DETOX Program
Hazardous Substances Fact Sheet

Flame Retardants

Content

1 Background

Flame-retarding agents should protect fabric from burning, without modifying the hand feel, color, and look of the fabric.[1] For the majority of apparel products, home textiles and shoes, flame retardants are neither needed nor desired. But even if there is no intended use, flame retardants may be present in products, caused by contamination or the use of other materials that were treated with flame retardants.
The group of flame retardants includes a variety of different chemicals which are necessary because the materials and products which are to be rendered fire safe are very different in nature and composition. Many of them can cause serious health effects like damages to the endocrine system and cancer. They are often persistent and bioaccumulative. Through migration over long distances by air and ocean currents they became widespread global environmental contaminants.

Even if for the majority of apparel products, home textiles and shoes, flame retardants are not needed nor desired, flame-retarding finishing has become increasingly important and in several countries, it is compulsory for some items. The different sources of contamination may also cause significant concentrations of flame retardants in common apparel and shoe products.

In contrast to many other textile auxiliaries and finishing agents, where only small quantities remain on the garment, a flame-retardant coating may account for up to 20 % of the product weight. As most flame retardants are not fixed to the matrix of consumer products and can leach out into the environment, considerable exposure is to be expected when wearing garments with a non-permanent finish.[2].

2 Definition

A range of chemically very diverse substances is used as flame retardants. Important chemical groups used in textile industry are:

- Halogenated flame retardants (bromated or chlorinated) include substances (groups) like:

CAS Number	Name
59536-65-1	Polybrominated biphenyls (PBBs)
Various CAS numbers	Polybrominated diphenyl ethers (PBDE)
Various CAS numbers	Polychlorinated biphenyls (PCBs)
Various CAS numbers	Polychlorinated terphenyls (PCTs)
Various CAS numbers	Polybrominated terphenyls (PBTs)
Various CAS numbers	Polychlorinated naphthalenes (PCNs)
Various CAS numbers	Polybrominated napthalenes (PBNs)
Various CAS numbers	Halogenated diarylalkanes
Various CAS number	Chlorinated paraffins (factsheet no. 11)

[1] Swedish Chemicals Agency (KEMI) 2004. Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications. Online available: https://www.kemi.se/Documents/Publikationer/Trycksaker/PM/PM5_04.pdf
[2] German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, BFR), 2012. Introduction to the problems surrounding garment textiles. Online available: http://www.bfr.bund.de/cm/349/introduction-to-the-problems-surrounding-garment-textiles.pdf

79-94-7	Tetrabromo-bisphenol A (TBBPA)

In the textile industry mainly brominated flame retardants (BFR) are used. Polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDEs) are the most common groups of BFRs[3, 4]. Substances falling under this group are for example:

CAS Number	Name
1163-19-5	Deca-bromodiphenyl ether (DecaBDE)
32534-81-9	Penta-bromodiphenyl ether (PentaBDE)

- Organophosphate flame retardants contain phosphate groups bound to carbon. Important examples are:

CAS Number	Name
545-55-1	Tris-(1-aziridinyl)-phosphine oxide (TEPA)
5412-25-9	BIS-(2,3-dibromopropyl)-phosphate
25155-23-1	Trixylyl phosphate
13674-87-8	Tris-(1,3-dichlorisopropyl)phosphate (TDCPP)

- Inorganic flame retardants include mineral /salt/ amine flame retardants containing e.g. aluminum, inorganic phosphorus (not bound to carbon), nitrogen, calcium, and magnesium.[5] Commonly used flame retardants of this group in the textile industry are for example:

CAS Number	Name
1303-86-2	Boron trioxide
11113-50-1; 10043-35-3	Boric acid
1309-64-4	Antimony trioxide

3 Legal Aspects

In the European Union (EU) the use of certain flame retardants are banned or restricted in textile articles.[6] Under the REACH regulation tris-(2,3-dibromo-propyl)-phosphate (TRIS), tris-(1-aziridinyl)-phosphine oxide (TEPA) and polybrominated biphenyls (PBB) are banned.[7][8]

[3] European Food Safety Authority 2014. Brominated Flame Retardants. Online available: http://www.efsa.europa.eu/en/topics/topic/bfr.htm

[4] Intertek, undated. For brands that care from make to wear. Online available: http://www.intertek.com/uploadedFiles/Intertek/Divisions/Consumer_Goods/Media/PDFs/Services/Eco-Textiles.pdf

[5] A PERKINS+WILL WHITE PAPER 2014. Healthy Environments: Strategies for Avoiding Flame Retardants in the Built Environment. Online available: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf

[6] Reach 1907/2006. Annex XVII, Limitations: 1. Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin.

