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Fire Safety Requirements and Alternatives to Brominated Flame-Retardants

A LOUS follow-up project

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Fire Safety Requirements and Alternatives to Brominated Flame-Retardants

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Foreword

The project *Fire Safety Requirements and Alternatives to Brominated Flame Retardants* was carried out from September 2014 to December 2014. The project is a follow-up on the recent survey of brominated flame-retardants, which was a part of the review of The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS). The main objective of this study is to provide background for the Danish EPA's Strategy for risk management of brominated flame-retardants.

The results are purely based on literature available to the public and information from the industry and trade organisations. No products have been subject to any form of analysis or testing.

The project was carried out by Danish Technological Institute (DTI), COWI A/S and the Danish Institute of Fire and Security Technology (DBI). The project was headed by Nils Nilsson, Danish Technological Institute.

The assessment of regulations, legislation and standards regarding fire safety was headed by DBI.

The project was financed by the Danish EPA.

Conclusion and Summary

Together with chlorinated flame-retardants, brominated flame-retardants (BFR) belong to the group of halogenated flame-retardants. The most frequently used halogenated flame-retardants have been under severe scrutiny for their toxicological and eco-toxicological properties. .

The main objective of this survey was to support the phase-out or reduction in the use of BFR by dissemination of information. In order to determine the possibilities for fulfilling the objective, this survey identifies the products and sectors with the highest consumption of brominated flame-retardants, maps trade standards as well as national, regional and international fire safety requirements and standards, including the fire safety test methods and criteria, and assesses the possibilities to substitute the brominated flame-retardants with non-halogenated flame-retardants.

The project was divided into four sections:

- Consumption of BFR
- Regulations and standards
- Screening of alternatives
- Health and environmental impact of alternatives

Consumption of BFR
According to the recent LOUS review of brominated flame-retardants, the most common additive BFRs are decabromodiphenyl ether (decaBDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD). In 1999, a comprehensive survey of the use of BFR demonstrated that imported articles containing BFR made up 330-660 tons, accounting for approximately 90% of the total content of BFR in end-user products. About 70% of this tonnage was used in electrical and electronic equipment. This is still believed to be the situation today. As most electrical and electronic equipment is produced outside of Denmark, the BFRs in these articles on the Danish market reflect the general use patterns in the EU and globally. The use of BFR in Denmark was found to be in building materials, EEE and transportation. In the Danish industry, the main application of BFRs in 1999 and 2012 was reactive brominated polyol, e.g., halogenated polyetherpolyol B, used for production of flame-retarded polyurethane foams for building insulation.

To narrow the screening of alternatives, it was decided to include only the most important product groups, based on the overall consumption of BFR. These were:

- Building materials
- Electric and electronic equipment
- Transportation and off-shore vessels

The included product groups are to some degree overlapping, meaning that some of the same polymeric material and appertaining non-halogenated flame-retardants are used in all three product groups. Consequently, it is to some degree possible to transfer knowledge regarding FRs from one product group to another.

Regulations and standards
Without standards, it would be impossible to compare products and the properties to each other. Like most other countries in the world, Denmark uses a classification system based on standards in especially the construction sector. Each country has its own national standards (which in some cases are identical to the European/International standards), but the European Union are working towards a unified standardization in all of Europe and they have already come a long way. However, there are still a lot of differences in the European countries in between and it should be remembered that this report has focused primarily on the Danish regulations.

Danish regulations specify demands to the fire behaviour properties of materials used in the building sector and electrical appliances (which are also applicable in EU). However, there are not any requirements to furniture or clothing (unless it is clothing specifically design to withstand fire) for the consumer market. Regulations in Denmark do not require any use of fire retardants (FR) but in many cases it is impossible to achieve the necessary fire safety properties without the use of FR. Thus, FR is basically a necessity in every electronic product due to the very strict regulation, which is primarily based on the American standard UL94.

Insulation products used in construction are divided into either combustible or non-combustible materials. By introducing FR in combustible insulation products, the fire performance properties can be improved, which allow a wider use of the specific product. This is also the case for coverings (both inside and outside of a building), where FR could improve the fire performance properties of a building material that would not be able to pass the fire performance criteria on its own. Thus FR enables the use of a wider range of products.

The transportation sector is regulated by international standards/conventions, which has been implemented in Denmark (given status as a national standard). Off shore vessels are regulated by SOLAS (Safety of Life at Sea), which is an international convention. SOLAS offers very strict requirements to all products on board and the use of FR in the sector is inevitable, as the requirements also extend to bedding components and other furniture.
Components and fixtures used in trains such as panelling and surfaces of the driver's desk are tested according to the European standard (EN45545), which also offers strict requirements that makes the use of FR a necessity. However the requirements for trains are more differentiated than those for offshore vessels, as there are three different hazard levels (HL), which are dependent on four different operational categories and four different design categories. Thus, the fire safety level varies between the three hazard levels.

Finally it can be concluded that standards are a necessity in order to secure an economical, reliable and uniform system that is beneficial to all countries. Therefore it is also essential that all standards are continuously updated, which most of them also are to a large extent

Screening of alternatives
This survey illustrates that alternative non-halogenated flame-retardants, appertaining polymer systems and production set-ups are already developed and on the market for a majority of the identified product types. However, it remains a challenge to substitute the brominated flame retardants for some application e.g. EPS insulation. The survey indicates that, the cost of using polymeric materials with non-brominated flame-retardants instead of brominated flame retardants is not significantly different for many applications; yet, substituting chemicals can involve significant costs, as industries must adapt their production processes, and have products and materials re-tested for all required performance and product standards.

Building materials
Building and construction materials have to meet a number of performance requirements, including fire protection and material properties. Modern buildings are commonly constructed with a large variety of materials and some may be flame retarded using BFR. In the screening of alternatives, a number of chemical and technical alternatives were identified and categorized into three groups:

Insulation
EPS/XPS are good thermal insulators and they are often used as building insulation material. The screening indicated that the high flammability of polystyrene could not yet be satisfactorily overcome with non-brominated flame-retardants. A brominated co-polymer of styrene and butadiene has been developed. According to the manufacturer, the brominated polymer is stable and not a persistent, bioaccumulative, toxic substance (opposed to HBCDDs that are presently used). Polyurethane foams are commonly flame retarded using reactive brominated polyols; however, the screening indicates that flame retardant requirements can be fulfilled by several different halogen-free flame-retardants, e.g., liquid phosphorous FR. Moreover, some other insulation materials, e.g., mineral wool, are inflammable and can be used for some the applications where EPS/XPS or polyurethane are used. For cavity walls, lofts and pitched roof insulation the mineral wools are typically the same price or less expensive than EPS.

Insulation	BFR	Chemical and technical alternatives	Comment
EPS and XPS	HBCDD	Inorganic wool	Inflammable (no need for FR). Technically and economically feasible for some applications
		Polyurethane foam	See below
		Wood fibre	Technically and economically feasible for some applications (mainly non-flame retarded EPS).
		Fire-resistive constructions	EPS/XPS without FR may be used. Not applicable for all purposes
Polyure-thane	Halogenated polyetherpolyol B Ester of TBBPA TBPH	Liquid phosphate FR (TEO, DEEP, DMPP, CDP)	Incorporated into the foam formulary.
		Solid (Expandable graphite and ammonium polyphosphate)	Used in combinations with liquid phosphate FR
		Wool	Inflammable (no need for FR). Technically and economically feasible for some applications
		Wood fibre	Technically and economically feasible for some applications
		EPS/XPS	See above
		Fire-resistive constructions	Polyurethane without FR may be used. Not applicable for all purposes

TECHNICAL AND CHEMICAL SUBSITUTIONS FOR EPS/XPS AND POLYURETHANE HBCDD

Cables

Non-brominated flame-retardants are already used in a wide range of base polymers, including halogen-free and halogenated polymers (e.g., PVC (poly-vinyl-chloride)). PVC is still the most important polymeric material used for cables. Modern low smoke, flame retardant (LSFR) PVC compounds have been developed by incorporating metal hydrate flame-retardants (e.g., magnesium dihydroxide and aluminium trihydroxide). In addition, zinc hydroxystannate and zinc borates are often used as synergistic flame-retardants. Moreover, phosphorous flame-retardants such as aryl phosphates and aryl alkyl phosphates may be used to reduce the flammability of the polymers. Besides flame retardant PVC and LSFR PVC the above-mentioned FR may also be used in chlorinated rubber like chloroprene and CSM. The following table summarizes relevant non-halogenated flame-retardants for PVC and other halogenated base polymers used for cables.

Flame retardant	Fire suppression function
Aluminium trihydroxide **and** **magnesium dihydrooxide**	Decompose during fire: - releasing water - absorbing energy - creating an oxide layer absorbing soot particles and HCl
Zinc-borates	Smoke suppressant in the condensed phase by forming a glass-like char
Zinc hydroxylstannate	Acts in the condensed as well as the gas phase
Aryl phosphates **and** **Aryl alkyl phosphates**	Reduce flammability of polymer

NON-HALOGENATED FLAME-RETARDANTS USED IN PVC COMPOUNDS AND OTHER HALOGENATED POLYMERS FOR CABLES

A number of halogen-free flame-retardants or low-smoke free-of-halogen polymer compounds can be used as an alternative to halogenated polymers. The by volume most frequently used compounds for halogen-free flame-retardant wire and cables are based on blends of EVA and LLPDE using aluminium trihydoxide as the sole flame retardant filler (loadings app. 60-65%).

Whenever special requirements are required, concerning abrasion and chemical or temperature resistance, thermoset type and thermoplastic compound can be used. Elastomers based on EPDM or EVM are commonly applied with 50-60% aluminium trihydorxide. Sometimes zinc borates are applied as flame-retardant synergist and inherent mineral filler. In addition, a number of other non-halogenated FRs might be used. In the table below, the relevant non-halogenated flame-retardants for halogen-free wire and cable compounds are summarized.

Flame retardant	Working function	Polymer
Aluminium trihydroxide **and** **magnesium dihydroxide**	Decompose during fire: - releasing water - absorbing energy - creating an oxide layer	**Polyolefins** - LDPE -EVA **Elastomers** - EPDM -TPU
Zinc-borates	Smoke suppressant in the condensed phase by forming a glass-like char	**Elastomers** - EPDM -TPU
Phosphorous flame-retardants	Reducing flammability	Used in fire-resistant coatings for cables, polyolefins and polyprolylene
Ammonium polyphosphates **Polyphosphonates** **Metal phosphinates** **Aryl phosphates** **Melamine derivates**	Char formation prevents heat transfer (intumescent products)	**Elastomers** TPE TPU Thermoplastic polyesters

NON-HALOGENATED FLAME-RETARDANTS FOR HALOGEN-FREE CABLES AND WIRES

Profiles, composites, film and sheets
Profiles, composites, film and sheets are used for versatile application and are manufactured by using different polymer materials and flame-retardants. For the majority of these products, the polymer can be flame retarded by using non-halogenated flame-retardants; however, non-BFR solutions are still missing for some application, e.g., thin film. An overview is presented in the table below.

In addition to substituting the type of flame retardant, it might be possible to substitute from an inherently flammable polymeric material to a less flammable material for some applications. For instance, metal profiles might be used instead of plastic for some applications e.g., cable trays.

Material	Application	Possible non-halogenated FR
Flexible PVC	Tarpaulins	Phosphate esters, zinc borate, aluminium trihydroxide
Rigid PVC	Profiles (windows, doors, trim)	
PC and blends, ABS	Sheets: Roofing, glazing, lighting Profiles: trim	Oligomeric phosphates and diphosphates, silicone compounds, potassium perfluorobutane sulphonate (KPBS), potassium diphenyl sulphone sulphonate (KSS)
Unsaturated polyester	Sheets (mould, facing)	Aluminium trihydroxide, melamine and melamine derivates, DMPP, cyclic phosphonate, phosphonate oligomers (transparent applications)

Polyolefins (PE, PP, EVA)	Thin film: roofing underlay, vapour barrier, scaffold sheeting, etc.	Alkyl phosphonates, hypophosphite salts
Polyolefins (HDPE, PP)	Rigid sheets: Aluminium Composites Panels, building scaffolds (walk ways) Pipes and cable trays	ATH, MDH, melamine polyphosphate
TPU	Thin film: roofing underlay	Alkyl phosphonates, polyphosphonates, phosphate esters
Copolyesters, copolyamides	Breathing film: roofing underlay	Polyphosphonates, metal phosphinate

NON-HALOGENNATED FLAME-RETARDANTS FOR PROFILES, COMPOSITES, AND FILM OF POLYMERIC MATERIAL

Electrical and electronic equipment
In the screening of alternatives, a number of technical alternatives were identified. For some applications, an inflammable material could be applied; however, for most applications that is not applicable. An alternative approach is to use technologies that detect and stop the fire at the earliest stage, by interrupting the power supply to the object and thus preventing fire. Examples are sensor technologies and artificial noses.

For the vast majority of applications, chemical alternatives to the use of brominated flame-retardants were identified. In general, EEE materials with non-halogenated FRs were found to be 10-30% more expensive than materials with brominated flame-retardants. However, substituting chemicals can involve significant costs, as industries must adapt their production processes, and have products re-tested for all required performance and product standards.

Wiring boards
Almost all electronic items contain a printed wiring board and most materials used for printed wiring boards need a flame retardant to fulfil the common fire safety classifications. Commonly, epoxy resins are used as circuit boards in printed wiring boards. Several companies have announced halogen-free products. Lower glass transition temperature (less stiffness), lower drill ability and increased cost are problems for some non-halogen printed wiring boards. However, there are a number of reactive nitrogen and phosphorous compounds and additive inorganic alternatives, mainly aluminium trihydroxide that are used on a commercial basis as alternative to non-halogen flame-retardants in epoxy resins instead of TBBPA.

Enclosures

Electrical installations and components are made of numerous types and blends of polymer; however, polyamides are often used. A large number of different FRs may be used to flame retard these products. An overview is given in the table below.

FR	Polymer	Content	Remark
Metal phosphinates	Glass fibre reinforced polyamides Glass fibre polyester	Up to 20%	Often combined with N-synergists
Melamine polyphosphate	Glass fibre reinforced polyamides	App. 25%	Used as synergists with phosphorous FR
Melamine cyanurate	Un-reinforced polyamide 66 Unfilled polyamide 6 Mineral-filled polyamide	5-10% (UL 94 V-0) 5-10% (UL 94 V-0) 13-16% (UL 94 V-0)	Used as synergists with phosphorous FR. Difficult to reach V-0 in glass filled polyamide
Red phosphorus	Glass fibre reinforced polyamides	5-8% (UL 94 V-0)	Limited to red and black plastic. Handling and safety issues; consequently, FR is stabilized and coated
Aryl phosphates/phosphonates	PC/ABS blends	10-20%	
Magnesium hydroxide	(low) Glass fibre reinforced polyamides	60% (UL 94 V-0)	Plastic difficult to process and stiff.
Ammonium polyphosphate	Polyolefins	20-30%	Often combined with N-synergists

OVERVIEW OF POSSIBLE NON-BFR FOR ELECTRIC ENCLOSURES.

Screening of alternatives – transportation and off-shore vessels

Transportation and off-shore vessels are very complex, and the various "products" are manufactured from a broad variety of components/materials that potentially contain BFR, including EEE, cables, interior parts textiles and seats. Many of these components have been examined previously in the report. Consequently, the screening of alternatives for transportation and off-shore vessels was less thorough with circular references to previous sections.

Health and environmental impact of alternatives

The European Commission-funded project ENFIRO investigated the substitution options for some BFRs and compared the hazard, exposure, fire and application performances. According to the LCA study of the ENFIRO project the waste phase was the most important difference between the selected BFRs and non-halogenated FRs. Especially the formation of brominated dioxins during improper electronic waste treatment had a strong negative impact on the LCA scores. Overall, the life cycle environmental performance of the non-halogenated FR scenario was better than for the BFR scenario.

Recommendations for further work

On the basis of this survey and a separate note elaborated on for the Danish EPA, it is recommended to use this survey as a base for the elaboration of an idea catalogue with the aim to promote and encourage the substitution of the BFRs with more environmental friendly alternatives, either as non-halogenated FRs or as other technical solutions.

From this survey, it appears that alternatives exist for the large application areas, but it is also clear that some of the most frequently used alternatives (e.g., organic phosphorous compounds) might have unwanted properties that rarely have been clarified.
On the basis of the above, we recommend that a possible phase two of the project should aim to prepare an idea catalogue/guide for the identified target group consisting of product developers, designers, purchasers and others who are involved in the development of products (including buildings) that today use bromated flame-retardants.

