(PFAS)

PER-AND POLY-FLUOROALKYL SUBSTANCES

Background

Per- and poly-fluoroalkyl substances (PFAS) are a broad class of thousands of man-made synthetic fluorinated chemicals used in various industries and consumer goods since the 1940s. PFAS do not occur naturally in the environment. The strong Carbon-Fluorine bonds present in this chemistry prevents them from degradation during usage and in the environment and hence they are known as "forever chemicals". PFAS are also easily transmitted in the environment across great distances from their point of release and some are hence included as Persistent Organic Pollutants (POP) under the Stockholm Convention.

Due to their extensive use, ability to migrate and persistence, they can be found in low concentrations in a range of food items as well as in the environment and in the blood of humans and other animals worldwide.[1,2]

Uses in textile & footwear supply chains[3,4]

- Durable oil and water repellant functional finishes.
- Soil release functional finishes.
- Mold release (injection molding process).
- Low friction treatments (Polishes, Lubricants, Waxes and Greases).
- Surfactant in softeners, defoamers, foam stabilizers, surface cleaning agents, coatings, digital printing, high-bond glues.
- Emulsifier in liquid suspensions – Dyestuff, textile finishing agents.

Harmful effects of PFAS[2,5-7]

(All these effects are not caused by every individual PFAS, but certain health and environmental hazards such as persistence are common properties of these substances)

- Very Persistent, Very Bioaccumulative (vPvB)
- Reprotoxic; capable of reducing fertility, damage to growth of foetuses or elevated blood pressure in pregnant women
- Associated with human cancers including prostate, kidney, and testicular cancers
- May potentially affect the human endocrine (hormonal) system
- Increased risk of obesity and/or high cholesterol, which can harm the liver
- Reduced capacity of the immune system to combat infections
- Developmental impacts in children such as low birth weight, premature puberty, bone abnormalities or behavioural alterations
- May have long term adverse impacts on aquatic environments

1. Chemistry and terminologies:

The term PFAS refers to fluorinated substances that have at least one fully fluorinated methyl ($-CF_3$) or methylene ($-CF_2-$) carbon atom (without any H/Cl/Br/I atom attached to it).[8] The chemistry is further divided into two types:[5]

- *Polymer PFAS:* where the Fluorine atoms are directly bonded to the carbon-only polymer backbone or a carbon-oxygen polymer backbone or where fluorinated side-chains branch out from the carbon polymer backbone. Fluoropolymers (like PTFE, ETFE) and fluorinated polymers (like fluorinated urethane polymers) that are used for repellent functional finishes in the textile and leather supply chain are examples of polymer PFAS.
- *Non-polymer PFAS* where:
    i. All hydrogen atoms on all carbon atoms in the alkyl chain attached to a functional group have been replaced with fluorine (Per Fluoroalkyl substances)

        » Examples:
        - Perfluoroalkyl carboxylic acids (PFCA), such as Per Fluoro Octanoic Acid (PFOA)
        - Per fluoroalkane sulfonic acids (PFSA), such as Per Fluoro Octane Sulphonate (PFOS)

These are further sub-divided into:

Long chain PFCA - 8 or more carbon atoms (7 or more carbons are Perfluorinated)
Long Chain PFSA - 6 or more carbon atoms (6 or more carbons are Perfluorinated)

Short chain PFCA - 7 or fewer carbon atoms (6 or fewer carbons are Perfluorinated)
Short chain PFSA - 5 or fewer carbon atoms (5 or fewer carbons are Perfluorinated)

ii. All hydrogen atoms on at least one -but not all- carbon atoms have been replaced with fluorine (Poly Fluoroalkyl substances)
    » Examples: Fluorotelomer alcohols (FTOH), Fluorotelomer carboxylic acids (FTCA)

2. Safer alternatives to fluorinated repellent functional finishes in the textile and footwear supply chain:

The chemical industry has worked on a number of fluorine-free substitutes due to the harmful concerns of PFAS. These chemical products can only impart the durable water repellancy and not oil repellancy. These formulations are based on following chemistries:[4,9]

- Paraffin
- Stearic acid-melamine
- Silicone
- Polyurethane
- Dendrimer
- Poly acrylates

The OECD offers some information on PFAS alternatives based on country-specific studies for alternatives, however they are not supported by the entire group of companies.[3,10] Any alternative selected must be carefully vetted to ensure a regrettable substitution is not made. Also, the chosen alternative must be conformant to the latest version of the ZDHC MRSL.