[7] German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, BFR), 2012. Introduction to the problems surrounding garment textiles. Online available: http://www.bfr.bund.de/cm/349/introduction-to-the-problems-surrounding-garment-textiles.pdf

[8] https://echa.europa.eu/addressing-chemicals-of-concern/restrictions/substances-restricted-under-reach

Several chemicals banned by the Stockholm Convention on Persistant Organic Pollutants (POPs) are halogenated flame retardants or their degradation products.[9] [10]

Suppliers of the REWE Group must ensure that they produce in full accordance with the legal requirements of the country where the production takes place, and the legal provisions of the European Union regarding final products. A comprehensive list with international regulation for individual hazardous substances can be found on the website of the American Apparel & Footwear Association (AAFA).[11]

4 Hazardous Properties and Exposure

4.1 Hazardous Properties

Contact to flame retardants can cause serious health impacts. Brominated Biphenyls (PBBs) can cause damages to the endocrine system and produce cancer. PBBs are listed by the European Commission as “endocrine disrupter Category 1” (Cat. 1 = Evidence for endocrine disruption in living organisms)[12]. The International Agency for the Research on Cancer (IARC) listed PBBs as “probably carcinogenic to humans” (Category 2A)[13].

PBDEs are endocrine-disrupting compounds, exerting effects on a number of hormonal systems, including the androgens, progestins and estrogens, though the major system affected by PBDEs is the thyroid hormone system.[14]

A typical representative of brominated flame retardants is deca-bromodiphenyl ether (DecaBDE). Exposure to DecaBDE and lower brominated transformation products may result in neurotoxic effects in mammals, including humans.[15] DecaBDE is persistent, bioaccumulative and toxic (PBT) and also very persistent and very bioaccumulative (vPvB) because it transforms to substances with these properties in the environment. Information from environmental monitoring shows that DecaBDE occurs widely in the environment and in wildlife.[16] It was added to the REACH Candidate List for authorization in December 2012[17].

Organophosphate flame retardants show health effects such as endocrine disruption[18], neurotoxicity[19] and some may cause cancer[20]. Reduced sperm counts and altered levels of

[9] Susan D. Shaw (Marine Environmental Research Institute, USA) et al. 2010. Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? Online available: http://greensciencepolicy.org/wp-content/uploads/2013/12/25-HFRs-benefit-v-risk-Review-of-Env-Health-2010-SHAW-BLUM-etal.pdf
[10] http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx
[11] https://www.wewear.org/rsl/ https://www.wewear.org/assets/1/7/RSL_v16_final_UPLOAD.pdf
[12] European Commission. Annex 13 - List of 146 substances with endocrine disruption classifications prepared in the Expert meeting. Online available: http://ec.europa.eu/environment/archives/docum/pdf/bkh_annex_13.pdf
[13] IARC undated. Agents Classified by the IARC Monographs. Online available: http://monographs.iarc.fr/ENG/Classification/ClassificationsGroupOrder.pdf
[14] Breast Cancer Fund, undated. Polybrominated Diphenyl Ethers. Online available: http://www.breastcancerfund.org/clear-science/radiation-chemicals-and-breast-cancer/polybrominated-diphenyl-ethers.html
[15] European Chemicals Agency (ECHA), undated. ECHA proposes a restriction on decaBDE, a brominated flame retardant used in plastics and textiles http://echa.europa.eu/documents/10162/bffac753-8ee1-47fa-86f9-5b7294a415e5
[16] European Chemicals Agency (ECHA), undated. ECHA proposes a restriction on decaBDE, a brominated flame retardant used in plastics and textiles http://echa.europa.eu/documents/10162/bffac753-8ee1-47fa-86f9-5b7294a415e5
[17] https://echa.europa.eu/candidate-list-table
[18] Cao, Z.; et al 2014. Distribution Patterns of Brominated, Chlorinated, and Phosphorus Flame Retardants with Particle Size in Indoor and Outdoor Dust and Implications for Human Exposure. Abstract online available: http://www.ncbi.nlm.nih.gov/pubmed/25010345. Mentioned in: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf
[19] Cequier, E. et al 2014. Occurrence of a Broad Range of Legacy and Emerging Flame Retardants in Indoor Environments in Norway. Mentioned in: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf
[20] ACC undated. Classes of Flame Retardants. Online available: http://flameretardants.americanchemistry.com/FAQs/Classes-of-Flame-Retardants.html

hormones related to fertility and thyroid function have been reported.[21] [22] Organophosphate flame retardants tend to be less persistent and bioaccumulative than halogenated flame retardants.[23]

Also flame retardants from the group of minerals, salts and amines can cause negative health effect and pose a risk to the environment, e.g. because of their high aquatic toxicity.

