, this list is restricted to those chemical species, which are most commonly used in the UK.⁷⁴ Furthermore, the list does not include those FR chemicals which are used mainly in the plastics sector like alumina trihydrate, zinc hydroxide, zinc borate, etc., which find little or no use in the UK furnishing sector. These are excluded because they are effective only at very high levels (with adverse effects on aesthetics), are ineffective on some fiber types and/or they cannot withstand the water-soak durability requirement.

Table 14: Typical Maximum (Rounded) Application Levels on Furnishing Fabrics.

| Fabric/Fibers | Formulation/Finish | Effective Element, % w/w Fabric | Total add-on of FR Agent, % |
|---|---|---------------------------------------|--------------------------------|
| Cotton Viscose Cellulosic blends with wool, synthetics, etc | Semi-durable P salt, e.g. ammonium polyphosphate | 3% P | 10% (25% as backcoating) |
| Cotton Viscose Cellulosic blends with wool, | TMPC | 3% P | 15% |

⁷⁴ US-NRC et al. (2000) "Flame-Retardant Composition in Fabrics: Their Durability and Permanence."

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| Fabric/Fibers | Formulation/Finish | Effective Element, % w/w Fabric | Total add-on of FR Agent, % |
|--|---|---|----------------------------------|
| synthetics, etc. | | | |
| Cotton Viscose Cellulosic blends with wool, synthetics, etc. | Phosphonic acid derivative, e.g. Pyrovatex | 2% P | 12% (excl. Resin component t) |
| Wool and wool- rich blends | Zirconium salt | 2.5% Zr | 6% |
| All fabrics | Sb-Br/DBDPO | 12% Br, 7% Sb | 25% |
| All fabrics | Sb-Br/HEXA | 12% Br, 7% Sb | 25% |
| All fabrics Polyester and blends | Chloroparaffins Cyclic phosphonates | 7% Cl 2% P (as 50% replacement for Sb/Br system) | 10% 12% |
| All fabrics | Aromatic phosphate plasticizer for backcoatings | | 30% |

TCEP replaced the historical use of pentaBDE⁷⁵ (EU RAR 2008a) but is currently not used anymore in the EU. TCEP has been replaced with TCPP and to some extent TDCP. TCEP may still be present as an impurity in other commercial flame retardants⁷⁶ or in imported articles.⁷⁷

Europur have stated during a consultation in preparation for a restriction proposal that "It is the requirements of the UK/Irish regulation to perform the Crib-5 test on the foam itself that trigger the need for relatively high flame-retardant use in the foam. In other jurisdictions where final consumer articles are required to pass a benchmark for flame retardancy, or in some EU member states for the non-residential market, lower levels of flame retardants might be used as the other components in the final article can contribute to flame retardancy as well. However, when the foam does require some flame retardancy to produce such a flame-retardant system the flame retardant of choice is TCPP, as it is liquid (i.e. easier to dose than melamine) and has less adverse impact on the mechanical/physical properties of the foam than other FR systems."

TCPP has been used as a drop-in replacement for TCEP (EU RAR 2008a). TCPP has a registered volume under REACH of $10\ 000\ -\ 100\ 000$ tonnes/year. The registered volume of TDCP under REACH is $1\ 000\ -\ 10\ 000$ tonnes per year.

⁷⁵ Pentabromodiphenyl ether (pentaBDE) is listed in Annex A (Elimination) of the Stockholm Convention (POPs).

⁷⁶ TCEP may still be present as an impurity in other commercial flame retardants such as TCPP, TDCP, V6 and V66 (ECHA 2010a; Danish EPA 2016b; TERA 2015; EUROPUR 2018).

To E.g., sample B18A in Danish EPA (2015) contained 4 700 mg/kg TCEP (0.5% w/w). This sample also contained 16 300 mg/kg TCPP as well as 13 000 mg/kg TDCP.

According to the draft EU RAR (2008), more than 40 000 tonnes of TCPP were consumed in the EU in the year 2000. Most TCPP (over 98%) was used as a flame retardant in the production of polyurethane (PUR) for use in construction and furniture. Most TCPP was used in rigid PUR foam (over 80%), mainly for construction applications. Flexible PUR applications, the focus of this restriction report, accounted for approximately 17%, corresponding to 6 800 tonnes (EU RAR 2008). The majority of the flexible PUR is destined for upholstery and bedding for the UK and Irish markets. TCPP is an all-round flame retardant for all types of flexible PUR foams (Danish EPA 2016⁷⁸). TCPP tends not to be used in flexible PUR for automotive applications owing to its volatility and 'fogging'⁷⁹ potential.

TDCP is more expensive than TCPP and is used mainly in foams for automotive applications, with some use in furniture (EU RAR 2008b). TDCP is a useful flame retardant for automotive uses on the basis of its low volatility and hence low fogging potential (EU RAR 2008b). It also offers good resistance to migration following moderate heat or humidity ageing (EU RAR 2008b).

In most Member States flame retardants are necessary to meet flammability standards for certain products on the furniture office, contract and public market, but only the UK and IE have flammability standards applicable to residential furniture and some childcare articles as well (EUROPUR 2018). These fire safety regulations are the main reason for the use of the OPFRs in childcare articles and residential furniture in the EU. Also in the other Member States the three OPFRs are present in childcare articles and furniture placed on the market, either through imports from the British Isles or non-EU countries, or possibly also from EU-producers who do not have separate production and supply for the British Isles but still wish to be present in that market.

⁷⁸ Danish EPA (2016). Chlorinated phosphorous-based flame retardants in children's articles containing foam. Background for content and possibilities for prevention in the EU. The Danish Environmental Protection Agency (Danish EPA), Environmental project No. 1855, Copenhagen, 2016. Available at http://www2.mst.dk/Udgiv/publications/2016/05/978-87-93435-69-8.pdf

⁷⁹ 'Fogging' is the condensation of substances used in vehicle interiors onto glass following volatilisation (EU RAR 2008b).

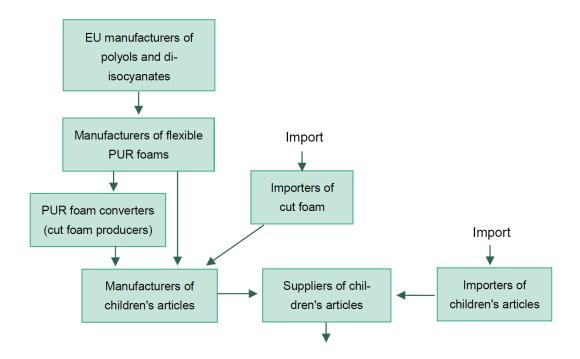


Figure 6. Overall supply chain for flexible PUR foams in children's articles (Source: Danish EPA 2016)

The three OPFRs are additive flame retardants, i.e. they are physically combined with the PUR foam being treated rather than chemically combined. The amount of flame retardant used in any given application depends on a number of factors such as the flame retardancy required for a given product, the effectiveness of the flame retardant and synergist within a given polymer system, the physical characteristics of the end product (e.g. colour, density, stability, etc.) and the use to which the end product will be put.