3. Important regulations:

Many nations across the world have regulations regarding the use of PFAS in products in the form of complete bans or limits. Uniform regulations for these substance class(es) currently exist in Europe in Regulation (EC) No. 1907/2006 REACH (Annex XVII; Candidate List) and Regulation (EU) 2019/1021 (POP Regulation),[11] among others.

Some important regulations are listed here for general reference with no intention to be used as a reference for any legal compliance purpose and this information is updated to the issue date of this document:[2,5]

- The Stockholm Convention regulates the global elimination of PFOS and its derivatives, PFOA, its salts and PFOA-related compounds, PFHxS, its salts and related compounds.
- In Switzerland, perfluorohexane-1-sulfonic acid, its salts and PFHxS-related compounds were already added to the national law to phase out the use in mixtures/ substances and products.
- In June 2019 and January 2020, two PFAS groups were identified as SVHCs. The SVHC identification was based on their persistence, mobility and toxicity, which were considered to pose a threat to human health and wildlife when exposed through the environment (including through drinking water). These groups are:

    - 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propionic acid, its salts and its acyl halides (HFPO-DA), a short-chain PFAS substitute for PFOA in fluoropolymer production
    - perfluorobutane sulfonic acid (PFBS) and its salts, a replacement of PFOS
- A few PFAS already have a harmonised classification and labelling under the CLP Regulation. These include:
    - perfluorooctanoic acid (PFOA)
    - ammonium pentadecafluorooctanoate (APFO)
    - perfluorononan-1-oic acid (PFNA) and its sodium and ammonium salts
    - nonadecafluorodecanoic acid (PFDA) and its sodium and ammonium salts
- The revision of the EU Drinking Water Directive, which came into force on January 12th, 2021, sets a limit for 20 perfluorinated acids in the range of C4-C13.
- The Safer Clothes and Textile Act (AB 1817), passed by California in the United States on 30th September 2022, bans the use of PFAS in textiles and textile articles, starting 01st January 2025.[12]

4. Relevance of the ZDHC MRSL:

The use of any formulation based on, or including PFAS, is not permitted (for fashion, sport or outdoor clothing and apparel and home textiles) as per the ZDHC MRSL V3.0 published in Nov 2022.[13]

PFAS for certain technical textiles

There may be certain critical (technical textile) end uses where legally or contractually mandated standards may only be achieved using PFAS (e.g. military, medical, protective clothing, transportation). Only fluorinated polymers based on C6 telomer chemistry with a minimized content of impurities may be applicated for these essential uses. Nevertheless, the chemical formulations within the chemical inventory of a Supplier will always be deemed ZDHC MRSL non-conformant and the ZDHC Supplier Platform will appraise the end uses of any PFAS within an inventory.

There are thousands of individual substances categorised as PFAS. For confirmatory testing as mentioned in the ZDHC MRSL V3.0, the procedures and substance series should be considered as mentioned in the relevant standards for textile and leather: EN 17681-1, 2022; EN 17681-2, 2022; EN ISO 23702-1, 2021; EN ISO 20137, 2022.

The below table is for information only about the broad class of PFAS substances.

Table 1 (for information only): Broad class of PFAS[14]