Example of hazard statements from a safety data sheet[24]:

Tris-(1,3-dichlorisopropyl)-phosphate (TDCPP), CAS 13674-87-8

- Classification according to Regulation (EC) No 1272/2008
- H351: Carcinogenicity (Category 2)

4.2 Exposure

The risk of a chemical for human health and the environment is not only determined by its toxicity but by the degree of exposure, too.

a) Workers

Workers involved in product manufacturing and end-of-life processes (recycling, incineration, landfilling) may be exposed to flame retardant chemicals that are applied to numerous consumer products.[25]

Flame retardants based on antimony trioxide usually contain halogenated organic synergists, such as decabromo- and/or pentabromodiphenyl ether, hexabromocyclododecane, chloroparaffins and/or PVC; thus posing additional risks to workers, consumers and the environment.[26]

Non-reactive, phosphor-organic flame retardant agents release volatile components like glycols, alcohols, glycol ether etc. or parts of the active substances. Inorganic flame retardant agents can release ammonia at high process temperatures (> 150 °C).

Formaldehyde is a problem with reactive phosphor-organic flame retardants. When processing with antimony trioxide containing-agents, special care should be taken with regard to dust emissions associated with dried pastes. Antimony trioxide is carcinogenic and can contain arsenic trioxide as a contaminant. [27]

b) Environment

[21] Environmental Health Perspectives 2013. New Details on Organophosphate Flame Retardants: Exposure in Men Appears Stable over Time. Online available: http://ehp.niehs.nih.gov/121-a168/

[22] Environmental Health Perspectives 2013. New Details on Organophosphate Flame Retardants: Exposure in Men Appears Stable over Time. Online available: http://ehp.niehs.nih.gov/121-a168/

[23] A PERKINS+WILL WHITE PAPER 2014. Healthy Environments: Strategies for Avoiding Flame Retardants in the Built Environment. Online available: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf

[24] http://www.sigmaaldrich.com/MSDS/MSDS/PleaseWaitMSDSPage.do?language=&country=DE&brand=FLUKA&productNumber=32951&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D13674-87-8%26interface%3DCAS%2520No.%26N%3D0%26mode%3Dmatch%2520partialmax%26lang%3Dde%26region%3DDE%26focus%3Dproduct

[25] US Environmantel Protection Ageny, undated. Other Organics. Online available: http://www.epa.gov/risk_assessment/expobox/chemicalclass/other-flam.htm

[26] A PERKINS+WILL WHITE PAPER 2014. Healthy Environments: Strategies for Avoiding Flame Retardants in the Built Environment. Online available: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf

[27] A PERKINS+WILL WHITE PAPER 2014. Healthy Environments: Strategies for Avoiding Flame Retardants in the Built Environment. Online available: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf

Halogenated flame retardants enter the environment through multiple pathways, such as emissions during manufacturing and combustion, leaching from landfills, or recycling at the end of the product's life. They have become widespread global contaminants.[28]

Flame retardants leaching out of products contaminate environment, air, soil and water. These contaminants enter the food chain where they mainly occur in food of animal origin, such as fish, meat, milk and derived products.[29]

Many flame retardants have a high aquatic toxicity. Even after waste water treatment, a part of the flame retardants is discharged by factories into rivers and lakes. 50% of the total amounts of organophosphate flame retardants entering a sewage treatment plants may pass it, and being emitted to water bodies via the effluent[30]. Organophosphate flame retardants are frequently detected in the environment and biota. Knowledge on their potential toxicological effects is limited.[31]

c) Consumers

Exposure to flame retardants occurs mainly through food, the inhalation or ingestion of household dust, and dermal contact with treated products. Considerable exposure is to be expected when wearing garments with a non-permanent finish.[32] Children may be exposed to high levels of dust in homes due to the amount of time they spend on the floor and the higher rate of hand-to-mouth contacts.[33].

Halogenated flame retardants were detected in human breast milk, body fat, fish, whales, seals, mussels, water and sediments of rivers, or eggs of wild birds. [34]

Flame retardants are not fixed to the products and are ubiquitous substances in both indoor and outdoor environments. They can enter our bodies via evaporation out of products and into the air and dust.[35]

5 Sources for Flame Retardants in production of textiles

a) Processing chemicals used in the factory

The direct use of flame retardants will cause a significant input of these substances in the supply chain.

