

Ministry of Environment of Denmark Environmental Protection Agency

Survey, control and risk assessment of flame retardants and other hazardous substances in textiles containing electronic parts

> Survey of chemical substances in consumer products No. 198

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Summary

An increasing number of textile products with electronic heating functions are available to consumers for use in their homes and for outdoor activities such as skiing or hunting. Since these products contain both electronic parts and heating functions, an increased risk of flammability can be expected, making the addition of flame retardants to these products likely.

The objective of this study is to provide insight into which flame retardants are used in textiles containing electronic parts, and to which extent these flame retardants are regulated by applicable European law. The study has a dual focus; on the one hand, it investigates whether legal requirements regarding use of regulated flame retardants in textiles containing electronic parts are complied with. One the other hand, the project investigates whether non-regulated flame retardants occur in textiles containing electronic parts and, if yes, whether these substances pose a health risk to consumers, especially to vulnerable groups such as children. Additionally, the study aims to clarify, whether textile products with electronic heating functions contained other hazardous substances specific for this product type.

By means of a literature survey, flame retardants used in textiles were identified, and their regulatory status was investigated. Legal requirements and standards regarding flammability were screened in a few selected countries; the United Kingdom (UK), Germany and Denmark. The UK was chosen due to its stringent flammability requirements for consumer articles, Germany due to its size of the market and Denmark due to the project scope. Legal requirements and standards regarding flammability may require or encourage the use of flame retardants, therefore, products labelled with any of these standards are more likely to contain flame retardants. The legal requirements and standards screening was therefore applied to support the identification of products containing flame retardants. Some relevant standards and regulations were identified and are applicable to some of the products in scope of this project. However, during the product survey, no products labelled or claimed to comply with any of these fire safety requirements or standards where identified.

In the product survey, information about 67 unique textile products with electronic heating functions available on the Danish market from 28 different manufacturers was listed. The products comprise a total of 22 different products categories, including home textiles such as heating blankets and clothing articles intended for outdoor use, e.g., gloves, socks, and jackets.

Out if the 67 listed products, 30 products were purchased for chemical analysis of flame retardants. Samples were taken as composite samples (including all textiles layers of an article) in the immediate vicinity of the electronic heating element. The analytical program comprised both regulated and non-regulated flame retardants, for which reference materials and analytical methods were available at the laboratory. The target analysis of flame retardants showed low concentrations of flame retardants in the products, indicating that the substances have not been added intentionally with the objective of achieving flame retardancy. Three flame retardants were found above the limit of detection: TCEP, TCPP and TPP. Flame retardants were detected in gloves, socks, a jacket, underwear, a vest, and a shirt with electronic heating functions. Banned flame retardants such as PBB and PBDE were not detected in any of the purchased articles. Even though additional regulatory action are underway for some of the flame retardants, the textile parts of the purchased articles seem currently to comply with current regulations under REACH, the POPs regulation, and the RoHS-Directive.

Additionally, a non-target GC-MS screening was performed to detect other substances in the products. Of the detected substances, many are fragments of plastic polymers used for textile

products, e.g., polyethyleneterephthalate (PET). Other substances are known additives in plastic polymers such as PET, PS or PVC, e.g., potentially hazardous substances such as benzophenones (UV-absorbers), aromatic amines (cleavage products from azo dyes) or adipates (plasticisers). The detected substances do not appear to be substantially different from substances that may be present in other non-electronic consumer textiles.

A hazard assessment of the three identified flame retardants, TCEP, TCPP and TPP, showed that the critical effects of the substances are effects on the kidneys, liver, thyroid, and body weight. The specific derived no effect levels (DNELs) are 0.013 mg/kg bw/d for TCEP (systemic effects on the kidneys), 0.07 mg/kg bw/d for TCPP (effects on liver and thyroid), and 0.04 mg/kg bw/d for TPP (decreased liver and body weight).

The exposure has been estimated using ECHA guidelines and focused on the dermal route for articles with direct skin contact, i.e., gloves, socks, and underwear. Dermal exposure has been calculated based on the measured concentrations in the articles (composite samples) as well as assuming that the whole amount of flame retardants is located in the inner layer of the article with direct skin contact. Only articles with clothing size specifically for adults were found to contain flame retardants, and children were therefore not considered a relevant exposure group.

The estimated exposure has been compared to the health-based reference values of the respective substances, yielding risk characterisation ratios (RCR). If the RCR < 1, the risk is considered to be controlled. The RCRs are presented in the table below.

			Exposure b measured c tions	ased on concentra-	Exposure bas centration in layer ^a	ed on con- the inner
	Product ID	Product	C _{prod} [g/cm ³]	RCR	C _{prod} [g/cm³]	RCR
TCEP	202011 - 3	Heated gloves	0.000041 / 0.000005 ^b	0.044 / 0.005	0.00032 / 0.00004 ^b	0.34 / 0.04
ТСРР	202011 - 3	Heated gloves	0.000005 / 0.000003 ^b	0.001 / 0.001	0.00004 / 0.00002 ^b	0.008 / 0.005
	202011 - 6	Heated socks	0.000003	0.001	-	-
ТРР	202011 - 15	Heated under- wear, top	0.000007	0.032	-	-
	202011 - 16	Heated under- wear, bottom	0.000005	0.004	-	-

^a Only applies to products consisting of multiple layers. The calculation of the inner layer concentration is described in section 6.3.2.2.

^b If the Relative Standard Deviation (RSD) between the measured concentration in duplicate samples exceeds 15%, the RCR is calculated for both values.

Since all RCR values are < 1, the risk assessment shows that the health risk following dermal exposure is controlled at the found concentrations of the flame retardants. A risk of exposure to flame retardants via textiles with electronic heating functions towards children is not indicated, as none of the articles, which reasonable could be expected to be used by children, contained any of the measured flame retardants.

1. Introduction

1.1 Background

An increasing number of textile products with electronic heating functions are available to consumers for use in multiple situations. For example, heating blankets have been on the market for many years, primarily aiming at assisting elderly people to keep warm and comfortable. During the recent years, with the development of smaller electronic power banks, an increasing number of products with heating functions for outdoor use are available, too, e.g., bicycle helmets, skiing socks and hunting vests. Since these products contain both electronic parts and heating functions, an increased risk of flammability can be expected, making the addition of flame retardants to these products likely.

The use of such products entails increased temperatures and possibly even sweating/humid conditions, which are circumstances that promote leaching and/or vaporisation of potentially added flame retardants and other hazardous substances. The presence of such substances in the products may thus lead to a risk for the consumer during the use phase.

Textiles are generally regulated through the REACH regulation, electronics are regulated through the RoHS Directive, and selected brominated flame retardants are regulated through the POP Regulation. All these legislations are therefore relevant for the regulation of flame retardants in textiles containing electronic parts.

1.2 Objective

The objective of this study is to provide insight into which flame retardants are used in textiles containing electronic parts, and to which extent these flame retardants are regulated by applicable European law. The study scope was limited to the textile parts of the relevant products and did not comprise electronic parts such as plastic casings and wiring. The study has a dual focus; on the one hand, it investigates whether legal requirements regarding use of regulated flame retardants in textiles containing electronic parts are complied with. One the other hand, the project investigates whether non-regulated flame retardants occur in textiles containing electronic parts and, if yes, whether these substances pose a health risk to consumers, especially to vulnerable groups such as children or unborn children. Additionally, the study aims to clarify, whether textile products with electronic heating functions differ in their content of hazardous substances from other textile products for consumers.

Thus, the study comprises a survey of relevant textile products including electronic parts, a survey of flame retardants and other hazardous substances in textiles including electronic parts, chemical analyses and a consumer health risk assessment.

The output of the study enables the EPA to decide on additional steps regarding potential legislative violations, as well as further regulation of flame retardants in consumer products. Also, the study provides the background for development of additional consumer advice regarding these products.

2. Methodology for data collection

The chapter describes the methodology and sources for the data collection on flame retardants, on other substances hazardous to human health and textile product with electronic parts.

2.1 Literature search

Data on detection of flame retardants and other hazardous substances in textiles with electronic parts were identified partly by searching via general web search engines and on websites of specific agencies and organisations, including:

- Danish Environmental Protection Agency
- Chemicals Inspectorate (KemI, Sweden)
- Environment Directorate (formerly SFT and Klif, Norway)
- Umweltbundesamt (UBA, Germany)
- Federal Institute for Risikobewertung (BfR, Germany)

Data from relevant reports and assessments by European (and international) Agencies were extracted. Data from relevant scientific publications cited within the agency reports were also extracted. Additionally, a systematic search of relevant scientific publications was conducted which is explained in the following.

For a systematic screening of relevant publications in literature databases two search strings were developed. One search string was developed to gather information on flame retardants and/or hazardous substances for the product type of textiles with heating function/electronic components. A second search string was developed to cover information on concentration of flame retardants and/or measurements thereof in textiles in general.

The searches were carried out in two scientific literature databases (EuropePMC and Pub-Med). The first search string resulted in 158 publications on PubMed and 184 publications on EuropePMC. The second search string resulted in further 95 publications on PubMed and 122 publications on EuropePMC. The combination of all search results revealed a total number of 321 individual publications (after removal of duplicates). The publications were screened for relevance according to title and abstract. In this first step, 272 publications were excluded based on a number of defined exclusion criteria. The remaining 49 publications were screened by full text. Within the full text screening another 35 papers were excluded, leaving 14 papers for data extraction.

Data from the 14 remaining relevant papers were extracted into an excel spreadsheet used for systematic collection of information on substances and on products within textiles with electronic parts. During the extraction process, two additional relevant publications were identified, as they were cited in some of the relevant papers, but not identified during the literature search.

2.2 Information from other sources

Further information sources, as listed in the following paragraphs, were screened for additional data on flame retardants identified in textiles and other hazardous substances in textiles with electronic parts.

2.2.1 ECHA SCIP database

The SCIP database lists articles containing substances of very high concern (SVHCs) on the Candidate List at a concentration above 0.1% weight by weight (w/w) placed on the EU market notified according to Article 9(1)(i) of the Waste Framework Directive 2008/98/EC. It currently (as of July 2023) contains more than 10 million reported articles. The list is searchable by article identity, article category, material & mixture category, SVHCs, concern/reason for inclusion and SCIP Number.

The article category is based on the combined nomenclature (CN) description and code integrated of the Tariff of the European Union (TARIC) list.¹ The following relevant article category was identified:

• 6301100000 Electric blanket (13 articles reported)

SVHCs reported in this article category were extracted into the excel spreadsheet.

Further, the article identity was searched by the following list of keywords:

- e-textile/ electronic textile/ electric textile
- smart textile/ smart clothing
- textile with heating function/ textile with heating component
- heating blanket/ electric blanket
- heated mat
- heated shoes/ heated insoles
- heated vest/ heated coat
- heated base layer
- heated clothing
- heated seat

Only for "heated seat", 25 articles were identified. From the article category and the description (most articles fall within the CN section "Vehicles, aircraft, vessels and associated transport equipment"), it was not possible to determine whether the articles are relevant for the scope of this study. The reported substances from the identified articles were therefore extracted as well.

2.2.2 SPIN (Nordic product register database)

The SPIN (Nordic product register database)² contains data about substances used in the Nordic countries. The database displays, if a substance is used in a specific country, in which amount or time frame it is used, and in which industry and in which function it is used. However, the information is displayed in such a way, that no information relevant in the scope of this project can be extracted from the database.

2.2.3 PINFA product selector

PINFA (Phosphorus, Inorganic and Nitrogen Flame Retardants Association) is a European industry association representing manufacturers and users of non-halogenated phosphorus, inorganic and nitrogen flame retardants (PIN FRs). The PINFA product selector³ is a collection of PIN FRs for different applications. PIN FRs for the application group of textiles/paints/adhesives were extracted into the excel spreadsheet.

¹ Consolidated text: Council Regulation (EEC) No 2658/87 of 23 July 1987 on the tariff and statistical nomenclature and on the Common Customs Tariff, <u>https://eur-lex.europa.eu/legal-con-</u> tent/EN/TXT/?uri=CELEX%3A01987R2658-20230617&gid=1690297318205

² www.SPIN2000.net

³ <u>https://www.pinfa.eu/product-selector/?_sft_product_group=3</u> (last accessed 25th July 2023)

2.3 Stakeholder Consultation

The aim of the stakeholder consultation was to get up-to-date information from leading manufacturers/industry associations about the use of flame retardants in textiles. Relevant stakeholders were identified during the literature analysis, by search for textile industry associations and in cooperation with the Danish EPA. The following stakeholders were identified as relevant and therefore contacted:

- Dansk Industri (industry association)
- Dansk Erhverv (industry association)
- Digital Europe (industry association)
- AENEAS (Association for European NanoElectronics ActivitieS, industry association)
- Dansk Mode & Textil (industry association)
- Textilforeningen (industry association)
- ELIS (textile service company)
- European Technology Platform for the Future of Textiles and Clothing (Textile ETP)
- European Textile Service Association (ETSA, industry association)
- European Apparel and Textile Confederation (EURATEX, industry association)
- European Branded Clothing Alliance (EBCA, industry association)
- European Man-Made Fibres Association (CIRFS, industry association)
- European bedding industries' association (EBIA, industry association)
- Europa Regina (industry association)
- WEAR (industry association)

Stakeholders were contacted via an email and each of them received an accompanying letter signed by Danish EPA and a set of questions about use of flame retardants in textiles. In total, 15 stakeholders were contacted. By the end of the stakeholder consultation, only three stakeholders provided their response. The information from these responses was only of limited relevance for the project and is not included in this project.

2.4 Screening for textile products containing electronic parts at retailers' websites

For identifying products on the Danish market, an open search using different words for textiles with heating function was done using general internet search, mimicking the approach a Danish consumer would take when intentionally looking for a textile product with heating function. Among the search results, retailer websites were chosen to cover a broad presentation of different retailers, e.g., outdoor equipment retailers, homeware retailers and electronics retailers.

For products available on the European and non-European market, the project teams reviewed products from two large, international online marketplaces. Consumers may encounter advertisements for products from such online marketplaces during general browsing the internet and become spontaneously inspired to buy such products. Furthermore, products displayed from such marketplaces can be cheaper than similar product types which are sold at Danish retailers, as well as the product ranges often are broader compared the assortments at Danish retailers, which could also be a reason for consumers to choose products from international marketplaces.

Identified products were listed in an excel sheet with information about the manufacturer, product type, country of origin, retailer, parameters for exposure considerations, information on flammability/flame retardance, price etc. Focus was on covering as many different manufacturers and product types as possible. That means, e.g., if a retailer offers several heating blankets, which are from the same manufacturer and of the same type, but available in different sizes, only information about one of the heating blankets from this retailer was noted down (the larger heating blanket due to exposure considerations).

3. Overview of legal requirements on flammability

The purpose of this chapter is to obtain indications of which products may contain flame retardants. As this study aims at purchasing textile products containing electronic parts for chemical analyses of flame retardants, this information can support the identification of products containing flame retardants.

Within EU regulation, there is no legal requirement to inform consumers about the presence of a flame retardant in an article, such as a textile product containing electronic parts, unless the flame retardant is on the EU candidate list of SVHC (Substances of Very High Concern) and present in a concentration above 0.1% weight by weight (according to Article 33 in REACH regulation⁴).

Legal requirements within certain countries or industry standards can provide indications, in which product types the addition of flame retardants is required. If there is a legal requirement or industry standard requiring that a certain product is flame retarded, there is a high chance that the product actually contains flame retardants.

Therefore, in consultation with the Danish EPA, legal requirements regarding flammability were screened in a few selected countries; the United Kingdom, Germany and Denmark. The UK was chosen due to its stringent flammability requirements as known from previous Danish EPA projects (i.e., Danish EPA 1999, Kjølholt et al. 2015), Germany due to the size of the market and Denmark due to the scope of the project. The legal requirements for textiles containing electronic parts were researched via desktop research.

3.1 Selected Member State specific legal requirements

3.1.1 UK regulations and standards

3.1.1.1 The Furniture and Furnishings (Fire) (Safety) Regulations 1988 (amended 1989, 1993 and 2010)⁵

The Furniture and Furnishings (Fire) (Safety) Regulations 1988 ensures that upholstery components and composites used for furniture supplied in the UK meet levels of fire resistance and are properly labelled. Products falling under the scope of the regulation are any products which contain upholstery used in furniture such as furniture intended for private use in a dwelling, children's furniture, beds, headboards of beds, sofa-beds, futons, other convertibles, nursery furniture, garden furniture, furniture in new caravans. Permanent covers for furniture as well as loose and stretch covers for furniture are also covered under the Regulation. As

⁴ Regulation (EC) No 1907/2006 <u>https://eur-lex.europa.eu/legal-con-tent/EN/TXT/?uri=CELEX%3A02006R1907-20230806#tocld25</u>

⁵ <u>The Furniture and Furnishings (Fire) (Safety) Regulations 1988 (legislation.gov.uk).</u> The text summarises relevant provisions from the initial act including amendments.

such, pads and blankets with heating function may be regarded as covers for furniture and should thus meet the requirements of fire resistance.

Products such as mattresses, bed-bases, pillows, cushions, sleeping bags, bed-clothing, loose covers for mattresses, pillowcases, curtains, carpets, and mats are excluded from the Regulation.

Interlines, upholstery, and covers falling under the scope of the Regulation must pass testing requirements, otherwise the products cannot be placed on the UK market. For example, upholstery must pass the cigarette resistance test, while permanent and loose covers must pass the match resistance test.

The requirements for fabric and leather covers, interlinings, fillings, and upholstery composites are set out by British Standard BS 5852: Part 1:1979 and BS 5852: Part 2: 1982. The general principle of these standards is that the products are subjected to smouldering and flaming ignition to test their flammability.

In order to show compliance and indicate fire resistance of the products falling under the scope of this regulation, all manufacturers, importers and retailers have the obligation to appropriately label their products. Display labels have to be attached to all new furniture (except for mattresses, bed-bases, pillows, cushions), as well as on loose and stretch covers for furniture.

FIGURE 3-1 below provides examples of display labels that need to be attached on prominent position based on the product's properties.

During the screening of products at retailers, products were reviewed with respect to whether any of the labels in FIGURE 3-1. were present. None of the reviewed products displayed any of the listed labels or was marketed with any of these labels.



FIGURE 3-1 Examples of display labels under the UK Furniture and Furnishings (Fire) (Safety) Regulation from 1988.

3.1.1.2 The Nightwear (Safety) Regulations 1985⁶

The Nightwear (Safety) Regulations 1985 lays down labelling requirements which indicate whether the nightwear meets the flammability requirements or not.

Products falling under the scope of this regulation are pyjamas, babies' garments, cotton terry towelling bath robes (being children's nightwear) and adults' nightwear. Bath robes and pyjamas with heating elements could potentially occur, however, such products have not been identified during the product screening, not even during a targeted search for such products (performed in August 2023). Underwear with heating elements could potentially be used as nightwear, but underwear is unlikely to be within the scope of the regulation (except babies' underwear).

Children's nightwear (pyjamas, babies' garments and cotton terry towelling bath robes) and adults nightwear must comply with flammability requirement performance of *British Standard BS 5722: Specification for flammability performance of fabrics and fabric assemblies used in sleepwear and dressing gowns* and labelled accordingly ("LOW FLAMMABILITY TO BS 5722"). It is not known whether the required flammability performance is to be reached by use of flame retardants or other means.

Nightwear that is "made of a fabric treated with flame retardant chemicals" has to, according to the regulation, be labelled with "DO NOT WASH AT MORE THAN 50°C. CHECK SUITABIL-ITY OF WASHING AGENT". The label "DO NOT WASH AT MORE THAN 50°C. CHECK SUITABILITY OF WASHING AGENT" would thus provide a clear indication for use of flame retardants in a textile product.

⁶ The Nightwear (Safety) Regulations 1985 (legislation.gov.uk)

Neither of the labels, however, was found in the product descriptions of the screened textile products with heating functions. It is possible though that such a label is attached to any of the screened products, but that the product property is not reported in the description on the websites.

3.1.2 Germany

In Germany textiles used in buildings accessible to the public are required to be flame retarded. This includes e.g. curtains for stages, seats and decoration. This is regulated on federal state level by the respective federal state ordinances on places of assembly (German: Versammlungsstättenverordnung). In order to prove compliance with these ordinances, the DIN 4102 or EN 13773 can be applied. These standards established flammability classes from 'easily flammable' to 'not flammable' for building products.

However, textile products mentioned in the ordinance are typically not heated and as such out of scope for this project. Specific standards or laws for textiles products in scope of the project could not be identified.

3.1.3 Denmark

In Denmark, no specific national regulations regarding the use of flame retardants or flammability for the products within the project scope have been identified.

More generally, the Product Safety Act (LOV no. 799 af $09/06/2020)^7$ indicates that only safe products can be placed on the market and that it is the responsibility of the marketing company that the products are safe for the consumer. In that respect, products must be safe both with respect to their flammability and their content of flame retardants.

3.1.4 EU standards

There are a variety of standards for fire safety available in Denmark and Europe. Below, all standards relevant for textiles are listed. The list is created from the standards listed in an earlier Danish EPA report on flame retardants (Andersen et al. 2014) and the website of Danish Standards has been checked for updated/newer standards.

Those of the standards that address textiles in general (e.g. DS/EN ISO 12952-1:2010 and DS/EN ISO 12952-2:2010) may be applicable to the products within the current project scope. The standards are not publicly available; therefore it has not been possible to check whether they contain any requirements regarding use of flame retardants. Typically, the standards only define criteria for flame retardancy or flammability of the products, but do not prescribe whether these criteria have to be achieved via use of flame retardants or by other means.

None of the reviewed products in the product screening was marketed with compliance to any of these standards based on the information on the retailers' websites.

DS/EN 597-1:1995 - **Furniture** - Assessment of the ignitability of mattresses and upholstered bed bases - Part 1: Ignition source: Smouldering cigarette

DS/EN 597-2:1995 - **Furniture** - Assessment of the ignitability of mattresses and upholstered bed bases - Part 2: Ignition source: Match flame equivalent

DS/EN 1021-1:2006 - **Furniture** - Assessment of the ignitability of upholstered furniture - Part 1: Ignition source smouldering cigarette

DS/EN 1021-2:2006 - **Furniture** - Assessment of the ignitability of upholstered furniture - Part 2: Ignition source match flame equivalent

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⁷ " Lov om produkter og markedsovervågning" <u>https://www.retsinformation.dk/eli/lta/2020/799</u>

DS/EN 1058.3:1977 - Materials - Coverings and linings - Ignition temperature and surface spread of flame

DS/EN 1101:1996 - Textiles and textiles products - Burning behaviour - **Curtains and drapes** Detailed procedure to determine the ignitability of vertically oriented specimens (small flame)

DS/EN 1101/A1:2005 - Textiles and textile products - Burning behaviour - **Curtains and drapes** - Detailed procedure to determine the ignitability of vertically oriented specimens (small flame)

DS/EN 1102:1996 - Textiles and textile products - Burning behaviour - **Curtains and drapes** - Detailed procedure to determine the flame spread of vertically oriented specimens

DS/EN 1103:2005 - **Textiles - Fabrics for apparel** - Detailed procedure to determine the burning behaviour

- DS/EN 1624:2000 Textiles and textile products Burning behaviour of **industrial and technical textiles** - Procedure to determine the flame spread of vertically oriented specimens
- DS/EN 1625:2000 Textiles and textile products Burning behaviour of **industrial and tech**nical textiles - Procedure to determine the ignitability of vertically oriented specimens
- DS/ISO 6925:1982 **Textile floor coverings** Burning behaviour Tablet test at ambient temperature

DS/EN ISO 6940:2004 - **Textile fabrics** - Burning behaviour - Determination of ease of ignition of **vertically oriented specimens**

DS/EN ISO 6941:2003 - Textile fabrics - Burning behaviour - Measurement of flame spread properties of vertically oriented specimens

DS/EN ISO 9239-1:2010 - Reaction to fire tests for **floorings** - Part 1: Determination of the burning behaviour using a radiant heat source

DS/ISO 9239-2:2003 - Reaction to fire tests for **floorings** - Part 2: Determination of flame spread at a heat flux level of 25 kw/m2

DS/EN ISO 12952-1:2010 - **Textiles** - Assessment of the ignitability of bedding items - Part 1: Ignition source: smouldering cigarette

DS/EN ISO 12952-2:2010 - **Textiles** - Assessment of the ignitability of bedding items - Part 2: Ignition source: match-flame equivalent

DS/EN 13772:2011 - Textiles and textile products – Burning behaviour – **Curtains and drapes** – Measurement of flame spread of vertically oriented specimens with large ignition source

DS/EN 13773:2003 - Textiles and textile products - Burning behaviour - **Curtains and drapes** - Classification scheme

DS/EN 14041/AC:2007 - Resilient, textile and laminate floor coverings - Essential characteristics

DS/EN 14533:2003 - Textiles and textile products - Burning behaviour of **bedding items** - Classification scheme

3.2 Conclusion on applicability of legal requirements for selecting products for chemical analysis

The purpose of this chapter is to obtain indications of which products may contain flame retardants based on whether any products are marked with certain labels or claimed to comply with any of the identified standards as this potentially could support the identification of products containing flame retardants.