3. Building and construction material

Manufacture of building and construction products is the second largest market for flame retardants. The main uses include Cable and Wire electrical insulation, thermal insulation, structural elements made from plastic/resins, and protective coatings for non-flammable structural elements (Steel structures, metal sheets, wood, plaster, concrete).

For the European plastic conversion industry, 20% of the polymer demand results from building and construction products. The main related polymer types are: PVC, EPS, HD/MD-PE, PUR. Except for rigid PVC, all these polymers are inherently flammable, and therefore typically need to be equipped with flame-retarding properties if used in construction.

Typical loading

Table 15 illustrates the typical loading of flame retardants in materials used for constructions, still representative for the last decade.²⁸

Table 15: Selected guide formulations for standard plastics.

| Plastic | guide formulations Recipe Flame retardant/Syn ergist | Concentration in % | Application | Meets Standard Fire class |
|--------------------------------|---|---------------------|---------------------------------|---------------------------------|
| Polyethylene | Decabromdiphen ylether or Ethylen-to- (pentabromphen yl) Aluminum hydroxide | 12 - 14 6-7 | Construction Foam | EN 13501 E |
| Polystyrene (EPS) | Hexabromocyclo dodecane Dicumyl peroxide | 1 – 2 0,5 – 0,75 | Construction Foam as composite | EN 13501 E B to D |
| Unsaturated Polyester resin | Aluminum hydroxide | 60 | Construction | EN 13501 E |
| Polyurethane Hard foam | Tris- (chloroisopropyl) phosphate Tetrabromophth alic acid diol Tris- (chloroisopropyl) phosphate | 20 11 7 | Construction | EN 13501 E |

Apart from EPS the loading is quite high (up to 60% for inorganics and up to 20% for organics) according to this source.

A more recent source states that flame retardants typically make up about 1-6% of the weight of the product, but may account for up to 20% in open cell spray foam insulation. This statement potentially refers to organic flame retardant only and misses out the high loading required for polyolefin material.

Cables and Electrical Wiring

According to information material from PINFA, for PVC cables and other halogenated polymers, antimony trioxide (ATO) is an efficient option for flame retardancy although it has the negative effect of releasing large amounts of black smoke. Therefore, low smoke flame retardant (LSFR) PVC compounds are being used by incorporating metal hydrate flame retardants such as aluminium (tri-)hydroxide (ATH) or magnesium (di-) hydroxide (MDH). Other compounds can be added in lower quantities to act as synergists, e.g. zinc hydroxystannates and zinc borates.

Table 16 shows a summary of flame retardants used for PVC and other halogenated polymers. 80

Table 16: Flame retardants used in PVC and other halogenated cable compounds.

| Flame retardant | Working Function | Polymers/compounds | Main Applications |
|---|--|---|--|
| Aluminium tri- hydroxide (ATH) Magnesium di- hydroxide (MDH) Zinc-borates Zinc Hydroxystannates | In case of a fire, these mineral flame retardants decompose • absorbing energy • releasing water (thus reducing fire intensity and diluting fire gases). • creating an oxide layer which adsorbs soot particles and HCI Zinc Borate is a smoke suppressant that works in the condensed phase by forming a glass-like char. Zinc Hydroxystannate works both in the gas phase (flame) and in the condensed phase (smoke) simultaneously | FR-PVC (Flame Retardant PVC) LSFR-PVC (Low Smoke Flame Retardant PVC) CPVC (Chlorinated PVC) CR (Chlorinated Rubber) | Electrical cables • Low voltage • Medium voltage Information cables • LAN cables • Telephone cables • Plenum cables • Plenum cables |
| Phosphorus flame retardants Aryl phosphates Aryl alkyl phosphates | Flame inhibition of phosphorus-based materials reduce the flammability of polymers. | LSFR-PVC (Low Smoke Flame Retardant PVC) CPVC (Chlorinated PVC) CR (Chlorinated Rubber) | Information cablesLAN cablesTelephone cablesPlenum cables |

⁸⁰ PINFA (2017). "Innovative and Sustainable Flame Retardants in Building and Construction." from https://www.pinfa.eu/wp-content/uploads/2018/05/pinfa_BC_edit-2017-web.pdf.

| Flame retardant | Working Function | Polymers/compounds | Main Applications |
|-----------------|------------------|--------------------|----------------------|
| | | | Control Cables |

Another important type of cables on the market are those that are non-halogenated. These are halogen-free flame retardant (HFFR) or low-smoke free of-halogen (LSFOH) cables. The polymers used for these cables are mostly mixtures of EVA (Poly-ethylene-co-vinyl-acetate) and LLDPE (Linear Low-Density Polyethylene) and the flame retardancy is offered by addition of ATH. To enable sufficient flame retardancy, a loading of 60-65% is required. In cases where there are specific requirements for abrasion and chemical or temperature resistance, elastomeric compounds can also be used such as EPDM (Poly-ethylene-propylene-diene-copolymer) or EVM (EVA grades with high contents of vinyl-acetate). These compounds are crosslinked and loaded with 50-60% ATH, sometimes in combination with synergists such as zink-borates. In some cases such as E-beam cross-linking for photovoltaic cables, magnesium hydroxide (MDH) is used instead of ATH. Lastly, thermoplastic base materials like TPU (Thermoplastic Poly-Urethane) are used for their good abrasion resistance. In this category, melamine derivatives, organic phosphate, phosphinates and metal hydrates, ATH or MDH are used in different quantities and combinations depending on the manufacturer. Table 17 offers an overview of the HFFR segment.

Table 17: Flame retardants used in HFFR type cables.

| Flame retardant | Working Function | Polymers/compounds | Main Applications |
|---|--|--|---|
| | | | Electrical cables |
| Aluminium trihydroxide (ATH) Magnesium dihydroxide (MDH) Aluminium oxide- hydroxide (AOH, boehmite) Zinc-borates Zinc- Hydroxystannates | In case of a fire, these mineral flame retardants decompose -absorbing energy. -releasing water (thus reducing fire intensity and diluting fire gases). -creating an oxide fire barrier against heat from the flame and to prevent burnable polymer decomposition products from reaching the flame. | Polyolefins Low-density polyethyl ene (LDPE) Polyethylene vinylacetate copolymer (EVA) Polyethylen-co-butene Polyethylen-co-octene Elastomers Natural Rubber (NR) PolyEthylene-Diene- Rubbers (EPDM) Poly-Styrene-Butadiene- Rubbers (SBR) Silicone rubbers (SiR) Thermoplastic Elastomers (TPE) | Low voltage Medium voltage PV cables Emergency lighting Control cables Fire alarm cables Information cables |
| | | | • LAN cables |

| Flame retardant | Working Function | Polymers/compounds | Main Applications |
|--|---|---|--|
| | | | • Telephone cables |
| Phosphorus flame retardants Phosphate esters (eg. Tricresyl phosphate TCP) | Flame inhibition and charring properties of phosphorus-based materials reduce the flammability of polymers. | Used in fire-resistant coatings for cables Polyolefins Polypropylene (PP) | Electrical cables • PV cables |
| Intumescent products based on: ammonium polyphosphates (APP), Polyphosphonates, metal phosphinates, aryl phosphates, Melamine Derivatives Red phosphorus | A char on the surface prevents heat transfer and protects the polymer below | Elastomers Thermoplastic Elastomers (TPE), Thermoplastic Poly Urethanes Thermoplastic Polyesters | Control cablesLift cablesFire alarm cables |