The idea catalogue is foreseen to address the following important information to the target group:

- Actual regulation of BFR, BFRs on various substance lists and requirements of environmental labels concerning BFR (can be extracted from the LOUS report)
- Knowledge of fire requirements and especially knowledge of requirements to halogens in general
- Which alternatives exist on the market for the various purposes and their advantages and disadvantages
- Status of products with the alternatives in question (i.a. what are the challenges regarding substitution)

1. Introduction

Together with chlorinated flame-retardants, brominated flame-retardants (BFR) belong to the group of halogenated flame-retardants. The most frequently used halogenated flame-retardants have been under severe scrutiny for their toxicological and eco-toxicological properties. Consequently, over the past 10-15 years, there has been a trend in specifically polymers (e.g., plastic, textiles) that are used for applications with a fire safety demand, to move from traditional halogenated “flame retarded polymers” (FRP) towards non-halogenated alternatives. The drive to change from halogenated FRPs (due to toxicological and environmental concerns) emerged in the middle of the last decade and in some cases, they were driven by the introduction of two new instruments: Restriction of Hazardous Substances Directive (RoHS; Directive 2002/95/EC) and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH; Regulation (EC) No 1907/2006).

Fire safety regulations and the associated standards are to a large extent the drivers for using flame-retardants; however, fire safety regulations do often not include any specific requirements for the use of halogenated flame-retardants or other flame-retardants. The regulations typically define some fire tests, which the material or articles should pass, but it is up to the manufacturers to decide how the requirements are to be met.

In this survey, present fire safety standards and regulations are listed and assessed. Furthermore, the main applications of brominated flame-retardants are identified and possible substitutions with non-halogenated flame-retardants and other technical solutions, such as substituting to an inherently non-flammable material, are highlighted. Only the halogen-free flame-retardants will be considered as substitutes for the brominated flame-retardants as the chlorinated flame-retardants also emit toxic fumes (Hydrochloric acid) and some are also toxic to the environment, e.g., chlorinated paraffins. Therefore, the chlorinated flame-retardants have not included in the survey as alternatives, because some of the chlorinated flame-retardants also appear to be persistent and bio accumulative.

The non-halogenated flame-retardants are commonly classified as:

- Inorganic: This class mainly comprises the metal hydroxides and is dominated by aluminium hydroxide and magnesium hydroxide. Other inorganic compounds like zinc borate are used to a much smaller extent. The function of the metal hydroxides is to liberate water as a fire extinguisher at elevated temperature (> 200°C or more).
- Phosphorous-based flame-retardants: include both organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorous.
- Nitrogen-based flame-retardants: are typically melamine and melamine derivatives. These flame-retardants are often combined with phosphorous-based flame-retardants. By making this combination it is possible to create intumescent flame retardant systems where the combustible material, e.g., plastic, is separated from the fire or heat source by an insulating foam formed at the surface of the material.

The Index of Flame Retardants (an international guide) contains more than 1000 flame retardant (including halogenated) products with trade name, chemical, application and manufacturer that describe around 200 chemicals used in commercial flame retardant products (Posner 2006). The combination of one or more flame-retardants in the same application makes the chemistry very complex. When taking the numerous different fire safety requirements for the various applications and the many different polymeric materials into account, the task of substitution is not a simple matter.

There are ways to achieve adequate fire performance and they are relevant when considering alternative solutions. They include:

- Use of alternative chemical flame-retardants
- Use of intrinsically or inherently flame retardant materials
- Product design – achieved by the selection and use of materials together with other components such as physical and thermal barriers, coatings and layer technologies, heat sinks, etc. How components are placed physically in relation to each other can give enhanced fire performance regarding the expected types of ignition source and flame and fire exposure

All of these approaches are potential alternatives to the use of BFRs and have been included in this survey.

1.1 Objective of the survey

The objective of this survey was to address the above-mentioned challenges by:

- Identifying the products and sectors with the highest consumption of brominated flame-retardants BFRs.
- Mapping of trade standards, as well as national, regional and international fire safety requirements. Assessing possibilities to substitute the brominated flame-retardants with non-halogenated flame-retardants.

Emphasis will be on the sectors and applications where the highest consumer exposure is foreseen. Moreover, focus will be to gather knowledge on the regulations and standards regarding fire safety regulations (e.g., ships and off-shore) and non-halogenated solutions that the Danish export industry, e.g., supplier/sub-supplier and purchasers of products can benefit from. For instance, a sub-supplier might demand that materials used as components or semi-manufactured articles shall be based on non-halogenated FRs - a consequence of knowing that possible alternatives exist. This knowledge is considered important as most plastic and textile raw materials, used for production export articles, are imported from Asia, who traditionally uses brominated flame-retardants. In addition, the export industry not only has to face Danish or European fire standards, but also needs knowledge about legislation and standards of the global export marked.

In addition, this survey will be used as a decision-making basis regarding the possibility to compile a catalogue that will promote and initiate the substitution of halogenated flame-retardants.

1.2 Survey methods

The survey was divided into four main sections:

- Polymeric materials and their use and properties
- Identification of major application areas of brominated flame-retardants
- Mapping of alternatives to brominated flame-retardants
- Assessment of regulations and standards on flame retardant safety requirements

1.2.1 Polymeric materials and their properties

Today, a large number of different polymeric materials are commercially available for a number of different applications. They are characterised by low weight and at the same time high technical performance and comfort.

The polymeric materials are easy to form in different shapes, and a number of specific production equipment has been developed for automated and reasonably priced processing of these materials.

One drawback is that most of the polymeric materials are easy to ignite and burn. In order to avoid fires in connection with many of the applications, flame-retardants must be added to the polymers or composites must be made with other materials to encapsulate the polymer materials. The short overview on polymeric materials is based on expert knowledge at DTI and recent literature on polymers.

1.2.2 Identification of major consumption of brominated flame-retardants
An identification of major consumers of brominated flame-retardants was carried out, with the purpose to identify the most important product types and sectors. The identification was based on:

- Previous surveys, scientific literature and reviews on brominated flame-retardants
- Interview with the Sector Group PINFA (Phosphorous, Inorganic and Nitrogen Flame Retardants Association)
- Data from European Flame Retardants Association

Finally, to focus the survey for the subsequent work, an exclusion of product sectors was carried out, based on exposure and overall consumption of brominated flame-retardants.

1.2.3 Assessment of flame retardant safety requirements
The assessment of fire safety requirements is based on a thorough research on standardizations and the organizations behind them. This report has its main focus on Danish regulations, however, many of the national standards have been directly extracted from large standardization organizations. The chapter focuses on three primary sectors, which are within construction, electrical appliances and transportation. Some of the most important regulations have been addressed in each sector in order to create a broad overview of the overall requirements to the products that are used.

1.2.4 Screening of alternatives to brominated flame-retardants
The screening of alternatives is based on:

- Previous surveys, scientific literature and reviews on brominated flame-retardants
- Interview with the Sector Group PINFA (Phosphorous, Inorganic and Nitrogen Flame Retardants Association)
- Brochures from the Sector Group PINFA
- Google search using combinations of a number of relevant key words in order to find commercially available flame retardant products

1.3 Structure of the report
The report reflects the main findings and the delimitation process throughout the project. This means that the chapters have been structured as described below:

- A short introduction to polymeric materials and their use and properties (Chapter 2)
- Identification of major application areas of brominated flame-retardants (Chapter 3)
- Assessment of regulations and standards regarding fire safety requirements (Chapter 4)
- Screening of alternatives – Building materials (Chapter 5)
- Screening of alternatives – Electronic and electrical equipment (Chapter 6)
- Screening of alternatives – Transportation and off-shore vessels (Chapter 7)

Flame-retardants are mainly used for flame retarding polymeric materials such as plastic and textiles; consequently, only an overview of polymeric material is given.

1.4 Abbreviations

- Acrylonitrile-butadien-styrene (ABS)
- Aluminium trihydroxide (ATH)
- Antimony trioxide (ATO)
- Bis(2-ethylhexyl)tetrabromo-phthalate (TBPH)
- bisphenol A bis-(dephenyl phosphate) (BDP)
- Brominated flame retardants (BFR)
- Butadiene acrylonitrile (NBR)
- European Committee for Standardization (CEN)
- European Committee for Electrotechnical Standards (CENELEC)
- Chloroprene (CR)
- Chlorosulfonated polyethylene (CSM)
- Conventional Index of Toxicity (CIT)
- Critical flux at extinguishment (CFE)
- Danish building regulation 2010 (BR10)
- Danish Standard (DS)
- decabromodiphenyl ether (decaBDE)
- Dibromoneopentyl glycol (DBNPG)
- Dihydrooxaphosphaphenanthrene (DOPO)
- Dimethyl metylphosphonate (DMPP)
- Electrical and electronic equipment (EEE)
- Epoxies (EP)
- Ethane bis (pentabromophenyl) (EBP)
- Rthylene bis(tetrabromophthalimide) (EBTBP)
- Ethylene propylene diene monomer (EPDM)
- European Committee for Electrotechnical Standards (CENELEC)
- European Committee for Standardization (CEN)
- European Flame Retardant Association (EFRA)
- European standards (EN)
- Ethylene vinyl acetate (EVA)
- Expanded polystyrene (EPS)
- Extruded polystyrene (XPS)
- Fire Growth Rate (FGR)
- Fire Hazard Level (HL)
- Fire retardants (FR)
- Fire Test Procedures (FTP)
- Flame retarded polymers (FRP)
- Glass fibers in UP (GUP)
- High-density polyethylene (HDPE)
- Heat sustained burning (average heat for sustained burning) (Q_{sb})
- Hexabromocyclododecane (HBCDD)
- High impact polystyrene (HIPS)
- International Electrotechnical Commission (IEC)
- International Maritime Organization (IMO)
- International Organization of Standardization (ISO)
- Isobutylene isoprene rubber (IIR)
- Linear low-density polyethylene (LLPDE)
- Low smoke flame retardant (LSFR)
- Maritime Safety Committee (MSC)
- Methylene diphenyl diisocyanate (MDI)
- Original equipment manufacturer (OEM)
- Peak heat release rate (Q_p)
- Poly(ethylene terephthalate) (PET)
- Poly(phenylene oxide) (PPO)
- Poly(vinylchloride) (PVC)
- Polyacetal (POM)
- Polyamides (PA 6, PA 6,6)
- polybrominated biphenyls (PBBs)
- polybrominated diphenyl ethers (PBDE)
- polybrominated diphenyl ethers (PBDEs)
- Polycarbonate (PC)

- Polyesters e.g. poly(butylene terephthalate) (PBT)
- Polyether block amide (PEBA)
- Polyethylene (PE)
- Polyolefinic elastomers blends (TPE-V)
- Polypropylene (PP)
- Polystyrene (PS)
- Polyurethane foams (PUR and PIR)
- Polyurethanes (PU)
- Resorcinol bis-(diphenyl phosphate) (RDP)
- Resorcinol bis(2,6-dixylenyl phosphate) (RDX)
- Resorcinol bis-(diphenyl phosphate) (RDP)
- Restriction of Hazardous Substances Directive (RoHS)
- Safety of Life at Sea (SOLAS)
- Sector Group PINFA (Phosphorous, Inorganic and Nitrogen Flame Retardants Association)
- Smoke Growth Rate (SMOGRA)
- Styrene butadiene rubber (SBR)
- Styrene copoplymers (TPE-S)
- Tetrabromobisphenol A (TBBPA)
- Technical Specifications (TS)
- Tetrabromophthalic anhydride (TEBR-Anh)
- Thermoplastic polyurethanes (TPU)
- Thermoplastic rubbers (TPE)
- Total heat release (THR and Q_t)
- Total Smoke Production (TSP)
- Triphenyl phosphate (TPP)
- Underwriters Laboratories (UL)
- Unsaturated polyesters (UP)
- Waste Electrical and Electronic Equipment (WEEE)

2. Polymeric materials and their use and properties

Most polymeric materials are inherently flammable. Depending on the use and type of polymeric material flame-retardants might be required. In this chapter, a short overview of polymeric materials is given, with emphasis on the polymeric materials mentioned throughout the survey.

2.1 Introduction

A polymer is a large molecule (macromolecule) composed of repeated structural units. The repeated unit is called a monomer. If the polymer is formed from one repeated monomer only, it is called a homopolymer. If different monomers are used for the polymerization, the polymer is called a copolymer (V. Goodship 2010, Saechtling 2007, G.W.Ehrenstein 2001).

Polymers can be categorized as either natural polymers (e.g., cellulose, silk, cotton, flax, natural rubber), modified natural polymers (e.g., rayon) or synthetic man-made polymers (e.g., thermoplastics, thermosets and rubbers).

In most cases, the synthetic polymers are based on long chains of carbon atoms (back bones) to which hydrogen or other chemical elements are attached. An exception is the silicon-based polymers, where the long backbones are made of silicon oxygen chains.

In most cases, the carbon based polymers are inherently easy to ignite and to burn, which means that it is necessary to add or incorporate monomers in the polymer backbones which retard and diminish the flammability of the polymer in case of fire.

A vast number of synthetic polymers have been developed to serve the modern society with low-weight polymeric materials with tailor-made functional properties. The polymers can easily be shaped by different processes (extrusion, injection moulding, thermoforming etc.) due to very good melt flow properties, and they can be manufactured in many different and complicated shapes compared to e.g. steel, glass, stone and concrete.

Polymeric materials can be categorised into three main groups:

- Thermoplastic plastics
- Thermoset plastics
- Rubbers

The thermoplastic polymers can easily be re-melted, reshaped, and recycled to new products.

The thermoset polymers form a big molecule, which cannot be re-melted because the molecule chains are locked together with tight chemical cross-links, which lock the structure and make recycling difficult. The same is the case for rubber, but the cross-links are few compared to the thermosets, which means that rubber has elastic properties because the lock of the polymer chains is very loose. Thermoplastic rubbers (TPE) behave like rubber because the molecule chains are restricted in their movements due to physical bonds in crystalline domains. As the lock is not a chemical bond, these TPEs can be recycled when the polymer is heated to a temperature high enough for melting the crystalline domains.

The most common thermoplastic polymers that are used are:

- Polypropylene (PP)
- Polyethylene (PE)
- Linear low-density polyethylene (LLDPE)
- Poly(vinylchloride) (PVC)
- Poly(ethylene terephthalate) (PET)
- Polystyrene (PS), expanded polystyrene (EPS), extruded polystyrene (XPS)

They are also called commodity plastics due to the high volume on the marked and the cheap price index.

Engineering thermoplastics are high performance thermoplastics, which are high performance materials with enhanced properties (thermal, mechanical, chemical and electrical). Examples of engineering thermoplastic polymers are:

- Acrylonitrile-butadien-styrene (ABS)
- Polyacetal (POM)
- Polyamides (PA 6, PA 6,6)
- Polycarbonate (PC)
- Poly(phenylene oxide) (PPO)
- Polyesters, e.g., poly(butylene terephthalate) (PBT)

From thermoplastic polymers, blends such as ABS/PC, ABS/PVC and PPO/PS can be made.

The thermoset plastics i.a. comprise:

- Epoxies (EP)
- Polyurethanes (PU, PIP)
- Unsaturated polyesters (UP)
- Melamines (MF)
- Phenolic (phenol-formaldehyde)

They have also been given the name "resins" as they solidify in the same way as some plant resins, but they are synthetic and are not derived from plants.

Regarding rubber, a number of synthetic types exist besides natural rubber. The most common types are listed below:

- Styrene butadiene rubber (SBR)
- Ethylene propylene diene monomer (EPDM)
- Isobutylene isoprene rubber (IIR)
- Butadiene acrylonitrile (NBR)
- Chloroprene (CR)
- Ethyl vinyl acetate (EVA)

Furthermore, the TPEs thermoplastic rubbers also exist in several different chemical types, depending on the type of monomer and polymeric structure:

- Thermoplastic polyolefine (TPO)
- Thermoplastic polyurethanes (TPU),
- Styrene-Butadiene-Styrene (SBS)
- Styrene-Ethylene-Butadiene-Styrene (SEBS)
- Polyether block amide (PEBA)

Reinforcement of plastics and rubber with fibres or fibre mats is common because mechanical properties can be enhanced e.g. by using glass fibres in UP (GUP). In many cases, additives and fillers are also added to the formulary for the polymeric resin to improve processing properties, electrical properties and ageing resistance.

2.2 Flammability of polymeric material and function of flame-retardants

The complexity in chemistry and material properties of polymers and polymer processing makes the topic of selecting the best flame retardant package in each application a complicated task.

First, it is very important that the polymeric-based products fulfil their technical performance after improving the fire resistance either by addition of the flame-retardants as an additive or after chemical bonding in the polymer structure. In many applications of polymeric materials, this is mandatory due to fire safety requirements and standards in end-use service (see Chapter 4). The process of mixing and blending polymers and additives in molten state is called compounding. Compounding is typically made in tween screw extruders for plastics and in specially mixing chambers for rubbers.

The amount of flame-retardant needed depends a lot on the chemical structure of the polymer and its behaviour upon heating and in the flame.

Some plastics and rubber ignite and burn with difficulty like PVC and CR rubber because of a high content of chlorine in the polymer chain, but they liberate toxic hydrochloride acid and dioxins during fire. POM burns in the flame and continues to burn on removal and ignite easily. POM melts, decomposes and liberates very toxic formaldehyde vapours. Polyethylene and polypropylene continue to burn after removal from a flame, and they melt and drip and the drops still burn after falling from the flame. Polystyrene ignites easily and continues to burn. Polyurethane plastic burns, melts and drips with the development of toxic fumes, e.g. HCN (Krause, Lange et al. 1979).