The chapter documents that some standards and regulations are available and applicable to some of the products in scope of this project, for example pads and blankets with heating function regarded as loose covers could be covered by the UK Furniture and Furnishings (Fire) (Safety) Regulations 1988, or the DS/EN ISO 12952 on ignitability of bedding items could apply to mattress pads).

However, during the product survey (chapter 5), no products labelled or claimed to comply with any of these regulations and standards were identified.

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4. Flame retardants in textiles

This chapter outlines which flame retardants are regulated either in general, for use in textiles or electronics. Additionally, based on the data collection methods as outlined in sections 2.1 – 2.3, all flame retardants identified in textiles and other hazardous substances in textiles with electronic parts were listed in an excel table including CAS no., relevant product and material types, and information source(s). Finally, this chapter also summarises available information on alternative flame retardants to restricted flame retardants.

4.1 Restricted flame retardants in textiles with electronic parts

Some flame retardants and other hazardous substances have already been phased out due to their hazardous properties. They are regulated under various European laws such as the POP-Regulation (2019/1021)⁸, the REACH-Regulation (1907/2006)⁹ as well as the RoHS-Directive (2011/65/EU)¹⁰.

As the products in focus of this project all contain electronics, they all fall under the RoHS-Directive and are as such prohibited from containing several flame retardants, metal compounds and phthalates above the respective concentration limits. Additionally, the products are regulated under the REACH-Regulation as "articles", and as such various other substance restrictions apply (e.g. tris(2,3 dibromopropyl)phosphate (CAS no. 126-72-7) is not to be used in textiles intended to come into contact with skin). A few flame retardants are also regulated under the POP-Regulation (2019/1021).

Relevant substance restrictions under any of the above-mentioned EU laws applicable to the identified products were researched by screening the respective legislative texts. TABLE 4-1 gives an overview of flame retardants for which the use in textiles is restricted or banned according to the POP-Regulation (2019/1021), Annex XIV (authorisation list) or Annex XVII (restriction list) of the REACH-Regulation (1907/2006) and/or the RoHS-Directive (2011/65/EU). Some of the listed substance groups comprise many individual substances. In this case, examples of specific substances from the substance group are given.

It should be noted that the here listed flame retardants are/have been used in various materials and are not necessarily textile-specific flame retardants. For example, the restrictions in the RoHS-Directive apply to 'homogeneous materials', which for the products in scope of the current study, could comprise, e.g., plastic casings and/or textile fibres.

⁸ Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants, https://eurlex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02019R1021-20230610

⁹ Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency

¹⁰ Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment

TABLE 4-1: List of restricted flame retardants applicable to the product group of textiles with electronic parts.

Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
Chlorinated ali- phatics	I ali- Dechlorane Plus (covering any 13560-89-9, Not included of its individual anti- and syn- 135821-74-8, Substance proposed to become subject to the POPs Regulation		Substance proposed to become subject to the POPs Regulation	Not included	
	isomers or any combination thereof)	13560-89-9		(listed under the Stockholm Convention, Annex A Elimination)	
Chlorinated or- ganophos- phates	Tris(2-chloroethyl) phosphate (TCEP)	115-96-8	Included in Annex XIV (Authorisation list)	Not included	Not included
Brominated ali- phatics	Hexabromocyclododecane (HBCDD), hexabromocy- clodecane (HBCD) and diaster- oisomers	25637-99-4, 3194-55-6, 134237-50-6, 134237-51-7, 134237-52-8	Included in Annex XIV (Authorisation list).	 Included in Annex 1 (Part A): 1. For the purposes of this entry, point (b) of Article 4(1) shall apply to concentrations of hexabromocyclododecane equal to or below 100 mg/kg (0,01 % by weight) where it is present in substances, mixtures, articles or as constituents of the flame-retarded articles, subject to review by the Commission by 22 March 2019 Included in Annex IV. 	Not included
Polybrominated Biphenyls (PBB)	Hexabromobiphenyl (HBB)	36355-01-8	Included in Annex XVII (Restriction list entry 8):	Included in Annex 1 (Part A) and Annex IV.	Restricted with concentration limit of 0.1%

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Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
	Nonabromo-1,1'-biphenyl, tetrabromo(tetrabromo- phenyl)benzene, decabromo-1,1'-biphenyl, 4-bromobiphenyl, 4,4'-dibromobiphenyl, 3-bromobiphenyl, other PBBs (except hexa- bromo-biphenyl)	27753-52-2, 27858-07-7, 13654-09-6, 92-66-0, 92-86-4, 2113-57-7, 59536-65-1	 Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into con- tact with the skin. Articles not complying with paragraph 1 shall not be placed on the market. 	Not included	
Polybrominated Diphenyl Ethers (PBDE)	Tetrabromodiphenyl ether	40088-47-9 and others	Not included	 Included in Annex 1 (Part A): For the purposes of this entry, point (b) of Article 4(1) shall apply to concentrations of the individual substance equal to an 	Restricted with concentration limit of 0.1%
	Pentabromodiphenyl ether	32534-81-9 and others		below 10 mg/kg (0.001 % by weight) where it is present in substances.	
	Hexabromodiphenyl ether	36483-60-0 and others	_	 For the purposes of the entries on tetra-, penta-, hexa-, hepta- and decaBDE, point (b) of Article 4(1) shall apply to the sum of the concentration of those sub- stances up to 500 mg/kg where they are 	
	Heptabromodiphenyl ether	68928-80-3 and others		present in mixtures or articles, subject to review and assessment by the Commis- sion by 16 July 2021. This review shall	

Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-F	Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
	Decabromodiphenyl ether (commercial mixture, c- decaBDE)	1163-19-5	Included in the candidate list .	as re 3. By pla lov re de or be pr th ac 4. elu th er 5. Us ion inu de th	sess, inter alia, all relevant impacts with egard to health and the environment. y way of derogation, the manufacturing, acing on the market and use of the fol- wing shall be allowed: [paragraph eads differently for decaBDE: By way of erogation, the manufacturing, placing in the market and use of decaBDE shall e allowed for the following purposes, rovided that Member States report to e Commission by December 2019 in ccordance with the Convention:] ectrical and electronic equipment within e scope of Directive 2011/65/EU [sev- ral more derogations for decaBDE] se of articles already in use in the Un- n before 25 August 2010 containing the dividual substance [15 July 2019 for ecaBDE] shall be allowed. Article 4(2), ird and fourth subparagraphs shall ap- y in relation to such articles.	

Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
	Diphenylether, octabromo de- rivative	32536-52-0	Included in Annex XVII (Restriction list entry 45):	Not included	
			1. Shall not be placed on the market, or used:		
			— as a substance,		
			 — as a constituent of other substances, or in mixtures, in concentrations greater than 0.1 % by weight. 		
			 Articles shall not be placed on the market if they, or flame-retardant parts thereof, contain this substance in concentrations greater than 0.1 % by weight. By way of derogation, paragraph 2 shall not apply: 		
			— to articles that were in use in the Community before 15 August 2004,		
			— to electrical and electronic equipment within the scope of Directive 2002/95/EC.		

Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)	
-	Tris (2,3 dibromopropyl) phos- phate	126-72-7	Included in Annex XVII (Restriction list en- try 4):	Not included	Not included	
			 Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin. Articles not complying with paragraph 1 shall not be placed on the market. 			
-	Tris(aziridinyl)phosphinoxide	545-55-1	Included in Annex XVII (Restriction list en- try 7):	Not include	Not included	
			 Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin. Articles not complying with paragraph 1 shall not be placed on the market. 			
-	Mirex	2385-85-5	Not included	Included in Annex 1 (Part A) and Annex IV.	Not included	

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Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
-	Hexachlorobutadiene (HCBD)	87-68-3	Not included	Included in Annex 1 (Part A):	Not included
				 Placing on the market and use of articles already in use before or on 10 July 2012 containing hexachlorobutadiene shall be allowed. Article 4(2), third and fourth subpara- graphs shall apply to articles referred to in point 1. Included in Annex III (Part B) and Annex IV. 	
-	Hexachlorobenzene (HCB)	118-74-1	Not included	Included in Annex 1 (Part A):	Not included
				For the purposes of this entry, Article 4(1), point (b), shall apply to concentrations of hexachlorobenzene equal to or below 10 mg/kg (0.001 % by weight) where it is present in substances, mixtures or arti- cles	
-	Pentachlorobenzene	608-93-5	Not included	Included in Annex 1 (Part A).	Not included

Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
-	Polychlorinated biphenyls (PCB)	group	Not included	Included in Annex 1 (Part A): Without prejudice to Directive 96/59/EC, arti- cles already in use at the time of the entry into force of this Regulation are allowed to be used.	Not included
				Member States shall identify and remove from use equipment (e.g. transformers, ca- pacitors or other receptacles containing liquid stocks) containing more than 0.005 % PCBs and volumes greater than 0.05 dm ³ , as soon as possible but no later than 31 December 2025.	
-	Polychlorinated naphthalenes (PCNs)	70776-03-3, and other	Not included	 Included in Annex III (Part B) and Annex IV. Included in Annex 1 (Part A): Placing on the market and use of articles already in use before or on 10 July 2012 containing polychlorinated naphthalenes shall be allowed. Article 4(2), third and fourth subparagraphs shall apply to articles referred to in point 1. Included in Annex III (Part B) and Annex IV 	Not included

Polychlorinated terphenyls (PCTs) 61788-33-8, and other Included in Annex XVII (Restriction list entry Not included) Not included Shall not be placed on the market, or used: - as substances, - as substances, - in mixtures, including waste oils, or in equipment, in concentrations greater than 50	Group	Substance	CAS no.	REACH-Regulation (1907/2006)	POP-Regulation (2019/1021)	RoHS-Directive (2011/65/EU)
ma/kg (0.005 % by weight).	-	Polychlorinated terphenyls (PCTs)	61788-33-8, and other	Included in Annex XVII (Restriction list entry 1): Shall not be placed on the market, or used: - as substances, - in mixtures, including waste oils, or in equipment, in concentrations greater than 50 mg/kg (0.005 % by weight).	Not included	Not included

4.2 Overview of flame retardants identified in textiles

TABLE 4-2 shows a list of flame retardants found in textiles that have been identified from literature. The table only contains flame retardants identified in studies, agency reports or databases, which were proven to be present in textiles via analytical measurements. This also includes publications where substances could be detected with measurements above the limit of detection (LoD) but below the limit of quantification (LoQ). Further information included in the table are the kind of materials the flame retardants were used in, at which concentrations they were measured, which year samples were taken, as well as the location where the samples were taken (generally divided into Europe = "EU", not sampled in Europe = "Non-EU", or both).

During the literature search, studies or reports addressing hazardous substances specifically in textiles with heating function could not be identified, documenting that literature about hazardous substances in this specific product type is not available. Therefore, the list given in TA-BLE 4-2 only includes flame retardants found within textiles and no other hazardous substances or SVHCs. Extensive literature on hazardous substances in textiles in general is available, e.g. in the Danish EPA study on chemical substances in textile products for (Kjølholt et al. 2015) and the review on hazardous substances in textiles provided by Nijkamp et al. (2014). It is not within the objective and scope of the current project to provide an updated review of hazardous substances in textiles in general.

From the ECHA SCIP database, no SVHCs reported in relevant articles (electric blankets and heated seats) were embedded in the textile material itself. For example, the most reported substance of concern "*Lead*" (CAS no. 12060-00-3) was reported to be included in the external electronic components of the articles (e.g., remote controller, electronic board, pin of power plug, diode).

In addition to the literature research, a stakeholder consultation was conducted. In total, 15 stakeholders were contacted via email. By the end of the consultation period, three stakeholders provided a response, however, no relevant information was received. While two stakeholders stated the study is not relevant for them, one stakeholder provided information only regarding the workwear (limited relevance for consumers) without specific information on the flame retardants used.

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
Organophos- phates (OP) (non- halogenated)	Triphenyl-phos- phate	TPP	115-86-6	Textiles and (polyure- thane) foam	Textiles: 18-350 mg/kg Foams: 43-15000 mg/kg	EU and Non- EU (2011- 2017)	(Kjølholt et al. 2015) (Hammel et al. 2017) (Poulsen, Merlin, and Schmidt, 2018) (Estill et al. 2020) (Rodgers et al. 2021) (van Bergen and Stone 2021)
	Tri-isobutyl phos- phate	TIBP	126-71-6	Foam	Foam of bike helmets: 2.5 mg/kg	EU and Non- EU (2017)	(Poulsen, Merlin, and Schmidt, 2018)
	Tri-n-butyl phosphate	TnBP or TBP	126-73-8	Foam	Upholstered furniture <loq< td=""><td>Non-EU (2015-2016)</td><td>(Rodgers et al. 2021)</td></loq<>	Non-EU (2015-2016)	(Rodgers et al. 2021)
	Tri-cresyl phosphate	TCP	1330-78-5	Padding	Carpet padding (post 2020): 0.005 weight %	Non-EU (2015-2017)	(Estill et al. 2020)
	Tri-propyl phosphate	TPrP	513-08-6	Foam	Upholstered furniture <loq< td=""><td>Non-EU (2015-2016)</td><td>(Rodgers et al. 2021)</td></loq<>	Non-EU (2015-2016)	(Rodgers et al. 2021)
	Isopropylated tri- phenyl phos- phates	lsopro-py- lated TPHPs	55864-04-5 55864-07-8 2502-15-0	Polyure- thane foam	Foams of child car seats, child mat- tress, sofa and love seats, chairs rocking chairs and recliners, mat- tress pads: >1 weight %	Non-EU (No exact date specified)	(Cooper et al. 2016)
	t-butylated phenyl phosphates	TBPP	78-33-1 115-87-7 981-40-8	Polyure- thane foam	Couch PU foam: 7.9 mg/kg Foams of child car seats, child mat- tress, sofa and love seats, chairs rocking chairs and recliners, mat- tress pads: >1 weight %	Non-EU (2010-2011)	(Stapleton et al. 2012) (Cooper et al. 2016)

TABLE 4-2: Inventory of flame retardants in textiles (entries coloured in purple show that the substance can be found in TABLE 4-1 on restricted flame retardants)

¹¹ Concentrations of the substances are given for the materials and not individual textiles/foams to keep the table concise, unless only one specific sample could be found. The boundary values of the ranges do not necessarily originate from the same source but are derived from different sources. If possible, the concentration is given in mg/kg and otherwise as stated in the original reference.

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
	Methylated phenyl phosphate	MPP	No CAS	Polyure- thane foam	Couch PU foam: 3.23 mg/kg	Non-EU (2010-2011)	(Stapleton et al. 2012)
Chlorinated organ- ophosphates (CI- OP)	Tris(2- chloroethyl) phos- phate	TCEP	115-96-8	Textiles and foam	Textiles: 20-173 mg/kg Foam: 1.1-1400 mg/kg	EU and Non- EU (2011-2017)	(Kjølholt et al. 2015) (Poulsen, Merlin, and Schmidt, 2018) (Estill et al. 2020) (Rodgers et al. 2021) (van Bergen and Stone 2021)
	Tris(1-chloroiso- propyl) phosphate (including tris(2- chloroisopropyl) phosphate and tris(2-chloro-1- methylethyl) phos- phate)	ТСРР	13674-84-5 (1244733-77- 4) ¹²	Textiles and (polyure- thane) foam	Textiles: 5.6-19000 mg/kg Foam: 21-46000 mg/kg	EU and Non- EU (2002-2017)	(Stapleton et al. 2009) (Kjølholt et al. 2015) (Cooper et al. 2016) (Hammel et al. 2017) (Poulsen, Merlin, and Schmidt, 2018) (Estill et al. 2020) (van Bergen and Stone 2021) (Rodgers et al. 2021)
	Tris(1,3- dichloroisopropyl) phosphate	TDCPP	13674-87-8	Textiles and (polyure- thane) foam	Textiles: 20-148000 mg/kg Foam: 150-88100 mg/kg	EU and Non- EU (2009- 2021)	(Stapleton et al. 2009) (Stapleton et al. 2012) (Kjølholt et al. 2015) (Cooper et al. 2016) (Hammel et al. 2017) (Poulsen, Merlin, and Schmidt, 2018)

¹² TCPP refers to the reaction product and not the individual isomer. The substance was previously registered with the CAS no. 13674-84-5, but is now registered as "reaction products of phosphoryl trichloride and 2-methyloxirane" with new CASno. 1244733-77-4 and ECno. 807-935-0. The substance itself has not changed, however, the new identifiers refer to a mixture of four isomers. In the cited literature, the substance is identified as TCPP/tris(1-chloroisopropyl) phosphate/CAS no. 13674-84-5.

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
							(Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021) (van Bergen and Stone 2021)
	2,2-bis(chlorome- thyl)tri- methylenebis(bis(2-chloro- ethyl)phosphate)	V6	38051-10-4	Fabric and (Polyure- thane) foam	Fabric: 2390 ppm Foam: 201 – 42500 ppm	Non-EU (2012-2013)	(Cooper et al. 2016) (van Bergen and Stone 2021)
	Tris(2-chloroethyl) phosphate / 2,2- bis(chlorome- thyl)tri- methylenebis(bis(2-chloroethyl) phosphate)	TCEP / V6	115-96-8 / 38051-10-4	Polyure- thane foam	Foam: 5470 – 36300 mg/kg	Non-EU (2010-2011)	(Stapleton et al. 2012)
Polybrominated Diphenyl ethers	2,2',4-Tribromodi- phenylether	BDE-17	147217-75-2	Foam	Upholstered furniture: Below LOQ	Non-EU (2015-2016)	(Rodgers et al. 2021)
(PBDEs)	1,4,4'-Tribromo- diphenylether	BDE-28	41318-75-6	Foam	Textiles: 0.119 – 4.26 mg/kg	Non-EU (2015-2016)	(Vojta et al. 2017) (Rodgers et al. 2021)
	2,2',4,4'-Tetrabro- modiphenyl-ether	BDE-47	5436-43-1	Textiles and foam	Textiles: 0.122 - 451 mg/kg Foam: 1.3 – 6400 mg/kg	EU and Non- EU (2012-2021)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021) (Norwegian EPA 2021) (van Bergen and Stone 2021)
	2,3',4,4'-Tetrabro- modiphenylether	BDE-66	189084-61-5	Textiles and Foam	Textiles: 0.44 – 33 mg/kg Gymnastics foam: 4.2 – 92 mg/kg	USA	(Vojta et al. 2017) (Ceballos et al. 2018)

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
	2,2',3,4,4'-Pen- tabromodiphenyl- ether	BDE-85	182346-21-0	Textiles and foam	Textiles: >=1000 ppm (old furniture) Foam: 0.45 – 520 mg/kg	Non-EU (2015-2017)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	2,2',4,4',5-Pen- tabromodiphenyl- ether	BDE-99	60348-60-9	Textiles and foam	Textiles: 451 mg/kg Foam: 1.8 – 11000 mg/kg	EU and Non- EU (2012-2021)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021) (Norwe- gian EPA 2021) (van Bergen and Stone 2021)
	Diphenylether pentabromo deri- vates	BDE-99 / BDE-100	60348-60-9 189084-64-8	Polyure- thane foam	Foams: 940 – 35000 mg/kg	Non-EU (2010-2011)	(Stapleton et al. 2012) (Cooper et al. 2016) (Hammel et al. 2017)
	2,2',4,4',6-Penta- bromodiphenyl- ether	BDE-100	189084-64-8	Foam	Foam:0.324 – 1900 mg/kg	Non-EU (2015-2017)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	2,2',4,4',5,5'-He- xabromodipheny- lether	BDE-153	68631-49-2	Foam	Gymnastics foam: 1.2 – 990 mg/kg	Non-EU (2015-2017)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	2,2',4,4',5,6'-He- xabromodipheny- lether	BDE-154	207122-15-4	Foam	Gymnastics foam: 1.1 – 850 mg/kg	Non-EU (2015-2017)	(Vojta et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	2,2',3,4,4',5',6- Heptabromodiphe- nylether	BDE-183	207122-16-5	Foam	Gymnastics foam: 3.2 – 5.12 mg/kg Upholstered furniture: Below LOQ	Non-EU (2015-2016)	(Vojta et al. 2017) (Ceballos et al. 2018) (Rodgers et al. 2021)

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Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
	2,2',3,3',4,4',5,6'- Octabromodiphe- nylether	BDE-196	446255-39-6	Textiles	Furniture textiles: 13 mg/kg	EU (2021)	(Norwegian EPA 2021)
	2,2',3,4,4',5,5',6- Octabromodiphe- nylether	BDE-203	337513-72-1	Textiles	Furniture textiles: 19.95 mg/kg	EU (2021)	(Norwegian EPA 2021)
	2,2',3,3',4,4',5,5',6 -Octabromodiphe- nylether	BDE-206	63387-28-0	Textiles	Furniture textiles: 908 mg/kg	EU (2021)	(Norwegian EPA 2021)
	2,2',3,3',4,4',5,6,6' -Nonabromodi- phenylether	BDE-207	437701-79-6	Textiles	Furniture textiles: 115 mg/kg	EU (2021)	(Norwegian EPA 2021)
	Decabromodiphe- nylether	DecaBDE / BDE-209	1163-19-5	Textiles and foam	Textiles: 150 – 30000 mg/kg Foam: 1.66-22000 mg/kg	EU and Non- EU (2012-2021)	(Vojta et al. 2017) (Abdallah et al. 2017) (Estill et al. 2020) (Norwegian EPA 2021) (van Bergen and Stone 2021)
Brominated ali- phatics	Hexabromocy- clodecane	HBCD	3194-55-6	Textiles and foam	Textiles: 0.3-42000 mg/kg Foam: <0.3 - 6700 mg/kg	EU (2015-2021)	(Abdallah et al. 2017) (Norwegian EPA 2021)
	α-Hexabromocy- clododecane	α-HBCDD	134237-50-6	Textiles and foam	Textiles: 0.32 – 19000 mg/kg Foam: 2.61 – 89 mg/kg	Non-EU (Not men- tioned)	(Kajiwara et al. 2009) (Vojta et al. 2017)
	β-Hexabromocy- clododecane	β-HBCDD	134237-51-7	Textiles and foam	Textiles: 0.05 – 7500 mg/kg Foam: 1.97 – 23.5 mg/kg	Non-EU (Not men- tioned)	(Kajiwara et al. 2009) (Vojta et al. 2017)
	γ-Hexabromocy- clododecane	γ-HBCDD	134237-52-8	Textiles and foam	Textiles: 2.1 – 18000 mg/kg Foam: 20.4 – 32.3 mg/kg	Non-EU (Not men- tioned)	(Kajiwara et al. 2009) (Vojta et al. 2017)
	Hexabromocy- clododecane	HBCDD	25637-99-4	Textiles	Furniture textiles: 451 mg/kg	EU (2021)	(Norwegian EPA 2021)

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
	Sum of α- and β - Tetrabromoethyl- cyclohexane	DBE- DBCH (TBECH)	3322-93-8	Foam	Foam: 6.32 – 89.0 mg/kg	Not mentioned (1981-2004)	(Vojta et al. 2017)
	Sum of α-and β - 1,2,5,6-Tetrabro- mocyclooctane	ТВСО	3194-57-8	Foam	Foam: 3.62 mg/kg	Not mentioned (2003)	(Vojta et al. 2017)
Chlorinated ali- phatics	syn-Dechlorane Plus	s-DDC- CO	13560-89-9	Foam, hanging, up- holstery ma- terial	Foam: 476 mg/kg hanging: 0.588 mg/kg upholstery material: 0.833 - 3.25 mg/kg	Not mentioned (1981-2004)	(Vojta et al. 2017)
	anti-Dechlorane Plus	a-DDC- CO	13560-89-9	Foam, cur- tain, uphol- stery mate- rial	Foam: 650 mg/kg Curtain: 0.923 mg/kg upholstery material: 1.85 - 2.58 mg/kg	Not mentioned (1981-2008)	(Vojta et al. 2017)
	Hexachlorocyclo- pentenyl-dibromo- cyclooctane	DBHCTD (HCDBC)	51936-55-1	Foam	Foam: 1470 mg/kg	Not mentioned (2004)	(Vojta et al. 2017)
Brominated aro- matics	2-Ethylhexyl- 2,3,4,5-tetra-bro- mobenzoate	TBB/ FM550	183658-27-7	(Polyure- thane) foam	Gymnastics foam with 2.4 weight % or 1970 – 29000 mg/kg	Non-EU 2014-2017	(Stapleton et al. 2011) (Cooper et al. 2016) (Hammel et al. 2017) (Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	Bis(2-ethylhexyl)- 2,3,4,5-tetra-bro- mophtalate / 2- Ethylhexyl-2,3,4,5- tetra-bromobenzo- ate	FM550	26040-51-7/ 183658-27-7	Polyure- thane foam	Foam in couches: 19.76 mg/kg	Non-EU (2010-2011)	(Stapleton et al. 2012)
	Bis(2-ethylhexyl)- 2,3,4,5-tetra-bro- mophtalate	BEH- TEBP/ TBPH/	26040-51-7	Polyure- thane foam	Foams of child car seats, child mat- tress, sofa and love seats, chairs,	Non-EU (2010-2017)	(Stapleton et al. 2012) (Cooper et al. 2016) (Hammel et al. 2017)

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electronic parts

Chemical group	Substance	Abbrevia- tion	CAS no.	Material	Concentrations ¹¹	Sampling lo- cation (year)	Information source(s)
		FM550			rocking chairs and recliners: >1 weight % or 510 – 12000 mg/kg		(Ceballos et al. 2018) (Estill et al. 2020) (Rodgers et al. 2021)
	1,2-Bis(2,4,6-tri- bromophe- noxy)ethan	BTBPE	37853-59-1	Textiles, Foam	Furniture: 25 mg/kg Foam: 290 mg/kg	EU and not mentioned (2004-2021)	(Vojta et al. 2017) (Norwegian EPA 2021)
	Decabromo-diphe- nylethan	DBDPE	84852-53-9	Textiles	Furniture: 566 mg/kg	EU (2021)	(Norwegian EPA 2021)
	Tetrabromo- bisphenol A	TBBA, TBBPA	79-94-7	Textiles	Furniture: 21 mg/kg	EU and Non- EU (2015-2021)	(Estill et al. 2020) (Norwegian EPA 2021)
	Pentabromotolu- ene	PBT	87-83-2	Foam	Foam: 0.97 - 5.21 mg/kg	Not mentioned (2003-2004)	(Vojta et al. 2017)
	2,3-Dibromopro- pyl-2,4,6-tribromo- phenyl ether	TBP- DBPE (DPTE)	35109-60-5	Foam	Foam: 37.1 mg/kg	Not mentioned (2004)	(Vojta et al. 2017)
	Hexabromoben- zene	HBB ¹³	87-82-1	Foam	Foam: 895 mg/kg	Not mentioned (2004)	(Vojta et al. 2017)

¹³ Attention: Same abbreviation may be used for hexabromobiphenyl (CAS no. 36355-01-8).