Profiles and composites

Plastics are increasingly used in the buildings and construction sector and there are a number of applications in which plastic composites are used. For certain use of plastic composites in interior applications, there is a need to comply with fire safety regulations. This includes use in wall partitions, counter tops, panels and translucent or transparent skylights and covers. The most common test is ASTM E 84, Class A, B, C.⁸⁰ For profiles and composites made out of thermoplastics and thermosets, Table 18 summarises the application and flame retardants used. A typical flame-retardant loading for facade decorating elements made out of aluminium and composites is 65-70wt.-% for mineral flame-retardant fillers.

Table 18: Flame retardant use in profiles and composites.

| Materials | Application | Flame retardant |
|----------------------------------|-------------------------------|---|
| Rigid PVC | Profiles- window, doors, trim | Stannates, zinc borate, ATH, AOH (boehmite), MDH |
| ABS, PC blends, Polycarbonate | Profiles- trim | poly(phosphonate-co-carbonates) Silicone compounds Phosphate esters Potassium perfluorobutane sulphonate (KPBS) Potassium diphenyl sulphone sulphonate (KSS) |
| HDPE, PP | Pipes | Intumescents (with some |

| Materials | Application | Flame retardant |
|---|---|---|
| | | limitations), ATH, MDH, boehmite |
| PP | Cable trays, skirting boards | Intumescents, EDAP, Melamine pyrophosphate, melamine Polyphosphate, ATH, MDH, AOH (boehmite) |
| Wood-Plastic Composites (WPC) | Decking, railings, roofing shingles, fencing, facings | APP, Melamine pyrophosphate, Melamine polyphosphate, Alkyl phosphonates, Melamine cyanurate |
| Aluminium Composite Panels (ACP) – inner layer made of PE, PE/EVA, Ethylene-co-polymers | Facade decoration | ATH, MDH |
| Unsaturated Polyesters (UP) | Laminate structures, Pultruded | ATH, APP, Intumescents, Phosphonate oligomers, DMPP, Various |
| | Profiles | melamine derivatives |
| Vinylester (VE) | Laminate structures, Pultruded profiles | ATH, APP, Intumescents, Phosphonate oligomers, DMPP |
| Ероху (ЕР) | Laminates, Panels, Adhesive layers, Tubes/pipes (filament winding) | ATH, AOH (boehmite), APP, Phosphonate oligomers, DOPO, Intumescents, Melamine phosphate, Melamine polyphosphate, Cyclic phosphonates, Phosphinates. |
| Polyurethane (PU) | Castings, Coatings, RIM parts | ATH, AOH (boehmite), APP, Phosphate esters, Phosphonate oligomers, Various melamine derivatives, Intumescents, Phosphorus Polyols, Alkyl phosphonates |
| Phenolics (PF) Laminates and profiles | Laminates and profiles | Excellent FST (fire, smoke, toxicity) performance without the use of FR additives. Sometime need addition of APP, Zinc borate, Melamine borate to improve smoke or suppress afterglow |
| Melamine resin (UF) | Laminates, wood particle | Excellent FST (fire, smoke, toxicity) performance without the use of FR |

| Materials | Application | Flame retardant |
|-----------|-------------|-----------------|
| | boards | additives. |

For thermoset based profiles and composites, the manufacturing method greatly influences the choice of suitable flame retardants according to PINFA. Composites manufactured by BMC (Bulk Moulding Compounds) generally supports high amounts of filler-type flame retardants whilst composites produced by pultrusion only allow a limited content of solid flame retardants in order to keep an acceptable viscosity. Resin infusion or VARTM (vacuum assisted resin transfer moulding) does not work well with fillers as theses tend to be filtered out when the resin is diffused through the fabrics. This technique therefore requires either liquid flame retardants (which have undesirable plasticising properties), reactive flame retardants which offer a limited number of options or speciality grades of ATH that are designed for to give very low viscosity increase and filtration tendency.

The large amount of different manufacturing techniques for these kind of composites results in an equally large variety of different formulations where combinations of different flame retardants are used. This is necessary to maintain compatibility with the process while achieving a certain set of properties.

Insulation Material

The flame retardants in foams can be divided in three families, namely;

- Additive liquid flame retardants. These can easily be added to the foam but can impact mechanic properties.
- Reactive liquid flame retardants that are incorporated into the polymer chain and becomes an integral part but may impact curing.
- Solid flame retardants that act as a filler which may affect physical and insulating properties. This group is often combined with liquid flame retardants.

Thermal insulation is usually made from polystyrene foam boards (EPS/XPS), rigid polyurethan foam panels (PUR) and Polyisocyanurate foams (PIR). Also, polyolefin foams are used, in particular for sound insulation and for pipe insulation. In addition to the organic foams, materials such as mineral wool or natural based materials (e.g. Cellulose) are applied. Polyisocyanurate (PIR) foams offer an inherently better fire resistance than PUR foams due to the higher amount of isocyanurate structures in the foam.⁸⁰

Due to the regulatory pressure on some of the most used flame retardants in this area (HBCD for PS; TCEP for PU; Decabromdiphenylther for polyethylene) the market for alternatives has emerged.

Table 19 below gives an overview of the non-halogenated flame retardants used in rigid PU foams.

Table 19: Overview of the non-halogenated flame retardants used in rigid PU foams.

| Flame retardants | Chemical name | Appearance | Phosphorus content [%] | Viscosity at 25°C [mPa.s] |
|-------------------------|---|------------|------------------------|---------------------------------|
| TEP | Triethyl phosphate | Liquid | 17.0 | 2 |
| DEEP | Diethyl ethyl phosphonate | Liquid | 18.6 | 2 |
| DMPP | Dimethyl propyl phosphonate | Liquid | 20.3 | 2 |
| CDP | Cresyl diphenyl phosphate | Liquid | 9.1 | 45 |
| Reactive P/N polyol | N,N-Dihydroxyethylamino- methan phosphoric acid ester | Liquid | 12.1 | 175 |
| Reactive P- Polyol 1 | Proprietary | Liquid | 11.5 | < 500 |
| Reactive P- Polyol 2 | Proprietary | Liquid | 19 | 2.200 |
| APP | Ammonium Polyphosphate | Solid | 31% P (15%N) | n.a |
| EG | Expandable Graphite | Solid | - | n.a |

For **polystyrene foams** (EPS and XPS) no non-halogenated flame retardants have yet been effective enough to fulfil fire retardancy requirements for this product group.⁸⁰ Meanwhile the brominated butadiene-styrene co-polymer is used as the main substitute for HBCDD in polystyrene isolation foams.