To summarize:

- Chlorinated plastics like PVC and CR rubber burn with difficulty due to the high content of chlorine (40 -60% w/w) but they emit toxic vapours such as HCl and dioxins and in the presence of humidity produce white smoke, which makes it difficult to navigate during fire.
- Polyoxymethylene (POM) and other plastics, which have formaldehyde as one of the monomers built into the chemical backbone, will liberate toxic formaldehyde vapour in a fire. Some types (phenolic resins), which are thermally rather stable, will in a fire also liberate toxic phenolic substances and create soot. Melamine and other amino plastics become charred in a fire and liberate ammonia and formaldehyde.
- Olephinic plastics like PP and PE burn easily with drop formation and the volatiles formed can be compared with the fumes from a candle. A fire can easily spread due to dripping of the plastic while still burning.
- Polystyrene and ABS are very sooty when they burn and liberate free styrene and ABS also liberates acrylonitrile.

- Polyurethane produces a yellow orange grey smoke and liberates toxic fumes due to the MDI or TDI monomer used for the manufacturing of the polymer.

As polymeric materials behave differently during fire and as there are certain demands for maintaining important functional properties, the optimum and most feasible way to make the polymeric materials inflammable is an art that demands high skills and great understanding of polymer chemistry.

In order to change from a brominated flame retardant polymeric product to a non- halogenated solution it is important that there is a close cooperation between the manufacturer of non-halogenated flame-retardants, the compounder of the resin formulary and the producer of the product as the process parameters (injection moulding, extrusion, vacuum forming etc.) must also be taken into consideration. Some plastics are processed at such high temperatures that some of the non-halogenated flame-retardants start to decompose for the same reason as their way of acting as flame-retardants e.g. liberate water or nitrogen. Often more than one type of flame-retardant is used in the resin because they will act as synergists.

The flame-retardants function either by physical or chemical suppression of the fire.

The physical function is either:

- Cooling (liberation of water). A typical example is aluminium trihydroxide
- Coating by the formation of a thermally insulating layer on the surface of the polymer (intumescence). Typical examples are phosphorous-based retardants
- Dilution by addition of substances that during fire form inert gases, which dilute the flammable material. Typical examples are melamine derivatives (liberation of nitrogen)

The chemical function is either in the gas phase or in the solid state. The halogenated flame-retardants are examples of substances, which function in the gas-phase, by a reaction between the highly reactive H· and OH· radicals and the formed hydrogen chloride/hydrogen bromide. Consequently, the highly reactive H· and OH· radicals are replaced by the less reactive halogen radical. By dissipating the energy of the ·OH radicals by trapping, the thermal balance is modified and that strongly reduces the combustion rate. Melamine polyphosphate in polypropylene is an example of solid-state phase by creating a thermal barrier between the burning and unburned parts.

The chemical function is either (Subramanian 2013):

- Degradation where no volatile gases are produced
- Removal of responsible elements so that flames can be prevented or removed
- Removal of heat generation by endothermic reactions
- Formation of a thermally insulating char layer on the surface of the polymer (intumescence)

Especially for the halogenated FRs it is practice to add antimony oxide as a synergist. By using a synergist, the amount of the halogenated FR can be reduced as the synergist boosts the effect of the flame-retardant. Antimone oxide forms antimony trichloride and antimony oxychloride in the presence of chlorinated FRs and the similar antimony tribromide and antimony oxybromide for BFRs. The volatile antimony halogenides, formed in the case of fire, both react directly in flame quenching by reacting with the flame propagating free radicals. Antimony oxide alone acts directly with hydrocarbons (like PE and PP) to form water and molecular hydrogen instead of free radicals, which will propagate the flame. As antimony oxide might tend to retain heat after flaming has ceased (after glow), and in that way serve as a source for reignition, it is desirable to use as little antimony oxide as possible. The ratio of FR to synergist for polyolefins (e.g., PE and PP) varies from 1:1 to 8:1.

Aluminium trihydrate might also be used as synergist with more efficient flame-retardants by cooling the temperature by liberating water. At the same time, the alumina is an excellent heat conductor and removes heat from the flame zone.

A combination of different types of flame-retardants is also a very common practice. However, in this case the benefit is that they act by different flame suppression mechanisms.

3. Use of brominated flame-retardants and cost of substitution

In this chapter, the major use of brominated flame-retardants is outlined with regard to sectors, products, materials and types of BFR. Based on these findings, recommendations are provided for focusing and narrowing down the subsequent work in this project (section 1.3).

3.1 The substance groups

Flame-retardants are added to polymeric materials, both natural and synthetic, to enhance the flame-retardant properties of the polymer. BFRs and the chlorinated flame-retardants act essentially in the gas phase by emitting low energy radicals such as Br• and Cl•. These species will substitute high-energy free radicals (H• and OH•) in the gas phase, quenching the exothermic radical reactions, which lead to flame formation (gas phase mechanism, see section 2.2).

A distinction between reactive and additive flame-retardants is made:

- Reactive flame-retardants are chemically built into the polymer backbone molecule, together with other monomers. This prevents the flame-retardants from migrating from the polymer and vaporizing at service temperatures, and therefore retardancy is retained during normal use. Reactive BFRs include tetrabromobisphenol A (TBBPA), tetrabromophthalic anhydride (TEBR-Anh), dibromoneopentyl glycol (DBNPG), and brominated polystyrene (catalysis of bromine and polystyrene). The parent BFRs (e.g., TBBPA) are present as unreacted substances at trace levels only in the final polymers (Lassen, Jensen et al. 2013).
- Additive flame-retardants are incorporated in the polymer during or more frequently after polymerization. The BFRs are present in the final polymer and may migrate from the polymers. The most frequently used additive brominated flame-retardants are polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD).

BFRs form a complex group of chemical substances, usually containing 50-85% bromine (by weight) and are commonly divided into the following five main classes:

- Aromatics, including TBBPA, PBDEs and polybrominated biphenyls (PBBs)
- Aliphatics, including a few BFRs that are used in relatively small quantities
- Cycloaliphatics, including HBCDD
- Polymeric, including brominated polystyrene and a brominated co-polymer of styrene and butadiene
- Inorganics (only includes ammonium bromide)

In the recent LOUS-review, 69 different BFRs were identified to be preregistered under REACH as well as 14 BFRs described in the literature (Lassen, Jensen et al. 2013).

Although BFRs are a highly diverse group of chemical substances, the flame retardancy mechanism is basically the same for all substances.

3.2 Production and use of brominated flame-retardants

The global production of BFR was 575.000 t/y in 2007 and is expected to increase to 595,000 t/y in 2015 (Morgan and Wilkie 2014); elsewhere the global production has been estimated to be far lower (Lassen, Jensen et al. 2013).

The BFRs presently account for approximately 20% of the total consumption of flame-retardants. The increase in production and consumption has primarily taken place in Asia; consequently, the consumption in Asia is presently four times the consumption in Europa. The market for BFRs is dominated by relatively few major global manufacturers and there is at present no production in Denmark (Lassen, Jensen et al. 2013). In Table 1, an overview is presented of the market consumption, by region, for the five most used BFRs.

BFRs are mainly used for electrical and electronic equipment. Other application areas include wiring and power distribution; textiles, carpets and furniture; building materials; means of transportation (vehicles, trains, airplanes, ships, etc.), and paint and coatings.

FR	Market demand (t/y)				
	Americas	Europe	Asia	Rest of the world	Total
C-pentaBDE	7100	150	150	100	7500
C-octaBDE	1500	610	1500	180	3790
C-decaBDE	24500	7600	23000	1050	56100
HBCDD	2800	9500	3900	500	16700
TBBPA	18000	11600	89400	600	119700
Total	53900	29460	117950	2430	203790

TABLE 1
MARKET DEMAND FOR PBDEs AND TWO OTHER MAJOR BROMINATED FLAME-RETARDANTS, BY REGION, IN 2001 (TONNES). BOTH C-pentaBDE AND C-octaBDE HAVE BEEN BANNED IN THE EU SINCE 2004. FROM JULY 2006, UNDER DIRECTIVE 2002/95/EC ALL NEW ELECTRICAL AND ELECTRONIC EQUIPMENT MUST NO LONGER CONTAIN PBBs AND PBDEs (EXCEPT decaBDE) IN CONCENTRATIONS ABOVE 0.1%. IN JULY 2008, AN EXEMPTION OF decaBDE WAS LIFTED (LASSEN, JENSEN ET AL. 2013).

A comprehensive survey of the use of BFR in Denmark was conducted in 1999 (Lassen and Løkke 1999). According to that survey, imported articles containing BFR made up 330-660 tonnes, accounting for approximately 90% of the total content of BFR in end-user products. About 70% of this tonnage was used in electrical and electronic equipment. That is believed to still be the situation today. As most electrical and electronic equipment is produced outside of Denmark, the BFRs in these articles on the Danish market reflect the general use patterns in the EU and globally.

In the Danish industry, the main application of BFRs in 1999 and 2012 was reactive brominated polyols, e.g., halogenated polyetherpolyol B, used for the production of flame-retarded polyurethane foam for building insulation.

3.3 Main BFRs and their use

According to the recent LOUS review, the most common BFRs are decabromodiphenyl ether (decaBDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD).
In the subsequent sections, the use of the main BFRs is outlined with emphasis on the product sectors on the Danish market. Please find references to the original data sources in the LOUS review (Lassen et al., 2013).

3.3.1 Building materials

In the Danish industry, the main application of BFRs in 1999 and 2012 was the use of reactive brominated polyols (e.g. brominated polyetherpolyol) and HBCDD used for production of flame-retarded foam-based articles for building insulation.

BFRs might be used in numerous building products/materials for building industry as specified below:

3.3.1.1 Insulation materials

The main part of HBCDD (90%) are used in the EU as flame-retardant in polystyrene (PS) and expanded PS (EPS) or extruded PS (XPS). According to a REACH Annex XV report for HBCDD, 170,000 tones are used for construction applications. Approximately 90-95% of the 30,000 t/y EPS that are used in Denmark (for all applications) is produced in Denmark while the rest is imported from Germany and Poland (Lassen, Jensen et al. 2013). EPS boards typically contain 0.5% by weight HBCDD in the final product with maximum concentrations of app. 0.7% (INEOS 2014). In EPS, HBCDD is typically used in combination with dicumyl peroxide as a synergist (concentration <0.5%). EPS is produced in a variety of densities and compressive strength providing a range of properties for specific applications. As a consequence, EPS might be used in buildings in a broad variety of applications, including:

- Roofs and ceilings
- Floors
- Walls
- Foundations

XPS is used in the construction industry as rigid thermal insulation for buildings and for road and railway constructions. In XPS produced in Europe, 3% HBCDD is used, whereas 0.5-3% HBCDD is used in XPS produced in Canada (Lassen, Maag et al. 2011).

Since November 2014, HBCDD has been included in Annex A to the Stockholm Convention; consequently, it is expected that the consumption of HBCDD will decrease significantly over the next 5 years although a time-limited exemption has been granted for the use of HBCDD in EPS/XPS for building applications.

Two groups of rigid polyurethane (PUR) are used, termed PIR and PUR. In the PUR foam, isocyanate is reacted with a polyether polyol, whereas a low-cost polyester derived polyol in the PIR foam is used in the reaction. In the PIR foam, the proportion of methylene diphenyl diisocyanate (MDI) is higher than for PUR (nearly by a factor of 2) and the isocyanates polymerize to some extent into polyisocyanurate trimers (hence the name PIR) (Lassen, Maag et al. 2011). Due to the aromatic polyester polyol, the PIR foams have relatively low flammability, low smoke generation and low cost; however, the liberation of toxic HCN is still a problem for PIR with maximum generation of HCN at 500° C to 600° C.

Polyurethane foams (PUR and PIR) have one of the best thermal isolation properties among foamed plastic materials. Furthermore, the insulation capability is stable over a long period and water adsorption is low. Therefore, polyurethane foam is the preferred insulation material in a number of sandwich constructions (e.g., cold stores, refrigerators). PUR/PIR foams are used both as factory-made insulation boards/blocks, as sandwich panels, and as spray insulation foamed directly at the building site. Halogenated polyetherpolyol B, esters of TBBPA (e.g. tetrabromobisphenol A bis(dibromo propyl ether)), bis(2-ethylhexyl)tetrabromo-phthalate (TBPH) and decaBDE may be used as flame-retardants in rigid polyurethane foams (Lassen, Jensen et al. 2013). According to the survey of BFR consumption in Denmark in 1999, 80-120 t/y brominated polyetherpolyol was used for the manufacture of rigid polyurethane foam.

3.3.1.2 Cables

Cables generally contain a substantial amount of inherently flammable polymer materials such as insulation and sheathing. Besides being a potential source of ignition due to electrical faults (e.g. overheating, arcing and short circuits), cables can contribute to the spread of fire because they form an interpenetrated network in modern buildings and can conduct heat via the conductor cores. Consequently, flame-retardants provide an essential function in the cables.

Thermoplastic elastomers and rubber, such as Chlorosulfonated polyethylene (CSM) and chloropene rubber are commonly used for cables sheaths and insulators due to their chemical and physical properties (elasticity, weather resistance and thermal insulation). High loadings of FR may affect their physical properties. As brominated flame-retardants are particularly efficient, they have generally been used. According to EFRA that includes ethane bis (pentabromophenyl) (EBP), ethylene bis(tetrabromophthalimide) (EBTBP), poly(pentabromobenzlyacrylate), and the polymeric poly brominated styrene copolymers, poly brominated styrene homopolymers and tetrabromophthalate esters.

3.3.1.3 Light-weight profiles and composites

Due to their high strength, durability and low-weight, plastic materials and especially reinforced plastic (glass or carbon filled) materials have developed and continue to displace traditional building materials like concrete and bricks. The use of plastic materials in the construction sector has increased due to their enhanced durability and easy maintenance compared to other materials (e.g. wood and metals). Both thermoplastic and thermoset plastic based profiles and composites are manufactured and flame-retardants are needed for many applications.

3.3.1.4 Film and sheets

Film and sheets used in the building and construction sector are made from different materials and they cover a large variety of articles, e.g. (Morgan 2010):

- Protective: building scaffolds, construction films
- Functional: moisture/vapour barrier, adhesive
- Structural: wind barrier, space parathion, roofing sheets
- Decorative: banners, artificial plants/trees

Depending on their final use (residential, public, industrial), film and sheets may be flame retarded and in some cases BFR, e.g., bis(2-ethylhexyl)tetrabromo-phthalate (TBPH) and decaBDE might be used as FRs (EPA 2014).

3.3.2 Electrical and electronic equipment

Electrical and electronic equipment (EEE) is by far the largest application area of BFRs. Currently, the RoHS directive restricts the use of polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in EEE. From July 2006, under Directive 2002/95/EC, all new electrical and electronic equipment must no longer contain PBBs and PBDEs (except decaBDE) in concentrations above 0.1%. In July 2008, an exemption for decaBDE was lifted.

In EEE, BFRs are mainly used in printed wiring boards, components (e.g. connectors), housing/covers and in cables.

3.3.2.1 Printed wiring boards

Almost all electronic equipment contains a printed wiring board. Epoxy resins are widely used as circuit boards for printed wiring boards. Several types of printed wiring boards exist, some being multi-layered and reinforced. TBBPA and derivatives are used as a reactive BFR in the manufacture of epoxy resins and in rigid epoxy-laminated printed wiring boards. In 2011, EFRA member companies sold TBBPA in a range of 1000-2,500 tonnes in Europe according to the 2012 VECAP report (VECAP 2012). Around 90% of that volume was used in printed circuit boards.

3.3.2.2 Electric enclosure

Electronic enclosures primarily include the enclosure of consumer and information technology, e.g., televisions, monitors, desktop and notebook computers and household appliances. These enclosures are made from various types of polymer resins with the main resins being high impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate/ABS blends and polyphenylene ether/HIPS blends. Depending on the application, the enclosures may be flame retarded and a wide range of BFR including HBCDD are used.

3.3.2.3 Electric installations and components

Connectors, switches and other internal parts made from plastic play an essential role in most electrical components. The product groups cover a wide range of applications and consequently numerous plastic types are applied. The type of plastics is governed by the end-use and requirement to the plastic.

3.3.2.4 Wire and cables

Wire and cables are found everywhere in buildings, means of transportation and in electronic and electrical equipment. Wire and cables may contribute to the spread of fire (as explained previously) and therefore, wire and cables are often flame-retarded.

3.3.3 Textiles, carpets and furniture

A survey of the use of flame-retardants in consumer textiles in Denmark has recently been conducted (Andersen, Møller et al. 2014). In the survey, more than 30 Danish companies (producers of furniture, carpets) responded to a questionnaire regarding the use of flame-retardants. No respondent claims to use BFRs in their products. In addition, 15 products (chairs, blankets, mattresses) were analysed and it was found that they did not contain BFRs. However, products from this category are to a large extent imported to Denmark, and thus imported products might contain BFRs even if the 15 products analysed were selected as representative for products on the Danish market. According to literature, various BFRs might be used in textiles. However, the main consumption of BFR is assumed to be for transportation and hotels/public premises in, e.g., carpets and curtains, including:

- DecaBDE to treat a wide range of textiles, including synthetic, blended and natural fibres.
- For use in textiles, HBCDD is formulated into polymer-based dispersions (e.g., acrylic or latex) of variable viscosity, which are then processed in the textile finishing industry. As HBCDD is applied to textiles as a surface coating, it may be released during textile wear and washing. Antimony trioxide is often used as a synergist in combination with HBCDD in the flame retardation of textiles. The typical loading of HBCDD in textile back coatings is 10-25% (United States EPA 2013).