4.3 Alternative flame retardants to restricted flame retardants in textiles

As some flame retardants are restricted due to their hazardous properties, several alternatives come into use to provide flame retardancy in products.

When pentabromodiphenylethers (subgroup under PBDE) were listed in Annex A of the Stockholm Convention, thus prohibiting their production and use, tris(2-chloroethyl) phosphate (TCEP) was used as replacement, which in turn, due to being identified as SVHC and subsequently included in the authorization list, was replaced by tris(1-chloroisopropyl) phosphate (TCPP) or tris(1,3-dichloroisopropyl) phosphate (TDCP). While a restriction intention for the intentional use as flame retardant in toys was initially prepared for TCPP, the intention was withdrawn in 2019, pending availability of new critical data. TCPP was in 2022 included on the CoRAP list¹⁴ for substance evaluation by the Danish EPA as the evaluating Member State Competent Authority. The conclusion of the substance evaluation was that the health concern is confirmed and a harmonized classification, as well as identification as SVHC and inclusion in the Restriction annex under REACH, is foreseen.¹⁵ TCPP was realized to be a multi constituent substance and as such received new identifiers (CAS no., EC no.) under which it is currently produced in the EU and/or imported into the EU in a tonnage of >10,000 to <100,000. TDCP is also still produced and/or imported into the EU in a tonnage of 1,000-10,000 t/year (ECHA 2023).

Since 2016, products (substances, mixtures, and articles) containing HBCD in concentrations of more than 100 mg/kg may no longer be produced or placed on the market in the EU according to the POP-Regulation (2019/1021). According to the German environmental agency (UBA), HBCD is easily replaceable in textiles because there are various possible ways to reduce flammability in this sector (Wurbs et al. 2017). Structure and density can influence flammability of fabrics. Further, fabrics can be made from poorly flammable fibre material such as polyaramids. UBA states that flame retardant alternatives include, for example, the permanent finishing of cellulose fibres with reactive flame retardants based on phosphorus, or inherently flame-retarded polyester fibres by means of chemically bound, phosphorus-containing flameretardant molecules. Specific examples used for the flame protection of cellulose are dimethylphosphono (N-methylol) propionamide, or tetrakis (hydroxymethyl)phosphonium urea ammonium salt. In the former case, the wet chemical treatment carries the drawback of releasing formaldehyde from the resin during the reaction between resin, flame retardant and cellulose polymer. However, in recent times, resins with very low or no formaldehyde emission were developed. Another drawback through this method and substance though is the discoloration of the textile product through the resin. The less commonly used substance tetrakis (hydroxymethyl)phosphonium urea ammonium salt can be regarded as wash-resistant through its polymerisation technique, however it requires a special ammonia-based preparation and a market license (Posner 2004).

Another possibility is flame retardancy through intumescent (swelling) systems. These systems are based on the formation of expanded coal or tar. This is achieved using three different components: acid source, carbon source and gas source. The acid can act as catalyst for the decomposition of the carbon source, or it can form or liberate acid itself when being heated. The carbon source mainly consists of polyols, which upon decomposition form a "carbon foam". Lastly, the gas component is usually a precursor, which liberates non-combustible or flammable gases like hydrochloric acid, ammonia, water, or carbon dioxide. Different suitable chemicals to

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¹⁴ Community rolling action plan (CoRAP), substances on the list are subject to substance evaluation by a Member State.

¹⁵ Substance Evaluation Conclusion document for Reaction products of phosphoryl trichloride and 2methyloxirane, CAS No 1244733-77-4, List No 807-935-0. EC No 807-935-0, <u>https://echa.europa.eu/documents/10162/9f7c76ef-d3fb-ebc1-dce6-c88a6bae9d14</u>.

act as such components includes for the acid source: Monoammonium phosphate, diammonium phosphate, ammonium polyphosphate, melamine phosphate, urea phosphate or other; for the carbon source: erythritol, pentaerythritol, arabitol, sorbitol, or other; and as a gas source: dicyandiamide, urea, melamine, or more (Posner 2004). Posner (2004) stated that the applications of these systems in textiles are still under development. Therefore, is not known whether there are any problems with the application of these systems. Updated information about such systems has not been identified during literature search in this project.

5. Survey of textiles containing electronic parts

5.1 Overview of textiles containing electronic parts at retailers

Products on the Danish market were identified from websites of several outdoor/hunting shops, a general consumer goods retailer, a fashion retailer, an electronics retailer and homeware suppliers (in total, 17 Danish retailers). Some of these retailers are actually European retailers, i.e. with activities in several EU countries, and provide several national websites for selected countries in Europe. If a European retailer provides a Danish websites, the retailer was counted as a Danish retailer. Additionally, relevant products from two international online marketplaces were added to the product list. The approach of the product survey aims to mimick how a typical Danish consumer would purchase such products on the internet (refer to method section 2.4).

In total, information about 67 unique products from 28 different manufacturers were listed. Generally, no information about use or type of flame retardants were provided in the product specifications. For a single product, a floor mat, the specifications note that the surface material is "flame-retardant" and another one, a space heater, is claimed to be fireproof. A few other products are advertised to be "RoHs approved" or are ecolabelled with the OEKOTEX label.

22 different product types were listed and include:

- heating blanket
- heating neck blanket
- heated sleeping bag
- heated sleeping pad
- heating mattress pad
- heating seat
- heating mat
- heated socks
- heated shoes
- heated soles
- heated gloves
- heated underwear
- heated jacket
- heated shawl
- heated vest
- heated shirt
- heated scarf
- heated cap
- heated ear warmers
- heated eye mask
- heating pads (usually to attach to or to be worn inside other clothing)
- space heater

All products are either powered with a power bank or plugged directly to a power socket. The products are generally targeted for use by adults but can in principle used by both adults and children.
The products are made from or in a combination of the following materials: acrylic, nylon, elastane, polyester, synthetic feathers, cotton, polyester fleece, synthetic wool, wool, PU coating, carbon fibre, suede, silica gel, synthetic leather and silicone. The manufacturers are companies located in Poland, Germany, Denmark, Sweden, United States, China, Spain and India. The location of the manufacturers is not always available from manufacturers' websites, but in many cases the Chinese name of a company led to the assumption that a manufacturer is located in China. Several European manufacturers inform on their websites, that they have production sites outside EU, e.g., in Asia, China or India. The prices of the listed products range from DKK 24 (a heating pad) to DKK 1,799 kr (heating soles).

5.2 Initial exposure assessment

In order to select products for purchase and chemical analyses, an initial exposure assessment was performed to identify products with the most significant exposure potential.

The products in TABLE 5-1 were evaluated qualitatively according to reasonable exposure duration, area of dermal contact, whether they are in direct or indirect contact with skin, whether exposure to children is likely, how common the products are, and the fabric material. For each of the exposure parameters, a rating was assigned (e.g., low, medium, high) and the average of the ratings resulted in an overall exposure score. The higher the overall exposure score, the higher is the initially assessed exposure potential.

The purpose with the rating on the mentioned parameter is solely to identify the most relevant products for purchase for the chemical analyses and the rating does not reflect actual exposure parameters for the risk assessment.

The reasoning behind the initial exposure parameters is based on reasonable worst-case considerations as follows:

- Exposure duration: Products that potentially are used overnight (>7 hours) receive the highest score of 3, while products designed for short-term use (<1 hour), i.e., a heated eye mask, receives the lowest score of 1. Products that are typically used for several hours during an outdoor activity, e.g., gloves, receive a medium score of 2, as it is anticipated that such outdoor activities usually will last between 1-7 hours.
- Contact area: A product which is designed to provide heat by radiation and which is not in contact with the skin, is assigned a score of 0, while products in contact with smaller parts of the body, e.g. hands or feet, are assigned a score of 1, and products covering larger parts of the body, e.g. a blanket or long-sleeve underwear, obtain a score of 2.
- Direct/indirect contact to skin: The potential for dermal exposure to flame retardants is increased when products are in direct contact with the skin, especially in the case where sweating can enhance exposure of flame retardants to the skin. Products potentially used with direct skin contact, e.g., socks and underwear, receive the higher score of 2. Other products can reasonably be expected to be used with one or several layers of fabric between the skin and the product, e.g., a jacket or vest, and are assigned a score of 1 for indirect contact to skin.
- Likelihood of children's exposure: None of the identified products were marketed for children as the target group. However, some products can be expected to be used by adults and children, e.g., blankets receive a score of 2, while products coming in specific sizes for adults, e.g., shirts, are less likely to be used for children and receive a score of 1.
- Common use and availability: The scoring of this parameter is based on the project team's subjective experience regarding how many different products and brands there are available for a given product type and how large the target group for a specific product type is. As example, heating socks are available at many retailers and from several different brands, and the potential user group comprises both outdoor-active people and people in general with a tendency to cold feet. Such products receive the higher score of 2. Other products appear rarer at retailers and probably have fewer potential users, e.g., a heated mat to place under

the desk against cold feet or a heated eye mask marketed for beauty and relaxation purpose. Such products receive a lower score of 1.

Material: In the case of natural fibres such as cotton or wool, the flame retardants are typically added via chemical post-treatment and as such "sit" on the surface of the fibre, leading to a higher potential for exposure, and are thus assigned the higher score of 3. In synthetic fibres, flame retardants are either present in the free space between the polymer molecules, but not covalently bound to the polymer matrix, presenting a leaching potential (and thus possible exposure), or built into the textile fibre via covalent bonding, meaning they cannot leach out of the fibre. Overall, synthetic fibres are assigned the lower score of 1. Products consisting of both natural and synthetic fibres are assigned the medium score of 2.

TABLE 5-1 Initial exposure assessment of textiles with electronic parts

Product type	Exposure duration 1 Low (<1 hr) 2 Medium (1 - 7 hr) 3 High (>7 hr)	Contact area be- tween product and body 0 No contact 1 Minor body parts 2 Large body parts	Direct/in- direct con- tact 1 Indirect 2 Direct	Estimation of likelihood of children's exposure 1 Not likely 2 Likely	Estimation of common use and availability of product 1 Not common 2 Common	Material 1 Synthetic fi- bers 2 Mix of syn- thetic and natu- ral fibers 3 Natural fibers	Likely use in combination with other products	Overall exposure score
Heating blanket	3	2	2	2	2	1	Neck blankets	2.0
Heating mattress pad	3	2	2	2	1	2	-	2.0
Heated sleeping bag	3	2	2	2	1	1	Сар	1.8
Heated shirt	3	2	2	1	2	1	Gloves, footwear, scarfs, cap	1.8
Heated underwear	3	2	2	1	2	1	Gloves, footwear, scarfs, cap	1.8
Heated socks	3	1	2	1	2	2	Gloves, underwear	1.8
Heating pads	2	1	2	2	2	2	Gloves, footwear, scarfs, cap	1.8
Heated gloves	2	1	2	1	2	2	Footwear, scarfs, underwear, cap	1.7
Heated scarf	2	1	2	1	1	3	Gloves, footwear, underwear, cap	1.7
Heating neck blanket	2	1	2	2	2	1	Blankets	1.7
Heated jacket	2	2	2	1	2	1	Gloves, footwear	1.7
Heated shawl	2	2	2	1	1	2	Gloves, footwear, underwear, cap	1.7

Heated vest	2	2	1	1	2	2	Gloves, footwear, scarfs, cap	1.7
Heating mat	3	1	1	2	1	2	-	1.7
Heated sleeping pad	3	2	1	2	1	1	-	1.7
Heating seat	3	1	1	2	2	1	Footwear	1.7
Heated eye mask	1	1	2	1	1	3	-	1.5
Heated shoes	3	1	1	1	1	2	Gloves, scarfs, underwear, cap	1.5
Heated soles	3	1	1	1	2	1	Gloves, scarfs, underwear, cap	1.5
Heated cap	2	1	2	1	1	1	Gloves, scarfs, underwear, footwear	1.3
Heated ear warmers	2	1	2	1	1	1	Gloves, scarfs, underwear, footwear	1.3
Space heater	3	0	1	2	1	1		1.3

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5.3 Selection of products for analysis

Within the project scope, it was foreseen to purchase 30 products, 20 at Danish retailers and 10 from foreign retailers.

In order to support the overall objective of the project, products with different use patterns, price ranges and high relevancy with respect to dermal contact and potential exposure. The products were selected in consultation with the Danish EPA based on the information found during the literature research, the stakeholder consultation, and the following selection criteria.

- Inclusion of products with different use patterns
- High exposure potential of the product (compare previous section 5.2 and TABLE 5-1)
- Products purchased from EU and non-EU retailers
- Products representing different brands/manufacturers
- Products representing different price classes

Additionally, the product types were grouped in products groups based on similar exposure conditions. Considering availability at Danish and also at international retailers, and at the same time aiming at obtaining three different products of any of the most relevant product types (overall score \geq 1.7, TABLE 5-1), products as displayed in TABLE 5-2 were bought.

Each product was purchased in triplicate, of which two specimens were used for chemical analysis and one specimen was stored for possible enforcement procedures.

Product group	Product types	No. of products for purchase in DK/EU	No. of products for purchase from non- EU countries
Blankets, mattress	Heating blanket	2	1
pads, sleeping bags	Heating mattress pad	2	1
	Heated sleeping bag	_c	3
Clothing with direct	Heated shirt	1 ^a	1
skin contact	Heated underwear	3ª	_b
Accessory clothing with	Heated socks	2	1
direct skin contact	Heated gloves	2	1
	Heating neck blanket	2	1
Clothing with indirect	Heated jacket	2	1
skin contact	Heated vest	2	1
Total		18	11

TABLE 5-2 Number of products purchased from each product group.

^a Additional shirts with electronic heating were not identified at Danish retailers. Instead, another set of heated underwear was purchased.

^b Product ordered, but shipping failed.

° Products were not available from DK/EU retailers and were instead ordered from non-EU countries.

6. Chemical analyses

For the chemical analyses, only the textile and possibly foam parts of the relevant products are included in the analysis program. Foams in consumer products have earlier been shown to contain various flame retardants (e.g., Kjølholt et al. 2015, Klinke et al. 2023). Plastic casings, wiring and other plastic parts in the products are excluded from the project scope.

6.1 Analytical program

The analysis for presence of flame retardants was conducted with gas chromatography–mass spectrometry (GC-MS) at The Danish Technological Institute. The analytical program was adjusted according to the substances found in the survey of flame retardants (see chapter 4), availability of analytical methods and reference material, as well as communication with the Danish EPA. The list of analytes included in the analytical program as well as their detection limits (LOD) can be seen in Appendix 1. The list comprises flame retardants from the following chemical groups: organophosphates (non-halogenated), halogenated organophosphates (chlorinated or brominated), brominated aromatics, PBB and PBDE.

Due to challenges with reference material, a few analytes could not be determined with sufficient certainty. These comprise the non-halogenated flame retardant 2-ethylhexyl)-diphenylphosphate (EHDP, CAS no. 1241-94-7), some PBB and certain PBDE (see Appendix 1).

6.2 Sampling method and preparation

Samples were taken from two specimens of each product for true duplicate determinations. From each specimen a sample of 10 cm² was taken, and the weight and thickness of the sample was noted. The thickness of the sample was measured with a digital calliper and indicates the thickness of the compressed material. This means that the material does not contain any air in the thickness measurements. For most products, the sample consists of several layers of materials, e.g. inner lining, wadding and outer fabric, a so-called composite sample. The sample was taken in the immediate vicinity of the electronic heating element.

The samples were extracted with dichloromethane/acetone with internal standard using ultrasound followed by mechanical shaking on a shaking table for 12 hours. The extract was subsequently analysed by capillary gas chromatography combined with mass spectrometry (GC-MS). The content of the selected flame retardants was determined quantitatively against specific reference substances.

6.3 Target analysis of flame retardants

6.3.1 Results

The results of flame retardants detected in the textile products above the LOD are shown in TABLE 6-1. The LODs are substance- and material-dependent and vary between 1 - 10 mg/kg (TABLE 6-1). The relative uncertainty of analysis is 15% according to the laboratory.

Of the 25 flame retardant substances, for which quantification was possible during the analysis, three substances were quantified at levels above LOD. These are: tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and triphenyl phosphate (TPP). TCEP and TCPP belong to the group of chlorinated organophosphates, while TPP is a nonhalogenated organophosphate.

Concentrations of the measured flame retardants range from <LOD - 120 mg/kg.

The presence of TCEP and TCPP was determined in one out of 29 products (a pair of gloves). TPP was determined in six products, comprising clothing only (underwear, socks, outerwear) at concentrations ranging from 5.5 - 15 mg/kg.

In some cases, matrix interference due to the sample material caused elevated LOD in the analysis. The elevated LODs are also listed in TABLE 6-1, however, it is noted, that the listing of an elevated LOD does not mean (or increase the likelihood) that a flame retardant is present in a given product.

Product ID	Product type	ТВР	TCEP	ТСРР	TDCP	ТРР	TEHP
		126-73-8	115-96-8	13674-84- 5	13674-87- 8	115-86-6	78-42-2
202011 – 1	Heated sleeping bag	-	-	-	-	-	-
202011 – 2	Heating neck blan- ket	-	-	-	-	-	-
202011 - 3	Heated gloves	-	120/ 14 ^b	15/ 8.6 ^b	-	<10	-
202011 - 4	Heated vest	-	-	-	-	<15	-
202011 - 5	Heating blanket	-	-	-	-	-	-
202011 - 6	Heated socks	-	-	-	-	5.5	-
202011 - 7	Heated jacket	-	-	-	-	11	-
202011 - 8	Heated shirt	-	-	-	-	<10	<100
202011 - 9	Heating mattress pad/underblanket	-	-	-	-	-	-
202011 - 10	Heating blanket	-	-	-	-	-	-
202011 - 11	Heating mattress pad/underblanket	-	-	-	-	-	-
202011 - 12	Heating mattress pad/underblanket	-	-	-	-	-	-
202011 - 13	Heating blanket	-	-	-	-	-	-
202011 - 14	Heated sleeping bag	-	-	-	-	-	-
202011 - 15	Heated underwear	-	-	-	-	9.2	-
202011 - 16	Heated underwear	-	-	-	-	13	-
202011 - 17	Heated socks	-	-	-	-	-	-
202011 - 18	Heated socks	-	-	-	-	-	-
202011 - 19	Heated gloves	-	-	-	-	-	-
202011 - 20	Heating neck blan- ket	-	-	-	-	-	-
202011 - 21	Heating neck blan- ket	-	-	-	-	-	-
202011 - 22	Heated vest	-	-	-	-	15	-
202011 - 23	Heated sleeping bag	-	-	-	-	-	-
202011 - 24	Heated shirt	-	-	-	-	10	-
202011 - 25	Heated underwear	-	-	-	<15	-	-
202011 - 26	Heated gloves	<5	-	-	<15	-	-
202011 - 27	Heated jacket	-	-	-	<15	-	-
202011 - 28	Heated vest	-	-	-	-	-	-
202011 - 29	Heated jacket	-	-	-	<20	-	-
LOD		1	10	5	10	5	10

TABLE 6-1. Concentrations^{a, c} of flame retardants in the textile products (mg/kg)

^a "–" means that the concentration is <LOD.

^b If the Relative Standard Deviation (RSD) between duplicate samples exceeds 15%, both results are given.

 $^{\mbox{\tiny c}}$ "<" means that the LOD is elevated due to interference from the sample matrix.

6.3.2 Discussion

6.3.2.1 Flame retardants in textile products with electronic parts

The number of flame retardants determined at concentrations >LOD is rather low (3/25 substances) and comprises TCEP, TCPP and TPP.

TCEP is on the candidate list under REACH and subject to authorisation under REACH (no exempted uses registered). TCEP has been detected in a pair of gloves, which was purchased from a non-EU retailer, and which presumably was manufactured outside EU, meaning that the use restrictions due to authorisation do not apply.

TCPP and TPP are currently not regulated with respect to use in textiles or in electronic products in the EU. However, TCPP is (along with TCEP and two other chlorinated phosphorous flame retardants) comprised by a restriction intention submitted by ECHA, which is currently pending availability of new critical data¹⁶. The substance evaluation under CoRAP led to the conclusion that the health concern regarding TCPP is confirmed and a harmonized classification, as well as identification as SVHC and inclusion in the Restriction annex under REACH, is foreseen.¹⁷ TPP is on the CoRAP list due to suspected endocrine disrupting effects, and the substance evaluation has led to the conclusion that TPP should be classified and included on the candidate list¹⁸.

Other regulated flame retardants, such as PBB or PBDE were not detected. It is noted that some substances belonging to the group of PBB and PBDE could not reliably be identi-fied/quantified during analysis. Since PBB and PBDE were generally not found, the occurrence of substances and congeners for which analytical results are not available, is not expected.

In conclusion, the textile parts of the purchased products seem to comply with current regulations under REACH, the POPs regulation, and the RoHS-Directive in regard to the content of flame retardants.

The number of products, in which flame retardants were determined at concentrations >LOD, is relatively low (7/29 products, corresponding to 24%). Products, in which flame retardants were determined at concentrations >LOD, were bought from Danish, EU as well as non-EU retailers (data not shown). The concentrations of flame retardants determined in the products were generally below 20 mg/kg (0.002% w/w), and only in one case exceeded 100 mg/kg (corresponding to 0.01%; TCEP was determined at 120 mg/kg = 0.012%).