For **polyolefin foams** that are used for HVAC applications (heating, ventilation, air conditioning), such as thermal insulation of pipes (both hot and cold fluids) and/or for sound insulation, the production method influences the choice of flame-retardant. Non-halogenated flame retardant alternatives include alkyl phosphonates and amino-ether based compounds.

For insulation materials made out of **renewable sources** such as hemp, cotton, cellulose, wool and flax, non-halogenated flame retardants that are used include mixtures of ammonium salts of various inorganic acids (i.e. Phosphate, Phosphonate, Sulphate, Sulphamate and others).⁸⁰ LANXESS product information suggest organophosphates like (Isopropylated or butylated) triphenyl phosphates and cresydiphenylphosphate.

Floor coverings (PVC)

PVC (Vinyl) floorings are used in buildings with various applications including healthcare, retail and hospitality, office and education or sport surface application areas. Advantage of PVC floorings are that there are easy to install, clean and maintain. Especially for hospitals hygiene has a very high priority. A variety of different PVC floorings is possible due to a wide variability of the formulations and material combinations including for example homogeneous,

heterogeneous and composite PVC coverings.⁸⁰ Flammability is one of the safety criteria of floor coverings. Table 20 gives an overview of the non-halogenated flame retardants used in PVC floorings.

Table 20: Overview of non-halogenated flame retardants used in PVC floorings.

| | Flame | | | |
|-----------|------------------------------------|------------|---|--|
| retardant | Chemical name | Appearance | Effectiveness | |
| | | | | |
| CDP | Cresyl diphenyl phosphate | Liquid | Flame inhibition and charring properties, plasticizing effect | |
| ТСР | Tricresyl phosphate | Liquid | Flame inhibition and charring properties, plasticizing effect | |
| DPO | Diphenyl 2-ethylhexyl phosphate | Liquid | Smoke inhibitor, plasticizing effect | |
| ТОР | Tri (2-ethylhexyl) phosphate | Liquid | Plasticizing effect, cold flexibility | |
| АТН | Aluminum trihydroxide | Powder | Flame inhibition through endothermic decomposition | |
| ZHS | Zinc Hydroxystannate | Powder | smoke suppression and flame inhibition | |

Floor coverings (Linoleum, Elastomers)

Linoleum flooring is easy to clean and very though. It can be used for many different application areas. Composition of linoleum as well as its technical characteristics and their testing are defined in EN standards. Whereas elastomers (blends of NBR (nitrile butadiene rubber) and EVA) are due to their soft and elastic properties ideal materials for gym mats and floor coverings. With suitable additives they can also exhibit good flame retardancy. In Table 21 some non-halogenated flame retardants used for linoleum and/or elastomers are shown.

Table 21: Non-halogenated flame retardants used in linoleum and elastomer floorings.

| Flame retardant | Chemical name | Appearance | Suitable Floorings | Effectiveness |
|--------------------|--------------------------|------------|------------------------|--|
| MDH | Magnesium hydroxide | Powder | Linoleum | Flame inhibition through endothermic decomposition |
| АТН | Aluminum trihydroxide | Powder | Linoleum Elastomers | Flame inhibition through endothermic decomposition |

Insulation products without flame retardants

Products without flame retardants are available in certain regions for certain applications where building code allows. California has new legislation allowing polystyrene insulation without flame retardants to be used below grade beneath cement slabs. Products for this application are exempted from meeting the open flame standard that plastic foam insulation must typically meet. Polystyrene insulation used elsewhere in a building still will require the addition of a flame retardant to meet the open flame testing standard. Other regions have building codes that consider assembly-level fire performance as opposed to an open flame test of the bare insulation. As a result, for example, flame retardant-free polystyrene boards dominate the market in Scandinavia. Scandinavia.

Films and sheets

The product group films and sheets compromise a wide variety of products used for different purposes in the building and construction sector. A rough division into segments can be;

- protective: i.e. building scaffolds, construction films, confinement films, tarpaulins etc.
- functional: i.e. vapour barrier films, adhesive films, greenhouse films, artificial grass, etc.
- structural: roofing sheets, wind barriers, films or sheets for space partition, etc.
- decorative: banners, printed films, artificial plants/trees, etc

Depending on the use, there may be a need for fire retardancy to meet fire safety regulations.

Structural Elements

Concrete, wood, plaster and steel structures are coated with special paints and sealants that contain fire retardants. Once applied, these form a thick, insulating, and non-flammable foam. These coatings protect the structural integrity of a building in case of a fire. It is important to secure structural elements from fire, especially those that serve as basis and support for a building. For example, steel loses its ability to support weight and collapses at a certain temperature.

4. Transport vehicles

In transport vehicles, polymeric materials are predominant and appear in a wide range of product forms, including moulded sheet or shapes, composite-faced honeycomb sandwiches, textile fibres (fabrics or carpets), foams, sealants, and adhesives. Interiors currently contain materials having different flammability's. They are selected according to their particular application and a variety of additional factors, such as availability, cost, and processability. Most of the polymers used need FRs to comply with the current fire standards.⁸²

Interior parts for transport applications, i.e. automobiles, aeroplanes, ships, are complex systems that include visible items, such as flooring, textiles, seats, lavatories, ceilings, sidewalls, stowage bins, bag racks, closets, dash boards, and windows, and items that are not visible to

⁸¹ Charbonnet, J., Weber, R. and Blum, A. (2020) 'Flammability standards for furniture, building insulation and electronics: Benefit and risk'

⁸² PINFA (2010). "Innovative and Sustainable Flame Retardants in Transportation." from https://www.pinfa.eu/wp-content/uploads/2018/05/PINFA_Transportation_Brochure_2010_Final_Version.pdf.

passengers, such as ducting, wiring, electrical & electronic components, insulation blankets, coatings, sealants, and adhesives.

Today, thanks to modern plastics technology, instrument panels are made of acrylonitrile-butadiene-styrene (ABS), ABS/polycarbonate (PC) alloys, PC, polypropylene (PP), modified polyphenylene ether (m-PPE), and SMA (styrene maleic anhydride) resins. These plastics allow for complex designs of items, such as airbag housings, centre stacks for instrument panels, and large, integrated instrument panel pieces. They are also used in manufacturing the rest of the automobile's interior trim. These plastics are also capable of eliminating the need for a steel support beam, allowing manufacturers to dramatically save costs of the instrument panel while substantially reducing its weight.