3.3.4 Transportation

It is characteristic for the transport sector that it uses rather complex vehicles such as cars, buses, trains and airplanes. High demand for fire safety is obvious. The vehicles are constructed from a broad variety of components, including EEE, wiring, textiles and various construction materials (e.g., steel and plastic composites).

From the above, it is obvious that some of these components may contain BFRs. Moreover, transportation is often subject to very strict regulations regarding fire safety requirements, which necessitate the use of vast amounts of FRs (and BFRs). According to literature, various BFRs may be applied in the transport sector:

- HBCDD and DecaBDE is used for the treatment of textiles in the transport sector. Moreover, brominated polyols are used for the treatment of polyurethane foam. These foams are mainly used in the transport sector (minor uses are textiles, EEE, insulation foam). C-PentaBDE has previously been used; however, has been banned for use in EU since 2004.
- decaBDE may be used in polyamides (e.g., nylon for injection moulding applications in transport such as wheel covers and handles, chair and seat belt mechanisms), polycarbonate (windows housings in trains and aircrafts, bumpers and headlamps in cars).

3.4 Selection of product groups for screening of alternatives

In the above section, the overall use of BFR was outlined and categorized into four product groups. To narrow down the screening of alternatives, it was decided to include the most important products groups, based on the overall consumption of BFR. The arguments are briefly summarized in the list below:

- EEEs are mainly produced outside of Europe and the use of FRs will mainly be affected by European/international legislation. EEE represents the largest consumption of BFRs and is a major exposure route. Therefore, it was decided to include EEE in the screening of alternatives.
- The above findings indicate that BFRs are only used to a limited degree in consumer textiles, carpets and furniture. Therefore, it was decided to exclude these products used in homes from the screening of alternatives.
- According to the above findings, the main use of BFR in the Danish industry is for building and construction materials. Consequently, it was decided to include building and construction materials in the screening of alternatives.
- The transportation sector is subject to strict regulation regarding flame-retardant safety requirements. Moreover, the “products” are manufactured from a broad variety of components /materials making it difficult to cover in depth. However, the transport sector is important because consumer exposure to BFR is considered to be high and recycling of various vehicles is an important issue, e.g., with a view to ELV 2000 /53/EC[1]. Consequently, the transportation and offshore vessels have been included. However, the screening of alternatives is less thorough with circular references to other listed application areas that are also used in the transport sector.

3.5 Summary of BFR use

According to the recent LOUS review of brominated flame-retardants, the most common BFRs are decabromodiphenyl ether (decaBDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCDD). A comprehensive survey of the use of BFR in 1999, demonstrated that imported articles containing BFR made up 330-660 tonnes, accounting for approximately 90% of the total content of BFR in end-user products in Denmark. About 70% of this tonnage was used in electrical and electronic equipment, 15% building material and 15% transportation. That is still believed to be the situation today. As most electrical and electronic equipment is produced outside of Denmark, the BFRs in these articles on the Danish market reflect the general use patterns in the EU and globally. In Denmark, BFR was used in building materials, EEE and transportation. In the Danish industry, the main application of BFRs in 1999 and 2012 was

[1] End of Life Vehicles Directive

reactive brominated polyols, e.g., halogenated polyetherpolyol B, used for the production of flame-retarded polyurethane foam for building insulation.

3.6 Cost of substituting BFRs with non-halogenated flame-retardants

This survey illustrates that alternative non-halogenated flame-retardants, appertaining polymer systems and production set-ups are already developed and available on the market for a majority of the identified product types.

Accurate cost estimations must be company-specific because the impact of substituting chemicals on complex product formulations is difficult to determine. Substituting chemicals can involve significant costs, as industries must adapt their production processes, and products and materials must be re-tested for all required performance and product standards. These tests are expensive, and according to PINFA, they might be a barrier to the substitution of BFR. Consequently, the most promising substitution will often be for newly designed products where the non-halogenated flame-retardants can be taken into consideration already in the design phase.

It is very difficult to make a price index for the non-halogenated flame-retardants compared to the brominated flame-retardants, because non-halogenated flame-retardants are very diverse substances (organic/inorganic) and available from a large number of suppliers. Moreover, flame-retardants are often used in combinations and the amount needed for fire protection differs according to the polymer and specific application.

Flame-retardants that either are more expensive per pound or require more flame-retardant to meet the fire safety standards will make the raw material costs increase. For some types of non-halogenated flame-retardants, e.g., mineral fillers, more flame-retardant is needed to meet the same fire safety standard. On the other hand, some of the phosphorous based flame-retardants are more expensive than the brominated flame-retardants. It must be stressed that while some of the assessed alternative flame-retardants included in this survey are currently manufactured in high volume, not all are currently available in quantities that would allow their immediate widespread use. Consequently, prices and availability may change if demand increases.

According to PINFA, the cost of using non-brominated flame-retardants is not significantly different for most product types. For EEE the materials with non-halogenated FRs are generally 10-30% more expensive than materials with brominated flame-retardants representing 1-5% of the finished product (Lassen, Jensen et al. 2013). The price of halogen-free alternatives to BFR-containing ABS e.g. ABS/PC blends is comparable to the price of non-halogenated flame retarded ABS on the market, but some 20-30 % higher than the cheapest ABS compounds with BFR; and the price of halogen-free grades of polyamide is basically the same as bromine containing grades (Lassen, Leisewitz et al. 2006).

3.7 Cost of substituting inherently flammable material or applying design-based solutions

Another way to achieve adequate fire performance is to use an inherently flame retardant material or to protect the flammable material with physical and thermal barriers, e.g., coatings and layer technologies, heat sinks, etc. The latter includes fire-resistive construction used for non-flame retarded EPS see section 5.1.2.1. However, for many applications these types of construction are not applicable for many purposes and the cost is very complex to deduce.

Substituting inherently flammable material is for some applications a technical and economical solution. In section 5.1.2, alternatives to flame retarded EPS and EXS was assessed. It was found that mineral wool and EPS are interchangeable for many applications. For cavity walls, lofts and pitched roof insulation, mineral wool typically has the same price or is less expensive than EPS. In

Table 2, a summary of the relative cost levels for the described alternatives to flame retarded EPS is presented, based on the findings from Lassen, Maage et al.

Technical solution	Price of functional unit compared to EPS*
Stone wool	0/10-30%
PIR/PUR	0/>30%
Wood fibre insulation boards	10-30%/>30%

***FUNCTIONAL UNIT: INSULATION THICKNESS WHICH PROVIDES THE SAME THERMAL RESISTANCE AS 10 CENTIMETRES OF EPS COVERED OUTER WALL INSULATION**

TABLE 2

SUMMARY OF COST OF ASSESSED INSULATION MATERIALS

4. Regulations and standards

This report has its primary focus around standards that affect the Danish society (developers/producers, contractors and consumers), regarding fire safety within some of the biggest segments of the entire industry affected by fire safety requirements: construction products, transportation and electrical appliances. A key purpose of this section is to create a bird-view of the relevant standards (and their content), which affect the above mentioned stakeholders. The section has been divided into subsection in order to make it easier to navigate between specific points of interest throughout the document.

4.1 Introduction

Many of the regulations and standards within the product areas in this survey that apply in Denmark are elaborated in detail below. It should be noted that the regulations and standards can have both regional and international origin, thus many of the regulations and standards that apply in Denmark are regulated by the European Union or other international communities. Standards are one of the key elements to secure a general optimization and efficiency in the society. The following is based on a well-defined description of standards, which is developed by Danish Standard (DS).

The official definition of a standard:

"A Document for all stakeholders which can be repeatedly used, that indicate regulations, guidance and specific characteristics in curtain activities from the results therefrom. The document is established with consensus and approval by a recognized organ. The intension of the document is to achieve optimal order for a specific purpose"

Standards are developed nationally, regionally and internationally, however it is noted that some specific companies have developed their own standards (not necessarily in relation to fire safety), which may be stricter than required by for example the European directives. IKEA and DELL are examples of companies who have created their own standards for their products amongst many others.

Standards are typically developed by technical committees with representatives from the industry who are part of a larger standardization organisation, such as for example ISO or CEN.
As seen in figure 1**Fejl! Henvisningskilde ikke fundet.** there different types of standards in relation to fire safety. One of them is standards for testing and the other is standards for classification. Both of them are needed in order to obtain a product classification, which is then used in the national regulations.

This document has its main focus around fire safety, where the standards play a key role. Regulations have determined a fire safety level, which is to be followed. Some are performance based (such as the Danish building regulations 2010, BR10) and others are prescriptive (such as Safety of Life at Sea, SOLAS). The performance based code in Denmark does not contain any specific requirements (which are measureable), instead it is stating that an adequate fire safety level has to be achieved. The prescriptive code (SOLAS) on the other hand lists specific requirements to each product and they have to comply with those requirements in all cases. The standards are the basis of documentation that is required when ensuring a sufficient fire safety level. Products can be classified through testing and held up against a classification system.

Figure 1 shows the three primary sectors (construction, electric and transport), each sector is linked to one or more standardization organizations. The figure is valid for Denmark/Europe, but the principles are similar in most countries around the world. For example the United States would have exchange CENELEC under electrical appliances with UL, which are two different organizations.

All official standards are published by the respective organizations and they are all available for purchase in both hard copy and electronic versions. The standards are continuously updated with different intervals of typically around every three to five years.

The standards used for testing include a variety of different testing methods, where a wide range of different parameters are obtained. The parameters include lateral flame spread, afterglow, burning droplets, smoke production and many more. The parameters are then held up against the acceptable values, which are typically given in the standards for classification.

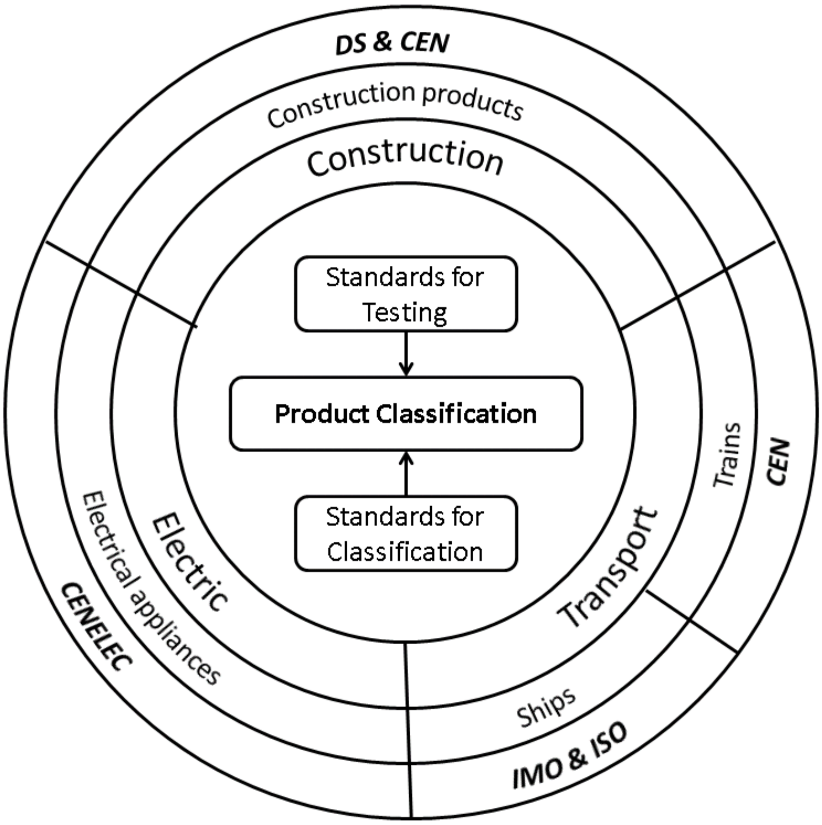

FIGURE 1: STANDARDS AND PRODUCT CLASSIFICATION IN THREE INDIVIDUAL SECTORS.

CEN (www.cen.eu)
The technical requirements to products which are given in the European standards are defined by the European Committee for Standardization (CEN) and European Committee for Electrotechnical Standards (CENELEC). The main purpose of the standards is to break down potential technical barriers that could block an open trade between European countries.

National standardization bodies that are part of CEN are obliged to implement the European standards (EN). Therefore, one European standard becomes the national standard in 33 different European countries.

CEN also develop Technical Specifications (TS), which are normative documents. These documents are not equivalent to European Standards and conflicts between technical specifications and national standards are allowed.

IEC (www.iec.ch)
Within the electrical field the International Electrotechnical Commission (IEC) has developed standards for the electrical market, in order to remove trade barriers.

ISO (www.iso.org)
All other technical fields are covered by the International Organization of Standardization (ISO). The aim of ISO is to promote the worldwide development of standards in order to eliminate trade barriers and to encourage cooperation in intellectual, scientific and economic activities. The members of the ISO Committees are the national standard organizations.

DS (www.ds.dk)
Danish Standard (DS) is the Danish organization of standardization. As the other standard organizations, DS is aiming at breaking down trade barriers, however DS has its main focus around the Danish interests.

IMO (SOLAS)
Safety on off shore vessels is regulated by Safety of Life at Sea (SOLAS), which is an international convention. SOLAS is divided into subchapters in the same manner as the Danish building regulations (BR10). Fire safety is covered in chapter II-2, which includes fire safety precautions for all ships. Furthermore specific requirements for passenger ships, freighters and tankers are also included. Some of the requirements for ships are regards to:

- Fire sections
- Use of combustibles materials
- Fire detection
- Escape routes
- Accessibility for fire fighting

Regulation 17 was introduced in chapter II-2 in year 2000. The supplement allows deviation from the prescriptive requirements in SOLAS given that the overall fire safety is secured by other means. It is required that the alternative solution is documented (performance based design).

UL (www.ul.com)
Underwriters Laboratories (UL) is an American global safety science organization. Basically the principles are the same as for the other standard organizations, however UL is primarily a safety organization and therefore also of great interest in relation to fire retardants.

Each country has its own regulation and that means that there are deviations in the requirements the countries in between. One of the biggest differences between Denmark and other countries is found within insulation materials in buildings. In Denmark all materials of a wall (e.g. brick, insulation material, concrete) have to live up to the requirements given individually, which means the all of the materials have to obtain a specific classification in individual testing. However in other countries it is allowed to test the entire wall as a unified system.

Another good example is the very strict regulations in the United Kingdom, where all furniture has to be treated with fire retardants before they can approved for the British market. In Denmark there are no requirements of usage of fire retardants in furniture.

4.2 Building materials and inventory

The use of combustible materials in buildings underlies the restrictions dictated by the national building code (Bygningsreglement 2010). The regulation is performance based with no specific requirements. However it is supported with a guidance of how to reach an adequate fire safety level (Eksempelsamling om brandsikring af byggeri, 2012), which is based on classification standards. Products have to comply with the regulations, thus testing of building materials is required. This section covers some of the most common construction products and their coherence with the standards.

4.2.1 Textiles

There are no fire requirements for clothing textiles unless the clothes are designed for protection against fire. Nor are there any requirements to furniture in buildings according to the Danish building regulation. However, some building types will introduce requirements to the floorings (carpets), which are elaborated in section 4.2.6 below. It should be noted that buildings, such as hotels or other building types with public premises, that are subjected to operational regulations[2] issued by the Danish fire brigade could potentially be met with some requirements to the textiles used in the building, such as curtains. Thus, the requirements are dependent on number of occupants and usage. For further elaboration, see statutory order on operations of hotels, education premises etc. (Bekendtgørelse om driftsmæssige forskrifter for hoteller m.v., plejeinstitutioner, forsamlingslokaler, undervisningslokaler, daginstitutioner og butikker. 2008).

Furthermore it is noted that requirements to textiles (and furniture) in general are very common in other countries, such as in the United Kingdom and in the transportation sector, including trains and off shore vessels, which elaborated in section 4.4 and 4.3.

4.2.2 Insulation material in buildings

According to the Danish building regulation 2010 (BR10) part 5.1 buildings generally must be built in a manner that satisfy the requirements for adequate protection against fire and fire spread. Examples of fire protection in buildings ("Eksempelsamling om brandsikring af byggeri, 2012" EBB12) part 3.2 suggests that insulation material, which has a material class equal or better than the B-s1,d0 class (according to EN13501-1, see more below) in general should be used. However, there are a number of examples of exceptions to where a material class worse than B-s1,d0 is applicable within certain building types and specific areas, that is for example in family homes or if the insulations material is covered with a fire safe construction (for example EI 60 A2-s1,d0). Thus, insulation material with high fire hazard is not entirely excluded from use in buildings. It should be noted that there are no requirements specifying the use of chemical retardants in any insulation products.

4.2.3 Walls and ceilings

Products that are used for wall- and ceiling surfaces are allocated a classification, which is obtained through material testing according to EN13501-1 – Fire classification of construction products and building elements – Part 1: Classification using data from reaction to fire tests. There are primarily three different material classifications that are commonly used in Denmark, that is A2-s1,d0; B-s1,d0 and D-s2,d2, see Table 1.