Examples:

[28] Susan D. Shaw (Marine Environmental Research Institute, USA) et al. 2010. Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? Online available: http://greensciencepolicy.org/wp-content/uploads/2013/12/25-HFRs-benefit-v-risk-Review-of-Env-Health-2010-SHAW-BLUM-etal.pdf

[29] European Food Safety Authority 2014. Brominated Flame Retardants. Online available: http://www.efsa.europa.eu/en/topics/topic/bfr.htm

[30] Umeå University, Sweden 2005. Levels and Sources of Organophosphorus Flame Retardants and Plasticizers in Indoor and Outdoor Environments. Online available: http://www.diva-portal.org/smash/get/diva2:144103/FULLTEXT01.pdf

[31] Xiaoshan Liu, Kyunghee Ji, Kyungho Choi 2012.Endocrine disruption potentials of organophosphate flame retardants and related mechanisms in H295R and MVLN cell lines and in zebrafish. Online available: http://www.sciencedirect.com/science/article/pii/S0166445X12000690

[32] German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, BFR), 2012. Introduction to the problems surrounding garment textiles. Online available: http://www.bfr.bund.de/cm/349/introduction-to-the-problems-surrounding-garment-textiles.pdf

[33] US Environmental Protection Agency, undated. Other Organics. Online available: http://www.epa.gov/risk_assessment/expobox/chemicalclass/other-flam.htm

[34] Kansas City 2011. The Most Common Flame Retardants, Part 2: Chlorinated. Online available: http://thesoftlanding.com/the-most-common-flame-retardants-part-2-chlorinated/#sthash.jLa4luKb.dpuf

[35] A PERKINS+WILL WHITE PAPER 2014. Healthy Environments: Strategies for Avoiding Flame Retardants in the Built Environment. Online available: http://transparency.perkinswill.com/Content/Whitepapers/PerkinsWill_FlameRertardantAlternatives.pdf

- Decabromo diphenyl ether (DecaBDE) is added primarily to coated textile materials, furniture and similar seating and bedding products but also other technical textiles.[36]
- Pentabromo diphenyl ethers (PentaBDE), CAS 32534-81-9 is added primarily to polyurethane foams in furniture, baby products, and automobile and aircraft interiors[37]
- PBDE is added to various plastic polymers as well as back coating for textiles (commercial furniture, automobile fabrics, and carpets).[38] Because of their high-volume use in consumer products over decades, they can be found at high levels in homes and public places..[39]

b) Raw materials used in the factory

Raw materials (synthetic fibers e.g.) and semi finished raw material that are bought by a factory and used in production may also contain halogenated flame retardants and should be controlled.

c) Contamination

Possible reasons for contamination are chemical impurities or unknown additives in processing chemicals and incoming water.

6 Alternative and Substitute Substances

All alternatives used as substitutes for hazardous substances must be free of hazardous properties. Some tools to identify hazardous properties of chemicals and to find safer alternatives are listed in the factsheet about hazardous substances.

There are flame-retardant man-made fibers which seem to cause very low exposure to flame retardants.

In general no flame retardant effect is needed for the products relevant for the REWE Group, as there is no demand for an additional flame retarding function.

In case flame retarding effects are needed, there are possibilities to substitute regularized flame retardants in textiles. Depending on the desired effect on flammability the options need to be discussed with the chemical manufacturer (taking the customer requirements and restrictions into account).

In order to minimize environmental and health effects and to use resources efficiently the use of best available technology (BAT[40]) in textiles industry is a standard requirement.
The Chemsec Textile Guide offers access to a list of hazardous and safer chemicals and should be taken into account for the selection and purchase of chemical products[41].

[36] Swedish Chemicals Agency (KEMI) 2004. Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications. Online available: https://www.kemi.se/Documents/Publikationer/Trycksaker/PM/PM5_04.pdf
[37] Susan D. Shaw (Marine Environmental Research Institute, USA) et al. 2010. Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? Online available: http://greensciencepolicy.org/wp-content/uploads/2013/12/25-HFRs-benefit-v-risk-Review-of-Env-Health-2010-SHAW-BLUM-etal.pdf
[38] Swedish Chemicals Agency (KEMI) 2004. Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications
Online available: https://www.kemi.se/Documents/Publikationer/Trycksaker/PM/PM5_04.pdf
[39] Susan D. Shaw (Marine Environmental Research Institute, USA) et al. 2010. Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? Online available: http://greensciencepolicy.org/wp-content/uploads/2013/12/25-HFRs-benefit-v-risk-Review-of-Env-Health-2010-SHAW-BLUM-etal.pdf
[40] European Commission: Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry July 2003
[41] ChemSec, undated. Textiles come with a toxic footprint. http://textileguide.chemsec.org/find/textiles-come-with-a-toxic-footprint/