The appropriate choice of the environmentally friendly flame retardant strongly depends on the application and the required fire standard.

| Application | Polymer | HFFR |
|---|---|--|
| | Polymer | IIIIX |
| Flooring | PVC Polyolefins Epoxy Phenolic resins Urethane elastomers Elastomers | ATH, isopropylated phosphate ester, CDP, zinc borate MDH, ATH, intumescent systems, new phosphonates ATH, APP, intumescents, ethylene diamine phosphate, melamine borate, DOPO Melamine borate, phosphate esters Aluminium phosphinate, melamine cyanurate, TPP, CDP, APP, melamine phosphate, melamine polyphosphate ATH, MDH, phosphate esters |
| Ceilings Sidewalls Panels Structural parts | UP resin VE resin Acrylate resin EP resin Phenolic resins | ATH, APP, EDAP, intumescent systems, DMPP ATH, APP ATH, APP, ATH, APP, intumescent systems ATH, APP, intumescent systems, DMPP, DOPO, cyclic phosphonate, new reactive phosphorus based containing epoxy groups Melamine borate, phosphate esters |
| Dashboard Instruments Instrument panels Instrument cluster housing Speaker grilles Gear knobs Console parts Trunk tailgates Steering wheels Air ducts Tubing Door trim / handle Pillar claddings Door pockets Door panels Chairs Other interior devices | PC ABS PC/ABS TPU TPE Polyamide, nylon Polyolefin Reinforced PP RIM UPR | Sulphonates TPP, RDP, and BDP TPP, RDP, and BDP APP, metal phosphinate, melamine cyanurate, melamine polyphosphates, TPP, CDP, zinc borate Metal phosphinate +N-synergist, intumescent systems Melamine cyanurate metal phosphinate +N-synergist Intumescent systems Intumescent systems APP, ATH, melamine phosphate, melamine polyphosphate, intumescent systems ATH, APP, EDAP, melamine phosphate, DMPP, intumescent systems |
| Insulation materials | r-PUR PIR | P-polyols, DMPP, APP, TEP RP, DMPP, APP, TEP |
| Coatings | 2K-PU, epoxy, acrylates | ATH, phosphate esters, APP |

| Application | Polymer | HFFR | |
|-----------------------|--------------------|--|--|
| Sealants (flame- | PUR, acrylics, | ATH, APP, RP, EDAP, melamine phosphate and - | |
| retarded and/or fire- | epoxy, elastomers, | , pyrophosphate, melamine polyphosphate, phosphate | |
| resistant) | PVC | esters, melamine borate, zinc borate | |

presents an overview of the main types of interior parts with their corresponding suitable polymers and flame retardants.

Table 22: Overview of the main types of interior parts with their corresponding suitable polymers and flame retardants.

| Application | Polymer | HFFR |
|---|---|--|
| | PVC | ATH, isopropylated phosphate ester, CDP, zinc borate |
| | Polyolefins Epoxy | MDH, ATH, intumescent systems, new phosphonates ATH, APP, intumescents, ethylene diamine phosphate, melamine borate, DOPO |
| Flooring | Phenolic resins Urethane elastomers | Melamine borate, phosphate esters Aluminium phosphinate, melamine cyanurate, TPP, CDP, APP, melamine phosphate, melamine |
| | Elastomers | polyphosphate ATH, MDH, phosphate esters |
| Collings | UP resin VE resin | ATH, APP, EDAP, intumescent systems, DMPP ATH, APP |
| Ceilings Sidewalls Panels Structural parts | Acrylate resin EP resin | ATH, APP, intumescent systems ATH, APP, intumescent systems, DMPP, DOPO, cyclic phosphonate, new reactive phosphorus based |
| · | Phenolic resins | containing epoxy groups Melamine borate, phosphate esters |
| Dashboard | PC | Sulphonates |
| Instruments Instrument panels | ABS PC/ABS | TPP, RDP, and BDP TPP, RDP, and BDP |
| Instrument cluster housing | TPU | APP, metal phosphinate, melamine cyanurate, melamine polyphosphates, TPP, CDP, zinc borate |
| Speaker grilles Gear knobs | TPE | Metal phosphinate +N-synergist, intumescent systems |
| Console parts | Polyamide, nylon | Melamine cyanurate metal phosphinate +N-synergist |
| Trunk tailgates Steering wheels | Polyolefin Reinforced PP | Intumescent systems Intumescent systems |
| Air ducts | RIM | APP, ATH, melamine phosphate, melamine |
| Tubing Door trim / handle Pillar claddings | UPR | polyphosphate, intumescent systems ATH, APP, EDAP, melamine phosphate, DMPP, intumescent systems |
| Door pockets Door panels Chairs | | |
| Other interior devices | w DUD | D polycle DMDD ADD TED |
| Insulation materials | r-PUR PIR | P-polyols, DMPP, APP, TEP RP, DMPP, APP, TEP |
| Coatings | 2K-PU, epoxy, acrylates | ATH, phosphate esters, APP |
| Sealants (flame- retarded and/or fire- resistant) | PUR, acrylics, epoxy, elastomers, PVC | ATH, APP, RP, EDAP, melamine phosphate and - pyrophosphate, melamine polyphosphate, phosphate esters, melamine borate, zinc borate |

The following table lists the substances that are most commonly used in textiles, according to PINFA. With a few exceptions, combinations of different substances must be used in order to meet the various requirements, including the necessary fire standard, but also other aspects,

such as the functionality of the textile, wash resistance, handling (soft, hard), etc.

| able 23: Lists the FRs that are most commonly used in textiles. | | | |
|---|-------------------------------|---------------------------------------|--|
| Substance | Physical form | Use | |
| Aluminium-tri-hydroxide (ATH) | Powder | Back-coating or added to polymer melt | |
| Aluminium phosphinate | Powder | Back-coating or impregnation | |
| Amino-Ether-HALS derivatives | Powder | Added to polymer melt | |
| Ammonium phosphate | Powder or aqueous solution | Back-coating or impregnation | |
| Ammonium polyphosphate | Powder | Back-coating | |
| Ammonium sulphamate | Powder or aqueous solution | Back-coating or impregnation | |
| Ammonium sulphate | Powder or aqueous solution | Back-coating or impregnation | |
| Cyclic phosphonate | Liquid | Impregnation Added to polymer melt | |
| Dicresyl phosphate | Liquid | Added to polymer melt | |
| Diethyl phosphinic acid, aluminium salt | Powder | Back-coating or added to polymer melt | |
| Guanidine phosphate | Powder or aqueous solution | Back-coating or impregnation | |
| Isopropyl phosphate ester | Liquid | Added to polymer melt | |
| Melamine | Powder | Back-coating | |
| Melamine cyanurate | Powder | Back-coating or added to polymer melt | |
| Melamine phosphate | Powder | Back-coating | |
| Melamine polyphosphate | Powder | Back-coating or added to polymer melt | |
| Methyl phosphonic acid, amidino-urea compound | Liquid | Back-coating or impregnation | |
| Oxaphosphorinane oxy-bis-dimethyl sulphide | Powder | Back-coating or added to polymer melt | |

| Substance | Physical form | Use |
|-------------------------------|-------------------------------|---------------------------------------|
| Potassium hexafluoro titanate | Powder | Reacted on fibre |
| Urea | Powder or aqueous solution | Impregnation |
| Zinc borate | Powder | Back-coating or added to polymer melt |
| Zirconium acetate | Liquid | Reacted on fibre |

Seats

The most common framework materials are polyamide (PA) and polypropylene (PP). Both polymer families are organically based materials and, hence, relatively easy to ignite and can burn heavily. However, both PA and PP usually pass the required FMVSS 302 fire test (horizontal flame propagation) at a certain thickness without the addition of a flame retardant.