[2] Statutory order on operations of hotels, education premises etc. (Bekendtgørelse om driftsmæssige forskrifter for hoteller m.v., plejeinstitutioner, forsamlingslokaler, undervisningslokaler, daginstitutioner og butikker. 2008).

Classification	Primary class	Secondary class: Smoke development	Secondary class: Burning droplets
A2-s1,d0	**A2** Building components with extremely limited contribution to fire. The classification is allocated with a subclass that specifies the specific material properties in relation to smoke (s) and droplets (d). **EN ISO 1716 (alternatively. EN ISO 1182):** EN ISO 1716 is most commonly used and the standard specifies a method to determine the gross heat of combustion. **EN13823:** Lateral Flame Spread (LFS) to the edge of the specimen is not allowed. $FIGRA_{0,2MJ} \leq 120$ W/s $THR_{600s} \leq 7{,}5$ MJ	**s1:** Very limited amount of smoke development **EN13823:** SMOGRA ≤ 30 m^2/s^2 and $TSP_{600s} \leq 200$ m^2	**d0:** **EN13823:** No burning droplets or particles within the first 600 s
B-s1,d0	**B** Building components with very limited contribution to fire. The classification is allocated with a subclass that specifies the specific material properties in relation to smoke (s) and droplets (d). **EN ISO 11925-2:** Flame exposure to the surface for 30 s of duration cannot lead to vertical flame spread that exceeds 150 mm from the starting point within the first 60 s. **EN 13823:** Lateral Flame Spread (LFS) to the edge of the specimen is not allowed. $FIGRA_{0,2MJ} \leq 120$ W/s $THR_{600s} \leq 7{,}5$ MJ	**s1:** Very limited amount of smoke development. **EN 13823:** SMOGRA ≤ 30 m^2/s^2 $TSP_{600s} \leq 200$ m^2	**d0:** **EN 13823:** No burning droplets or particles within the first 600 s
D-s2,d2	**D** Building components with some contribution to fire are allowed. The classification is allocated with a subclass that specifies the specific material properties in relation to smoke (s) and droplets (d). **EN ISO 11925-2:** Flame exposure to the surface for 30 s of duration cannot lead to vertical flame spread that exceeds 150 mm from the starting point within the first 60 s. **EN13823:** $FIGRA_{0,4MJ} \leq 750$ W/s	**s2:** Limited amount of smoke development. **EN13823:** SMOGRA ≤ 180 m^2/s^2 and $TSP_{600s} \leq 200$ m^2	**d2:** **EN13823:** No restrictions to the amount of burning droplets or particles

Note: FIGRA = Fire Growth Rate, SMOGRA = Smoke Growth Rate, THR = Total Heat Release, TSP = Total Smoke Production.

TABLE 1
TYPICAL CLASSIFICATIONS USED IN DENMARK WITH RESPECTIVE PRIMARY CLASS AND SECONDARY CLASSES.

4.2.4 Coverings

A covering is the outer most part of a wall and/or ceiling construction. The covering is allocated to one of two primary covering classes according to the classification standard EN1350-1:

- Covering class K_1 10 (for regular coverings)
- Covering class K_2 10/30/60 (fire protection systems by fire protection materials)

Both regular coverings and fire protection systems are allocated with a sub-classification, which is depending on the material that is used in the system, see table 2. Denmark operates with two sub covering classes for regular coverings and three sub covering classes for fire protection systems see table 2. It is noticed that a fire protection system cannot contribute to the fire for either 10, 30 or 60 minutes, whereas the covering class k_1 to some extend can.

Covering	Remark
K_1 10 B-s1,d0 [Class 1 covering]	Covering that protects the underlying material for at least 10 min and furthermore is based on materials that meet the corresponding classification requirements in table 1.
K_1 10 D-s2,d2 [Class 2 covering]	Covering that protects the underlying material for at least 10 min and furthermore is based on materials that meet the corresponding classification requirements in table 1.
K_2 10 A2-s1,d0 [10 minutes fire protection system]	Fire protection system that protects the underlying material for at least 10 min and furthermore is based on materials that meet the corresponding classification requirements in table 1.
K_2 30 A2-s1,d0 [30 minutes fire protection system]	Fire protection system that protects the underlying material for at least 30 min and furthermore is based on materials that meet the corresponding classification requirements in table 1.
K_2 60 A2-s1,d0 [60 minutes fire protection system]	Fire protection system that protects the underlying material for at least 60 min and furthermore is based on materials that meet the corresponding classification requirements in table 1.

TABLE 2
TYPICAL COVERING CLASSES AND FIRE PROTECTION SYSTEMS USED IN DENMARK.

K_1 and K_2 coverings are required to be tested according to EN 14135, in which the test conditions and the criteria for the different classes are given. Performance requirements for both covering classes with and without underlying cavity are listed in table 3 and table 4. Note that the substrate is the material being tested.

Covering	Specification requirements	Remark
K_1	During the test the mean temperature measured on the lower side of the substrate shall not exceed the initial temperature by more than 250 °C and the maximum temperature measured at any point of this side shall not exceed the initial temperature by more than 270 °C. After the test there shall be no burnt material, charred material, melted material or shrunk material at any point of the substrate.	Any covering shall be tested on the specific substrate unless the substrate has a density of at least 300 kg/m³. Then the test can be performed on a chipboard with a density of (680 ± 50) kg/m³ and a thickness of (19 ± 2) mm. It is always a possibility to carry out the test on the specific substrate.
K_2	During the test the mean temperature measured on the lower side of the substrate shall not exceed the initial temperature by more than 250 °C and the maximum temperature measured at any point of this side shall not exceed the initial temperature by more than 270 °C. After the test there shall be no burnt material or charred material at any point of the substrate.	The test shall be performed on a chipboard with a density of (680 ± 50) kg/m³ and a thickness of (19 ± 2) mm. It is always a possibility to carry out the test on the specific substrate.

TABLE 3
COVERINGSCLASS AND FIRE PROTECTION SYSTEM WITHOUT UNDERLYING CAVITY

Covering	Specification requirements	Remark
K_1	During the test the mean temperature measured on the lower side of the substrate *and the mean temperature measured on the unexposed side of the covering* shall not exceed the initial temperature by more the 250 °C and the maximum temperature measured at any point of this side shall not exceed the initial temperature by more than 270 °C. After the test there shall be no burnt material, charred material, melted material or shrunk material at any point of the substrate *or at any point of the unexposed side of the covering*.	Any covering shall be tested on the specific substrate unless the substrate has a density of at least 300 kg/m³. Then the test can be performed on a chipboard with a density of (680 ± 50) kg/m³ and a thickness of (19 ± 2) mm. It is always a possibility to carry out the test on the specific substrate.
K_2	During the test the mean temperature measured on the lower side of the substrate *and the mean temperature measured on the unexposed side of the covering* shall not exceed the initial temperature by more than 250 °C and the maximum temperature measured at any point of this side shall not exceed the initial temperature by more than 270 °C. After the test there shall be no burnt material or charred material at any point of the substrate *or at any point of the unexposed side of the covering*.	The test shall be performed on a chipboard with a density of (680 ± 50) kg/m³ and a thickness of (19 ± 2) mm. It is always a possibility to carry out the test on the specific substrate.

TABLE 4
COVERINGSCLASS AND FIRE PROTECTION SYSTEM WITH UNDERLYING CAVITY

4.2.5 Roof coverings

Roof coverings are divided into classes in a European classification system according the European standard DS/EN 13501-5: *"Fire classification of construction products and building elements – Part 5: Classification using data from external fire exposure to roof tests"*.

In Denmark there is primarily a distinction between whether a roof covering has obtained the classification BROOF (t2) or not. The roof coverings are tested according to the method given in DS/CEN/TS 1187:2012 where two wind scenarios (2 and 4 m/s) are analysed. The classification BROOF (t2) is obtained when:

1. The mean damage length of the roof covering and substrate is less than 550 mm measured from the center of the burning crib.
2. The maximum damage length of the roof covering and substrate is less than 800 mm measured from the center of the burning crib.

4.2.6 Floorings

Floorings are divided into classes in a European classification system according the European standard DS/EN EN13501-1 – Fire classification of construction products and building elements – Part 1: Classification using data from reaction to fire tests. According to the exemplified practice in Denmark (Eksempelsamling om brandsikring af byggeri. 2012) there is typically a distinguish between either no demand or a class D_{fl}-s1 flooring. A product applying for class D_{fl} has to be tested in accordance with EN ISO 9239-1 and EN ISO 11925-2 with 15 s exposure time. In order to obtain the classification D_{fl} the following criteria must be satisfied:

- Under condition of surface flame attack with 15 s exposure time, there shall be no flame spread in excess of 150 mm vertically from the point of application of the test flame within 20 s from the time of application
- Critical heat flux ≥ 3,0 kW/m^2

Class D_{fl}-s1 flooring is only required in usage category 3 (e.g. rooms with many persons who do not know the escape routes in the building) and in escape routes. See 4.2.3 for a description of both fire class D and sub-class s1.

4.3 Off shore vessels

The use of combustible materials on ships underlie the restrictions dictated by the International Convention for the Safety of Life at Sea (SOLAS 1974), which is directly related to the International Code for Application of Fire Test Procedures (2010 FTP Code (resolution MSC.[3]307(88)). The code covers all larger ships in international waters and is signed by most countries, hereunder Denmark at the SOLAS convention in 1948. The FTP Code provides requirements for the following tests of interest in relation to fire retardants:

- Test procedure for non-combustibility
- Test procedure for smoke and toxicity
- Test procedure for surface flammability (all surface material, including paint and primary deck coverings)
- Test procedure for vertically supported textiles and films
- Test procedure for upholstered furniture
- Test procedure for bedding components

The following elaborates the content of the above mentioned test procedures and parts of it is extracted from the 2010 FTP code (resolution MSC.307 (88)).

[3] MSC: Maritime Safety Committee, which is a part of the International Maritime Organization.

4.3.1 Test procedure and criteria for non-combustibility

The test (EN 1716 and ISO 1182) provides a method for evaluating the non-combustibility of a product. This test has been adopted in the 2010 FTP Code, thus they have not created their own test procedure for non-combustibility.

A product is classified as non-combustible if the following criteria are satisfied:

- The average furnace thermocouple temperature rise does not exceed 30 °C
- The average specimen surface thermocouple temperature rise does not exceed 30 °C
- The average duration of sustained flaming does not exceed 10 s.
- The average mass loss does not exceed 50%

Materials that are classified as non-combustible according to (EN 1716 or ISO 1182) can be used in any application without further requirements to the fire safety performance.

4.3.2 Test procedure for smoke and toxicity

The test is described in 210 FTP Code Annex 1 part 2 and provides methods for evaluating the development of smoke and toxicity of products in the event of fire. Part 2 is always carried out in correlation with part 5. That is unless the following products with the following results have been obtained (based on 2010 FTP CODE Annex 1: Part 5, 2.7):

"Surface materials and primary deck coverings with both the total heat release (Q_t) of not more than 0.2 KJ and the peak heat release rate (Q_p) of not more than 1.0 kW (both values determined in accordance with part 5 of annex 1) are considered to comply with the requirements of part 2 of annex 1 without further testing."

	Classification criteria for smoke
1	For materials used as surface of bulkheads, linings or ceilings, the D_m shall not exceed 200 in any condition.
2	For materials used as primary deck coverings, the D_m shall not exceed 400 in any condition.
3	For materials used as floor coverings, the D_m shall not exceed 500 in any condition.
4	For plastic pipes, the D_m shall not exceed 400 in any condition.

Note: An average (D_m) of the maximum specific optical density of smoke ($D_{s\,max}$) of three tests, see 2010 FTP Code Annex 1 part 2: 2.4.1.

TABLE 5
CLASSIFICATION CRITERIA FOR SMOKE ACCORDING TO THE SMOKE AND TOXICITY TEST GIVEN IN THE 2010 FTP CODE.

Gas component	Reference concentration [ppm]
NO_x	350
CO	1.450
HF	600
HCL	600
HBr	600
HCN	140
SO_2	120 (200 for floor coverings)
Note: The average value of the maximum value of the gas concentration measured, see 2010 FTP Code Annex 1 part 2: 2.4.2.	

TABLE 6
CLASSIFICATION CRITERIA FOR TOXICITY ACCORDING TO THE SMOKE AND TOXICITY TEST GIVEN IN THE 2010 FTP CODE.

4.3.3 Test procedure and criteria for surface flammability (surface material and primary deck coverings)

The test provides methods for evaluating flammability characteristics of 155 mm x 800 mm specimens in vertical orientation.

The specimens are exposed to a graded radiant heat flux field supplied by a gas-fired radiant panel. Means are provided for observing the times to ignition, spread and extinguishment of flame along the length of the specimen as well as measuring the compensated millivolt signal of the stack gas thermocouples as the burning progresses. Experimental results are reported in terms of:

- heat for sustained burning
- critical heat flux at extinguishment
- heat release of specimen during burning
- Amount of burning droplets

The surface flammability criteria are given in the table below. Material having average values for all the surface flammability criteria that comply with the values in the table below, are considered to meet the requirement for low flame spread in compliance with the relevant regulations in chapter II-2 of the convention, which is the chapter regarding fire safety in SOLAS.

	Bulkhead, wall and ceiling linings	Floor coverings	Primary deck coverings
CFE [kW/m²]	≥ 20.0	≥ 7.0	≥ 7.0
Q_{sb} [MJ/m²]	≥ 1.5	≥ 0.25	≥ 0.25
Q_t [MJ]	≤ 0.7	≤ 2.0	≤ 2.0
Q_p [kW]	≤ 4.0	≤ 10.0	≤ 10.0
Burning droplets	Not produced	No more than 10 burning drops	Not produced
Note: CFE = Critical Flux of Extinguishment, Q_{sb} = Heat sustained burning, Q_t = Total heat release, Q_p = Peak heat release rate			

TABLE 7
SURFACE FLAMMABILITY CRITERIA FOR: BULKHEAD, WALL AND CEILING LININGS, FLOOR COVERINGS AND PRIMARY DECK COVERINGS [FROM 2010 FTP CODE].

It is noted that the only difference between the primary deck coverings and the regular floor coverings is that a maximum of 10 burning droplets are allowed for regular floor coverings.

4.3.4 Test procedure and criteria for vertically supported textiles and films

In general it has been decided that drapes, curtains and other textile materials are required to have qualities of resistance to flame propagation, not inferior to those of wool (0.8 kg/m^2].

At least 10 specimens measuring 220 mm x 170 mm must be tested, five in each perpendicular direction of the fabric.

Products which show one or several of the following characteristics obtained by the fire test specified in the 2010 FTP Code part 7 shall be considered unsuitable for use as curtains, draperies or free hanging fabric product for use in rooms containing furniture and furnishings of restricted fire risk as defined in the relevant regulations of chapter II-2 of the convention (SOLAS):

- An after-flame time greater than 5 sec. for any of the 10 or more specimens tested with a surface application of the pilot flame.
- Burn through to any edge of any of the 10 or more specimens tested with a surface application of the pilot flame.
- Ignition of cotton wool below the specimen in any of the 10 or more specimens tested.
- An average char length in excess of 150 mm observed in any of the batches of five specimens tested by either surface or edge ignition.
- The occurrence of a surface flash propagating more than 100 mm from the point of ignition with or without charring of the base fabric.

4.3.5 Test procedure and criteria for upholstered furniture

In the 2010 FTP Code part 8 it is stated that the test procedure prescribes methods for examining the ignitability, in defined circumstances, of an assembly of upholstered materials. These materials are combined together in a way intended to be generally representative of their end use in upholstered seating, and ignition sources are a smouldering cigarette and a flame representing a burning match. Corresponding performance criteria are given in the table below.

Test	Performance criteria
Smouldering cigarette [2010FTP Code, Part 8, 7.2]	A successful result is obtained when the cigarette test has been carried out twice with no observation of progressive smouldering or flaming within a period of 60 min. Unless the test piece fails the final examination (see below)
Propane flame [2010FTP Code, Part 8, 7.3]	A successful result is obtained when the propane flame test has been carried out twice with no observation of progressive smouldering or flaming 120 s after the burner tube has been removed. Unless the test piece fails the final examination (see below)
The final examination	A final examination is required if the above tests are successful. Immediately after completion of the test the assembly must be dismantled and examined for internal progressive smouldering. If any sign of internal progressive smouldering is observed the test fails.

TABLE 8
MOST IMPORTANT TESTS AND PERFORMANCE CRITERIA FOR UPHOLSTERED FURNITURE

4.3.6 Test procedure and criteria for bedding components

Bedding components are tested similarly to upholstered furniture – with a cigarette test and a propane flame test. Specific test procedures and fail criteria can be found in the 2010 FTP Code part 9. However the criteria differentiate a little from one another.

4.4 Trains

Fire safety on trains is covered by the standard EN 45545-x, which was updated thoroughly in 2013. The standard must be given the status of a national standard, either by publication of an identical text or by endorsement. Potentially conflicting national standards must be withdrawn by 2016.