Substances	CAS No.
Perfluoroalkyl Carboxylic Acids and Derivatives - PFCA	
Perfluorocarboxylic acids and its salts	Several
Perfluorobutanoic acid	375-22-4
Perfluorohexanoic acid and its salts	Several
Perfluorohexanoic acid (PFHxA)	307-24-4
Perfluoroheptanoic acid and its salts	Several
Perfluoroheptanoic acid	375-85-9
Perfluorooctanoic acid and its salts	Several
Perfluorooctanoic acid (PFOA)	335-67-1
Ammonium pentadecafluoro octanoate	3825-26-1
Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8- pentadecafluoro-, sodium salt (1:1)	335-95-5
Potassium perfluorooctanoate	2395-00-8
Perfluorononanoic acid and its salts	Several
Perfluorononanoic acid	375-95-1
Sodium salts of perfluorononan-1-oic-acid	21049-39-8
Ammonium salts of perfluorononan-1-oic-acid	4149-60-4
Perfluorodecanoic acid and its salts	Several
Perfluorodecanoic acid	335-76-2
Ammonium nonadecafluoro-decanoate	3108-42-7
Decanoic acid, nonadecafluoro-, sodium salt	3830-45-3
Perfluoroundecanoic acid and its salts	Several
Perfluoroundecanoic acid	2058-94-8
Perfluorododecanoic acid and its salts	Several

Table 1 (for information only): Broad class of PFAS[14]

Substances	CAS No.
Perfluorododecanoic acid	307-55-1
Perfluorotridecanoic acid and its salts	Several
Perfluorotridecanoic acid	72629-94-8
Perfluorotetradecanoic acid and its salts	Several
Perfluorotetradecanoic acid	376-06-7
Perfluorohexanoic acid related substances	Several
Perfluorohexylethyl alcohols	Several
Perfluorohexyl-ethanol	647-42-7
Perfluorohexylethyl olefins	Several
Perfluorohexylethene	25291-17-2
Perfluorohexylethyl halides	Several
Tridecafluoro-1-iodohexane	355-43-1
1H,1H,2H,2H-Perfluorooctyliodide	2043-57-4
Perfluorohexylethyl acrylates or methacrylates	Several
Perfluorohexylethyl polymers	Several
Perfluorooctanoic acid related substances	Several
Methyl perfluorooctanoate	376-27-2
Ethyl perfluorooctanoate	3108-24-5
Perfluorooctylethyl alcohols	Several
Perfluorooctylethanol	678-39-7
Perfluorooctylethyl olefins	Several
Perfluorooctylethene	21652-58-4
Perfluorooctylethyl halides	Several

Table 1 (for information only): Broad class of PFAS[14]

Substances	CAS No.
Heptadecafluoro-1-iodooctane	507-63-1
1H,1H,2H,2H-Perfluorodecyliodide	2043-53-0
Pentadecafluorooctyl fluoride	335-66-0
Perfluorooctylethyl acrylate or methacrylate	Several
Perfluorooctylethyl polymers	Several
Perfluoroalkyl compounds, branched	Several
2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid, its salts and its acyl halides	Several
2,3,3,3-tetrafluoro-2-(heptafluoro-propoxy) propionic acid	13252-13-6
Potassium 2,3,3,3-tetrafluoro-2-(heptafluoro-propoxy) propionate	67118-55-2
Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate	62037-80-3
2,3,3,3-tetrafluoro-2-(heptafluoro-propoxy) propionyl fluoride	2062-98-8
Perfluoroalkyl Sulfonic Acids and Derivatives - PFSA	
Perfluorobutane sulfonic acid and its derivatives	Several
Perfluorobutane sulfonic acid and its salts	Several
Perfluorobutane sulfonic acid	375-73-5
Perfluorobutane sulfonates	45187-15-3
Perfluorohexane sulfonic acid and its derivatives	Several
Perfluorohexane sulphonic acid and its salts	Several
Perfluorohexane sulfonic acid	355-46-4
Perfluorohexane sulfonate	108427-53-8
Potassium perfluorohexane-1-sulphonate	3871-99-6
Ammonium perfluorohexane-1-sulphonate	68259-08-5

Table 1 (for information only): Broad class of PFAS[14]