Cables

Halogen-free flame retardant (HFFR) or low-smoke free-of halogen (LSFOH) polymer compounds can be used in many ways to produce safe and functional cables. Selected polymers and the corresponding flame retardants, together with some general facts about the flame-retardant (FR) systems, are presented in Table 24.

Table 24: Polymers and the corresponding flame retardants that are used in HFFR-cables. The last columns contains some general facts about the flame-retardant (FR) systems.

| Flame retardant | Polymers | Applications and effectiveness |
|--|---|--|
| Aluminium tri-hydroxide (ATH) Magnesium di-hydroxide (MDH) Aluminium oxide-hydroxide (AOH, boehmite) Also coated grades are available. | Low-density polyethylene (LDPE) Ethylene vinyl acetate (EVA) Polyolefins Elastomers Silicone rubbers (SiR) | In case of a fire, these mineral flame retardants decompose – absorbing energy. – releasing water (thus reducing fire intensity and diluting fire gases). – creating an oxide fire barrier against heat from the flame and to prevent burnable polymer decomposition products from reaching the flame. |
| Phosphorus flame retardants Phosphate esters (eg. tricresyl phosphate TCP) Intumescent products based on: ammonium polyphosphates (APP), | Used in fire-resistant coatings for cables Polyolefins Elastomers Thermoplastic Elastomers (TPE) | Flame inhibition and charring properties of phosphorus-based materials reduce the flammability of polymers. A char on the surface prevents heat transfer and protects polymer below. |

| Flame retardant | Polymers | Applications and effectiveness |
|-------------------------------------|--------------------|---|
| metal phosphinates, aryl phosphates | Polypropylene (PP) | |
| Melamine phosphate | | |
| Red phosphorus | | |
| Melamine Cyanurate (MC) | Polyamides (PA) | Results in polymer decomposition without flaming, especially in PA. |

In Europe, the main mineral flame retardant for this application is magnesium hydroxide (MDH), whereas in the USA, the use of aluminium hydroxide (ATH) for automotive XLPE cables (cross linked polyethylene cable) are more common.

In HFFR PE cable compounds, intumescent FR systems and finely grained metal phosphinates can be used. Depending on the Shore hardness and the overall balance of required properties, dosage should range between 20 and 30% metal phosphinate. A combination with nitrogen synergists can further improve the FR system and small amounts of PTFE can prevent dripping of burning material during the fire.

Typical polymer compounds for insulation of the metal wire or glass fibre for cables in public transport are XLPE, PVC, or Ethylene propylene rubber (EPR), but also PA, TPE, SiR, or fluoropolymers can be used. For the sheathing compound, typical polymers are Polyolefins, PE, PP, EVA or PVC.

Appendix 2. Fire safety standards and legislation

National regulations and fire safety standards vary across countries in Europe for the different sectors in which flame retardants are used. The European Commission has taken steps towards a level of harmonisation through regulations and standards such as the General Product Safety Directive (Directive 2001/95/EC), the Constructions Products Regulation (Regulation (EU) 305/2011), the Directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment, the Directive 95/28/EC on the burning behaviour of materials used in the interior construction of certain categories of motor vehicles or the Regulation (EU) 1007/2011 on fibre names and related labelling and marking of the fibre composition.

Fire safety standards do not specify the use of a certain flame retardant nor do they require the use of flame retardants. Instead, materials or products need to meet the performance tests set in relevant fire safety standards (certain materials are inherently not flammable).

On the other hand, ecolabels and voluntary product assessment schemes often have requirements excluding either chemicals with certain classifications or the use of certain types of substances, e.g. halogenated flame retardants. As an example, in the Blue Angel criteria for low-emission textile floor coverings⁸³, the use of halogenated compounds is prohibited. Furthermore, the criteria specify that inorganic ammonium phosphates, other dehydrating minerals (e.g. aluminium hydrate) or expandable graphite can be used as flame retardants if necessary while antimony oxides may not. Instead of a list of banned substances, the ecolabel TCO uses GreenScreen benchmark scores as a way to define acceptable substances. Substances with BM score 2 or higher are accepted.⁸⁴

There are also manufacturers or brand owners that have their own burn resistance specifications. An example is Volvo that has a specification⁸⁵ for cars, trucks and busses that is built on the US FMVSS 302 standard as well as the ISO 3795 standard.

1. Electric and electronic devices

Directive 2011/65/EU restricts the use of certain hazardous substances (Annex II of the Directive) in electrical and electronic equipment. However, the list of substances is currently limited to Lead (0.1%), Mercury (0.1%), Cadmium (0,01%), Hexavalent chromium (0,1%), Polybrominated biphenyls (PBB) (0,1%) and Polybrominated diphenyl ethers (PBDE) (0,1%).

The International Electrotechnical Commission (IEC) develops and publishes international standards for all electrical, electronic and related technologies. They serve as a basis for national standardization and as a reference to draft international tenders and contracts.

One of the most important conformity assessment schemes is the Certification Body (CB) Scheme. It is based on the principle of mutual recognition through certification using internationally recognized standards. With its 53 members, the "International Electrotechnical

⁸³ Criteria DE-UX 128 https://produktinfo.blauer-engel.de/uploads/criteriafile/en/DE-UZ%20128-201602-en%20Criteria-V4.pdf

https://tcocertified.com/industry/accepted-substance-list/

⁸⁵ Volvo standard STD 104-0001 https://webstd.volvo.com/webstd/docs/104-0001.pdf

Committee for Conformity Testing to Standards for Electrical Equipment" (IECEE) is a global network of National Certification Bodies (NCBs) that has agreed on mutual recognition of CB test certificates and reports.

The CB Scheme is based on the use of international (IEC) standards and on many specific product categories introduced by the introduced by the IECEE. Examples include IEC 60065 "Audio, video and similar and similar electronic equipment - Safety requirements" or IEC 60335 " Safety of electrical equipment for household and similar purposes". If a product is already UL-listed, classified, recognized or has a test mark such as the German GS or VDE test marks, this is usually sufficient for the CB Scheme to be granted. In some cases, additional tests are necessary to comply with national deviations.

The most common test for EEE is the UL 94. This is a standard that measures the burn characteristics of plastic materials. This standard is for testing plastic materials to ensure they meet the required resistance to burning for a specific application and typically for enclosures made out of plastic. There are several tests that are outlined and defined in UL 94:

- horizontal burning test; HB
- vertical burning test 50W; V-0, V-1 or V-2
- vertical burning test 500W; 5VA or 5VB
- thin material vertical burning test; VTM-0, VTM-1, or VTM-2
- horizontal burning foamed material test; HBF, HF-1, or HF-2

From the information collected within this project, the vertical burning (V-0, V-1 and V-2) test seems to be the most widely used. For this test, V-0 is the highest of the scores and to achieve this, burning must stop within 10 seconds on a vertical specimen and drips of particles are allowed as long as they are not inflamed. For a V-1 score, burning must cease within 30 seconds and drips of particles are allowed as long as they are not inflamed. For V-2, burning must cease within 30 seconds but drips of flaming particles are allowed.