All railway vehicles are assigned a Fire Hazard Level (HL) according to EN 45545-2 (from 2013), which is determined from the operation category and the design category according to table 10 and table 11.

The operation category ranges from 1-4 and is dependent on the design of tracks of where the train is operating (underground section or elevated structures) and the evacuation strategy (immediate evacuation, evacuation at next station or other suitable stopping point). It should be noted that if a vehicle is operating in more than one operation category, or changes its services, it shall fulfil the requirements of all the relevant operation categories.

The design category is dependent on the type of vehicle and is classified as given in table 10.

Design category	Description
A	Automatic vehicles having no emergency trained staff on board
D	Double decked vehicles
S	Sleeping and couchette cars
N	All other vehicles

TABLE 10
DESIGN CATEGORIES AND THEIR DESCRIPTION [FROM EN45545-1].

Fire Hazard Levels				
Operation category	**Design category**			
	N	**A**	**D**	**S**
1	HL 1	HL 1	HL 1	HL 2
2	HL 2	HL 2	HL 2	HL 2
3	HL 2	HL 2	HL 2	HL 3

TABEL 11
FIRE HAZARD LEVELS DETERMINED FROM THE OPERATIONAL CATEGORY AND THE DESIGN CATEGORY [FROM EN45545-1].

It is noticeable that almost all products used in trains have to be tested for toxic fumes (both the specific listed products and the non-listed products). The gas components of interest and there reference concentration is given in table 11 below.

4.4.1 Requirements to listed products

EN 45545-2 presents a variety of common products that are used in railway vehicles. Each product is assigned with a reference to a specific requirement, which again is elaborated in another table.

Example:

1. The fire hazard level is determined.
2. The specific listed product is located (in EN 45545-2) and the requirement is noted.
3. The requirement is located (in EN 45545-2) and the testing methods and criteria are determined in relation to the fire hazard level.

Item No	Name	Description	Requirement
IN5	Driver's desk	Panelling and surfaces of the drivers desk	R1

TABLE 31
EXAMPLE OF DETERMINATION OF THE REQUIREMENT TO A SPECIFIC PRODUCT

Requirement	Method: Condition parameters	HL1	HL2	HL3
R1	ISO 5658-2 CFE [kWm^{-2}] *(Critical Flux at Extinguishment)*	20	20	20
R1	ISO 5660-1: 50 kWm^{-2}	-	90	60
R1	ISO 5659-2: 50 kWm^{-2} CIT at 4 and 8 min	1,2	0,9	0,75
R1	See all requirements in EN 45545-2	...	...	...

TABLE 42
EXAMPLE OF DETERMINATION OF THE SPECIFIC CRITICAL VALUES OF A PRODUCT IN ITS REQUIRED TEST

4.4.2 Requirements to non- listed products

Non-listed products have to be tested according to the following table according to EN45545-2.

Exposed area	Location	Requirement
> 0.20 m²	Interior	R1
> 0.20 m²	Exterior	R7
≤ 0.20 m²	Interior	R22
≤ 0.20 m²	Exterior	R23

TABLE 53
REFERENCES TO SPECIFIC REQUIREMENTS TO NON-LISTED PRODUCTS

Toxic fume requirements to all products used in trains are defined in term of Conventional Index of Toxicity (CIT). According to EN45545-2 the following 8 gas components shall be analysed:

Gas component	Reference concentration [mg/m3]
CO_2	72000
CO	1380
HF	25
HCL	75
HBr	99
HCN	55
SO_2	262
NO_2	38

TABLE 64
GASCOMPONENTS LISTED AS TOXIC FUMES AND THEIR REFERENCE CONCENTRATIONS

The CIT for specific listed products are given as:

$$CIT = 0.0805 \cdot \sum_{i=1}^{i=8} \left(\frac{c_i}{C_i}\right)$$

Where,
c_i = concentration of the ith gas in the chamber [mg/m3]
C_i = reference concentration of the ith gas [mg/m3]
i = the gas components in the table above

The calculated CIT value must not exceed the maximum CIT value specified in the requirements given in 4.4.1, which is dependent on the fire hazard level.

Products used in trains are also tested in relation to their smoke production. The testing method is the same as the one used for off shore vessel, which is based on EN ISO 5659-2.

4.5 Electrical appliances

Regular electrical appliances in homes such as TV-sets, dvd-players, etc. are regulated by "Sikkerhedsstyrelsen" in Denmark, which is based on the European/International standard EN/IEC 60065. The standard describes a series of different test methods which evolves from the American standard UL94. The classification system is elaborated in table 15 and performance criteria in table 16 below.

In general there are three different tests for regular products – two vertical burning tests and one horizontal burning test. The required classification criteria (and test method) is individually determined dependent on the specific product.

Classification	Test method
UL94(V-0) **UL94(V-1)** **UL94(V-2)**	Five specimens of 127 mm x 12.7 mm are derived from the product of interest and tested individually of each other. The specimen is placed 305 mm above a sheet of cotton supported by a metal mesh. The flame (19 mm) is applied for 10 sec and it is noted for how long the test specimen continues burning. Immediately after self-extinguishing the procedure is carried out one more time.
UL94(V-5)	Five specimens of 127 mm x 12.7 mm are derived from the product of interest and tested individually of each other. The flame (127 mm) is applied for 5 s and removed for 5 s (repeated five times) and it is noted for how long the test specimen continues burning/after glowing.
UL94(HB)	Three specimens of 127 mm x 12.7 mm are derived from the product of interest and tested individually of each other. The flame (25 mm) is applied for 30 s and it is noted for how long the test specimen continues burning. After extinguishing of the flame it is noted how much of the specimen that has been burned.

TABLE 75
UNDERWRITERS LABORATORIES (UL) CLASSIFICATION AND TESTING METHOD FOR ELECTRICAL PRODUCTS

Classification	Performance criteria
UL94(V-0)	• None of the five test specimens must burn for more than 10 s when the flame is removed. • The total burning time of the 10 ignition test must not exceed a total of 50 s. • No test specimen must burn with a flame or afterglow to the clamp that holds the specimen. • No burning droplets must ignite the cotton underneath the test specimen. • The afterglow time must not exceed 30 s. in any of the tests.
UL94(V-1)	• None of the five test specimens must burn for more than 30 s after the flame has been removed. • The total burning time of the 10 ignition tests must not exceed a total of 250 s. • No test specimen must burn with a flame or afterglow to the clamp that holds the specimen. • No burning droplets must ignite the cotton underneath the test specimen. • The afterglow time must not exceed 60 s in any of the tests.
UL94(V-2)	• None of the five test specimens must burn for more than 30 s when the flame is removed. • The total burning time of the 10 ignition test must not exceed a total of 250 s. • No test specimen must burn with a flame or afterglow to the clamp that holds the specimen. • Burning droplets ignites the cotton underneath the test specimen. • The afterglow time must not exceed 60 s. in any of the tests.

UL94(V-5)	• None of the five test specimens must burn for more than 60 s after the fifth ignition. • No droplets from the test specimen	
UL94(HB)	• The speed of burning does not exceed 38.1 mm per minute when the test specimen thickness is 3.05-12.7 mm. **OR** • The speed of burning does not exceed (76.2 mm per minute when the thickness of the specimen is less than 3.05 mm. **OR** • Burning finishes before the flame reaches the 100 mm reference mark.	

TABLE 86
UNDERWRITERS LABORATORIES (UL) CLASSIFICATION AND PERFORMANCE CRITERIA FOR ELECTRICAL PRODUCTS

4.6 Discussion and conclusion

Without standards, it would be impossible to compare products and the properties to each other. Like most other countries in the world, Denmark uses a classification system based on standards in especially the construction sector. Each country has its own national standards (which in some cases are identical to the European/International standards), but the European Union are working towards a unified standardization in all of Europe and they have already come a long way. However, there are still a lot of differences in the European countries in between and it should be remembered that this report has focused primarily on the Danish regulations.

Danish regulations specify demands to the fire behaviour properties of materials used in the building sector and electrical appliances (which are also applicable in EU). However, there are not any requirements to furniture or clothing (unless it is clothing specifically design to withstand fire) for the consumer market. Regulations in Denmark do not require any use of fire retardants (FR) but in many cases it is impossible to achieve the necessary fire safety properties without the use of FR. Thus, FR is basically a necessity in every electronic product due to the very strict regulation, which is primarily based on the American standard UL94.

Insulation products used in construction are divided into either combustible or non-combustible materials. By introducing FR in combustible insulation products, the fire performance properties can be improved, which allow a wider use of the specific product. This is also the case for coverings (both inside and outside of a building), where FR could improve the fire performance properties of a building material that would not be able to pass the fire performance criteria on its own. Thus FR enables the use of a wider range of products.

The transportation sector is regulated by international standards/conventions, which has been implemented in Denmark (given status as a national standard). Off shore vessels are regulated by SOLAS (Safety of Life at Sea), which is an international convention. SOLAS offers very strict requirements to all products on board and the use of FR in the sector is inevitable, as the requirements also extend to bedding components and other furniture.

Components and fixtures used in trains such as panelling and surfaces of the driver's desk are tested according to the European standard (EN45545), which also offers strict requirements that makes the use of FR a necessity. However the requirements for trains are more differentiated than those for offshore vessels, as there are three different hazard levels (HL), which are dependent on four different operational categories and four different design categories. Thus, the fire safety level varies between the three hazard levels.

Finally it can be concluded that standards are a necessity in order to secure an economical, reliable and uniform system that is beneficial to all countries. Therefore it is also essential that all standards are continuously updated, which most of them also are to a large extent.

5. Screening of alternatives – building materials

Building and construction materials have to meet a number of performance requirements, including fire protection and material properties. Modern buildings are commonly constructed using a large variety of materials and some may be flame retarded using BFR (see section 3.3.1). In the subsequent sections, alternative flame-retardants are assessed for each of the product groups. An examination of non-halogenated flame-retardants for textiles can be found in section 7.5.

5.1 Insulation materials – EPS and XPS

The main brominated flame retardant used for expanded polystyrene (EPS) and extruded polystyrene (XPS) is HBCDD. In this section, a number of alternatives to HBCDD flame retarded EPS and XPS is outlined. The identified alternatives have been divided into two categories:

- Alternative substances to HBCDD as a flame retardant in EPS and XPS
- Alternative to EPS and XPS as an insulation material

5.1.1 Alternative substances to HBCDD

HBCDD has been included in Annex A to the Stockholm Convention (exemption has been granted for the use of HBCDD in EPS/XPS for building application). HBCDD is subject to authorisation under REACH and there is a sunset date in 2015 after which HBCDD must not be used at all unless authorisation is given; consequently, the manufacturers of EPS and XPS may be forced to substitute HBCDD in the future.

The compatibility of the flame-retardant with EPS and XPS is essential for the function. Consequently, the alternative substances must be compatible and not affect the key properties of EPS and XPS, in particular the insulation properties. Furthermore, the flame-retardant must thermally decompose before EPS/XPS and have low migration rates in EPS/XPS to sustain the flame retardancy of the material.

5.1.1.1 Non-halogenated

According to a research programme carried out by Plastic Europe, brominated substances are the only present possibility, because other FRs are known to not provide adequate fire retardancy at concentrations that do not affect EPS properties or are not compatible with the EPS manufacturing process or the EPS material (INEOS 2014).

A similar conclusion was reached by ECHA in 2008 (ECHA 2008), reporting that, at present, no suitable FR is available to replace HBCDD in XPS or EPS (alternative BFRs have been introduced recently as described below). In addition, the association PINFA states in their latest brochure “The high flammability of polystyrene materials cannot yet be satisfactory overcome with PIN FR’s”, which are Phosphorous, Inorganic and Nitrogen Flame Retardants (Morgan 2010).

5.1.1.2 BFR

Trials have been undertaken by a number of EPS producers to substitute HBCDD with a brominated co-polymer of styrene and butadiene (CAS 1195978-93-8). The trials indicate that the substances could be technically and potentially economically feasible (INEOS 2014). The brominated polymer has been developed by Dow Chemical Company and is now being manufactured under license by the manufacturers that currently supply HBCDD. According to Dow, the brominated polymer is stable and not a persistent, bio accumulative toxic substance (as opposed to HBCDD).

5.1.2 Alternatives to flame retarded polystyrene

A number of alternative building insulation materials may be used in place of the flame retarded EPS and XPS. In the figure below, the application areas for different insulation materials according to the German standard DIN V 4108-10 are presented.

Table 3.3 Application areas for different insulation materials according to the German standard DIN V 4108-10 (after GDI, 2007)

Application area	Mineral wool	EPS	XPS	PUR	Wood wool
Pitched roof					
On the rafter	•	•	•	•	•
Between the rafter	•	•	-	•	-
Below the rafter	•	•	•	•	•
Flat roof					
Sloping roof	•	•	-	•	-
Green roof	only DAA *	only DAA *	•	only DAA*	-
Parking deck	-	only DAA * a)	• a)	only DAA *a)	-
Roof terrace	-	only DAA*	•	only DAA*	-
Steel profile tin roof	•	•	only DAA	•	-
Ceiling/floor					
Top ceiling - walkable	b)	b)	•	b)	•
Top ceiling - not walkable	•	•	Only DI **	•	•
Basement ceiling	•	•	•	•	•
Floor - below screed without requirements for footfall noise reduction	•	•	•	•	•
Floor - below screed with footfall noise requirements	•	•	-	-	-
Industry floors	-	•	•	•	•
Walls					
Internal insulation	•	•	•	•	•
Cavity insulation	•	•	•	•	
ETICS (external thermal insulation composite systems)	c)	c)	-	c)	c)
Base insulation – thermal bridge insulation	•	•	•	•	•
Ventilated façades	•	•	•	•	•
Wood and timber frame building	•	•	-	•	•
House partition walls with requirements for noise reduction	•	c)	-	-	-
Room partitioning wall	•	-	-	-	•
Perimeter					
Floor batt against the ground	-	c), d)	• d)	c)	-
Wall against the ground	-	c)	• e)	c)	-

* Only for roofs where the insulation is under seal which protect against the weather (DAA) – not for inverted roofs where the insulation is not protected (DUK).

** Only for internal insulation of the ceiling (the underside) or the roof, insulation at rafter / support structure, suspended ceilings, etc (DI)

a) Insulation must meet the requirements regarding static/dynamic compressive strength/pressure resistance. Manufacturer's instructions must be observed.

b) Additional load-distributing layer required.

c) Regulated by general approvals by the building authorities

d) Additional general approvals by the building authorities regarding weight-carrying foundation slabs.

e) Additional general approvals by the building authorities when used in water under pressure.

Original includes also abbreviations on application type and data on multi—layered wood wool boards.

IMAGE 1
APPLICATION AREAS FOR DIFFERENT INSULATION MATERIALS ACCORDING TO THE GERMAN STANDARD DIN V 4108-10. (LASSEN, MAAG ET AL. 2011). DIN: DEUTCHES INSTITUT FÜR NORMUNG. GDI: GOTTLIEB DUTTWEILER INSTITUT. WOOD WOOL BOARDS MENTIONED IN THE IMAGE ARE OF THE RELATIVELY ROUGH, HEAVY TYPE WITH CONCRETE OR MAGNESITE BINDER. THESE DIFFER FROM THE WOOD FIBRE BOARDS THAT ARE DESCRIBED IN THE SUBSEQUENT SECTION.

As seen in the above figure, the insulation materials are interchangeable for most of the applications. However, the combination of low weight and effect of moisture on the insulation value and mechanical properties makes EPS and XPS advantageous for some types of application, e.g., applications where the insulation material is in direct contact with the ground (perimeter insulation). However, for some of these applications EPS or XPS is commonly placed between a concrete slab and the insulation materials are well concealed from fire exposure. For these purposes, there is no reason to use FR (see section 5.1.2.1). Moreover, it must be noticed that some of the other insulation materials also might contain brominated flame-retardants or other “problematic” substances (see section 5.1.2.3).

In terms of market volume, the major insulation materials apart from EPS/XPS are mineral wool, fibre glass wool and PUR. In addition, a number of other insulation materials may be used. In the sections below, the other insulation materials and techniques are briefly described.

5.1.2.1 Fire-resistive constructions

Non-flame retarded EPS may be used when thermal barriers are applied (preventing the EPS from catching fire). A commonly used construction is as ground or floor insulation below a concrete layer; however, walls and other more open constructions may also be made with non-flame retarded EPS if thermal barriers, such as bricks, concrete, plasterboards, metal sheets, are applied (Lassen, Maag et al. 2011).

5.1.2.2 Inorganic wool and natural fibres

It is technically feasible for end-users to replace EPS/XPS with wool products in many building applications. Four different types of inorganic wool are commonly used, namely stone, minerals and slag. Over the past decade, stone wool and slag wool have together met just over half of the world’s demand for insulation (Lassen, Maag et al. 2011). These insulation materials are inherently inflammable, and consequently little or no flame-retardants are needed. Moreover, wood fibre insulation boards, made from, e.g., wood fibre, flax, hemp or cellulose/paper are marketed for use in most normal building applications where EPS is used - often flame-retarded with inorganic salts.

5.1.2.3 Foam

For insulation in buildings, PIR foams takes up the majority of the market.