For a few of the restricted flame retardants, concentration limits in articles are defined in the applicable regulations (see section 4.1). Under the POPs Regulation, the concentration limit of PBDE in articles is 500 mg/kg (0.05%), under RoHS, the concentration limit in electrical and electronic equipment is 0.1%, and under REACH, the concentration limit for octaBDE is set at 0.1% in articles. For TCEP, no concentration limit is defined. The concentration limits are usually set at levels below functionality, but still allow for trace contamination. The flame retardants found during the analysis are below the established concentration limits. It is noted, that the substances for which concentration limits apply, are not the same that have been found during the analysis in this study, and the comparison with established concentration limits is merely included to provide a sense of the order of magnitude of the found concentrations.

¹⁶ https://echa.europa.eu/da/registry-of-restriction-intentions/-/dislist/details/0b0236e1829a30b8

¹⁷ Substance Evaluation Conclusion document for Reaction products of phosphoryl trichloride and 2methyloxirane, CAS No 1244733-77-4, List No 807-935-0. EC No 807-935-0, <u>https://echa.europa.eu/documents/10162/9f7c76ef-d3fb-ebc1-dce6-c88a6bae9d14</u>.

¹⁸ https://echa.europa.eu/documents/10162/916779d9-ec10-07fa-f178-9562bdd7dedc

ECHA (2023a) identifies concentrations of 5-25% organic flame retardants as drivers for exposure via release of the flame retardant from intact materials. In the survey on flame retardants by the Danish EPA (Andersen et al. 2014), the typical use of halogenated phosphorous-based flame retardants (e.g., TCPP or TCEP) in textiles is given as 50-100 g/kg (5-10%). Compared to these figures, it is assessed as unlikely that the flame retardants occurring in the analysed products in this study are added for an intentional flame retardancy effect, but rather occur as impurities. It is not known, where the impurities stem from, but handling flame retardants at the production site or use of recycled polymer products in the production could lead to the presence of flame retardants in low concentrations in the products investigated here. Also, it is not known whether flame retardants occur in the electronic parts or plastic casings of the products, and whether their potential presence in these parts may impact the presence of flame retardants in the textile parts. Contamination of the samples during analyses could be excluded due to analytical procedures.

Even though the number of purchased products is relatively small to allow a general conclusion, the results indicate that it is not common practice to add flame retardants to textile products containing electronic parts. This perception is supported by the low concentrations of flame retardants determined in the products, which were generally below 20 mg/kg (0.002% w/w), and only in one case exceeding 100 mg/kg.

6.3.2.2 Recalculation of concentration from composite samples to single layer

Many of the analysed products consist of several layers. Most products are made of one to three layers, while some products comprise of four to six layers. A pair of gloves (product 202011-3), for example, consists of five layers comprising an outer fabric with glued on foam, wadding, felt fabric with heating element, another layer of wadding and an inner lining. As the samples were taken as composite samples (containing all layers), a dilution through the sample can be anticipated in multilayer products, if flame retardants are only present in one of the layers.

To account for this dilution, the measured concentrations of flame retardants can be recalculated assuming that the total measured concentration of flame retardant is situated only in the inner layer of the article, thus being in direct contact with the skin. This approach presents a worst-case scenario of exposure.

The theoretical concentration of flame retardant in the inner layer is recalculated and converted to a mass/volume unit (mg/cm³), which is the unit to be used as input for the exposure calculation (see Equation 6-1 and Equation 6-2).

$Conc_{innerlayer}\left[\frac{mg}{cm^3}\right] = Conc_{prod}\left[\frac{mg}{kg}\right] \times \frac{Mass_{sample}\left[kg\right]}{Vol_{innerlayer}\left[cm^3\right]}$	Equation 6-1
$Vol_{inner\ layer} = Height \times Width \times Thickness_{inner\ layer}$	Equation 6-2

As an example, the mass and dimensions for the gloves sample (product 202011-3) are given in TABLE 6-2.

TABLE 6-2. Dimensions and mass of glove sample (product 202011-3).

Parameter [unit]	Value
Mass m (sample) [kg]	0.0079
Height [cm]	10
Width [cm]	10

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Thickness (inner layer) [cm]	0.030
Thickness (sample) [cm]	0.233

Applying the above equations to the gloves (product 202011-3) with a measured TCEP concentration of 120 mg/kg, the concentration of TCEP in the inner layer can be calculated as follows:

 $Conc_{inner\,layer} = 120 \frac{mg}{kg} \times \frac{0.0079 \, kg}{10 * 10 * 0.03 \, cm^3} = 0.316 \, \frac{mg}{cm^3} = 0.00032 \, \frac{g}{cm^3}$

Hence, in the case of the gloves (product 202011-3), a measured concentration of TCEP of 120 mg/kg in the product, corresponds to a concentration of 0.00032 g/cm³ in the inner layer.

Similarly, a measured concentration of TCPP of 15 mg/kg in the gloves (product 202011-3), corresponds to a concentration of 0.00004 g/cm³ in the inner layer.

The socks and underwear (products 202011-6, 202011-15 and 202011-16) in which TPP was detected, only consist of one layer. Hence, for these products, the measured concentration reflects the concentration in the textile layer, which is in contact with the skin. Thus, it is not relevant to conduct an additional calculation to derive the inner layer concentration.

For comparison with the analytical results, the concentration in the inner layer can also be converted to mg/kg by assuming the same density of the inner layer and the whole sample. Using the density (Equation 6-3) and the volume of the inner layer, the sample concentration can be converted to the concentration in the inner layer (Equation 6-4). The example below shows the calculation for the glove sample in which 120 mg/kg TCEP were measured:

Equation 6-4

 $d_{sample} = \frac{m_{sample}}{V_{sample}} = \frac{0.0079 \, kg}{10 cm \times 10 cm \times 0.233 cm} = 0.00034 \, kg/cm^3$ Equation 6-3

$$C_{inner\,layer} \left[\frac{mg}{kg} \right] = \frac{m_{FR}[mg]}{m_{inner\,layer}[kg]}$$
$$= \frac{C_{sample} \left[\frac{mg}{kg} \right] \times m_{sample}[kg]}{V_{inner\,layer}[cm^3] \times d_{sample} \left[\frac{kg}{cm^3} \right]}$$
$$= \frac{120 \frac{mg}{kg} \times 0.0079 \, kg}{3 \, cm^3 \times 0.00034 \frac{kg}{cm^3}} = 932 \, mg/kg$$

Where m_{FR} is the mass of the flame retardant in the sample and d is the density of the sample (assumed equal to density of inner layer).

Thus, based on the worst-case assumption that the whole amount of flame retardant is concentrated in the inner layer of the glove, the concentration is about eight times higher.

6.3.3 Conclusion

Overall, the results and the discussion allow for the following conclusions:

- Flame retardants may occur in textiles with electronic parts, but their occurrence does not appear significant in terms of concentration levels.
- The concentrations found in the products are low and do not indicate intentional addition of flame retardants to the products with the objective of achieving flame retardancy.

- Product samples were taken as composite samples, and a dilution of flame retardants through the sample can be anticipated for multilayer products. The theoretical concentration, corresponding to that all flame retardant is present in the inner layer with skin contact, is about eight times higher for the glove sample, in which flame retardants were measured. These concentrations are included in the risk assessment.
- The consumer health risk assessment (chapter 7) concludes whether the found concentrations in the products may cause a health risk for the consumers based on worst-case assumptions.

6.4 GC-MS non-target screening analysis for additional compounds

Apart from the quantitative analysis of flame retardants, the output from the GC-MS analysis was reviewed further to identify additional compounds.

The objective of the analysis of the GC-MS chromatograms is to obtain additional data about presence of potentially hazardous substances. The identified substances are to be compared with the substances found in other consumer textile products in order to evaluate whether the presence of substances in textiles with electronic heating functions differs from other textile types.

The chromatographs from the GC-MS screening were reviewed for all 29 products, and the substances resulting in the 10-20 highest peaks were aimed to be identified by The Danish Technological Institute using the NIST¹⁹ mass spectral library. Concentrations were determined semi-quantitatively against internal standards.

6.4.1 Results of GC-MS screening analysis

Generally, substances were identified with three categories of certainty:

- Category A: Confident and confirmed identification with NIST hit rate ≥80%. The substance is identified by name, CAS no. (or NIST no. if CAS no. is not available for the substance in the library). It is noted that also for category A substances, some uncertainty remains regarding the precise substance identification.
- Category B: Partial identification. The substance is identified by chemical class of the compound, a fragment of the substance or by a compound bound to the substance. In some cases (especially for larger molecules with complicated structures), a suitable name for a chemical class was not available. In such cases, a substance name was chosen as class name, and CAS or NIST no. is not provided.

Category C: Unidentified substance.

An overview of the number of substances identified per category and per article is given in TA-BLE 6-3 below. About one third (118) of all substances (292) could be identified with adequate certainty to allow conclusion on specific substance identification.

A full list of all substances identified in the analysed articles can be seen in Appendix 2.

¹⁹ National Institute of Standards and Technology (NIST) is an agency of the U.S. Department of Commerce.

⁴⁸ The Danish Environmental Protection Agency / Survey, control and risk assessment of flame retardants and other substances of concern in textiles containing electronic parts

TABLE 6-3. Overview of the number of substances and articles in the GC-MS screening.

Parameter	Number
Category A substances (identification with high certainty)	118
Category B substances (identification with low certainty)	47
Category C substances (not identified)	127
Total number of peaks (substances) reviewed	292
Number of articles in GC-MS screening	29
Number of substances (all categories) per article, mean (range)	13 (6 – 20)

Substances, that were detected commonly (in three or more articles) and were identified by CAS/NIST no. or chemical class, are listed in TABLE 6-4 below, together with the number of articles in which the substance was identified and the indicated concentration ranges.

Additionally, information about the likely origin and/or function of the substances is shown in the table to evaluate, whether the presence of the substance may be specific for textile products with heating function or whether such substances may also be expected in other consumer textiles articles. A main source for this information is the Danish EPA report from 2015 on textile articles for children (Kjølholt et al., 2015), as a corresponding GC-MS method as in the current study was used on textiles and foam samples from consumer articles. Additional sources for information on the substances were the reports on hazardous chemicals in textiles by the Swedish Chemicals Agency (Keml 2013, 2014), RIVM (Nijkamp et al., 2014), ECHA's list on plastic additives²⁰ and the Danish database in chemicals consumer articles²¹. If no information could be retrieved from these sources, information about the substances' presence in textiles was sought via the Pubchem Hazardous Substances Data Bank (HSDB)²², ECHA chemicals database²³ or additional literature sources identified via general search engine (Google, Google Scholar). Substances that were identified as hazardous in the mentioned publications and/or for which harmonised classifications for health hazards were available from the ECHA chemicals database, are also recognised as hazardous in the current study, and the the hazard information is mentioned in TABLE 6-4 below. Finally, a conclusion on whether the substance can be considered specific for textile with electronic parts is provided.

Only substances identified in three or more products were included in TABLE 6-4. This demarcation was chosen to evaluate the presence of 'common' (present in three or more products) substances in textiles with heating function, and to focus resources for the review on the most relevant substances. The identification of flame retardants is not discussed in this section, as results from the targeted analyses are reported in the previous section 6.3.

²⁰ <u>https://echa.europa.eu/mapping-exercise-plastic-additives-initiative</u>

²¹ https://vidensbank.mst.dk/v2/

²² <u>https://pubchem.ncbi.nlm.nih.gov/source/11933</u>

²³ <u>https://echa.europa.eu/information-on-chemicals</u>

TABLE 6-4 Substances in textiles with heating function identified during the non-target GC-MS screening.

Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
1	Unidentified, possibly part of polyeth- ylene terephthalate	-	29	130 - 1700	An "unidentified, possibly part of polyethylene terephthalate" (PET) substance, was identified in all 29 articles. PET is a commonly used polymer used for textiles, and the analysed articles consist, according to the product descriptions, either entirely or partially of polyester. PET is a common polyester type and the presence of PET related substances can be explained through the presence of the polymer and some degree of degradation of the polymer through the sample treatment, resulting in PET fragments. Hazard or classification information for this unidentified substance could not be identified. The presence of the substance is not considered to be specific for textiles with electronic heating functions.
2	Unidentified, hydroxybenzophenone	-	22	43 - 310	Several benzophenone-related substances were identified. Benzophenones are used as UV- absorbers and -stabilisers in textiles (Kjølholt et al., 2015). Benzophenones were also detected in other consumer textiles articles. For example, Kjølholt et al. (2015) identified benzophenone in baby carriers. Some benzophenones are suspected of being carcinogenic, endocrine disrupt- ing and/or harmful to the unborn child, while others are not considered to be problematic to the same degree (Kjølholt et al., 2015). More detailed hazard information could not be identified, as the substance could not be precisely defined. Since benzophenones are known to be used as UV-filters in textiles, their presence is not considered to be specific for textiles with electronic heating functions.
3	3,6,13,16-tetraoxatricy- clo[16.2.2.2(8,11)]tetracosa- 8,10,18,20,21,23-hexaene-2,7,12,17- tetrone	998398-77-0	14	25 - 550	Terephthalate/PET related, see row no. 1

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Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
4	Benzenamine, 2-chloro-4,6-dinitro-	3531-19-9	13	34 - 170	Benzenamine, 2-chloro-4,6-dinitro- (CAS no. 3531-19-9) is also known as 6-Chlor-2,4-di- nitroaniline). It is a halogenated, aromatic amine (AA). Aromatic amines may be released from azo dyes and are therefore recognised as indicators for azodyes (KemI, 2014; Kjølholt et al., 2015; Brüschweiler & Merlot, 2017).
					In the quantitative analysis of amines in Kjølholt et al. (2015), AA were measured in both car safety seats and baby carriers. 6-Chlor-2,4-dinitroaniline was not measured in the quantitative analysis of AA but identified during the GC-MS screening in textile and foam samples of several car safety seats and baby carriers.
					Azo dyes, which may release any of the 22 regulated carcinogenic AAs are banned from cloth- ing textiles in the European Union (Annex XVII of the REACH regulation; No, 1907/2006, entry 43 and Appendix 8). 6-Chlor-2,4-dinitroaniline is not comprised by this regulation but Brüschweiler & Merlot (2017) investigated the mutagenicity potential of unregulated AA and found mutagenic properties for many unregulated AA. The substance does not have a harmo- nised classification, but the majority of notifiers inform that the substance is fatal if swallowed (Acute Tox. 2, H300), is fatal in contact with skin (Acute Tox. 1, H310), is fatal if inhaled (Acute Tox. 330), and may cause damage to organs through prolonged or repeated exposure (STOT RE, H373).
					Considering that the substance most likely is present as a cleavage product from azodyes, which use is know from other consumer textiles, the presence of AA in the articles with heating function is therefore not considered to be specific for this type of product.

Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
5	Benzoic acid	65-85-0	11	9.2 - 200	Benzoic acid is a the simplest of all benzene-based carboxylic acids. Benzoic acid and related substances have been identified in numerous articles in the GC-MS screening.
					Benzoic acid esters may be used as carriers for certain dyeing processes (Keml, 2013), and so- dium salts of benzoic acids also function as direct dyestuffs in textiles (Keml, 2014). Derivatives of benzoic acid (different benzoates) are also used as plasticisers in different polymers (ECHA plast additive initiative). The origin of benzoic acid identified in the samples is therefore expected to be related to the textiles dyeing or origin from degradation of larger molecules containing a benzoic acid moiety during analytical sample handling.
					Benzoic acid and related substances were not identified in other consumer articles. However, it is likely, that the substance could not be identified in corresponding analyses (e.g., Kjølholt et al., 2015), because of low concentrations and because short retention times (retention times not shown here) often impede the identification of low-molecular, volatile substance in GC-MS screenings.
					The substance has a harmonised classification as skin irritant (Skin Irrit. 2, H315), for causing damage to organs through prolonged or repeated exposure (lungs via inhalation, STOT RE 1, H372), and for causing serious eye damage (Eye Dam. 1, H318).
_					Based on the available information on function of benzoic acid and related substances, it is expected that the presence of these substances is not specific to textiles with heating functions.
6	Unidentified, hydroxybenzophenone	-	10	60 - 180	See above, row no. 2
7	Isophthalic acid	121-91-5	9	58 - 350	Isophthalic acid is, as phthalic acid and terephthalic acid, an isomer of benzenedicarboxylic acid. It may occur as an impurity in PET fabric or be added intentionally to the polymer to decrease crystallinity (Arnkvist, 2023). According to the notifications provided by companies to ECHA in REACH registrations, no hazards have been classified for this substance.
					The concentration indicated here is rather low, and the presence in expected to be linked to the polymers (polyester) used in the articles and not expected to be specific for textiles with heating functions.

Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
8	Benzenepropanoic acid, 3-(1,1-di- methylethyl)-4-hydroxy-5-methyl-, 1,2- ethanediylbis(oxy-2,1-ethanediyl) ester	36443-68-2	8	69 - 230	The substance is listed as an antioxidant in several plastic types in the ECHA Plastic-Additives- Initiative ⁴ , also for some plastic types used in textiles (e.g. PUR, PS). This may explain the pres- ence in the textile articles analysed in the current project. Other information regarding the pres- ence of this substances in textiles has not been identified. It is noted that the substance appears in concentrations (≤0.023%), which are within the typical concentration range 0.005 - 3.0% for this type of antioxidant according to ECHA Plastic-Additives-Initiative. According to the notifica- tions provided by companies to ECHA in REACH registrations, no health hazards have been classified for this substance. Considering the function of this substance, it is considered unlikely that the substance is specific for textiles with heating functions.
9	Benzoic acid, 2-(1-oxopropyl)-	2360-45-4	8	82 - 1600	See above, row no. 5.
10	Benzene, 1,1'-methylenebis[4-isocya- nato-	101-68-8	7	52 - 710	The substance is a diisocyanate commonly abbreviated as MDI or 4,4-MDI. MDI is like other iso- cyanates a precursor in the manufacturing of polyurethane (PUR), e.g., for waterproof clothing. MDI was identified in several foam samples from textile articles in Kjølholt et al. (2015), both in car safety seats, baby carriers and baby mattresses. In addition, MDI has also previously been shown to migrate from children's jackets and gloves (Tønning et al., 2009) and was identified in textile face masks (Poulsen et al., 2021). However, Kjølholt et al. (2015) also conclude that the conventional GC-MS screening is not suitable for identification of isocyanates, as the sub- stances, despite indications of their presence in the samples at the GC-MS screening, were not found in concentrations above 1 mg/kg in any of the samples examined by the specific quantita- tive analysis. MDI has a harmonised classification for causing serious eye irritation (Eye Irrit. 2, H319), is harmful if inhaled (Acute Tox. 4, H332), is suspected of causing cancer (Carc. 2, H351), may cause damage to organs through prolonged or repeated exposure (STOT RE 2, H373), causes
					skin irritation (Skin Irrit. 2, H315), may cause an allergic skin reaction (Skin Sens. 1, H317), may cause allergy or asthma symptoms or breathing difficulties if inhaled (Resp. Sens. 1, H334) and may cause respiratory irritation (STOT SE 3, H335).
					The substance does not appear to be specific to textiles with heating functions, but its presence in textiles articles may be linked to outdoor articles (with waterproof properties) or articles containing foam.

Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
11	Unidentified, hydroxybenzophenone	-	6	28 - 55	See above, row no. 2
12	Cyclohexane, 1,3,5-triphenyl-	28336-57-4	6	38 - 380	No specific information has been identified for this substance. In HSDB, it is mentioned that the substance can occur as impurity in polystyrene (PS). It is a PS oligomer (a trimer), which can form during (bio)degradation of PS (Tsochatzis et al., 2021). It is thereforeanticipated that the low levels of the substance identified here origins from its presence as impurity or possibly degradation. No hazard or classification information is available for this substance.
					functions.
13	1,4-Benzenedicarboxylic acid, bis(2-	6422-86-2	5	6 44 - 580	Also Bis(2-ethylhexyl) terephthalate (DEHT), plasticiser.
	ethylhexyl) ester				Terephthalate/PET related, see row no. 1
14	3,6,13,16-tetraoxatricy- clo[16.2.2.2(8,11)]tetracosa- 8,10,18,20,21,23-hexaene-2,7,12,17- tetrone	-	4	74 - 430	Terephthalate/PET related, see row no. 1
15	3-Butenyl adipate	998445-98-6	4	48 - 250	Adipates are used as plasticisers in PUR or soft PVC. According to the ECHA Plastic-Additives- Initiative, adipates are typically added in the concentration range 10-35% (100,000-350,000 mg/kg), which is far above the indicated concentration range for the articles in this study. Addi- tional information about this specific substance was not identified. It appears likely that the iden- tified adipate results from impurities and/or contamination of the polymers used in the articles. No hazard or classification information is available for this substance.
					The presence of the substance is thus anticipated be linked to the material, rather than to the specific product type of textiles with heating function.
16	Unidentified, possibly part of polyethyl- eneterephthalate	-	4	99 - 2200	Terephthalate/PET related, see row no. 1. The substance is listed separately here due to longer retention time (data on retention time not presented here).

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Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
17	tri(2-Ethylhexyl) trimellitate	3319-31-1	4	. 30 - 83	The substances (also called tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate) is a plasticiser used in soft PVC used at typical concentrations of 35% (350,000 mg/kg) according to the ECHA Plastic-Additives-Initiative. Textile articles may be coated with soft PVC, e.g., for water repellence or as imitation leather. The substance has been detected earlier in (playing) mats used in childcare centers (Vium et al., 2015), while detections in consumer articles have not been identified. According to the majority of notifications provided by companies to ECHA in CLP notifications no hazards have been classified. As the substance is a PVC plasticiser, it is not anticipated to be specifically linked to textiles with heating function.
18	9-Octadecenoic acid	2027-47-6	3	30 - 82	The substance is better known as oleic acid. Oleic acid is a fatty acid and mostly used to make soaps and detergents, but also mentioned in relation to waterproof fabrics, and as a plasticiser (HSDB entry on oleic acid, CAS no. 112-80-1, 2027-47-6 and 99148-48-8). Fatty acid esters are also used as preparation agents in the manufacturing of synthetic fibres, and fatty acids may occur as degradation products and impurities from production in textiles (Kemi, 2013). According to the majority of notifications provided by companies to ECHA in CLP notifications no hazards have been classified. The presence of oleic acid in the articles is not anticipated to be specifically linked to textiles with heating function.
19	Butenyl Butanediol Adipate	998445-98-8	3	92 - 160	Adipate, see row no. 15
20	Irigenin, trimethyl ether	50901-35-4	3	38 - 96	Neither information with relevancy for textiles nor hazard information could be retrieved for this substance.
21	2H-1,3-Pyrimidine-2-ketene, 2,5-dime- thyl-1,6-diphenyl-4-(p-tolyl)-	998149-41-5	3	53 - 270	Neither information with relevancy for textiles nor hazard information could be retrieved for this substance.
22	Adipic acid, cyclobutyl nonyl ester	998324-27-7	3	39 - 120	Related to adipates, see row no. 15
23	bis(Butenyl) adipate	998445-98-7	3	21 - 95	Adipate, see row no. 15
24	Butanediol adipate	998445-98-5	3	170 - 420	Adipate, see row no. 15
25	Ethanone, 1-[3,5-bis(phenyl- methoxy)phenyl]-	28924-21-2	3	43 - 290	Synonym: 3,5-bis(benzyloxy)acetophenone. No information with relevancy for textiles was re- trieved for this substance. According to the majority of notifications provided by companies to ECHA in CLP notifications no hazards have been classified.

Row no.	Substances ¹	CAS or NIST no. ²	No. of articles	Indicated concen- tration (mg/kg) range ³	Information on origin and/or function, and evaluation of content of hazardous substances
26	Tributyl acetylcitrate	77-90-7	3	57 – 340	Tributyl acetylcitrate is used as a plasticiser in PUR or soft PVC. According to the ECHA Plastic- Additives-Initiative, the substances is typically added in the concentration range 10-35% (100,000-350,000 mg/kg), which is far above the indicated concentration range for the articles in this study. According to an entry in the HSDB (entry on CAS no. 77-90-7), the substance is used as plasticiser in packaging films for food. The substance was also identified in the screening by Kjølholt et al. (2015) in a foam sample from a baby mattress, and a textile and foam sample from a car safety seat. According to the notifications provided by companies to ECHA in REACH registrations no hazards have been classified. There are no indications that link this substance specifically to functionality required for textiles.

¹ Some substance names occur more than once in the table. This is due to that the name presumably covers different substances within same chemical class or the substance could not be identified.