In addition to UL 94, the limiting oxygen index (LOI) is a common test for EEE. In this burn test the specimen is mounted in a cylinder which is supplied with an oxygen and nitrogen mixture from the bottom and a flame from the top. The LOI value is the lowest oxygen concentration which will sustain burning of the specimen. The LOI value gives an indication how well a material burns where e.g. a LOI of around 20 or lower (the natural concentration of oxygen in air is 21%) indicates that the test material is easily ignitable.

Performance needs in cables and wires

A large amount of wiring is present in buildings and transport vehicles, usually bundled together and hidden in walls, ceilings or behind panels. The fire properties of cables are of great importance from a fire safety perspective. As a result, power and communication cables have been included.

The material in cables other than the conductor is generally made out of flammable polymers including the insulation, sheathing or bedding. The content in combination with the risk for being a source of ignition through e.g. short circuits, arcing or overheating triggers the use of flame retardants in cables.

There are a number of standards used for cables and fire safety. The table below shows a

summary.

Table 25: Summary or fire safety standards used for cables

| Table 25: Summary or fire safety standards used for cables | | | | | |
|--|--------------------------------|--|--|--|--|
| Test type | Standard | Tested parameters | | | |
| Fire resistance | IEC 60331 | Circuit integrity, resistance to fire, water, mechanical shock | | | |
| | BS 6387 | | | | |
| | UL 2196 | | | | |
| | VDE 0472/841 | | | | |
| | IEC 60332-1 | Burning Length | | | |
| | UL 1581-VW1 | Heat Release | | | |
| | FT1 | | | | |
| | FT2 | | | | |
| - 1 | IEC 60332-3 | | | | |
| Flame propagation | EN50399 | | | | |
| | BS4066 | | | | |
| | UL1666 | | | | |
| | NFPA262 | | | | |
| | UL910 | | | | |
| | UEC 61034 | Smoke emission on cable | | | |
| | EN50269 | | | | |
| | BS 7672 | | | | |
| Construction and the | ASTM 2843 | | | | |
| Smoke acidity | ASTME E-662 | | | | |
| | IEC 60754 | | | | |
| | EN 50297- 2-3 | | | | |
| | BS6425 | | | | |
| Flame retardancy | LOI: ASTM D 2863 / EN ISO 4589 | Acid gas emission on material | | | |

| Test type | Standard | Tested parameters |
|-----------|---------------------------|-------------------|
| | CTI: EN ISO 4589-3 | |
| | Cone Calorimetry ISO 5660 | |

2. Textiles

Specific standards have to be met for some protective work clothing, firefighter apparel and military garments where these textiles need to act as a protective barrier against fire.

Also, fabrics, textile surfaces or other cloth for typical applications in advertising, exhibition and stage constructions or in show business and event and institutional locations have to be fire-resistant. This is of special importance when the fabric has to be washed since a fabric made with flame retardants might lose its fire-resistant properties after several times of washing or cleaning, while an inherently flame-retardant fibre will not.

Fire safety requirements apply to furniture in several EU Member States (see Table 27). A distinction should be made between furniture for the residential market and furniture for office, contract and public markets because for the latter stricter fire safety requirements apply (e.g. requiring often meeting the open-flame test).

An overview of the standards for textiles is available in

Table 26. The standards for textiles in upholsteries and seating in transport vehicles are covered in section 4 to Appendix 2.

EU legislation relevant to textiles are the General Product Safety Directive 2001/95/EC which includes children's clothing, the Personal Protective Equipment (PPE) Regulation (EU) 2016/425 which includes fire-proof clothing and the Regulation (EU) 1007/2011 on fibre names and related labelling and marking of the fibre composition of textile products which requires to declare the fire behaviour of textiles.

The European Commission is also working on an EU strategy for sustainable and circular textiles⁸⁶ to ensure that by 2030 textiles products placed on the EU market are free of hazardous substances as well as long-lived and recyclable and produced in respect of social rights and the environment. Specific measures will include ecodesign requirements for textiles.

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⁸⁶ https://environment.ec.europa.eu/publications/textiles-strategy_en

Table 26: Overview of fire safety standards for textiles

| | y standards for textiles Standard Name | Description | |
|--|--|--|--|
| Firefighting | EN 469 | | |
| Automobile racing | EN ISO 14460:1999 | Protective clothing for automobile racing drivers — Protection against heat and flame | |
| Protective work clothing | EN 340 ISO 694d2:2002 EN 367 EN 470 EN 533 EN ISO 11612:2008 EN ISO 15025:2002 | Protective clothing, general requirements Protective clothing against heat and fire convection Protection against heat and flames, determination of heat transmission on exposure to flame Protective clothing for use in welding and allied processes Protection against heat and flames, limited flame spread materials and material assemblies Protective clothing for workers exposed to heat Protective clothing against heat and flames. Test procedure for limited flame spread | |
| Apparel other than protective clothing | EN 1103 | Burning behaviour of textiles for apparel - other than protective clothing - before and after cleansing | |
| Curtains and drapes | EN 13772 | Burning behavior of curtains and drapes | |
| Bedding | EN ISO 12952-1 EN ISO 12952-2 EN 597-1 | Assessment of the ignitability of several bedding items (smoldering cigarette) Assessment of the ignitability of several bedding items (matchflame equivalent) | |

| | Standard Name Description | |
|-----------------------|-------------------------------|--|
| | EN 597-2 | Mattresses and upholstered bed bases (smoldering cigarette) |
| | | Mattresses and upholstered bed bases (match-flame equivalent) |
| | EN 1021-1 | Upholstered furniture – Ignition source smouldering cigarette |
| | EN 1021-2 | Upholstered furniture – Ignition source match flame equivalent |
| | EN 597-1 | |
| Upholstered furniture | EN 597-2 | Mattresses and upholstered bed bases – Ignition source smouldering cigarette |
| | DIN 4102 (Germany) | Mattresses and upholstered bed bases – Ignition source match flame equivalent |
| | UNI 9175 (Classe Uno) (Italy) | Defines fire behavior classes for building materials. This standard is applicable to a wide range of materials, including composite materials, |
| | NFP 92 501-507 (France) | coverings, and decorative materials, which are very often used in furniture products |
| | Italian UNI 9175 (Classe Uno) | Determines and classifies the flammability performance of the components of upholstered furniture and products, such as chairs, sofas, mattresses, bed bases, bean bags, and similar types of furniture. |
| | | Sets testing methods for decoration materials, |

| Standard Name | Description | |
|---------------|---|--|
| | composite materials, fillings, fabric coverings, and other components used in furniture. It includes reaction to fire, electrical burner, speed of a flame, and other testing methods | |
| | The combustion of upholstered furniture is evaluated in presence of or without flame and/or glow. This gives an indication of the reaction to fire of furniture exposed to a small ignition source. | |