PUR and PIR foam can be used in several ways:

- As a spray insulation, foamed directly on the building site
- Factory-made insulation blocks/boards
- In combination with rigid facings as a constructional material or sandwich panel

Both materials may emit toxic fumes if burnt and the manufacturing process involves the use of isocyanates (persistent material) (INEOS 2014). The PUR/PIR foams share some of the key properties of EPS in terms of density and water resistance; consequently, the PIR/PUR foams are applicable for most of the applications where EPS and XPS have a significant market share. However, it must be noted that PUR/PIR foams may be flame retarded by using brominated flame-retardants, e.g., reactive brominated polyols.

Phenolic foams have been used for structural applications for more than two decades, and they share some of the same material properties as EPS. Therefore, phenolic foams are applicable for most of the applications where EPS and XPS have a significant market share; however, due to higher prices the market for phenolic foams is smaller. BFR may be applied as a flame-retardant.

5.1.3 Summary

Table 9 lists the chemical and technical substitutions for EPS and XPS fire retarded with HBCDD. In section 3.7, a cost assessment is presented of technical substitutions for EPS and XPS fire retarded with HBCDD.

Alternative	Applications	Comment
Fire-resistive construction	Used when thermal barriers are applied	
Inorganic wool and natural fibres	Technically and economically feasible in many applications. Not applicable for perimeter applications	Most inorganic wool is inherently inflammable; therefore, no FR is needed. Natural fibres are commonly fire-retarded using inorganic salts.
Foam	Applicable for most of the applications	Polyurethane and phenolic foams may contain halogenated flame-retardants.
Brominated co-polymer of styrene and butadiene	Technically feasible and potentially economically feasible	According to manufacturer the brominated polymer is stable and not a persistent, bioaccumulative, toxic substances

TABLE 9
TECHNICAL AND CHEMICAL SUBSITUTIONS FOR EPS AND XPS FIRE-RETARDED WITH HBCDD

5.2 Insulation material – polyurethane

In order to pass various fire standards, flame-retardants must be added to polyurethane foams. However, the addition of FR must not have an impact on the curing process, the shelf-life, or the mechanical and insulation properties of the polyurethane product. Tris(chloroisopropyl) phosphate is the principal FR used in rigid PUR foams (Weil and Levchik 2009). However, the flame-retardant requirements can be fulfilled by several different halogen-free flame-retardants.

Liquid phosphorous flame-retardants are the most commonly used. Dimethyl methylphosphonate has been used for many years, but has been withdrawn from the market due to mutagenic concerns (Morgan and Wilkie 2014). However, a number of different liquid phosphorous flame-retardants, e.g. triethyl phosphate, diethyl ethyl phosphonate, dimethyl propyl phosphonate and cresyl diphenyl phosphate are available for polyurethane. Although the polyurethane industry prefers liquid FR, due to handling, the use of solid FR, e.g. expandable graphite and ammonium polyphosphate, is sometimes a more economical way to achieve flame retardancy. Usually triethyl phosphate or some other low viscosity liquid FR is used in combination with solid FR to improve processability. There is some market interest in reactive flame-retardants (such as the reaction product of diethyl phosphite, formaldehyde and diethanlamine), especially in roofing applications in hot environments.

The non-halogenated FR for polyurethane can be classified into three groups:

- Additive liquid FR, e.g., triethyl phosphate. Incorporated into the foam formulary and not chemically bond to the polymer backbone. Can impact the mechanical properties because it acts as a plasticizer.
- Reactive liquid FR. Incorporated into the polymer chain and becomes part of the polymer backbone. Can impact the curing of the polyurethane foam.
- Solid flame-retardants (filler), e.g., expandable graphite and ammonium polyphosphate. Can impact the physical and insulation properties.

5.3 Cables

Non-brominated flame-retardants are already used in a wide range of base polymers, including halogen-free and halogenated polymers (e.g., PVC).

PVC (poly-vinyl-chloride) is still the most important polymeric material used for cables. Antimony trioxide (ATO) is a very effective flame-retardant for flexible PVC when ignitability and flame propagation are considered because it acts synergistically with the chlorine in PVC. However, PVC cables containing ATO release significantly more black smoke than non-flame retardant PVC cables, and ATO has a critical environment and health profile (Morgan 2010). Therefore, modern low smoke flame retardants (LSFR) PVC compound have been developed by incorporating metal hydrate flame-retardants (e.g., magnesium dihydroxide and aluminium trihydroxide). In addition, zinc hydroxystannates and zinc borates are often used as synergistic flame-retardants. Moreover, phosphorous flame-retardants such as aryl phosphates (e.g., tricresyl phosphate) and aryl alkyl phosphates (e.g., 2-ethylhexyl diphenyl phosphate) may be used to reduce the flammability of the polymers. Besides flame-retardant PVC and LSFR PVC the above-mentioned FR may also be used in chlorinated rubber like chloroprene and CSM (Morgan 2010). Table 10 summarizes relevant non-halogenated flame-retardants for PVC and other halogenated base polymers used for cables.

Flame retardant	Fire suppression function
Aluminium trihydroxide **and** **magnesium dihydrooxide**	Decompose during fire: - releasing water - absorbing energy - creating an oxide layer absorbing soot particles and HCl
Zinc-borates	Smoke suppressant in the condensed phase by forming a glass-like char
Zinc hydroxystannates	Acts both in the condensed and gas phase
Aryl phosphates **and** **Aryl alkyl phosphates**	Reduce flammability of polymer

TABLE 10
NON-HALOGENATED FLAME-RETARDANTS USED IN PVC COMPOUNDS AND OTHER HALOGENATED POLYMERS FOR CABLES.

A number of halogen-free flame retardant or low-smoke free-of-halogen polymer compound can be used as an alternative to halogenated polymers. The most frequently used compounds by volume used for halogen-free flame-retardant wire and cables are based on blends of EVA and LLPDE using aluminium trihydoxide as the sole flame-retardant filler (loadings app. 60-65%). The use of low-smoke free-of-halogen polymer compound for cables in Europe has been widespread since the 1980s (ANXIER 2012), and especially in the transportation sector where the protection of people and equipment from toxic and corrosive gas is critical.

Whenever special requirements are required, concerning abrasion and chemical or temperature resistance (e.g., lifts and photovoltaic modules), thermoset type and thermoplastic compounds can be used. Elastomers based on EPDM or EVM are commonly applied with 50-60% aluminium trihydorxide. Sometimes zinc borates are applied as a flame-retardant synergist and inherent mineral filler. Finally, non-halogenated FR like melamine derivates (i.e., salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid), organic phosphates (e.g., aryl phosphates), phosphinates (e.g., aluminium phosphinates) and metal hydrates (e.g., aluminium trihydroxide and magnesium dihydorxide) are used in different ratios for thermoplastic materials like TPU. Table 11 summarizes relevant non-halogenated flame-retardants for halogen-free wire and cable compounds.

Flame-retardant	Working function	Polymer
Aluminium trihydroxide **and** **magnesium dihydroxide**	Decompose during fire: - releasing water - absorbing energy - creating an oxide layer	**Polyolefins** - LDPE -EVA **Elastomers** - EPDM -TPU
Zinc-borates	Smoke suppressant in the condensed phase by forming a glass-like char	**Elastomers** - EPDM -TPU
Phosphorous flame-retardants	Reducing flammability	Used in fire-resistant coatings for cables, polyolefins and polyprpolylene
Ammonium polyphosphates **Polyphosphonates** **Metal phosphinates** **Aryl phosphates** **Melamine derivates**	Char formation prevents heat transfer (intumescent products)	**Elastomers** TPE TPU Thermoplastic polyesters

TABLE 11
NON-HALOGENATED FLAME-RETARDANTS FOR HALOGEN-FREE CABLES AND WIRES

5.4 Profiles, composites, film and sheets

For the majority of thick films (e.g., protection), the polymer can be flame-retarded using non-halogenated flame-retardants. However, mineral fillers are used at high concentration reducing the physical and mechanical properties of the materials. Similarly, intumescent systems by nature require a certain thickness to develop an effective char. Consequently, non-BFR solutions are still lacking for thin film. Profiles, composites, film and sheets are used for versatile applications and are therefore manufactured using different polymer materials and flame-retardants. An overview is presented in the text below and summarized in Table 12.

Polycarbonate and blends of polycarbonate and ABS are used for sheets as well as profiles. The oligomer phosphonates and diphosphates (e.g., RDP and BDP) are preferred for use in PC and PC/ABS blends because of a lower tendency to juicing at high temperature (Weil and Levchik 2009). For the same reason, aromatic phosphate esters have limited use in polycarbonate. Using a commercially available diphospahtes give a UL 94 V-0 rating (the highest fire safety rating in the Underwriters Laboratory classification; see chapter 4) in PC at 9% loading. Several patents indicate that diphosphates may be most useful in combination with silicone compounds.

Moreover, polycarbonates can be flame-retarded with very low levels (<1%) of various sulphonate salt, which today is widely used by a number of manufacturers. Especially, potassium salts of diphenyl sulphone mono- and disulphonates have proven very efficient and applicable (Weil and Levchik 2009).

Unsaturated polyester is used for the manufacturing of various types of sheets, including mould, facing. Aluminium trihydroxide is used as filler in unsaturated thermosetting resins, such as polyester. The use of triethyl phosphate and dimethyl metylphosphonate (DMPP) as low liquid additives for ATH (aluminium trihydroxide)-filled polyester resins have been commercially available for decades. Similarly, melamine derivates or combinations of melamine derivates with ATH have been used as flame and smoke inhibitors in polyester resins.

Polyolefins such as polyethylene, polypropylene and copolymers with vinyl monomers such as vinyl acetate may be used for both thin films and rigid sheets. Several none-halogenated flame-retardants may be used including mineral fillers such as aluminium trihydroxide and magnesium dihydroxide. The flame-retardant performance of the mineral filler can be synergized by zinc borate. In addition, numerous intumescent phosphorous-based additive systems, including melamine polyphosphate and a combination of ammonium polyphosphate with a char-forming nitrogenous resin are commercially available.

In addition to substituting the type of flame retardant, it is possible to substitute from an inherently flammable polymeric material to a less flammable material for some applications. For instance, metal profiles might be used instead of plastic for some applications, e.g., cable trays.

Material	Application	Possible non-halogenated FR
Flexible PVC	Tarpaulins	Phosphate esters, zinc borate, aluminium trihydroxide
Rigid PVC	Profiles (windows, doors, trim)	
PC and blends, ABS	Sheets: Roofing, glazing, lighting Profiles: trim	Oligomeric phosphates and diphosphates, silicone compounds, potassium perfluorobutane sulphonate (KPBS), potassium diphenyl sulphone sulphonate (KSS)
Unsaturated polyester	Sheets (mould, facing)	Aluminium trihydroxide, melamine and melamine derivates, DMPP, cyclic phosphonate, phosphonate oligomers (transparent applications)
Polyolefins (PE, PP, EVA)	Thin films: roofing underlay, vapour barrier, scaffold sheeting, etc.	Alkyl phosphonates, hypophosphite salts
Polyolefins (HDPE, PP)	Rigid sheets: Aluminium composites panels, building scaffolds (walkways) Pipes and cable trays	ATH, MDH, melamine polyphosphate
TPU	Thin film: roofing underlay	Alkyl phosphonates, polyphosphonates, phosphate esters
Copolyesters, copolyamides	Breathing film: roofing underlay	Polyphosphonates, metal phosphinate

TABLE 12
NON-HALOGENNATED FLAME-RETARDANTS FOR PROFILES, COMPOSITES, AND FILM OF POLYMERIC MATERIAL

6. Screening of alternatives – electrical equipment

In addition to governmental and international restrictions on the use of certain flame-retardants, a large number (more than 25 worldwide) of eco-labels have been introduced as voluntary measures in order to promote environmentally friendly products. According to PINFA, some eco-labels have prohibited the use of halogenated flame-retardants in their criteria for electronic products. Some of the Nordic Ecolabelling product groups address all brominated flame-retardants as a whole in the criteria, while other in the Nordic system and the EU-Ecolabel criteria focus on specific brominated flame-retardants or brominated flame-retardants assigned specific risk phrases.

Moreover, the electronics organization HDPUG (high-density packaging user group) has developed a guideline for halogen free alternatives for electronic equipment.

Due to the increasing focus on BFR - both through legalization and through eco-label systems – a number of original equipment manufacturers (OEMs) have developed plans for phasing out BFR. An overview of stated objectives and timelines for various electronics OEMs based on the availability of suitable alternatives are presented in the Image 2. Most of the timelines have already been exceeded; however, it is unknown how many of the commitments have been fulfilled.

In section 3.6, the costs related to the substitution of BFRs with non-halogenated flame-retardants have been assessed.

halogen specification	PVC		Br, Cl and their compounds	
OEM	**specification**	**timeline**	**specification**	**timeline**
Nokia	not intentionally added		Br < 900 ppm, Cl < 900 ppm	all products by 2008
Sony-Ericsson	banned	exclusion by end of 2006	Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	all new products by end of 2006
Lenovo	banned (> 25 g part)	new product from 2009		all products from 2009
Dell	not intentionally added (> 25g part)		Br < 900 ppm, Cl < 900 ppm	all products from 2009
LG	< 100 ppm	begin phase out in 2008; exclusion from all products 2010	Br < 900 ppm, total halogen < 1500 ppm	all products from 2010
Sony	banned (FFC and package)			
Samsung	banned (package)			all mobile phone products from 2010
Toshiba	not intentionally added	begin phase out 2009		begin 2009
Wistron			Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	begin 2008 3Q
Apple	not intentionally added (> 25 g part)		Br < 900 ppm, Cl < 900 ppm, Br+Cl < 1500 ppm	all products by the end of 2008
HP	Cl < 900 ppm	all new computing products from 2009	Br < 900 ppm	all new computing products from 2009
Intel	1000 ppm (reporting threshold only)		not intentionally added	

IMAGE 2
HALOGEN-FREE COMMITMENTS AND TIMELINES FOR VARIOUS ELECTRONICS OEMS BASED ON THE AVAILABILITY OF SUITABLE ALTERNATIVES (DÖRING, DIEDERICHS ET AL. 2010). IT IS UNKNOWN IF THE CONCENTRATION IS CALCULATED ACCORDING TO THE WEIGHT OF THE COMPONENT OR THE TOTAL WEIGHT OF THE PRODUCT. MOST OF THE TIMELINES HAVE ALREADY BEEN EXCEEDED; HOWEVER, IT IS UNKNOWN HOW MANY OF THE COMMITMENTS HAVE BEEN FULFILLED.

6.1 Printed wiring boards

Almost all electronic items contain a printed wiring board and most materials used for printed wiring boards need a flame-retardant to fulfil the common fire safety classifications. Commonly, epoxy resins are used as circuit boards in printed wiring boards; however, epoxy resins are also used elsewhere in electronics.

Several types of printed wiring boards exist; designated FR-1, FR-2, FR-3 and so on. The FR-4 is predominant (epoxy resin with glass reinforcement). TBBPA is used in an estimated 95% of all FR-4 epoxy wiring boards (Weil and Levchik 2009). Flexible printed circuit boards are used for computer peripherals and mobile devices such as cell phones. The flexible printed circuits are made from epoxy, polyurethane, polyamide, polyester or acrylic resin and usually contain polymeric brominated FR, e.g., brominated epoxy or phenoxy resins (Döring, Diederichs et al. 2010).

Several companies have announced the use of halogen-free materials. Lower glass transition temperatures (less stiffness), lower drillability and increased costs, remain problems for non-halogen FR-4 printed wiring boards (Weil and Levchik 2009). However, there are a number of reactive nitrogen and phosphorous compounds and additive inorganic alternatives (mainly aluminium trihydroxide) that are used commercially as alternatives to non-halogen flame-retardants in epoxy resins instead of TBBPA.

6.1.1 Substitution of resin polymer

Substituting the resin polymer with a base material, such as epoxy-novolac resins, with higher thermal resistance makes it easier to achieve the technical requirements with non-brominated flame-retardants. Such formulations are available and have been proposed for sealing as well as for printed wiring boards. By using the modified epoxy resin, printed wiring boards can be made with similar properties and costs according to Hitachi Chemical and Motorola. Similarly, Sony has used a high heat resistant high-char-forming epoxy resin with a mineral filler to produce a halogen-free flame retardant for printed wiring boards (Weil and Levchik 2009).

6.1.2 Non-reactive flame-retardants

Metal hydroxides, such as aluminium trihydroxide and metal phosphinates/polyphosphates may be used (Döring, Diederichs et al. 2010). However, it has been challenging to reach a sufficient level for FR-4 without sacrificing the physical properties of the material (thermal stability, copper adhesion). Especially in Japan, high loads of ATH and in some cases magnesium oxide have been used, but problems in the laminating process may occur. Hitachi chemical has developed special grades of ATH with improved thermal stability achieved by special crystallization, and a bialkylsilane treatment has been developed showing promising results. Furthermore, the combination of red phosphorous and mineral filler has also turned out to be very efficient (Weil and Levchik 2009).

In addition, metal phosphinates might be used for printed wiring boards. However, in order to reach American Underwriters Laboratories UL94 V0 classification, nitrogen-synergist such as melamine polyphosphate is required (Döring, Diederichs et al. 2010).