Differentiation between substances was made based on diverging retention times in the analysis (retention times not shown here).

² If CAS no. was not available, substance is identified with NIST no. NIST no. start with "998".

³ Concentrations were quantified against an internal standard and do thus not represent precisely quantified concentrations

⁴ ECHA Plastic-Additives-Initiative https://echa.europa.eu/mapping-exercise-plastic-additives-initiative

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6.4.2 Discussion and conclusion on the GC-MS non-target screening

About one third (118) of the reviewed peaks (292) in the GC-MS non-target screening could be identified with adequate certainty to allow conclusion on specific substance identification.

Overall, the commonly identified substances as presented in TABLE 6-4 can be assigned to three groups:

- Many of the substances identified in the non-target screening are related to the type of polymer used for textile products, e.g., unidentified components, which appear to be fragments of the polymers such as polyethyleneterephthalate (PET). For these substances, information on hazards is not readily available. These substances are not considered specific for textiles with heating functions, as they relate to polymers used for textiles.
- 2) Other substances are known additives in polymers such as PET, PS or PVC, e.g., hazardous substances such as benzophenones (UV-absorbers), aromatic amines (cleavage products from azo dyes) or adipates (plasticisers). Generally, these substances occur at low concentrations, which indicates that they are present as impurities rather than intentionally added. Also these substances are not considered specific for textiles with heating functions, as they relate to plastic polymers.
- 3) The substance MDI is an isocyanate, which is a precursor in the manufacturing of PUR. PUR is used for waterproof coatings in outdoor clothing. MDI is a recognised hazardous substance due to (amongst others) suspected carcinogenic, skin and respiratory sensitising properties. MDI was identified in seven out of the 29 analysed articles, hereunder in socks (2 articles), shirts (2 articles), underwear (2 articles) and a vest. Only the latter article is intended for use as outer layer in outdoor settings, where waterproof properties may be desirable. The presence of MDI in articles such as socks and underwear is not plausible and the identification may be due to contamination rather than intentional use of PUR. Additionally, it is noted that some uncertainty in the identification of Category A-substances remains and that the non-target GC-MS screening method has earlier been shown not to be suitable for isocyanates (TABLE 6-4, row 10). It is therefore not possible to conclude, whether isocyanates are commonly present hazardous substances in textiles with electronic heating functions.

Most articles comprised by the current study were exclusively or partially made of polyester according to the product descriptions on the retailers or manufacturers' websites. Other listed materials were synthetic polymers such as acryl, nylon, spandex and elastan, while a few also contained cotton layers. PVC or PUR were not listed as used materials in the product descriptions. However, PVC and PUR may still occur as labels or prints on the textile articles. Detailed information to which extent the samples contained labels or prints were not monitored in the study and the information is therefore not available.

The results of the GC-MS non-target screening indicate that certain hazardous substances such as benzophenones, aromatic amines, benzoic acid and MDI can be present in textiles with electronic heating functions. However, most of these substances have also been identified in other consumer textiles products. Generally, the concentrations appear to be low and do thus indicate impurities or contamination rather than intentionally used additives. It is therefore considered unlikely, that the presence of this substances is specifically related to the functionality of textiles with electronic heating functions.

Thus, based on the identified substances in the non-target screening, the presence of hazardous substances in textiles with electronic heating functions cannot be excluded. However, textile products with electronic heating functions do not appear to contain hazardous substances that are specific for this product type.

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7. Consumer health risk assessment

As reported in TABLE 6-1, TCEP, TCPP and TPP are the only flame retardants that were detected above the LOD in the analysed consumer products. Hence, the consumer health risk assessment will focus on these three substances.

The substance identification through the analysis of the GC-MS chromatographs purely serves the objective of obtaining additional data about presence of potentially hazardous substances, and these substances were not in the scope for the risk assessment.

7.1 Hazard assessment

In the following sections, the phosphorus-based flame retardants TCEP, TCPP and TPP are described in terms of their harmonised classification according to the CLP Regulation, their physicochemical properties as well as their toxicity and therefrom derived DNEL (Derived No Effect Level).

7.1.1 TCEP

Classification

According to the EU harmonized classification²⁴ (CLP Regulation 1272/2008), TCEP is classified as Acute Tox. 4; H302, Carc. 2; H351, Aquatic Chronic 2; H411 and Repr. 1B; H360F. The majority of the notified self-classifications have the same hazard categories and phrases, none has a more hazardous profile, but one is lacking Repr. 1B.

Substance identity and physicochemical properties

The physical and chemical properties of TCEP are described in TABLE 7-1.

Parameter	Description	Source
Substance name	Tris(2-chloroethyl) phosphate	ECHA Substance Infocard
CAS no.	115-96-8	ECHA Substance Infocard
Structure		ECHA Substance Infocard
Chemical group	Chlorinated organophosphates	
Vapour pressure (in- terpretation)	1.14×10 ⁻³ Pa at 20.0 °C (non-volatile)	EU RAR (2009) and ECHA CHEM

TABLE 7-1. Identification and physicochemical properties of TCEP.

²⁴ ECHA C&L inventory accessed on 2nd April 2024. URL: <u>https://echa.europa.eu/da/information-on-chemi-cals/cl-inventory-database/-/discli/details/68691</u>

Parameter	Description	Source
Molecular weight	378.39 g/mol	ECHA CHEMI
LogPow	1.7 at 20.0 °C	ECHA CHEM
CLP classification	Aquatic chronic 2 – H411 Carc. 2 – H351 Repr. 1B – H360F Acute Tox. 4 – H302 ²⁵	ECHA C&L inventory

Substance toxicity

Toxicity studies on TCEP have been summarized in earlier consumer risk assessments by the Danish EPA; Andersen et al. (2014) and Kjølholt et al. (2015), who based the hazard information on the EU risk assessment report on the same substance (EU RAR, 2009). Available ECHA dossiers have also been checked for updated information and since no studies were newer than 2015, the information therefrom was not regarded in this assessment.

From the available data, the following can be summarized:

- Kjølholt et al. (2015) report an absorption of approximately 90% following oral ingestion. In the EU risk assessment, the oral, dermal and inhalation absorption rates are assumed to be 100% as a worst-case scenario (EU RAR, 2009).
- Based on animal studies, TCEP is not considered to be corrosive nor to be a skin or eye irritant (EU RAR, 2009).
- TCEP is concluded not to be mutagenic (Kjølholt et al., 2015; EU RAR, 2009).
- TCEP is concluded to be toxic to reproduction (Kjølholt et al., 2015). A No Observed Adverse Effect Level (NOAEL) of 175 mg/kg bw/d has been identified for impairment of reproduction in both sexes of mice (Gulati et al., 1991, cited in EU RAR, 2009). The identified NOAELs for developmental toxicity and maternal toxicity in rats are 200 mg/kg bw/d and 100 mg/kg bw/d, respectively (Kawashima et al., 1983, cited in EU RAR, 2009).
- TCEP is concluded to be carcinogenic with a Lowest Observed Adverse Effect Level (LOAEL) of 12 mg/kg bw/d. This conclusion is based on a number of carcinogenicity studies in rats and mice following established guidelines. Kjølholt et al. (2015) report: "TCEP causes benign and malignant tumours in multiple organs in rats and mice. The carcinogenicity of TCEP is considered to be related to nongenotoxic mechanisms and effects on the kidneys (increased cell growth)."
- Based on repeated dose toxicity tests described in the EU RAR (2009), the effects on kidneys are assessed to be the most sensitive endpoint.

To ensure that the toxicological data on TCEP used for the risk assessment is updated, a literature search using the Google search engine was conducted on 12th of March 2024 using the search terms: "hazard assessment" OR "risk assessment" OR "health assessment" OR "toxicological profile" AND "TCEP" OR "Tris (2-chloroethyl) phosphate" OR "115-96-8". The search results were filtrated by year, so only publications from 2015 and onwards were included.

A study on health risks from dietary exposure to organophosphorus flame retardants by Plichta et al. (2022), has reported the hazard potential of TCEP. According to the cited sources (ATDSR, 2012; US-EPA, 2009; Ali et al., 2012), the reference dose (RfD) ranges from 0.007 mg/kg bw/d to 0.2 mg/kg bw/d based on effects on the kidneys (and in one study also on the liver) in rats. Likewise, a publication by the Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS, 2017) reports that TCEP is a suspected carcinogen, may impair fertility and has toxic effects on the kidney, liver and brain following oral treatment of rats and mice (EU RAR, 2009; ATDSR, 2012; US EPA, 2015a; 2015b). A recent study by

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²⁵ There are specific cut-off values for the substances with respect to the selected hazard class.

Ding et al. (2024) reports a RfD of 0.007 mg/kg bw/d (cited from Sun et al., 2019), however, the endpoint is not reported.

Since the cited sources in Plichta et al. (2022) and NICNAS (2017) are either older than Kjølholt et al. (2015) or do not comprise hazard information newer than 2015, and because the endpoint for the RfD reported by Sun et al. (2019) is not given, the conclusion that TCEP is carcinogenic, nongenotoxic and that the critical endpoint is effects on the kidneys, remains unchanged.

Critical effect and derivation of DNEL

According to the REACH guidelines, the effect specific DNEL is calculated as the most critical NOAEL divided by the product of assessment factors (AF) (ECHA, 2012a).

Kjølholt et al. (2015) have derived a DNEL of 0.013 mg/kg bw/d for systemic effects based on a LOAEL for kidney damage of 12 mg/kg bw/d from an 18-month oral carcinogenicity study in mice (EU RAR, 2009) and using an AF of 900 (10 for interspecies variation, 10 for intraspecies variation, 3 for extrapolation from LOAEL to NOAEL and 3 to account for the lack of knowledge on the mode of action of TCEP and hence the uncertainty regarding TCEP's role in tumour formation in humans). In this case, oral toxicity data are used to assess dermal exposure and therefore no additional route-to-route AF is needed. This is in accordance with the ECHA guideline for calculation of DNEL (ECHA, 2012a). Since newer or more relevant information is not available, the DNEL derived by Kjølholt et al. (2015) is used in the present risk assessment.

7.1.2 TCPP

Classification

There is no harmonized classification for TCPP or any of its isomers. However, according to the ECHA C&L inventory, 137 notifiers have self-classified TCPP as Acute Tox. 4; H302 and Aquatic Chronic 3; H412 in a joint submission. There are two aggregated notifications and 175 notifiers in total²⁶. The previous identifier (CAS no. 13674-84-5) is self-classified as Acute Tox. 4; H302, Aquatic Chronic 3; H412, Eye Irrit. 2; H319 and Skin Irrit. 2; H315. There are seven aggregated notifications and 739 notifiers²⁷.

Substance identity and physicochemical properties

The physical and chemical properties of TCPP are described in TABLE 7-2.

The chemical identifiers of TCPP were adapted upon a comprehensive compliance check under REACH in 2016, because the previous identifier contained a mixture of isomers (ECHA, 2023c). Hence, two CAS numbers are mentioned in TABLE 7-2.

Parameter	Description	Source
Substance name	Reaction products of phosphoryl trichloride and 2- methyloxirane (Tris(2-chloro-1-methylethyl) phosphate)	ECHA Substance Info- card
CAS no.	1244733-77-4	ECHA Substance Info- card

TABLE 7-2. Identification and physicochemical properties of TCPP.

²⁶ ECHA C&L inventory accessed on 13th March 2024. URL: <u>https://echa.europa.eu/da/information-on-che-micals/cl-inventory-database/-/discli/details/245118</u>

²⁷ ECHA C&L inventory accessed on 13th March 2024. URL: <u>https://echa.europa.eu/da/information-on-che-micals/cl-inventory-database/-/discli/details/12076</u>

Description (13674-84-5) ²⁸	Source
$CI \rightarrow H_{3}C \rightarrow H_{3}$	ECHA Substance Info- card
Chlorinated organophosphates	
1.4×10 ⁻³ Pa at 25.0 °C (non-volatile)	ECHA CHEM
391.56 g/mol	ECHA CHEM
2.68 at 30 °C and pH 7.1	ECHA CHEM
No harmonized classification Self-classification (CAS no. 1244733-77-4): Acute Tox. 4 – H302 Aquatic Chronic 3 – H412	ECHA C&L inventory
	Description (13674-84-5) 28 $(13674-84-5) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-73) 28$ $(13674-84-84) 28$ $(13674-84-84) 28$ $(13674-84-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(13674-84) 28$ $(1367$

Substance toxicity

Toxicity studies on TCPP have been summarized in earlier consumer risk assessments by the Danish EPA; Andersen et al. (2014) and Kjølholt et al. (2015), who based the hazard information on the EU risk assessment report on TCPP (EU RAR, 2008). Additionally, a substance evaluationperformed by Denmark as evaluating Member State was concluded and published in 2023. The substance evaluation focused on clarifying concerns regarding the carcinogenicity, reproductive toxicity, and endocrine disrupting potential of TCPP. (ECHA, 2023c). For this matter, newly generated subchronic and chronic exposure studies in rats and mice from the US National Toxicology Programme was considered (NTP, 2023).

As the substance was included in CoRAP for substance evaluation in 2022, this report is assumed to contain all relevant studies for the in the report assessed endpoints published from 2015 until its publication in August 2023. An additional literature search using the Google search engine has been conducted on 13th of March 2024 using the search terms "hazard assessment" OR "risk assessment" OR "health assessment" OR "toxicological profile" AND "TCPP" OR "Tris (2-chloro-1-methylethyl) phosphate" OR "Tris(2-chloro-1-methylethyl) phosphate" OR "1244733-77-4" OR "13674-84-5". Search results were filtered by publication year 2015-2024. From this search no new relevant studies were found.

From the available data, the following can be concluded:

• The absorption of TCPP following oral ingestion is approximately 80% and the substance is readily distributed to tissues, the highest concentration being in the liver and kidneys (NTP, 2023; EU RAR, 2008).

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²⁸ The substance was previously registered with the CAS no. 13674-84-5, but is now registered as "reaction products of phosphoryl trichloride and 2-methyloxirane" with new CAS no. 1244733-77-4 and EC no. 807-935-0). The substance itself has not changed, however, the new identifiers refer to a mixture of four isomers, with TCPP being the main constituent.

- Dermal absorption is approximately 40% (Kjølholt et al., 2015).
- TCPP is not mutagenic (NTP, 2023; Andersen et al., 2014).
- A repeated dose study shows a NOAEL of 100 mg/kg bw/d regarding liver effects following a 28-day oral gavage study in rats (Bayer, 1991, cited in EU RAR, 2008). Another 90-day feed study in rats found a LOAEL of 52 mg/kg bw/d in males regarding effects on liver and thyroid and a NOAEL of 171 mg/kg bw/d in females regarding liver weights (Stauffer Chemical Co., 1981, cited in EU RAR, 2008).
- Based on a two-year carcinogenicity study in rats and mice conducted by the US National Toxicology Programme (NTP, 2023), TCPP is identified to be a non-genotoxic carcinogen (ECHA, 2023c). The results from the male and female rats (Sprague Dawley) as well as the male mice (B6C3F1/N mice) demonstrate that TCPP had some evidence of carcinogenic activity, meanwhile the results from female mice (B6C3F1/N mice) show clear evidence of carcinogenic activity based on the increased incidence of liver neoplasm. The NOAEL from the two-year study in female mice was 2500 ppm, which was the lowest within the study.
- TCPP is identified to exhibit developmental toxicity, based on six studies in rats and one study in rabbits. Effects observed include, decrease in mean number of offspring, decreased offspring weight, skeletal malformations in offspring and increased offspring mortality (ECHA, 2023c).
- Based on 12 *in vitro* and two *in vivo* studies, TCPP is identified as an endocrine disruptor (ED) on the sex hormonal system. TCPP shows effects on the female reproductive system and sexual maturation, altering the estrous cyclicity, pituitary, uterine and ovary weights, and timing of the vaginal opening (ECHA, 2023c). NTP (2023) reports: *"F1 males and females had LOAELs of 85 and 99 mg/kg bw/d, respectively. This assignment was based on a significant decrease in kidney weights in males and pituitary weights in females".* Hence, it is concluded that the available information is sufficient to conclude that TCPP is an endocrine disrupting chemical ECHA (2023c).

Critical effect and derivation of DNEL

Based on the available studies, the liver and thyroid are assessed to be the most sensitive endpoints with a LOAEL of 52 mg/kg bw/d based on a 90-day feed study in rats (EU RAR 2008).

From this LOAEL, Andersen et al. (2014) have derived a DNEL of 0.07 mg/kg bw/d by first recalculating the LOAEL to the internal dose (80% of the oral uptake, corresponding to 41.6 mg/kg bw/d) and thereafter dividing this value with an overall AF of 600 (4 for interspecies variation in rats, 2.5 for other interspecies variation, 10 for intraspecies variation, 2 for conversion from subchronic to chronic exposure and 3 for conversion to NOAEL from LOAEL). No additional route-to-route AF is needed in this case as oral toxicity data are used to assess dermal exposure. This is in line with the guideline method for deriving DNEL described by ECHA (ECHA, 2012a). Hence, this DNEL is used for further risk assessment.

7.1.3 TPP

Classification

TPP does not have a harmonised hazard classification. However, according to the ECHA C&L inventory, 113 notifiers have self-classified TPP as Aquatic Acute 1; H400 and Aquatic Chronic 1; H410 in a joint submission. There are 26 aggregated notifications and 1466 notifiers in to-tal²⁹.

²⁹ ECHA C&L inventory accessed on 13th March 2024. URL: <u>https://echa.europa.eu/da/information-on-che-micals/cl-inventory-database/-/discli/details/63257</u>

Substance identity and physicochemical properties

The physical and chemical properties of TPP are described in TABLE 7-3.

Parameter	Description	Source
Substance name	Triphenyl phosphate	ECHA Substance Infocard
CAS no.	115-86-6	ECHA Substance Infocard
Structure		ECHA Substance Infocard
Chemical group	Chlorinated organophosphates	
Vapour pressure (in- terpretation)	1×10 ⁻³ Pa at 25.0 °C (non-volatile)	ECHA CHEM
Molecular weight	390.27 g/mol	ECHA CHEM
LogPow	4.6 at 20.0 °C	ECHA CHEM
CLP classification	No harmonized classification	ECHA C&L inventory
	Self-classification:	
	Aquatic Acute 1 – H400	
	Aquatic Chronic 1 – H410	

TABLE 7-3. Identification and physicochemical properties of TPP.

Substance toxicity

As TPP was not included in the hazard assessments of the earlier consumer risk assessments by the Danish EPA, a literature search was conducted on 14th of March 2024 using the Google search engine and the following search terms: "hazard assessment" OR "risk assessment" OR "health assessment" OR "toxicological profile" AND "TPP" OR "Triphenyl-phosphate" OR "Triphenyl phosphate" OR "115-86-6". The period of publication was not specified in the search.

From the literature search, several relevant reports from authorities were found, including risk evaluations by the UK Environment Agency; Brooke et al. (2009), and Institute for Environmental Science and Research Limited, prepared for the New Zealand Ministry of Health; Fowles and Curtis (2022), as well as a substance evaluation conclusion conducted by the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) on behalf of evaluating Member State France (ECHA, 2023b). While the substance evaluation focused on clarifying concerns regarding the endocrine disrupting potential of TPP (ECHA, 2023b), the risk evaluation conducted by the UK Environment Agency (UK EA), considered all toxicological endpoints. This initial evaluation of TPP was conducted before UK's withdrawal from the EU, whereafter the evaluation of the substance was transferred to France (ANSES, 2023). In the substance evaluation, it is concluded that TPP should be identified as a SVHC and be subject to the authorization list, because the endocrine disrupting effects pose risks to the environment. France has subsequently submitted a dossier proposing the identification of TPP as a SVHC (France, 2024). Moreover, it is mentioned in the substance evaluation report (ECHA, 2023b) that the US NTP is currently conducting a one-generation reproductive toxicity study on TPP to generate knowledge on the hazards for human health regarding endocrine disrupting effects.

The following information on the toxicity of TPP has been extracted from the above-mentioned reports as well as the available dossiers on TPP from ECHA CHEM.

Toxicokinetics

The UK EA reports that *"TPP is metabolized by hydrolysis in rat liver homogenate to the major metabolite diphenyl phosphate"* (Sasaki et al., 1984, cited in Brooke et al., 2009). No studies of a reasonable quality are available on dermal absorption of TPP. Hence, in the risk assessment, a worst-case scenario of 100% dermal absorption is assumed.

Acute toxicity

TPP is not concluded to cause irritation, sensitisation nor to be corrosive (Brooke et al., 2009; Fowles and Curtis, 2022; ECHA, 2022).

Brooke et al. (2009) report that TPP exhibits a low level of acute toxicity irrespective of route of administration: Oral LD_{50} values in rats, mice, rabbits, guinea pigs and hens range from 3,000 to above 20,000 mg/kg bw, while the dermal LD_{50} in rabbits is greater than 7,900 mg/kg bw. Studies on intraperitoneal or subcutaneous routes of administration confirm that toxicity of TPP is low (Brooke et al., 2009). No reliable studies on inhalation toxicity are available (Brooke et al., 2009; ECHA, 2022).

Repeated dose toxicity

A repeated dose study of dermal toxicity in the ECHA registration dossier (Unnamed, 1979³⁰, cited by ECHA, 2022) reports a NOAEL of 1000 mg/kg bw/d in rabbits treated with TPP for 21 days.

Brooke et al. (2009) note, that none of the available repeated dose studies on neurotoxicity have been conducted according to OECD test guidelines, however, a limited number of studies allow for a weight of evidence approach. Hence, TPP was not shown to induce neurotoxicity in studies on hens, cats, and rats. For hens, Ciba-Geigy (1980; cited in Brooke et al., 2009, original reference not available) reports a NOEL > 12.5 mg/kg bw/d administered by gavage for 21 days, while a study in the ECHA dossier (Unnamed, 1956³¹, cited in ECHA, 2022) reports a NOAEL > 500 mg/kg bw/d administered by one subcutaneous injection). For cats, Wills et al. (1979) report a NOAEL > 1,000 mg/kg bw/d following one subcutaneous injection. For rats, Sobotka et al. (1986; cited in Brooke et al., 2009) identified a NOAEL > 711 mg/kg bw/d based on exposure to TPP in feed for 120 days.

There are no data to evaluate specific target organ systemic toxicity following repeated exposure to TPP. Based on decreased bodyweight and increased liver weight in a 35-day feed study in rat, the NOAEL for repeated dose toxicity is 70 mg/kg bw/d (Sutton et al., 1960, cited in Brooke et al., 2009). In the study, the tested doses were initially set to 0.5% w/w and 5.0% w/w, corresponding to 350 and 3,500 mg/kg bw/d, respectively. However, after three days, animals refused feed and lost weight, and therefore the high dose was lowered to 0.1% w/w corresponding to 70 mg/kg bw/d.

Fowles and Curtis (2022) report a LOEL for reduced growth rate of 161 mg/kg bw/d (based on Sobotka et al., 1986) and 517 mg/kg bw/d (based on Hinton et al., 1987).

The NOAEL for immunotoxicity is 700 mg/kg bw/d based on a subchronic rat study with dietary exposure to TPP (Hinton et al., 1987, cited in Fowles and Curtis, 2022).

³⁰ <u>https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15972/7/6/4</u>

³¹ https://echa.europa.eu/da/registration-dossier/-/registered-dossier/15972/7/3/5

Mutagenicity

ECHA CHEM provides four key *in vitro* studies conducted similar to or according to OECD guidelines showing no mutagenic effect of TPP. No *in vivo* data are available in the ECHA dossiers.

Carcinogenicity

No long-term carcinogenicity bioassays are available for TPP (Brooke et al., 2009; Fowles & Curtis, 2022). One 24-week mouse study from 1977 is considered inadequate due to a low survival rate of treated animals and the short duration of the study. The study injected doses of 20, 40 or 80 mg TPP intraperitoneally 18, 3 and 1 times (3 times per week), respectively, in 6–8-week-old mice (20 mice per treatment group). In the group treated 3 times with 40 mg TPP only 3/20 mice survived (Theiss et al., 1977, cited in Brooke et al., 2009 and ECHA, 2022).

Toxicity to reproduction

Based on a study following OECD test guideline 414, TPP is not concluded to affect fertility and fetal development in rats. The parental NOAEL for fertility and developmental toxicity is greater than 690 mg/kg bw/d (Welsh et al., 1987, cited in Brooke et al., 2009).

Endocrine disrupting properties

ECHA (2023b) conclude that there is a lack of *in vivo* data on endocrine disrupting effects of TPP. Hence, the authors refer to an ongoing one-generation reproductive toxicity study conducted by the US NTP.