| Country | Building | standards in Europe towards the i Reference regulations | Furniture | Requirement | Test methods |
|----------------|-------------|--|---------------|--|---------------------------|
| France | Domestic | N°200-164 | Bedding | Cigarette test | EN ISO 12952-1 and 2 |
| | Public | U 23 (Health) | Bedding | Cigarette test | EN ISO 12952-1 and 2 |
| | | | Mattress | Cigarette test | EN 597-1 |
| | | AM18 (Spectacle) | Seat | No ignition by 20g paper cushion equivalent burner | |
| | | | | No ignition of the frame | NF P92501/NF P92507 M3 |
| | | GPEMD1 – 90 (Prisons) | Mattress | Cigarette test | EN 597-1 |
| | | | | Match test | EN 597-2 |
| | | | | No ignition by higher ignition sources | |
| Ireland and UK | Domestic | Furniture and Furnishing Regulations | Seat/mattress | Cigarette test | EN 1021-1 |
| | regulations | Regulations | Covering | Match test | EN 1021-2 |
| | | | Filling | Crib 5 | BS 5852 |
| | Public | BS7176 | Seat | Cigarette test | EN 1021-1 |
| | | | | Match test | EN 1021-2 |
| | | | | No ignition by higher ignition sources | BS 5852 |

⁸⁷ https://www.fireseat.eng.ed.ac.uk/sites/fireseat.eng.ed.ac.uk/files/images/04-Guillaume.pdf

| Country | Building | Reference regulations | Furniture | Requirement | Test methods |
|----------|----------|---|------------------------------------|---|--|
| | | BS7177 | Mattress | Cigarette test | EN 1021-1 |
| | | | | Match test | EN 1021-2 |
| | | | | No ignition by higher ignition sources in function of the level of hazard | BS 5852 |
| Italy | Public | DM/26/06/1984 | Seat / Mattress | No ignition by a 40 mm high flame during (s) 20, 80, 140 | CSE RF 4/83 |
| Finland | Domestic | 743/1990, 479/96 | Seat | Cigarette test | EN 1021-1 |
| | Public | Ministry of Interior Guideline A:56, 1988 | Seat | Cigarette and match tests | EN 1021-1, EN 1021- 2 |
| Sweden | All | Recommendations from consumer agency | Seat | Cigarette test | EN 1021-1 |
| | | consums: agent, | Mattress | Cigarette test | EN 597-1 |
| Norway | All | CPR Decree 07/09/1990 | Seat | Cigarette test | EN 1021-1 |
| | | | Mattress | Cigarette test | EN 597-1 |
| Spain | Public | As French regulations | | | |
| Portugal | Public | As French regulations | | | |
| US | Domestic | Federal Mattress Flammability Standard | Upholstered furniture, mattress | Cigarette test | 16 CFR Code of Federal Regulations – Part 1632 (FF4-72, as amended) |

3. Building and construction material

The Constructions Products Regulation (Regulation (EU) 305/2011) sets out the conditions for the marketing of construction products. It also sets out methods and criteria for assessing and expressing the performance of construction products and the conditions for the use of CE marking.

Classification and testing of the fire behaviour of building materials and components is now mainly carried out according to the European classification system in accordance with EN 13501 ("Fire classification of construction products and building elements") and the standards on the fire behaviour of building products listed therein.²⁸

The standard applies to three categories:

- construction products, excluding floorings and linear pipe thermal insulation products
- floorings
- linear pipe thermal insulation products.

Construction products have five European reaction to fire test methods. Based on the test results the products are divided into seven main classes: A1, A2, B, C, D, E and F for construction products excluding floorings and linear pipe thermal insulation products. Classes for floorings are A1fl, A2fl, Bfl, Cfl, Dfl, Efl and Ffl and for linear pipe insulations A1L, A2L, BL, CL, DL, EL and FL.

Class A defines non-combustible materials, class B for combustible materials with very limited contribution to fire, class C for combustible materials with limited contribution to fire, class D for materials with medium contribution to fire, class E for combustible materials with high contribution to fire and class F for combustible materials that are easily flammable.

The corresponding Euroclasses, are the prerequisite for CE marking and ensure their use in all states of the European Union.

The additional criteria for smoke emission, which can be applied by the Member States at their own discretion, could prove problematic, as virtually all plastics are classified in the worst class s3. For cables as construction products, the application of the acidity criterion by individual member states for certain applications could mean the exclusion of all cables containing halogens.

Textile floor coverings which are installed 'wall-to-wall' are considered to be construction products and therefore regulated across the EU by the Construction Products Regulation. The corresponding requirements can be found in the harmonised standard EN 14041. If a flame retardant has to be used so that a product complies with a certain fire class, an annual inspection must be carried out by an independently certified third party. The CE Marking framework documents this information.

4. Transport vehicles

Polymers and textiles are increasingly used in transport vehicles due their advantageous properties in terms of engineering possibilities and light weight. Engineering thermoplastics are nowadays used also in high temperature environments such as the engine compartment of cars. The use of electronics in cars and transport vehicles is also increasing which in turn increases the use of plastics in cables as well as electrical and electronic parts. For passenger comfort, textile surfaces, carpets, and upholstered seats are an important aspect.

Special fire protection requirements are placed worldwide on materials and parts and parts in the interiors of passenger cars, trucks and buses. Testing is carried out in accordance with Federal Motor Vehicle Safety Standard (FMVSS) 302 and in Germany in accordance with the corresponding test to DIN 75200. In addition, Directive 95/28/EC deals with the burning behaviour of materials used in the interior construction of certain categories of motor vehicle. The standard ISO 3795 is used.

The most important fire protection requirements and tests for rail vehicles in Europe come from the technical committee CEN/TC 256 for railway applications. The system requires fire testing according to EN 45545-2 which has its own set of requirements for applications inside and outside the railway carriage, from R1 until R28. These in turn points towards different ISO standards such as ISO 5658-2 regarding spread of flame and ISO 5659-2 regarding smoke generation.

For shipping applications, the International Maritime Organization (IMO) has implemented the FTP Code -"International Code for Application of Fire Test Procedures, 2010" according to IMO-Resolution MSC.307(88) . This code covers fire tests of materials and components for use on ships and yachts and specifies a number of ISO standards for the different part of the vessels.

For aircraft, there are stringent fire safety requirements. The U.S. Federal Aviation Administration have developed the Federal Aviation Regulations (FAR) that most countries have adopted. FAR contains several test requirements applicable for interior applications such as the vertical bunsen burner test, the OSU heat release test, in addition to smoke density and toxicity tests. For seat testing the Oil Burner test is applied.

Appendix 3. Inventory of registered flame retardants

The list below contains registered substances with explicit reference/evidence of being used as additive, reactive or polymeric flame retardants.



EUROPEAN CHEMICALS AGENCY P.O. BOX 400, FI-00121 HELSINKI, FINLANDECHA.EUROPA.EU