6.1.3 Reactive flame-retardants

A large number of patent and non-patent citations, both industrial and academic, are found for various reactive phosphorous compounds in epoxy resin. Especially dihydrooxaphosphaphenanthrene (DOPO) has been well-studied and is marketed by several manufacturers for use in epoxy resins. According to PINFA, DOPO can be regarded as the major building block used to make phosphorous containing epoxy resins with an increasing global capacity (Döring, Diederichs et al. 2010). A commercial FR, based on a phosphorous and melamine structure, is claimed to have physical properties identical to the standard FR-4 made with TBBPA. Similarly, a commercial high %P aromatic phosphonate oligomer has been developed. The FR is commonly used in combinations with ATH and AOH (Weil and Levchik 2009).

6.2 Electric enclosures

Electric enclosures must fulfil a number of requirements, such as processability, thermal, mechanical and hydrolytic stability and fire safety standards. Moreover, the polymer resin must be recyclable and must comply with legislation (RoHS and WEEE directives). Enclosures made from PC/ABS and PPE/HIPS blends can fulfil the requirements using a number of aromatic phosphate esters, e.g., triphenyl phosphate (TPP), resorcinol bis-(diphenyl phosphate) (RDP), bisphenol A bis-(dephenyl phosphate) (BDP) and resorcinol bis(2,6-dixylenyl phosphate) (RDX) (Weil and Levchik 2009; Döring, Diederichs et al. 2010). The required loadings depend on the types of polymer and composition (ratios), but typically they vary between 8-15% in PC/ABS blends including an anti-dripping agent typically <0.5%. The oligomeric phosphates or diphosphates (e.g. RDP and BDP) are preferred for use in PC/ABS blends because of a lower tendency to migration at high temperatures

(Weil and Levchik 2009). However, non-halogen flame-retardants for pure HIPS remain a challenge.

6.3 Electric installations and components

Electrical installations and components are made from numerous types and blends of polymer; however, polyamides are often used. A large number of different FRs may be used for flame retarded polyamides; they have been summarized in Table 13.

Various salts of dialkylphosphinic acids are commercially available. Aluminium diethylphosphinate, is the leading member of the phosphinate flame-retardant group and can be used in 15-18% to reach the American Underwriters Laboratories rating UL94 V-0 in polyamide. Nitrogen synergists, such as melamine polyphosphate, are highly effective with phosphinate salts (Weil and Levchik 2009). Moreover, zinc borate may be used in combination with aluminium diethylphosphinate and melamine polyphosphate (Morgan and Wilkie 2014). Magnesium hydroxide can successfully be used to flame retard polyamide (polyamide 6) to a V-0 rating. However, a loading of 60% is needed for glass-filled polyamides, which makes the plastic difficult to process. Magnesium hydroxide is only used for polyamide with low loading of glass.

Ratings of V-0 can be obtained at 5-10 % melamine cyanurate in unreinforced polyamide (Morgan and Wilkie 2014) and up to 20% for V2 in low-glass filled polyamide. Moreover, melamine polyphosphate has proven especially suited for glass-fibre reinforced polyamide 66 (Weil and Levchik 2009).

FR	Polymer	Content	Remark
Metal phosphinates	Glass-fibre reinforced polyamide Glass-fibre polyester	Up to 20%	Often combined with N-synergists
Melamine polyphosphate	Glass-fibre reinforced polyamides	App. 25%	Used as synergists with phosphorous FR
Melamine cyanurate	Un-reinforced polyamide 66 Unfilled polyamide 6 Mineral-filled polyamide	5-10% (UL 94 V-0) 5-10% (UL 94 V-0) 13-16% (UL 94 V-0)	Used as synergists with phosphorous FR. Difficult to reach V-0 in glass filled polyamide
Red phosphorus	Glass-fibre reinforced polyamides	5-8% (UL 94 V-0)	Limited to red and black plastic. Handling and safety issues; consequently, FR is stabilized and coated
Aryl phosphates/phosphonates	PC/ABS blends	10-20%	
Magnesium hydroxide	(low) Glass-fibre reinforced polyamides	60% (UL 94 V-0)	Plastic difficult to process and stiff.
Ammonium polyphosphate	Polyolefins	20-30%	Often combined with N-synergists

TABLE 13
OVERVIEW OF POSSIBLE NON-BFR FOR ELECTRIC ENCLOSURES.

6.4 Wire and cables

In section 5.3, alternatives to BFR in wire and cables used for building and construction were assessed. The underlying principles for wire and cables in EEE are not very different, and therefore it has not been further elaborated in this section.

6.5 Sensor technologies for electronic and electrical equipment

It is well-known that flame-retardants are used to prevent a fire in the early stages. If the fire evolves, e.g. an explosive fire, the flame-retardants are ineffective. Therefore, an alternative approach is to develop technologies that detect and stop the fire at the earliest stage by interrupting the power supply to the object and thus preventing fire. Below, a number of existing or emerging technologies are listed:

- Sensor technology will be able to register a heat increase in electric appliances. Temperature rise might be the first sign of failure in a circuit and thus constitute a risk to the occurrence of fire.
- Nanotechnology based coating can be designed to release nano-sized particles at defined conditions. Similarly, sensors capable of detecting the released particles are being developed. Presently, DTU Nanotech is working on research projects aiming to develop sensors with semi-porous/thin films, which can measure emission from surfaces.
- Artificial noses can be calibrated to recognize odours from known components. Surfaces can be designed to release certain odours under certain conditions.

7. Screeing of alternatives – transport and off-shore vessels

Transportation vehicles and off-shore vessels are manufactured from a large variety of components. Many of these components have been examined previously in this report. Consequently, the screening of alternatives for transportation and off-shore vessels is less thorough with circular references to previous sections.

7.1 Introduction

Many examples exist of catastrophic fires in cars, buses, trains, airplanes and off-shore vessels in the past. This is why a number of fire safety requirements exist for these vehicles. Generally, the risk is related to the ease of escape from the vehicle in case of fire. That is why the fire safety demands increase from cars to bus, to train, to ship and to airplane. However, it should be stressed that fire in cars often is a result of a car crash due to an accident, which also makes it difficult for the passengers to escape from the fire.

As vehicle interiors mainly are made of plastic and textiles, which burn easily, it is necessary to prevent these materials from burning by using flame-retardants.

In a fire, plastics and textiles can release toxic volatile substances such as HCN, NOX and CO, but in a fire the halogenated flame-retardants can also liberate toxic fumes such as HCl and HBr that generate white smoke in the presence of water vapour. It is very important to avoid that, as the passengers must orient themselves and find the exit. Therefore, mineral FRs are commonly used due to depression of heavy smoke.

Other considerations are the end-of-life for vehicles. It is important that the materials can be recycled into new products, and therefore toxic substances and substances harmful to the environment in the plastics and textiles in the vehicles should be avoided.

It is important that the flame-retardants that are applied are safe in use and do not prevent recycling of the materials.

This issue can best be solved by using non-halogenated flame-retardants in the transport sector.

The same is the case for off-shore vessels where the avoidance of fire is of utmost importance as both gas and oil very easily can be ignited in a fire with a catastrophic result.

Transportation and off-shore vessels are very complex, and the various “products” are manufactured from a broad variety of components/materials. In the below text, an overview is given of the type of plastic and textiles that are used for vehicles, and which type of none-halogenated flame-retardants may be applied. The overview is based on a recently published brochure from PINFA (Döring, Bykov et al. 2010).

7.2 Electrical and electronic equipment

Modern individual, public and goods transport vehicles all contain electrical and electronic devices. Depending on the type of vehicle, this includes:

- Electrical installations and components, e.g.:
  - Connectors
  - Switches and switchgears
- Electrical devices and circuit boards, e.g.:
  - Safety (airbags, ABS, collision avoidance)
  - Comfort (climate, noise and suspension control)
  - Convenience (steering, navigation, information and communication)
  - Performance (engine/emission control)
- Housing materials

The application of none-halogenated flame-retardants in electrical and electronic equipment has been covered in chapter 6.

7.3 Cables

Cables are used for transmitting energy and growing amounts of data, and modern transportation is unthinkable without cables. For instance, the typical passenger car contained 45 m of cables in 1955 and today a car has up to 1,500-5,000 m of cables (Döring, Bykov et al. 2010). Depending on the use cable in a vehicle, different standards have to be complied with, and the materials have to be chosen according to mechanical and thermal stress during installation and service life (including distance to engine and exposure to different media such as oil, acid). For instance, cables for trains have to comply with severe standards for fire resistance and low smoke development, see section 4.4. For this reason, higher amounts of mineral FR (e.g. aluminium trihydroxide) are normally used compared to cables for the automotive industry. Consequently, the choice of polymer and type of flame-retardant depend on the application, for instance different types of polymeric materials are used if the cable is stationary or none-stationary (e.g., exposed to torsion forces). However, the type and use of non-halogenated flame-retardants do not differ much from cables used in the construction sector. These cables have been covered in section 5.3.

7.4 Interior parts

Interior parts used for transport applications are very complex products and include visible items, such as flooring, celling and sidewalls as well as items that are not visible to passengers such as ducting and insulation. During the last decades, plastic has revolutionized the interior design of most transport vehicles. Plastic materials are durable and flexible, enabling the manufacturing of single-piece and lightweight components. Many different types of polymeric materials are used. In the table below an overview of some of the main types of interior parts with their corresponding suitable polymers are listed. Please note that the same polymeric materials are used across different product groups, e.g., electronic equipment and building materials.

Application	Polymer	Info on none-halogenated flame-retardants
Ceilings, sidewalls, panels, and other structural parts	PVC	Section 5.3 5.4
	Polyolefins	Section 5.3, 5.4, 6.3
	Elastomers	Section 5.3
Dashboards, instruments, chairs, console parts, air ducts and other interior devices	PC	Section 6.2, 6.3
	ABS and PC/ABS	Section 5.3 5.4 6.2 6.3
	TPU	Section 5.3 5.4
	TPE	Section 5.4
	Polyamide	Section 6.3
	Polyolefins	Section 5.3, 5.4, 6.3
Insulation	PUR and PIR	Section 5.2

TABLE 14
INTERIOR PARTS FOR TRANSPORTATION AND TYPE OF POLYMER AND POSSIBLE USE OF NON-BFR (CROSSREFERENCE)

7.5 Textiles

Textiles and fabrics can be described as flexible materials consisting of a network of fibres. Textiles may be made of homogeneous fibres or blends and can be of different origin (animal, vegetal, mineral or synthetic). Textiles are used in a variety of ways in different vehicles, e.g.:

- Seat covers
- Insulation
- Carpets/floor covers
- Belts
- Curtains
- Airbags
- Wall coverings

Moreover, textiles are also used for other applications, such as interiors and for the building and construction sector.

There are no fire requirements for clothing textiles and furniture in buildings according to the Danish building regulation; however, when used for vehicles they are often flame-retarded. Flame-retarding textiles are fairly complex, and include both non-durable treatment and durable treatment. In the durable treatment, FR is chemically bound (cross-linking) to the polymer and in the non-durable treatment FR is deposited on the surface. The non-durable treatment is not resistant to washing, whereas the durable FR treatment can be retained after a minimum of 50 washing cycles. A list of non-halogenated flame-retardants used in transportation textiles according to the sector group PINFA is presented in Image 3 (Döring, Bykov et al. 2010).

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
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

IMAGE 3
NON-HALOGENATED FLAME RETARDANT SYSTEMS FOR TEXTILE APPLICATIONS IN TRANSPORTATION. IN BACK-COATING THE FR IS APPLIED ON THE BACKING OF THE MATERIAL, E.G. IN CARPETS.

7.6 Seats

Seats are a part of all transportation systems. Most seats are built using three main components: the framework, a foam and the covering.

Most frameworks are made of either metal or plastic. Frameworks made from metal are inherently flame-resistant and can therefore be used without flame-retardants. On the other hand, framework made of plastic, mainly polyamide or polypropylene, are easy to ignite. Depending on the use, the framework might be flame-retarded to pass the required fire standards. None-halogenated flame-retardants for polypropylene and polyamide are presented in section 5.4 and 6.3.

Flexible polyurethane foams are often used for seats, either as slab stock or as moulded foam. Polyurethane foams are inherently flammable; consequently, flame-retardants must be added to polyurethane to meet the fire standards. For a detailed description of the standards, see chapter 4. Phosphorous-based FR, liquid or solid, are most commonly used for automotive seating. Furthermore, for aeroplanes seats, the foam must be protected by a fire-proof layer (usually expandable graphite).

The covering protects the foam and framework. Usually textiles or natural or artificial (soft PVC and PUR) leather are used as covering. Various types of non-halogenated FR for textiles is listed in Image 3 in the preceding section.

8. Health and environmental impact of alternatives

The level of available human health and environmental information varies widely according to flame retardant chemical. A number of studies and projects have been undertaken with the aim to assess the health and environmental profiles of non-halogenated flame-retardants as a substitute to the brominated flame-retardants. The vast majority of these studies/projects was included in the recent LOUS review of brominated flame-retardants, including the finished parts of the comprehensive ENFIRO project and the screening undertaken by US EPA. Consequently, the health and environmental impact is only briefly assessed, highlighting the findings from the ENFIRO project and LOUS review. Please find detailed information and references to the original data sources in the LOUS review of brominated flame-retardants.

The European Commission-funded project ENFIRO investigated the substitution options for some BFRs and compared the hazard, exposure, fire, and application performances. Some of the results of the ENFIRO project are still not available, whereas others have already been published. The section below gives a short summary of the published results.

The ENFIRO project included a total of 14 non-halogenated flame-retardants as alternatives to decaBDE, TBBPA, and brominated polystyrenes. These flame-retardants were studied in five applications - printed circuit boards, electronic components, injection moulded products, textile coatings and intumescent paint. From the initial selection of 14 alternative flame-retardants, seven (ammonium polyphosphate, aluminium diethylphosphinate, aluminium trihydroxide, DOPO, melamine polyphosphate, zinc stannate, zinc hydroxyl stannate) were found to be of less concern. Bioaccumulation of the inorganic non-halogenated flame-retardants was found to not be a concern, but BDP was found to be persistent. Environmental fate models predicted that the organic non-halogenated flame-retardants would be found primarily in soil, sediments and dust and to a lesser degree in water and air. Controlled air emission experiments showed that all organic non-halogenated flame-retardants were emitted from polymers at elevated temperature, but not at lower temperatures. The risk assessments showed that some non-halogenated flame-retardants show less risk to the environment and human health. The lower risk was found to be caused by lower hazards of the non-halogenated flame-retardants, and a lower exposure. According to the LCA study of the ENFIRO project the waste phase was the most important difference between the selected BFRs and non-halogenated FRs. Especially the formation of brominated dioxins during improper electronics waste treatment had a strong negative impact on the LCA scores. Overall, the life cycle environmental performance of the non-halogenated FR scenario was better than for the BFR scenario (Leonards, Brandsma et al. 2013).

In general, there is a lack of knowledge regarding the environmental and health impact of the non-halogenated flame-retardants. One reason for this lack of knowledge is that the non-halogenated flame-retardants are a group of very different chemical structures, and they are often added as blends to obtain synergistic effects. They have to be compatible with the polymer they have to protect against fire. Depending on the flammability of the polymer, they can be added in rather high amounts. One should bear in mind that the polymer might be a mixture of polymers and that each polymeric material is based on a formulary with a number of other additives like antioxidants, UV stabilizers, biocides and fillers or even more. The polymer must have good processing properties for the process, e.g., extrusion or injection moulding and the non-halogenated FRs must be stable at the process temperature. Therefore, many different formulations (so-called compounds) exist for the different applications even for the same polymer, e.g., ABS. The formulary is in general a commercial secret so it is very difficult from case to case to evaluate or obtain valid data for a health and environmental assessment. In most cases, the knowledge of the fate of plastic waste (which has been fire-retarded by non-halogenated FRs) plays an important role for the LCA analysis and is not well-known. In future, it is therefore necessary to gather more data for the environmental and health impact of the non- halogenated FRs.

In Morgan 2014, there are suggestions to the experimental methodology for non-halogenated flame-retardant screening for the future R&D in search for more or better non-halogenated FRs.

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Fire Safety Requirements and Alternatives to Brominated Flame-Retardants

This is a survey that identifies the products and sectors with the highest consumption of brominated flame retardants (BFRs), maps trade standards as well as national, regional and international fire safety standards, including the fire safety test methods and criteria, and assesses the possibilities to substitute the BFRs with non-halogenated flame retardants. It is a follow-up of the Danish EPA's List of Undesired Substances (LOUS) review 2012-2015. The background for implementing this project was the results from a survey of brominated flame retardants under LOUS (Environmental Project no. 1536 in 2014). Three sectors were identified as relevant in the follow-up survey: building materials, electric and electronic equipment as well as transportation and off-shore vessels. It was concluded that alternative non-halogenated flame-retardants, appertaining polymer systems and production set-ups are already developed and on the market for a majority of the identified product types. However substituting chemicals can involve significant costs, as industries must adapt their production processes, and have products and materials re-tested for all required performance and product standards.

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