Critical effect and derivation of DNEL

The most critical effects are decreased body weight and increased liver weight with a NOAEL of 70 mg/kg bw/d. This NOAEL was found in a sub-chronic study by Sutton et al. (1960; cited by Brooke et al., 2009), in which rats were exposed to TPP via feed for 35 days.

Brooke et al. (2009) note that none of the available repeated dose toxicity studies have been conducted according to OECD guidelines, which prescribe chronic studies to be of a duration of 6–24 months (OECD, 2018). Hence, it is necessary to apply an AF to extrapolate from the 35-day rat study describing a subacute effect to a chronic effect. The default AF for this extrapolation is 6 (ECHA, 2012a). Furthermore, interspecies variation and intraspecies variation need to be considered. For this, the default AF of 10 is applied for both interspecies and intraspecies variation, respectively (ECHA, 2012a). Moreover, an AF of 3 is proposed to account for the knowledge gap regarding the endocrine disrupting properties of TPP. In this case, oral toxicity data are used to assess dermal exposure and therefore no additional route-to-route AF factor is needed. Multiplying the AFs yields an overall AF of 1800.

Hence, the DNEL for decreased body weight and increased liver weight is 0.04 mg/kg bw/d. This value will be used in the further risk assessment of TPP.

7.2 Exposure and risk assessment

Calculations of the potential consumer exposure to the flame retardants, TCEP, TCPP and TPP, contained in the textiles with electronic parts is based on worst-case scenarios. Based on the intended use of the articles, dermal exposure is the most relevant exposure pathway.

Inhalation exposure is not accounted for in the exposure and risk assessment. Potential exposure to flame retardants in textiles via inhalation is dependent on the vaporization rate of each of the substances. Substances with higher vapour pressure will vaporize more readily at a given temperature than substances with lower vapour pressure. Based on the definition in the EU Industrial Emissions Directive, substances with a vapour pressure of 0.01 kPa or lower at 20°C are regarded as non-volatile. For comparison, the vapour pressure for water at 20°C is 2.3 kPa. All three flame retardants identified in the products analysed in this study have a vapour pressure below the cut-off value of 0.01 kPa. For example, TCPP has the highest vapour pressure amongst the three flame retardants in the study with a value of 1.4×10⁻³ Pa at 25.0 °C. Additionally, the articles in which flame retardants where detected, are intended for outdoor use (e.g. gloves, jacket, vest, long sleeve/long pants underwear for e.g. skiing or hunting), where good venting conditions exist, even though underwear with heating function may also be used indoor. Taking the low vapour pressure and the intended outdoor use of the products into consideration, the calculation of an exposure estimate via the inhalational route is not considered relevant. This is in line with previous studies on flame retardants, which also did not include inhalation exposure assessments (Kjølholt et al., 2015; Poulsen et al., 2018) or concluded a negligible risk based on inhalation exposure estimates for adults (Andersen et al., 2014).

Flame retardants have been detected in gloves, socks, a jacket, underwear, a vest and a shirt with electronic heating functions (see section 6.3.1). Based on the highest concentrations found and highest exposure potential via direct skin contact, the exposure estimates are derived for gloves, underwear, and socks, as well as the combined exposure to these articles. The combined exposure of multiple garments is only assessed in those specific cases where the flame retardant under evaluation was detected in several products the chemical analyses.

The exposure time for all three product categories is conservatively assumed to be eight hours, corresponding to that the products are worn during a whole day of outdoor activity, such as hunting or skiing (exposure time only needed for tier 2 assessment).

7.2.1 Exposure calculation based on measured concentrations in the articles

One method for calculating the dermal exposure to a substance in clothing is to base the calculation on the concentration of the substance in the textile article and therefrom estimate the amount of substance that can possibly migrate into the skin. As a worst-case scenario in the initial risk assessment, it is assumed that the dermal absorption is 100%, i.e. the dermal dose on the skin is also what is entering the body. The dermal dose is therefore transferred to the risk assessment and compared with the hazard data (DNEL values). This comparison indicates if the exposure could pose a risk for causing health effects or not.

According to ECHA guidelines on consumer exposure assessment, the dermal exposure to a substance migrating from an article is calculated according to the following equations (ECHA, 2012b). The parameters used are explained in TABLE 7-4.

$C_{der} = \frac{C_{prod} \times 1000 \frac{\text{mg}}{\text{g}}}{D}$	Equation 7-1
$L_{der} = C_{der} \times TH_{der}$	Equation 7-2
$D_{der} = \frac{L_{der} \times A_{skin} \times n}{BW}$	Equation 7-3

TABLE 7-4. Parameters used for exposure calculations	(ECHA,	2012b; Kjølholt e	t al., 2015).
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Parameter	Description	Unit
A _{skin}	Surface area of the exposed skin	cm ²
BW	Body weight (Assumed to be 60 kg for adults as a worst-case scenario)	Kg
C _{der}	Dermal concentration: Concentration of substance on skin	mg/cm ³
C _{prod}	Product concentration: Concentration of substance in product	g/cm ³
D	Dilution factor (For articles, D = 1)	-

Parameter	Description	Unit
D _{der}	Dermal dose (external): Amount of substance per bodyweight that can potentially be taken up	mg/kg bw/d
L _{der}	Dermal load: Amount of substance on skin area per event	mg/cm ²
n	Frequency of use; mean number of events per day (Assumed to be 1)	d-1
TH_{der}	Thickness of product layer on skin (Default value for articles is 0.001 cm)	Cm

A calculation example for exposure to TCEP in gloves, using the method described by ECHA (2012b), is explained in the following:

In a sample of gloves, a product concentration, C_{prod} , of 120 mg/kg TCEP has been measured (see TABLE 6-1). The unit of C_{prod} is converted from mg/kg to g/cm³ using the dimensions and weight of the sample, which were recorded prior to analysis. The volume of the glove sample is 23.3 cm³, while the mean weight of the duplicate glove samples is 0.008 kg.

 $C_{prod} \left[g/cm^3 \right] = \frac{C_{prod} \left[mg/kg \right] \times weight of sample \left[kg \right]}{volume of sample \left[cm^3 \right] \times 1000 \frac{mg}{g}} = \frac{120 \text{ mg/kg} \times 0.008 \text{ kg}}{23.3 \text{ cm}^3 \times 1000} = 0.0004 \text{ g/cm}^3$

From the product concentration, C_{prod} , the dermal concentration, C_{der} , i.e., the concentration of TCEP on the skin, is calculated using Equation 7-1.

$$C_{der} = \frac{C_{prod} \times 1000 \, mg/g}{D} = \frac{0.00041 \, \text{g/cm}^3 \times 1000 \, \text{mg/g}}{1} = 0.04 \, \text{mg/cm}^3$$

From the dermal concentration, C_{der} , the dermal load, L_{der} , i.e., the amount of substance on a given skin area can be calculated by taking into account the thickness of the product layer on the skin, according to Equation 7-2.

$$L_{der} = C_{der} \times TH_{der} = 0.04 \text{ mg/cm}^3 \times 0.001 \text{ cm} = 0.000041 \text{ mg/cm}^2$$

Finally, the dermal dose, D_{der}, i.e., the amount of substance per bodyweight that may be taken up through dermal absorption can be calculated according to Equation 7-3. The skin area is estimated according to the ECHA guideline on consumer exposure assessment (ECHA, 2012b) to be 840 cm² for males³². Furthermore, the bodyweight is assumed to be 60 kg (as a worst-case scenario to take female consumers into account), and that one event of exposure occurs per day.

$$D_{der} = \frac{L_{der} \times A_{skin} \times n}{BW} = \frac{0.000041 \text{ mg/cm}^2 \times 840 \text{ cm}^2 \times 1 \text{ d}^{-1}}{60 \text{ kg}} = 0.0006 \text{ mg/kg bw/d}$$

Using this method, the dermal doses for TCEP, TCPP and TPP have been calculated in the samples of gloves, underwear, and socks where the respective flame retardants exceeded the LOD in the chemical analysis (see TABLE 6-1 for the results). The dermal doses are presented in TABLE 7-5.

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³² In version 3.0 of the ECHA Guidance on Consumer exposure assessment (Chapter R.15) from 2016, the values for skin area and body weight are presented in example R-15-1.

TABLE 7-5. Dermal doses [in mg/kg bw/d and g/cm³] of TCEP, TCPP and TPP based on data from respective textiles in which the flame retardants were detected ^a.

	Product ID	Product	C _{prod} [mg/kg]	C _{prod} [g/cm³]	D _{der} [mg/kg bw/d]
TCEP	202011 - 3	Heated gloves	120 / 14 ^b	0.000041 / 0.000005	0.0006 / 0.00007 ^b
ТСРР	202011 - 3	Heated gloves	15 / 8.6 ^b	0.000005 / 0.000003	0.00007 / 0.00004 ^b
	202011 - 6	Heated socks	5.5	0.000003	0.00005
TPP	202011 - 15	Heated underwear, top	13	0.000007	0.0002
	202011 - 16	Heated underwear, bottom	9.2	0.000005	0.001

^a Assumptions: Bodyweight = 60 kg; Exposure events per day = 1; Skin area estimated according to ECHA guideline (ECHA, 2012b; Nordic Council of Ministers, 2011).

^b If the Relative Standard Deviation (RSD) between the measured concentration in duplicate samples exceeds 15%, both results are given in TABLE 6-1 and hence, the dermal dose is calculated for both values.

7.2.2 Exposure calculation based on calculated concentration in the inner layer

As described in section 6.3.2.2, a worst-case scenario for dermal exposure can be made by assuming that the total measured concentration of flame retardant is situated only in the inner layer of the article, thus being in direct contact with the skin. The calculation of the concentrations in the inner layer are reported in section 6.3.2.2. Applying Equation 7-1 – Equation 7-3 to the concentrations of flame retardants in the inner layer of the samples yield the worst-case dermal doses.

The concentrations in the inner layer as well as the dermal doses are reported in TABLE 7-6 for the glove samples. It was not relevant to calculate the concentration in the inner layer for other the samples of socks and underwear, as they consist of one layer only.

Comparing the concentrations in the product (C_{prod} [g/cm³] in TABLE 7-5 and $C_{prod, inner layer}$ [g/cm³] in TABLE 7-6), it can be seen that the assumption that all flame retardant is present in the inner layer of the glove, makes an approximately 8-fold difference in exposure (e.g. for the glove sample with 120 mg/kg TCEP: 0.00032 g/cm³ / 0.000041 g/cm³ = 7.8).

TABLE 7-6. Worst-case dermal doses of TCEP and TCPP derived from assuming that all of the substance is situated in the inner layer of the article.

	Product ID	Product	C _{prod, inner layer} [g/cm ³]	D _{der, worst-case} [mg/kg bw/d]
TCEP	202011 - 3	Heated gloves	0.00032 / 0.00004 ^b	0.0044 / 0.0005 ^b
ТСРР	202011 - 3	Heated gloves	0.00004 / 0.00002 ^b	0.0006 / 0.0003 ^b

^b If the Relative Standard Deviation (RSD) between the measured concentration in duplicate samples exceeds 15%, both results are given in TABLE 6-1 and hence, the dermal dose is calculated for both values.

7.2.3 Risk assessment

To assess the risk of the dermal doses of flame retardants that may migrate into the skin, a risk characterization ratio (RCR) is calculated according to Equation 7-4. If the RCR is less than one, the risk can be said to be controlled, while the opposite is the case, if the RCR is above one.

$$RCR = \frac{D_{der}}{DNEL}$$

Equation 7-4

The RCR values are reported in TABLE 7-7 both for the exposure estimates based on the measured concentrations in the articles as well as for the calculated concentrations in the inner layer.

			Exposure based on measured concentra- tions		Exposure based on con- centration in the inner layer ^a	
	Product ID	Product	C _{prod} [g/cm³]	RCR	C _{prod} [g/cm³]	RCR
TCEP	202011 - 3	Heated gloves	0.000041 / 0.000005 ^b	0.044 / 0.005	0.00032 / 0.00004 ^b	0.34 / 0.04
ТСРР	202011 - 3	Heated gloves	0.000005 / 0.000003 ^b	0.001 / 0.001	0.00004 / 0.00002 ^b	0.008 / 0.005
ТРР	202011 - 6	Heated socks	0.000003	0.001	-	-
	202011 - 15	Heated under- wear, top	0.000007	0.032	-	-
	202011 - 16	Heated under- wear, bottom	0.000005	0.004	-	-

TABLE 7-7. Risk Characterization Ratios (RCRs) for the estimated as well as worst-case exposure concentrations of flame retardants in gloves, socks, and underwear.

^a Only applies to products consisting of multiple layers. The calculation of the inner layer concentration is described in section 6.3.2.2.

^b If the Relative Standard Deviation (RSD) between the measured concentration in duplicate samples exceeds 15%, both results are given in TABLE 6-1 and hence, the RCR is calculated for both values.

- Not calculated for single layer products.

For TCEP and TCPP, the RCR values are less than one for both replicates of the heated gloves. This is the case both if the exposure is based on the concentration in the whole article as well as if it is assumed that the whole amount of substance is contained in the inner layer of the gloves. Hence, the dermal risk towards TCEP and TCPP is found to be controlled.

All RCR for exposure to TPP in the risk assessment are less than one, indicating no risk of TPP due to dermal exposure from the single layer products, i.e., socks and underwear.

7.2.4 Risk from combined exposure and mixture toxicity

As a reasonable worst-case scenario, it may be assumed that a consumer is wearing several textiles articles with electronic heating functions at the same time. Only TPP was found in several garments, and the combined exposure from wearing several textiles articles is only assessed for this substance. The products containing TPP were socks and a full set of underwear (i.e., both top and bottom). Wearing all these garments at the same time would cover the major parts of the body except hands, neck, and head. Combined exposure can be assessed by summing the relevant RCRs.

 $Total RCR_{TPP} = RCR_{TPP \ socks} + RCR_{TPP \ UW \ top} + RCR_{TPP \ UW \ bottom}$ = 0.001 + 0.032 + 0.004 = 0.037

As the combined exposure to TPP yields a total RCR well below one, no risk is concluded.

Additionally, a consumer may be exposed simultaneously to several flame retardants, when using an article containing several flame retardants or using several articles each containing different flame retardants. Thus, a consumer using both gloves, socks and underwear will be exposed to TCEP, TCPP and TPP at the same time. It may be plausible that the three investigated flame retardants may have similar mode of action, as their respective critical effects are on kidney, liver and thyroid as well as liver weight and bodyweight. Mixture Assessment Factors (MAF) may be used to assess the risk from several substances and different concepts

have been developed to account for potential mixture risks (e.g., Backhaus, 2023). However, knowledge gaps regarding the mode of action of the flame retardants exist, and specific methodologies for assessing the risk for the mixture of flame retardants have not been identified (e.g., ECHA, 2018; ECHA 2022). Hence, mixture toxicity could not be assessed quantitatively. Qualitatively, regarding the overall magnitude of RCR for the single substances, a risk from simultaneous exposure to the three flame retardants during simultaneous use of several textile articles with heating function is not expected.

7.3 Discussion and conclusion

The exposure assessment presents a worst-case approach, assuming that all the substance present in the product layer on the skin is taken up.

The exposure assessment does not account for fraction of flame retardant in the product available for migration, nor does it consider absorptions factors to account for the fraction of substance taken up by the skin, the amount of substance leaching per use event or exposure time. This is in accordance with the tier 1 approach as outlined in the ECHA guidance (ECHA, 2012b), where such factors only become relevant in a higher tier calculation.

In the exposure calculation, the thickness of product layer on the skin (TH) is the determining factor for calculating the dermal load. The default value for articles (TH = 0.001 cm) has been applied, while for mixtures, the default value is TH = 0.01 cm. Applying a higher TH would lead to a direct proportional increase in RCR, e.g. a TH of 0.01 cm, would yield RCR a factor ten larger than the ones presented in TABLE 7-7. Still, those RCR would be below one.

Analytical migration results from a sweat simulant have not been available for the exposure assessment. Migration via sweat is a relevant exposure model for the textile articles of this study, as sweating is likely to occur when using textiles with heating function. Migration models account for migration as the 'leachable fraction' of substance that migrates to the skin per unit amount of product over a certain time period, but do not consider TH, because this parameter is of limited relevance in migration modelling. As the here applied tier 1 method uses for the whole amount of substance in the article irrespective of exposure time for calculation of the dermal load, it is considered – despite its limitations – to be sufficiently robust to reflect potential dermal exposure.

As discussed in section 6.3.2.1, the concentrations found in the products are below the levels of functionality and below levels of concentration limits of other flame retardants, for which concentration limits are defined. This indicates that the flame retardants in the analysed textile articles with heating function are most likely present as impurities rather than intentionally added. The conclusions of the risk assessment indicate that the concentrations of flame retardants at impurity levels found in the consumer products investigated in this project, do not lead to health risks for the intended users of the products. No specific attention has been paid to specific vulnerable sub-populations, such as children, as none of the identified products containing flame retardants were marketed for children as the target group. The risk from dermal exposure to flame retardants in textiles with electronic heating function was therefore assessed only for adult consumers.

Consumers may be exposed to flame retardants from various sources, e.g., textiles, furniture and indoor construction material (ECHA, 2023a). Cumulative exposure from other potential sources has not been considered in this project. It is considered unlikely that textiles with heating functions contribute significantly to the cumulative exposure from various sources, as the calculated exposure estimates, including several worst-case assumptions made in this assessment, are well below the health-based reference values. Worst-case assumptions in the scenario are:

- The leakage of the flame retardants from the products over time is not considered, but the exposure assessment is instead assuming a concentration corresponding to what is in the newly bought products.
- For products made of several types of material layers, it is assumed that the entire amount of the flame retardant is situated in the inner layer of the product being in direct contact with the skin.
- The default parameters for skin area and body weight presented in the ECHA Guidance on consumer exposure assessment were used in this project (ECHA, 2012b) to assess the potential consumer exposure from the evaluated products. Other publications are available presenting different values for these body parameters. The Nordic Exposure Group published in 2023 a report on Existing default values and recommendations for exposure assessment (NEXPO, 2023). This reports reviews and evaluate input data used for exposure assessment and concludes on which recommended values to use. Comparing the input data from these two sources concludes that ECHA data is more conservative and can be seen as a worst case. The calculations made in this report are therefore based on the ECHA values according to the current guideline.
- Another aspect worth to highlight is that the analytical results in some cases report deviating results in the duplicate samples analysed. For example, for the glove duplicates showed a Relative Standard Deviation (RSD) exceeding 15% when comparing the two analytical results (120 / 14 mg/kg). The highest concentration identified is used in the exposure assessment.

In conclusion, the risk of health effects arising from dermal exposure to the flame retardants TCEP, TCPP and TPP, due to the use of textiles with electronic heating functions, is assessed to be acceptable.
8. Overall conclusion

The study investigated whether legal requirements regarding use of regulated flame retardants in textiles with electronic heating are complied with. Banned flame retardants such as PBB and PBDE were not detected in any of the purchased articles. Three organophosphorus flame retardants, TCEP, TCPP and TPP were detected at low, but quantifiable concentrations in 7 out of 29 articles. TCEP is on the candidate list under REACH and subject to authorisation under REACH, however, the article, in which TCEP was found, was presumably manufactured outside EU, meaning that the use restrictions due to authorisation do not apply. TCPP and TPP are currently not regulated with respect to use in textiles or in electronic products in the EU, even though regulatory actions are underway for both substances.

Overall, the textile parts of the purchased articles complied with current regulations under REACH, the POPs regulation, and the RoHS-Directive considering the content of flame retardants.

The study also investigated whether non-regulated flame retardants pose a health risk to consumers within the intended user population. 29 articles were purchased from Danish and non-EU retailers and samples were analysed for their content of flame retardants. Only articles with clothing size specifically for adults were found to contain flame retardants, and a risk of exposure to flame retardants via textiles with electronic heating functions towards children is therefore not indicated. Consequently, children were not considered as a relevant exposure group. The risk from dermal exposure to flame retardants in textiles with electronic heating function was assessed for adult consumers. For all assessed articles (gloves, socks, longsleeve and long pant underwear), the RCR were well below one, meaning that the risk is acceptable.

Additionally, the study investigated whether textiles with electronic heating functions contain hazardous substances that are specific for this product type. compared to substances found in other consumer textiles. A literature review did not reveal useful information on hazardous substances for the specific product type. Hence, substances were identified through a non-target screening of the purchased textiles with electronic heating functions and subsequent comparison of the findings with available information from literature about chemicals in textiles. The results of the non-target screening do not indicate that textile products with electronic heating functions contain hazardous substances which are specific for this product type.

References

Abdallah, Mohamed Abou-Elwafa, Daniel S. Drage, Martin Sharkey, Harald Berresheim, and Stuart Harrad, 2017. "A Rapid Method for the Determination of Brominated Flame Retardant Concentrations in Plastics and Textiles Entering the Waste Stream." *Journal of Separation Science* 40 (19): 3873–81. <u>https://doi.org/10.1002/jssc.201700497</u>.

Ali, N., Dirtu, A. C., Van den Eede, N., Goosey, E., Harrad, S., Neels, H., Mannetje, A., Coakley, J., Douwes, J. and Covaci, A., 2012. Occurrence of alternative flame retardants in indoor dust from New Zealand: Indoor sources and human exposure assessment. Chemosphere, vol. 88(11), pp. 1276-1282. DOI: <u>https://doi.org/10.1016/j.chemosphere.2012.03.100</u>

Andersen, Dorthe Nørgaard, Lise Møller, Poul Bo Larsen and Pia Brunn Poulsen. 2014. Survey, health and environmental assessment of flame retardants in textiles Survey of chemical substances in consumer products No. 126, 2014. <u>https://www2.mst.dk/Udgiv/publica-tions/2014/03/978-87-93178-35-9.pdf</u>

Arnqvist, K., 2023. Risk assessment of non-intentionally added substances in polyester yarn made from recycled polyethylene terephthalate (PET). KTH, School of Engineering Sciences in Chemistry, Biotechnology and Health (CBH).

ATDSR, 2012. Toxicological profile for phosphate ester flame retardants. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.

Backhaus, T. (2023). The mixture assessment or allocation factor: conceptual background, estimation algorithms and a case study example. Environmental Sciences Europe, 35(1), 55.

Bayer, 1991. 28-d study - full details needed. Bayer AG. Cited in EU RAR, 2008.

Bergen, Saskia van, and Alex Stone. 2021. "Flame Retardants in General Consumer and Children's Products." Washington State Department of Ecology.

Brooke, D. N., Crookes, M. J., Quarterman, P. and Burns, J., 2009. "Environmental risk evaluation report: Triphenyl phosphate (CAS no. 115-86-6)". UK Environment Agency. Product code: SCHO0809BQUK-E-P. URL: <u>https://assets.publishing.service.gov.uk/me-</u> <u>dia/5a7c2054ed915d210ade1bd3/scho0809bquk-e-e.pdf</u>

Brüschweiler, B. J., & Merlot, C., 2017. Azo dyes in clothing textiles can be cleaved into a series of mutagenic aromatic amines which are not regulated yet. Regulatory Toxicology and Pharmacology, 88, 214-226.

Ceballos, Diana M., Kendra Broadwater, Elena Page, Gerry Croteau, and Mark J. La Guardia. 2018. "Occupational Exposure to Polybrominated Diphenyl Ethers (PBDEs) and Other Flame Retardant Foam Additives at Gymnastics Studios: Before, during and after the Replacement of Pit Foam with PBDE-Free Foams." *Environment International* 116 (July): 1–9. https://doi.org/10.1016/j.envint.2018.03.035.

Cooper, Ellen M., Gretchen Kroeger, Katherine Davis, Charlotte R. Clark, P. Lee Ferguson, and Heather M. Stapleton. 2016. "Results from Screening Polyurethane Foam Based Con-

sumer Products for Flame Retardant Chemicals: Assessing Impacts on the Change in the Furniture Flammability Standards." *Environmental Science & Technology* 50 (19): 10653–60. <u>https://doi.org/10.1021/acs.est.6b01602</u>.

Ding, J., He, W., Sha, W., Shan, G., Zhu, L., Zhu, L. and Feng, J., 2024. Physiologically based toxicokinetic modelling of Tri(2-chloroethyl) phosphate (TCEP) in mice accounting for multiple exposure routes. Ecotoxicology and Environmental Safety, vol. 271, 115976. DOI: https://doi.org/10.1016/j.ecoenv.2024.115976

ECHA, 2009. Member state committee support document for identification of tris (2-chloroethyl) phosphate as a substance of very high concern because of its CMR properties. 27 November 2009, European Chemicals Agency. URL: <u>https://www.echa.europa.eu/docu-</u> <u>ments/10162/6d09755f-7fcb-4a00-b7ce-91ab45a2e5af</u>

ECHA, 2012a. Guidance on information requirements and chemical safety assessment. Chapter R.8: Characterisation of dose [concentration]-response for human health. Version 2.1, November 2012, European Chemicals Agency.

ECHA, 2012b. Guidance on information requirements and chemical safety assessment. Chapter R.15: Consumer exposure estimation. Version 2.1, April 2012, European Chemicals Agency.

ECHA, 2018. Screening report an assessment of whether the use of TCEP, TVPP and TDCP in articles should be restricted. Version 3, April 2018, European Chemicals Agency. URL: https://echa.europa.eu/documents/10162/13641/screening_report_tcep_td-cp_en.pdf/e0960aa7-f703-499c-24ff-fba627060698

ECHA, 2022. Assessment of regulatory needs Group Name: Chlorinated trialkyl phosphates. Version 1, July 2022, European Chemicals Agency. URL: https://echa.europa.eu/documents/10162/1654cf7e-5cc1-1294-3685-9dded917c5fc ECHA, 2023a. Flame retardant strategy. European Chemicals Agency. URL: https://echa.europa.eu/documents/10162/2082415/flame retardants strategy en.pdf/

ECHA, 2023a. Regulatory strategy for flame retardants. European Chemicals Agency. ISBN: 978-92-9468-261-1.

ECHA, 2023b. Substance Evaluation Conclusion as required by REACH Article 48 and Evaluation Report for triphenyl phosphate, EC No. 204-112-2, CAS RN 115-86-6. Evaluation Member State: France. French Agency for Food, Environmental and Occupational Health Safety.

ECHA, 2023c. Substance Evaluation Conclusion as required by REACH Article 48 and Evaluation Report for Reaction products of phosphoryl trichloride and 2-methyloxirane, CAS No 1244733-77-4, List No 807-935-0 (formerly identified with EC No 237-158-7 and List No 911-815-4). Evaluating Member State: Denmark. Danish Environmental Protection Agency.

Estill, Cheryl Fairfield, Jonathan Slone, Alexander Mayer, I-Chen Chen, and Mark J. La Guardia. 2020. "Worker Exposure to Flame Retardants in Manufacturing, Construction and Service Industries." *Environment International* 135 (February): 105349. <u>https://doi.org/10.1016/j.envint.2019.105349</u>.

EU RAR, 2008. Risk Assessment Report on tris (2-chloro-1-methylethyl) phosphate, TCPP. May 2008. URL: <u>https://echa.europa.eu/documents/10162/13630/trd_rar_ire-</u> land tccp_en.pdf/315063b0-593d-4703-9519-562c258506e6 EU RAR, 2009. Risk Assessment Report on tris (2-chloroethyl) phosphate, TCEP. July 2009. URL: <u>https://echa.europa.eu/documents/10162/2663989d-1795-44a1-8f50-153a81133258</u>

Fowles, J. and Curtis, A., 2022. Health Risk Assessment: Triphenyl phosphate in nail polish. Institute for Environmental Science and Research Limited (ESR) prepared for New Zealand Ministry of Health.

France, 2024. Annex XV report: Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH article 57 – Triphenyl phosphate. Submitted by: France. URL: <u>https://echa.europa.eu/documents/10162/d6e2e15e-41af-b344-90c3-3c8875aa4b31</u>

Gulati DK, Hommel Barnes L, Chapin RE and Heindel J, 1991. Tris(2-chlorethyl)phosphate Reproduction and Fertility Assessment in Swiss CD-1 Mice when Administered via Gavage. Final Report, Contract No NTP-NO1-ES-65142, Study No NTP-89-RACB-070; NTIS/PB92129170. Cited in EU RAR, 2009.

Hammel, Stephanie C., Kate Hoffman, Amelia M. Lorenzo, Albert Chen, Allison L. Phillips, Craig M. Butt, Julie Ann Sosa, Thomas F. Webster, and Heather M. Stapleton. 2017. "Associations between Flame Retardant Applications in Furniture Foam, House Dust Levels, and Residents' Serum Levels." *Environment International* 107 (October): 181–89. https://doi.org/10.1016/j.envint.2017.07.015.

Hinton, D. M., Jessop, J. J., Arnold, A., Albert, R. H. and Hines, F. A., 1987. Evaluation of immunotoxicity in a subchronic feeding study of triphenyl phosphate. Toxicology and Industrial Health, 3(1), 71-89. Cited in Brooke et al., 2009 and Fowles and Curtis, 2022.

Kajiwara, Natsuko, Minekazu Sueoka, Toshio Ohiwa, and Hidetaka Takigami. 2009. "Determination of Flame-Retardant Hexabromocyclododecane Diastereomers in Textiles." *Chemosphere* 74 (11): 1485–89. <u>https://doi.org/10.1016/j.chemosphere.2008.11.046</u>.

Kawashima K, Tanaka S, Nakaura S, Nagao S, Endo T, Onada K, Takanaka A and Omori Y, 1983. Effect of Oral Administration of Tris(2-chloroethyl)phosphate to Pregnant rats on Prenatal and Postnatal Developments. Eisli Shikenjo Hokuku, 101, 655-61. Cited in EU RAR, 2009.

Kemi, 2013. Hazardous chemicals in textiles – report of a government assignment. Swedish Chemicals Agency.

Kemi, 2014. Chemicals in textiles – Risks to human health and the environment. Report from a government assignment. Report 6/14, Swedish Chemicals Agency

Kjølholt, Jesper, Marlies Warming, Carsten Lassen, Sonja Hagen Mikkelsen, Anna Brinch, Inge Bondgaard Nielsen, and Eva Jakobsen. 2015. "Chemical Substances in Car Safety Seats and Other Textile Products for Children - Survey of Chemical Substances in Consumer Products No. 135, 2015." The Danish Environmental Protection Agency.

Klinke et al., 2023. Survey and risk assessment of chemicals from gaming equipment. Survey of chemical substances in consumer products No. 191. URL: <u>https://mst.dk/service/publika-tioner/publikationsarkiv/2023/apr/survey-and-risk-assessment-of-chemicals-from-gaming-equipment/</u>

NICNAS, 2017. Ethanol, 2-chloro-, phosphate (3:1): Human health tier III assessment. CAS No. 115-96-8. National Industrial Chemicals Notification and Assessment Scheme on behalf of

Australian Government Department of Health and the Australian Government Department of the Environment and Energy.

Nordic Council of Ministers, 2023. Existing Default Values and Recommendations for Exposure Assessment. URL: http://dx.doi.org/10.6027/temanord2023-508

Norwegian EPA. 2021. "Environmental Pollutants in Post-Consumer Plastics." Norwegian Environment Agency.

NTP, 2023. NTP Technical Report on the Toxicology and Carcinogenesis Studies of an Isomeric Mixture of Tris(chloropropyl) Phosphate Administered in Feed to Sprague Dawley (Hsd: Sprague Dawley® SD®) Rats and B6C3F1/N Mice. National Toxicology Program. U.S. Department of Health and Human Services.

OECD, 2018. OECD Guideline 452: Chronic Toxicity Studies. DOI: https://doi.org/10.1787/9789264071209-en

Plichta, V., Steinwider, J., Vogel, N., Weber, T., Kolossa-Gehring, M., Murínová, L. P., Wimmerová, S., Tratnik, J. S., Horvat, M., Koppen, G., Govarts, E., Gilles, L., Martin, L. R., Schoeters, G., Covaci, A., Fillol, C., Rambaud, L., Jensen, T. K. and Rascher-Gabernig, E., 2022. Risk Assessment of Dietary Exposure to Organophosphorus Flame Retardants in Children by Using HBM-Data. Toxics, vol. 10, 234. DOI: 10.3390/toxics10050234

Posner, S., 2014. Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications. PM Nr 5/04, Swedish Chemicals Inspectorate.

Poulsen, Pia Brunn, Charlotte Merlin, and Anders Schmidt, 2018. "Mapping and Risk Assessment of Chemical Substances in Bicycle Helmets." Danish Environmental Protection Agency.

Poulsen, Pia Brunn, Lisbeth E. Knudsen, Susann Geschke, Rikke Munch Gelardi, Christiane Borregaard, Mie Osten-feldt and Charlotte Merlin, 2021. Survey and risk assessment of chemicals in textile face masks. Kortlægning af kemiske stoffer i forbruger produkter Nr. 187, 2021

Rodgers, Kathryn M., Deborah Bennett, Rebecca Moran, Kristin Knox, Tasha Stoiber, Ranjit Gill, Thomas M. Young, Arlene Blum, and Robin E. Dodson. 2021. "Do Flame Retardant Concentrations Change in Dust after Older Upholstered Furniture Is Replaced?" *Environment International* 153 (August): 106513. <u>https://doi.org/10.1016/j.envint.2021.106513</u>.

Sasaki, K., Suzuki, T., Takeda, M. and Uchiyama, M., 1984. "Metabolism of phosphoric acid triesters by rat liver homogenate". Bulletin of Environmental Contamination and Toxicology, 33, 281-288. Cited in Brooke et al., 2009.

Sobotka, T. J., Brodie, R. E., Arnold, A., West, G. L. and O'Donell, M. W., 1986. Neuromotor function in rats during subchronic dietary exposure to triphenyl phosphate. Neurobehavioural Toxicology and Teratology, vol. 8, pp. 7-10. Cited in Brooke et al., 2009.

Stapleton, Heather M., Smriti Sharma, Gordon Getzinger, P. Lee Ferguson, Michelle Gabriel, Thomas F. Webster, and Arlene Blum. 2012. "Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out." *Environmental Science & Technology* 46 (24): 13432–39. <u>https://doi.org/10.1021/es303471d</u>.

Stapleton, Heather M., Susan Klosterhaus, Alex Keller, P. Lee Ferguson, Saskia van Bergen, Ellen Cooper, Thomas F. Webster, and Arlene Blum. 2011. "Identification of Flame Retardants

in Polyurethane Foam Collected from Baby Products." *Environmental Science & Technology* 45 (12): 5323–31. <u>https://doi.org/10.1021/es2007462</u>.

Stapleton, Heather M., Susan Klosterhaus, Sarah Eagle, Jennifer Fuh, John D. Meeker, Arlene Blum, and Thomas F. Webster. 2009. "Detection of Organophosphate Flame Retardants in Furniture Foam and U.S. House Dust." *Environmental Science & Technology* 43 (19): 7490– 95. <u>https://doi.org/10.1021/es9014019</u>.

Stauffer Chemical Co., 1981. Fyrol PCF 3-month dietary sub-chronic toxicity study in rats (Unpublished report). Cited in EU RAR, 2008.

Sun, Y., Liu, L., Sverko, E., Li, Y., Li, H., Huo, C., Ma, W., Song, W. and Zhang, Z., 2019. Organophosphate flame retardants in college dormitory dust of northern Chinese cities: Occurrence, human exposure and risk assessment. Science of the Total Environment, vol. 665, pp. 731-738. DOI: <u>https://doi.org/10.1016/j.scitotenv.2019.02.098</u>. Cited in Ding et al., 2024.

Sutton, W. L., Terhaar, C. J., Miller, F. A., Scherberger, R. F., Riley, E. C., Roudabush, R. L. and Fassett, D. W., 1960. Studies on the industrial hygiene and toxicology of triphenyl phosphate. Arch Environ. Health. Vol. 1, pp. 33-46. Cited in Fowles and Curtis, 2022 and Brooke et al., 2009.

Theiss, J. C., Stoner, G. D., Shimkin, M. B. and Weisburger, E. K., 1977. Test for carcinogenicity of organic contaminants of United States drinking water by pulmonary tumor response in strain A mice. Cancer Research, 37, 2717-2720. Cited in Brooke et al., 2009.

Tsochatzis, E., Lopes, J. A., Gika, H., & Theodoridis, G., 2020. Polystyrene biodegradation by Tenebrio molitor larvae: identification of generated substances using a GC-MS untargeted screening method. Polymers, 13(1), 17.

Tønning, K., Jacobsen, E., Pedersen, E., Strange, M., Poulsen, P. B., Møller, L., & Boyd, H. B. (2009). 2-åriges udsættelse for kemiske stoffer. Kortlægning af kemiske stoffer i forbrugerprodukter, 103, 2009.

US-EPA, 2009. Provisional Peer-Reviewed Toxicity Values for Tris(2-chloroethyl) phosphate (TCEP) EPA/690/ R-09/069F; U.S. Environmental Protection Agency.

US EPA. 2014. "Flame Retardant Alternatives for Hexabromocyclododecane (HBCD)." U.S. Environmental Protection Agency.

US-EPA, 2015a. TSCA Work Plan Chemical Problem Formulation and Initial Assessment: Chlorinated Phosphate Ester Cluster Flame Retardants. U.S. Environmental Protection Agency. Cited in NICNAS, 2017.

US-EPA, 2015b. Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update. U.S. Environmental Protection Agency. Cited in NICNAS, 2017.

Vium, K.S.R., Heckmanm L., Nielsen, I., Tønning, K., Larsen, P. B., & Engelund, D. E. H., 2015. How Child Care Centres Apply Material from Used Products. Survey of chemical substances in consumer products No. 143, 2015.

Vojta, Šimon, Jitka Bečanová, Lisa Melymuk, Klára Komprdová, Jiří Kohoutek, Petr Kukučka, and Jana Klánová. 2017. "Screening for Halogenated Flame Retardants in European Consumer Products, Building Materials and Wastes." *Chemosphere* 168 (February): 457–66. https://doi.org/10.1016/j.chemosphere.2016.11.032.

Welsh, J. J., Collins, T. F. X., Whitby, K. E., Black, T. N. and Arnold, A., 1987. Teratogenic potential of triphenyl phosphate in sprague-dawley (spartan) rats. Toxicology and Industrial Health, 3, 357-369. Cited in Brooke et al., 2009.

Wills, J. H., Barron, K., Groblewski, G. E., Benitz, K. F. and Johnson, M. K., 1979. Does triphenyl phosphate produce delayed neurotoxic effects? Toxicology Letters Vol. 4(1), pp. 21-24. DOI: https://doi.org/10.1016/0378-4274(79)90025-0

Wurbs, Beer, Bolland, and Debiak, 2017. "Hexabromocyclododecane (HBCD) Answers to Frequently Asked Questions." German Environment Agency (UBA).

Appendix 1. List of flame retardants analytes

TABLE 0-1. List of analytes in the analytical program, as well as information on whether regulatory restrictions apply, whether quantification succeeded during analyses and LOD.

Analytes in the analytical program	CAS no.	Substance restrictions ¹	Analytes quantified ²	LOD (mg/kg)
Organophosphates (OP) (non-halogenated)				
2-Ethylhexyl-Diphenylphosphate (EHDP)	1241-94-7	No	No	10
Tributylphosphate (TBP)	126-73-8	No	Yes	1
Tricresyl phosphate (TCP)	1330-78-5	No	Yes	10
Triisobutylphosphat (TIBP)	126-71-6	No	Yes	10
Tri-o-cresyl phosphate	78-30-8	No	Yes	1
Triphenylphosphate (TPP)	115-86-6	No	Yes	5
Tris(2-butoxyethyl)phosphate (TBEP)	78-51-3	No	Yes	10
Tris(2-ethylhexyl) phosphate (TEHP)	78-42-2	No	Yes	10
Halogenated organophosphates				
Tris(1,3-dichloroisopropyl)phosphate (TDCP)	13674-87-8	No	Yes	10
Tris(2-chloroethyl)phosphate (TCEP)	115-96-8	No	Yes	10
Tris(2-chloroisopropyl)phosphate (TCPP)	1244733-77-4 (13674-84-5)	No	Yes	5
Tris (2,3 dibromopropyl) phosphate	126-72-7	Yes	Yes	10
Brominated aromatics				
Tetrabromobisphenol-A (TBBPA)	79-94-7	No	Yes	10
1,2-Bis(2,4,6-tribromo-phenoxy)ethane (BTBPE)	37853-59-1	No	Yes	10
Polybrominated Biphenyls (PBB)				
2,2',5,5'-TetraBB # 52				10
2,2',4,5,5'-PentaBB # 101	67888-96-4	Yes	Yes	1
2,2',4,4',5,5'-HexaBB # 153	59080-40-9	Yes	Yes	10
2,2',3,4,4',5,5'-HeptaBB # BB 180	67733-52-2	Yes	No	10
2,2',3,3',4,4',5,5'-OctaBB # BB 194	67889-00-3	Yes	No	10
2,2',3,3',4,4',5,5',6-NonaBB # BB 206	69278-62-2	Yes	No	10
DecaBB # 209	13654-09-6	Yes	Yes	10
Polybrominated Diphenyl Ethers (PBDE)				
2,4,4'-TriBDE (BDE-28)	41318-75-6	Yes	Yes	10
2,2',4,4'-TetraBDE (BDE-47)	5436-43-1	Yes	Yes	10
2,2',4,4',5-PentaBDE (BDE-99)	60348-60-9	Yes	Yes	10
2,2',4,4',6-PentaBDE (BDE-100)	189084-64-8	Yes	Yes	10
2,2',4,4',5,5'-HexaBDE (BDE-153)	68631-49-2	Yes	Yes	10
2,2',4,4',5,6'-HexaBDE (BDE-154)	207122-15-4	Yes	Yes	10
2,2',3',4,4',5',6-HeptaBDE (BDE-183)	207122-16-5	Yes	Yes	10
DecaBDE-209	1163-19-5	Yes	Yes	10
Other PBDE (other congeners of tetraBDE, pen- taBDE, hexaBDE, heptaBDE and congeners of oc-	-	Yes	No	10

taBDE and nonaBDE)

¹ Restrictions of the substance in products according to the provision under the REACH regulation, POPs regulation and/or RoHS-directive, compare with TABLE 4-1

² Yes - substance could be quantified in the chemical analysis (however, that does not mean that the substance also was detected in any of the samples). No - substance could not be quantified due to problems with reference material.

Appendix 2. Results of GC-MS screening

TABLE 0-2. Sample ID 202011 - 1, Heated sleeping bag.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	200
5-Formylsalicylaldehyde	7.699	3328-70-9	430
Isophthalic acid	7.860	121-91-5	180
N-(p-Methoxyphenyl)maleimide	8.690	1081-17-0	160
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	1600
Terephthalic acid	9.195	100-21-0	86
Isophthalic acid, di(2-methylprop-2-en-1-yl) ester	9.847	998343-95-8	150
Succinic acid, di(3-chlorophenyl) ester	10.149	998329-97-5	120
Diethylene glycol dibenzoate	11.803	120-55-8	120 / -
1,4-Benzenedicarboxylic acid, bis(2- ethylhexyl) ester	12.999	6422-86-2	580
Unidentified	13.206	-	130
Unidentified	13.697	-	210
Unidentified	14.551	-	430
Unidentified	14.802	-	140
Unidentified, hydroxybenzophenone	15.368	-	180
Unidentified	15.625	-	310
Unidentified	15.914	-	170
Unidentified	18.313	-	160
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	550
Unidentified, possibly part of polyethylene- terphthalate	26.392	-	99

TABLE 0-3. Sample ID 202011 - 2, Heating neck blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	63
Isophthalic acid	7.860	121-91-5	63 / 34
Benzaldehyde, 2-ethoxy-	8.889	613-69-4	210
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	240
Isophthalic acid, di(2-methylprop-2-en-1-yl) ester	9.847	998343-95-8	56
1,4-Benzenedicarboxylic acid, bis(2- ethylhexyl) ester	12.999	6422-86-2	44 / -
Unidentified	13.690	-	130

14.533	998398-77-0	170
14.791	-	32
15.368	-	180
15.596	-	150
15.638	3319-31-1	30
15.894	-	42
25.057	-	720
	14.533 14.791 15.368 15.596 15.638 15.894 25.057	14.533 998398-77-0 14.791 - 15.368 - 15.596 - 15.638 3319-31-1 15.894 - 25.057 -

TABLE 0-4. Sample ID 202011 – 3, Heated gloves.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	97
ortho-Hydroxypropiophenone	7.752	610-99-1	320
Unidentified, benzoic acid type	7.796	-	110
Isophthalic acid	7.860	121-91-5	350
Tri(2-chloroethyl) phosphate	8.418	115-96-8	43 / -
Unidentified	8.894	-	54
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	82
4-(Butoxycarbonyl)benzoic acid	9.005	1818-06-0	57
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	57
Dibutyl phthalate	9.578	84-74-2	34
Unidentified	11.729	-	140
Didecan-2-yl phthalate	13.252	28029-89-2	160
Unidentified	13.696	-	120
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.521	998398-77-0*	430
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	110
Unidentified, hydroxybenzophenone	15.368	-	220
Unidentified, hydroxybenzophenone	15.435	-	100
Unidentified, hydroxybenzophenone	15.481	-	44
Unidentified	23.067	-	100
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1100

TABLE 0-5. Sample ID 202011 – 4, Heated vest.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	55
1,2-Benzenedicarboxylic acid	5.370	88-99-3	45
1,3-Benzodioxole-5-carboxylic acid, methyl ester	7.372	326-56-7	48 / -

Isophthalic acid	7.860	121-91-5	85 / -
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	140 / -
2-((2-(2-Methoxyethoxy)ethoxy)carbonyl)ben- zoic acid	9.156	207790-01-0	100
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	94
Benzenamine, 2-bromo-4,6-dinitro-	9.699	1817-73-8	77
Unidentified	10.595	-	55
Unidentified	11.001	-	50
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	60
Unidentified	12.618	-	52
Unidentified, adipate	13.566	-	46
Unidentified	13.687	-	80
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	230 / 56
Unidentified, hydroxybenzophenone	15.368	-	150
3,6,9,12,15-Oxabicyclo(15,3)heneicosa- 1(21),17,19-triene-2,16-dione	16.759	65745-83-7	44
Unidentified	16.994	-	- / 51
Unidentified	18.307	-	270
Unidentified	23.313	-	42
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	820

TABLE 0-6. Sample ID 202011 – 5, Heating blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
1,4-Benzenedicarboxylic acid, bis(2- ethylhexyl) ester	12.999	6422-86-2	60
13-Docosenamide, (Z)-	13.018	112-84-5	25
Didecan-2-yl phthalate	13.252	28029-89-2	50
Unidentified	13.683	-	85
9-Octadecenoic acid	14.382	2027-47-6	30
Unidentified	14.613	-	24
Unidentified, hydroxybenzophenone	15.368	-	160
tri(2-Ethylhexyl) trimellitate	15.638	3319-31-1	39
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1200
Unidentified, possibly part of polyethylene- terphthalate	26.392	-	130 / -

TABLE 0-7. Sample ID 202011 – 6, Heated socks.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)	
3-Butenyl adipate	8.372	998445-98-6		74
1,6-Dioxacyclododecane-7,12-dione	8.532	777-95-7		150

n-Hexadecanoic acid	9.677	57-10-3	86
Adipate Dimethylolpropane	9.921	998445-99-1	120
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	89 / 29
Unidentified	10.404	-	100
Unidentified	10.442	-	100
Unidentified, adipate	10.792	-	140
Butanediol adipate	11.195	998445-98-5	170
Adipic acid, dicyclopentylmethyl ester	11.663	998324-78-8	170
Unidentified, adipate	12.048	-	360
Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1- dimethylpropyl)-	12.689	25973-55-1	160
Hexanedioic acid, dicyclohexyl ester	12.801	849-99-0	110
Unidentified, adipate	13.584	-	120
Octacosanol	14.234	557-61-9	75
Unidentified, adipate	14.308	-	240
Long chained alcohol	15.062	36653-82-4	- / 78
Unidentified, adipate	15.132	-	150
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl)	20.087	36443-68-2	150
Unidentified	22.055	-	65
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	320

TABLE 0-8. Sample ID 202011 – 7, Heated jacket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	50
p-Nitroaniline	7.455	100-01-6	83
Isophthalic acid	7.860	121-91-5	58
Benzyl Benzoate	8.568	120-51-4	130
Benzonitrile, 2-amino-5-nitro-	8.592	17420-30-3	53
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	130
2-propenamide, N-[2-[ethyl(3- methylphenyl)amino]ethyl]-	9.327	998396-39-8	45
7-(Ethyl)amino-4-methylcoumarin	9.955	998395-85-1	68
Benzenamine, 4,4'-methylenebis-	10.307	101-77-9	78
1,4-benzenediamine, N4-(2-aminoethyl)-N4- ethyl-2-methyl-	10.496	998400-28-4	130
Pyrido[3,4-d]pyridazine-4,5(3H,6H)-dione, 1- (2-furfuryl)-7-methyl-	11.011	-	- / 50
Unidentified	11.472	-	200
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	- / 120
Adipate Ethylene glycol	13.016	998445-97-5	46
Unidentified	13.259	-	51
Unidentified, adipate	13.571	-	64

Unidentified	13.691	-	55 / -
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	210
Unidentified, hydroxybenzophenone	15.368	-	120
Unidentified, flavonoid	15.411	-	55
Unidentified, flavonoid	16.294	-	48
Unidentified	21.545	-	64
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	540

TABLE 0-9. Sample ID 202011 – 8, Heated shirt.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Isophthalic acid	7.860	121-91-5	110
bis(Butenyl) adipate	8.359	998445-98-7	43 / 95
3-Butenyl adipate	8.372	998445-98-6	74 / 170
2-((But-3-enyloxy)carbonyl)benzoic acid	8.943	113793-34-3	310
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	120 / 220
4-(Butoxycarbonyl)benzoic acid	9.005	1818-06-0	200
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	71
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	310 / 710
Ethylene glycol - Adipate - Diethylene glycol	11.910	998446-00-6	74 / 130
Unidentified	13.124	-	46 / 81
Unidentified, adipate	13.580	-	47 / 100
Unidentified	13.705	-	93
Adipic acid, cyclobutyl nonyl ester	13.928	998324-27-7	53 / 120
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	190
Unidentified, hydroxybenzophenone	15.368	-	280
Unidentified, hydroxybenzophenone	15.435	-	78
Unidentified, silane	17.115	-	95
Unidentified, xanthone	17.779	-	100
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl) ester	20.087	36443-68-2	140
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	890

TABLE 0-10. Sample ID 202011 – 9, Heating mattress pad/underblanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)	
Benzoic acid	4.421	65-85-0		74
1-Dodecanol	6.851	112-53-8	:	38
1,2-propanedione,1-(3,4-methylenedioxy)phe- nyl	7.733	998378-93-0	1	10

Isophthalic acid	7.860	121-91-5	110
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	290
1,4-Benzenedicarboxylic acid, bis(2-hydroxy- ethyl) ester	9.358	959-26-2	42
Unidentified	13.694	-	150
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-tet- rone	14.521	998398-77-0*	90
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	550
Unidentified, hydroxybenzophenone	15.368	-	270
Unidentified, hydroxybenzophenone	15.435	-	100
Unidentified, hydroxybenzophenone	15.481	-	55
tri(2-Ethylhexyl) trimellitate	15.638	3319-31-1	50 / 27
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	130
Unidentified, possibly part of polyethylene- terphthalate	26.392	-	2200

TABLE 0-11. Sample ID 202011 – 10, Heating blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	18
2-Propenoic acid, octyl ester	4.942	2499-59-4	31 / -
Glutaric acid, butyl 2-ethylhexyl ester	9.695	998358-23-4	13 / -
2H-Azepin-2-one, hexahydro-1-methyl-	9.917	2556-73-2	12 / -
Glutaric acid, di(2-ethylhexyl) ester	11.164	998358-24-7	27 / -
Unidentified	11.342	-	25 / -
2-Ethylhexyl stearate	12.842	22047-49-0	15
Unidentified	13.581	-	12 / -
Unidentified	13.686	-	62
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	55 / 22
Unidentified	14.635	-	39 / -
Unidentified, hydroxybenzophenone	15.368	-	110
Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)	15.626	31570-04-4	- / 24
tri(2-Ethylhexyl) trimellitate	15.638	3319-31-1	83 / -
Tris(2,4-di-tert-butylphenyl) phosphate	16.694	95906-11-9	45
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1700

TABLE 0-12. Sample ID 202011 – 11, Heating mattress pad/underblanket.

Component	Retention time	CAS/ NIST no.	Concentration
	(min)		(mg/kg)

Benzoic acid	4.421	65-85-0	16
Dimethyl palmitamine	9.453	112-69-6	7
1-Heptadecene	10.281	6765-39-5	11
Unidentified	10.599	-	- / 8.8
Unidentified	13.678	-	97
cis-9-Octadecenoic acid, propyl ester	14.377	998405-15-0	75
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	94
trans-9-Octadecenoic acid, pentyl ester	14.774	998405-19-1	11
Unidentified, hydroxybenzophenone	15.368	-	160
Unidentified	15.383	-	7
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1600 / 890
Unidentified	28.154	-	22

TABLE 0-13. Sample ID 202011 – 12, heating mattress pad/underblanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	9
Botran	8.257	99-30-9	7
Cyclotetradecane	9.276	295-17-0	9
Unidentified	10.599	-	9
Hexanedioic acid, bis(2-ethylhexyl) ester	11.602	103-23-1	9
Unidentified, siloxane	11.883	-	7.4 / -
Bis(2-ethylhexyl) phthalate	12.163	117-81-7	16
Unidentified	13.677	-	89
Unidentified, hydroxybenzophenone	15.435	-	140
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1700
Unidentified	28.133	-	10

TABLE 0-14. Sample ID 202011 – 13, Heating blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	88
Isophthalic acid	7.860	121-91-5	120
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	380 / 650
Unidentified	12.340	-	37
Unidentified	13.682	-	140
Unidentified	13.938	-	- / 39
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-tet- rone	14.521	998398-77-0*	100

3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	490
Unidentified, hydroxybenzophenone	15.368	-	270
Unidentified, hydroxybenzophenone	15.435	-	110
Unidentified, hydroxybenzophenone	15.481	-	46
Unidentified	23.009	-	120 / 58
Unidentified	23.349	-	120 / 240
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1000 / 600
Unidentified	28.050	-	45

TABLE 0-15. Sample ID 202011 – 14, Heating sleeping bag.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzoic acid	4.421	65-85-0	28
3-Octadecene, (E)-	8.868	-	- / 28
Benzoic acid, 2-(1-oxopropyl)-	8.950	2360-45-4	89 / 35
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	37
Unidentified	11.031	-	26
Unidentified	13.687	-	94
Unidentified	14.347	-	26
9-Octadecenoic acid	14.382	2027-47-6	82
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	25 / 14
9,10-Anthracenedione, 1-amino-4-hydroxy-2- phenoxy-	14.863	17418-58-5	36
Unidentified, hydroxybenzophenone	15.368	-	56
Unidentified, hydroxybenzophenone	15.435	-	180
Unidentified	18.290	-	140
Unidentified	22.015	998402-76-6	70
Unidentified	23.340	-	35
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	850 / 1600
Unidentified	28.215	-	33

TABLE 0-16. Sample ID 202011 – 15, heated underwear.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	54
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	82
2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester	10.904	141-02-6	43
Unidentified, adipate	13.562	-	110
1,6,11,16,21-Pentaoxacyclopentacosane	13.895	56890-57-4	62
Carbonic acid, 2-ethylhexyl tridecyl ester	14.039	998383-77-0	96

Branched alcohol, C15	14.203	-	110
Branched alcohol, C16	14.266	-	120
Stearic acid, tridecyl ester	14.289 – 14.528	998438-99-2	320 / 190
Carbonic acid, undecyl vinyl ester	14.425	998382-54-9	130
Carbonic acid, tridecyl vinyl ester	14.466	998382-54-7	68
Unidentified, phtalate	14.961	-	120
Unidentified, hydroxybenzophenone	15.435	-	60
1,6,11,16,21,26-Hexaoxacyclotriacontane	15.833	64001-05-4	54
1,6,11,16,21,26,31-Heptaoxacyclopenta- triacontane	18.734	66055-34-3	43
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl) ester	20.087	36443-68-2	150
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	75 / 600

TABLE 0-17. Sample ID 202011 – 16, Heated underwear.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Methanone, (1-hydroxycyclohexyl)phenyl-	8.151	947-19-3	41
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	34
Benzenamine, 2,6-dibromo-4-nitro-	9.353	827-94-1	43
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	52
Hexadecanoic acid, decyl ester	12.679	42232-27-9	57
Stearic acid, isohexyl ester	13.402	998438-98-6	270
Unidentified, adipate	13.559	-	86
Unidentified	13.674	-	41
2H-1,3-Pyrimidine-2-ketene, 2,5-dimethyl-1,6- diphenyl-4-(p-tolyl)-	13.705	-	30
1,6,11,16,21-Pentaoxacyclopentacosane	13.895	56890-57-4	49
Unidentified, phtalate	14.959	-	230
3',4',5'-Tribromobenzo[1',2'-b]-1,4-diazabicy- clo[2.2.2]octene	15.394	108958-99-2	54
Unidentified, hydroxybenzophenone	15.435	-	69
1,6,11,16,21,26-Hexaoxacyclotriacontane	15.833	64001-05-4	49
Unidentified, flavorid	16.274	-	38
Unidentified	16.994	-	370
Unidentified	17.068	-	340
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl) ester	20.087	36443-68-2	230
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	640

TABLE 0-18. Sample ID 202011 – 17, Heated socks.

Component	Retention time	CAS/ NIST no.	Concentration
	(min)		(mg/kg)

Benzene, 1,1'-(1,3-propanediyl)bis-	7.926	1081-75-0	34
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	54
Terephthalic acid, di(but-3-enyl) ester	9.766	998356-36-8	32
Terephthalic acid, di(but-2-enyl) ester	9.884	998356-47-7	51
Long chained alcohol	10.247	2425-77-6	31
Unidentified	10.970	-	48
Unidentified	11.668	998210-95-2	36
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	200 / 380
Unidentified	13.189	1700-29-4	36
Unidentified	13.628	-	58
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-tet- rone	14.533	998398-77-0	68
Unidentified	14.755	-	28 / -
Unidentified, silane	15.276	-	120
Irigenin, trimethyl ether	16.195	50901-35-4	38
Unidentified	16.305	-	56
Unidentified	17.620	-	44
Unidentified	18.267	-	250
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl) ester	20.087	36443-68-2	69
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	620

TABLE 0-19. Sample ID 202011 – 18, Heated socks.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
3-(2-Oxocyclohexyl)propionaldehyde	8.003	2568-20-9	22
bis(Butenyl) adipate	8.359	998445-98-7	21
3-Butenyl adipate	8.372	998445-98-6	48
1,6-Dioxacyclododecane-7,12-dione	8.523	777-95-7	67
Benzene, 1,1'-methylenebis[4-isocyanato-	9.882	-	33
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	170
Butanediol adipate	11.195	998445-98-5	420
Unidentified	11.241	-	52
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	130
Butenyl Butanediol Adipate	13.540	-	270
2H-1,3-Pyrimidine-2-ketene, 2,5-dimethyl-1,6- diphenyl-4-(p-tolyl)-	13.665	-	21
Adipic acid, cyclobutyl nonyl ester	13.928	998324-27-7	39
Butenyl Butanediol Adipate	15.050	998445-98-8	92
Unidentified, hydroxybenzophenone	15.481	-	28
Unidentified, adipate	20.483	-	170
Unidentified, adipate acid	21.175	-	21

TABLE 0-20. Sample ID 202011 – 19, Heated gloves.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Botran	8.257	99-30-9	140
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	110
Benzenamine, 2-bromo-4,6-dinitro-	9.699	1817-73-8	290 / 160
Ethanone, 1-(4-hydroxyphenyl)-2-phenyl-	9.717	2491-32-9	78 / 150
Benzoic acid, 4-amino-, 2-methylbutyl ester	10.153	998375-46-2	78
1-Octadecanol	10.231	112-92-5	68 / -
9-Octadecenoic acid, (E)-	10.559	112-79-8	590 / -
Octadecanoic acid	10.638	57-11-4	99 / -
Benzenesulfonamide, N-(3-hydroxyphenyl)-	10.658	59149-19-8	- / 60
Unidentified	10.943	-	- / 60
Unidentified	11.823	-	110
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	90
Phthalic acid, di(2-propylpentyl) ester	12.121	998377-93-5	- / 100
1,4-Benzenedicarboxylic acid, bis(2- ethylhexyl) ester	12.999	6422-86-3	- / 58
Unidentified, Silane	15.281	-	90
Unidentified	15.317	-	- / 240
Unidentified	15.336	-	260 / -
Unidentified	16.223	-	73
Unidentified	16.717	-	90 /150
Unidentified	16.886	6676-90-0	83 / 240
9-Octadecenoic acid (Z)-, octyl ester	17.715	32953-65-4	100 / -
Unidentified, silane	18.202	-	- / 64
Benzenepropanoic acid, 3-(1,1-dimethylethyl)- 4-hydroxy-5-methyl-, 1,2-ethanediylbis(oxy- 2,1-ethanediyl) ester	20.087	36443-68-2	150
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	760

TABLE 0-21. Sample ID 202011 – 20, Heating neck blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Cyclohexane, 1,3,5-triphenyl-	11.824	28336-57-4	38 / -
Unidentified	13.621	-	70
Unidentified, hydroxybenzophenone	15.368	-	110
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1100

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TABLE 0-22. Sample ID 202011 – 21, Heating neck blanket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Octacosane	13.103	630-02-4	38
Unidentified	13.543	-	69
Unidentified, hydroxybenzophenone	15.368	-	120
Propanenitrile, 3-[[2-(acetyloxy)ethyl][4-[(2,6- dichloro-4-nitrophenyl)azo]phenyl]amino]-	17.363	5261-31-4	66
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1400

TABLE 0-23. Sample ID 202011 – 22, Heated vest.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzene, 1,3-diisocyanato-2-methyl-	5.766	91-08-7	64
Benzene, 2,4-diisocyanato-1-methyl-	5.800	584-84-9	220
2-Methylglutaconic acid, diethyl ester	7.959	998222-04-3	110
1,2-Benzenedicarboxylic acid, bis(2- methylpropyl) ester	8.991	84-69-5	170
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	130
Tributyl acetylcitrate	10.842	77-90-7	- / 57
Unidentified	11.816	-	53
Unidentified	12.631	-	60
Unidentified, Adipate	13.434	-	130
Unidentified	13.547	-	65
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-tet- rone	14.521	998398-77-0*	74
propanenitrile, 3-[ethyl[4-[2-(4-nitrophenyl)dia- zenyl]phenyl]amino]-	14.532	998403-08-7	58
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0	370
9,10-Anthracenedione, 1-amino-4-hydroxy-2- phenoxy-	14.863	17418-58-5	65
Unidentified, hydroxybenzophenone	15.368	-	170
Unidentified, hydroxybenzophenone	15.435	-	88
Unidentified, hydroxybenzophenone	15.481	-	65 / -
Unidentified	18.089	-	470
Unidentified	20.251	-	- / 55
Unidentified	22.619	-	74 / -
Unidentified	22.951	-	150 / 57
Unidentified, possibly part of polyethylene- terphthalate	25.057	-	1300

TABLE 0-24. Sample ID 202011 – 23, Heated sleeping bag.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)	
Unidentified	11.595	-		47
Unidentified	13.546	-		75
9-Octadecenoic acid	14.382	2027-47-6		59
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetra- cosa-8,10,18,20,21,23-hexaene-2,7,12,17-te- trone	14.533	998398-77-0		63
Unidentified, hydroxybenzophenone	15.368	-		160
Unidentified	18.060	-		260
Unidentified	22.015	998402-76-6		110
Unidentified, possibly part of polyethylene- terphthalate	25.057	-		610
Unidentified, possibly part of polyethylene- terphthalate	26.392	-		650

TABLE 0-25. Sample ID 202011 – 24, Heated shirt.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzene, 1,3-diisocyanato-2-methyl-	5.766	91-08-7	83
Benzene, 2,4-diisocyanato-1-methyl-	5.800	584-84-9	250
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	68 / -
Benzene, 1,1'-methylenebis[4-isocyanato-	10.290	101-68-8	65
Butanediol adipate	11.195	998445-98-5	- / 62
Ethylene glycol - Adipate - Diethylene glycol	11.910	998446-00-6	77
Unidentified	12.635	-	97
Unidentified	13.551	-	65 / -
2H-1,3-Pyrimidine-2-ketene, 2,5-dimethyl-1,6- diphenyl-4-(p-tolyl)-	13.604	998149-41-5	270
4H-Cyclo- propa[5',6']benz[1',2':7,8]azuleno[5,6]oxiren-4- one, 8,8a-bis(acetyloxy)-2a-[(acety- loxy)methyl]-1,1a,1b,1c,2a,3,3a,6a,6b,7,8,8a- dodecahydro-6b-hydroxy-3a-methoxy-1,1,5,7- tetramethyl-, [1aR-(1a.al- pha.,1b.beta.,1c.beta.,2a.beta.,3a.al- pha.,6a.al	14.003	-	140
Coumarine, 6-(4-nitrophenylazo)-	14.233	998270-84-9	95
Unidentified	14.959	-	76
Unidentified	15.047	-	71 / 130
Butenyl Butanediol Adipate	15.050	998445-98-8	160
Unidentified, hydroxybenzophenone	15.368	-	120
Ethanone, 1-[3,5-bis(phenylmethoxy)phenyl]-	15.437	28924-21-2	290
Unidentified	15.568	-	- / 79
Unidentified	15.908	-	91 / -
Irigenin, trimethyl ether	16.195	50901-35-4	96
Unidentified	18.225	-	1400

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Octaethylene glycol monododecyl ether	10.927	-	110
Octan-2-yl palmitate	11.977	55194-81-5	240
2-Ethylhexyl stearate	12.842	22047-49-0	180
1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	12.999	6422-86-2	49 / 26
2H-1,3-Pyrimidine-2-ketene, 2,5-dimethyl-1,6-diphe- nyl-4-(p-tolyl)-	13.604	998149-41-5	53
Unidentified aliphatic hydrocerbons, C14-C30	7.9-17.2	-	8300
3',4',5'-Tribromobenzo[1',2'-b]-1,4-diazabicy- clo[2.2.2]octene	15.187	-	39
Unidentified, hydroxybenzophenone	15.368	-	43
Ethanone, 1-[3,5-bis(phenylmethoxy)phenyl]-	15.437	28924-21-2	43
Irigenin, trimethyl ether	16.195	50901-35-4	46
Unidentified	16.745	-	140
Unidentified	16.765	-	36 / -
Unidentified	18.121	-	490
Benzenepropanoic acid, 3-(1,1-dimethylethyl)-4-hy- droxy-5-methyl-, 1,2-ethanediylbis(oxy-2,1-etha- nediyl) ester	20.087	36443-68-2	96
Unidentified, possibly part of polyethyleneterphthalate	25.057	-	740

TABLE 0-26. Sample ID 202011 – 25, Heated underwear.

TABLE 0-27. Sample ID 202011 – 26, Heated gloves.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
n-Hexadecanoic acid	9.677	57-10-3	47 / -
cis-Vaccenic acid	10.411	506-17-2	77 / -
2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester	10.904	141-02-6	130
Unidentified	13.546	-	80
Unidentified	14.231	-	31 / -
Unidentified	15.025	-	- / 32
Unidentified, hydroxybenzophenone	15.368	-	140
Ethanone, 1-[3,5-bis(phenylmethoxy)phenyl]-	15.398	-	60 / 100
Unidentified	17.331	-	34
Unidentified	18.063	-	280
Benzenepropanoic acid, 3-(1,1-dimethylethyl)-4-hy- droxy-5-methyl-, 1,2-ethanediylbis(oxy-2,1-etha- nediyl) ester	20.087	36443-68-2	170
Unidentified, possibly part of polyethyleneterphthalate	25.057	-	700

TABLE 0-28. Sample ID 202011 - 27, Heated jacket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	35
1-Propene-1,2,3-tricarboxylic acid, tributyl ester	10.400	7568-58-3	39
Tributyl acetylcitrate	10.842	77-90-7	200 / 340
Unidentified	11.594	-	60
Unidentified	13.540	-	39
2H-1,3-Pyrimidine-2-ketene, 2,5-dimethyl-1,6-diphe- nyl-4-(p-tolyl)-	13.604	998149-41-5	33 / -
Unidentified, hydroxybenzophenone	15.368	-	110
Unidentified	15.978	-	33
5,5'-Dimethoxy-3,3'-dimethyl-2,2'-binaphthalene- 1,1',4,4'-tetrone	16.025	54215-49-5	35
Unidentified	16.121	-	130
Unidentified	16.775	-	97
Unidentified	17.389	-	51
Unidentified	18.067	-	330
Unidentified, possibly part of polyethyleneterphthalate	25.057	-	1100

TABLE 0-29. Sample ID 202011 – 28, Heated vest.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
Isophthalic acid	7.860	121-91-5	62
2-((But-3-enyloxy)carbonyl)benzoic acid	8.943	113793-34-3	73
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	66
Unidentified	11.599	-	150
Unidentified	13.546	-	85
Unidentified	13.587	-	96
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetracosa- 8,10,18,20,21,23-hexaene-2,7,12,17-tetrone	13.661	998398-77-0*	- / 44
3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetracosa- 8,10,18,20,21,23-hexaene-2,7,12,17-tetrone	14.533	998398-77-0	230
Unidentified	14.654	-	52
Unidentified, hydroxybenzophenone	15.368	-	310
Unidentified	15.408	-	57
Unidentified, hydroxybenzophenone	15.435	-	120
Unidentified, hydroxybenzophenone	15.481	-	50
Unidentified	16.050	-	55
Unidentified, silane	16.804		150
Unidentified	17.435		170
Unidentified	18.127	-	860
Unidentified	22.883	-	51
Unidentified, possibly part of polyethyleneterphthalate	25.057	-	900

TABLE 0-30. Sample ID 202011 – 29, Heated jacket.

Component	Retention time (min)	CAS/ NIST no.	Concentration (mg/kg)
bis(Butenyl) adipate	8.359	998445-98-7	81
3-Butenyl adipate	8.372	998445-98-6	250
Benzenamine, 2-chloro-4,6-dinitro-	9.190	3531-19-9	170
Terephthalic acid, di(but-3-enyl) ester	9.766	998356-36-8	52 / 110
Tributyl acetylcitrate	10.842	77-90-7	130 / 70
Unidentified	10.876	-	59
Unidentified	11.594	-	87 / 39
Unidentified	11.821	-	95
Unidentified	13.435	-	180
Unidentified	13.587	-	81
Adipic acid, cyclobutyl nonyl ester	13.928	998324-27-7	120
Unidentified	13.993	-	130
Unidentified	14.212	-	66
propanenitrile, 3-[ethyl[4-[2-(4-nitrophenyl)diaze- nyl]phenyl]amino]-	14.532	998403-08-7	170 / 98
Butenyl Butanediol Adipate	15.050	998545-98-8	160
Unidentified, hydroxybenzophenone	15.368	-	130
Ethanone, 1-[3,5-bis(phenylmethoxy)phenyl]-	15.437	28924-21-2	69 / 130
Unidentified	16.152	-	83 / -
Unidentified	16.169	-	- / 320
Unidentified, silane	16.801		250 / 99
Unidentified	17.419		180 / 42
Unidentified	18.170	-	1400
Unidentified, adipate	20.259	-	69
Unidentified, possibly part of polyethyleneterphthalate	25.057	-	590

Survey, control and risk assessment of flame retardants and other hazardous substances in textiles containing electronic parts

Textile products with electronic heating functions are available to consumers for use at home and for outdoor activities. Since these products contain electronic parts and heating functions, an increased risk of flammability can be expected, making the addition of flame retardants to these products likely.

The objective of this study is to provide insight into which flame retardants are used in textiles containing electronic parts, whether these flame retardants are regulated by applicable European law, and whether they pose a health risk to consumers. The study also investigates if textile products with electronic parts contain other hazardous substances specific for this product type.

In the product survey, information about 67 textile products were listed comprising, amongst others, blankets, mattress pads, gloves, socks, and jackets with heating functions. A selection of products was purchased for chemical analysis. Three flame retardants (TCEP, TCPP and TPP) were quantified at low concentrations, indicating that the substances had not been added to achieve flame retardancy. Banned flame retardants such as PBB and PBDE were not detected.

Additionally, non-target screenings were conducted to detect other substances. Of the detected substances, many are fragments of polyester or substances known as additives in polyester, PS or PVC polymers. These substances have been evaluated to be non-specific for the product type textiles with electronic parts.

The health risk characterisation shows risk ratios below one. Thus, the assessment shows that the health risk for consumers' use of textiles with electronic parts is controlled for the measured concentrations of flame retardants.



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