Substances	CAS No.
Tridecafluorohexanesulphonic acid, compound with 2,2'-iminodiethanol (1:1)	70225-16-0
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, lithium salt (1:1)	55120-77-9
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, zinc salt	70136-72-0
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compd. with N,N-diethylethanamine (1:1)	72033-41-1
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, sodium salt	82382-12-5
Iodonium, bis[(1,1- dimethylethyl)phenyl]-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic acid (1:1) (9CI)	866621-50-3
Sulfonium, (4-methylphenyl)diphenyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	910606-39-2
Sulfonium, [4-[(2-methyl-1-oxo-2- propenyl)oxy]phenyl]diphenyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic acid (1:1)	911027-69-5
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, cesium salt (1:1)	92011-17-1
1-Butanaminium, N,N,N-tributyl-, salt with1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid	108427-54-9
Ethanaminium, N,N,N-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic acid (1:1)	108427-55-0
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compd. with pyrrolidine (1:1)	1187817-57-7
Beta-Cyclodextrin, compd. with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid ion(1-) (1:1)	1329995-45-0
Gamma-Cyclodextrin, compd. with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid ion(1-) (1:1)	1329995-69-8
Methanaminium, N,N,N-trimethyl-, salt with1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid (1:1)	189274-31-5
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, compd.with 2-methyl-2-propanamine (1:1)	202189-84-2
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, gallium salt (9CI)	341035-71-0
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, scandium(3+) salt (3:1)	350836-93-0
Sulfonium, tris[4-(1,1- dimethylethyl)phenyl]-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic	425670-70-8

Table 1 (for information only): Broad class of PFAS[14]

Substances	CAS No.
Iodonium, bis[4-(1,1- dimethylpropyl)phenyl]-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic	421555-74-0
Sulfonium, (thiodi-4,1- phenylene)bis[diphenyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonic	421555-73-9
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, neodymium(3+) salt (3:1)	41184-65-0
1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, yttrium(3+) salt (3:1)	41242-12-0
Sulfonium, [4-[(2-methyl-1-oxo-2- propen-1-yl)oxy]phenyl]diphenyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonate (1:1)	911027-68-4
Dibenzo[k,n][1,4,7,10,13]tetraoxathiacy clopentadecinium, 19-[4-(1,1- dimethylethyl)phenyl]-6,7,9,10,12,13- hexahydro-, 1,1,2,2,3,3,4,4,5,5,6,6,6- tridecafluoro-1-hexanesulfonate (1:1)	928049-42-7
Phosphonium, triphenyl(phenylmethyl)-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	1000597-52-3
Ethanaminium, N-[4-[[4-(diethylamino)phenyl][4-(ethylamino)-1-naphthalenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-ethyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonate (1:1)	1310480-24-0
Methanaminium, N-[4-[[4-(dimethylamino)phenyl][4-(ethylamino)-1-naphthalenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonate (1:1)	1310480-27-3
Methanaminium, N-[4-[[4-(dimethylamino)phenyl][4-(phenylamino)-1-naphthalenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1- hexanesulfonate (1:1)	1310480-28-4
Sulfonium, triphenyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	144116-10-9
Quinolinium, 1-(carboxymethyl)-4-[2-[4- [4-(2,2-diphenylethenyl) phenyl]- 1,2,3,3a,4,8b-hexahydrocyclopent[b]indol-7- yl]ethenyl]-, 1,1,2,2,3,3,4,4,5,5,6,6,6- tridecafluoro-1-hexanesulfonate (1:1)	1462414-59-0
Iodonium, diphenyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	153443-35-7
Iodonium, bis[4-(1,1-dimethylethyl)phenyl]-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	213740-81-9
Sulfonium, bis(4-methylphenyl)phenyl-, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonate (1:1)	341548-85-4
Perfluorohexane sulfon amides	Several

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Substances	CAS No.
Perfluorohexane sulfon amide	41997-13-1
Perfluorohexane sulfon halides	Several
Perfluorohexanesulphonyl fluoride	423-50-7
Perfluorooctane sulfonic acid and its derivatives	Several
Perfluorooctane sulphonic acid and its salts	Several
Diethanolamine perfluorooctane sulfonate	70225-14-8
Ammonium perfluorooctane sulfonate	29081-56-9
Lithium perfluorooctane sulfonate	29457-72-5
Perfluorooctane sulfonic acid	1763-23-1
Perfluorooctane sulfonate	45298-90-6
Potassium heptadecafluoro-octane-1- sulphonate	2795-39-3
Ethanaminium, N,N,N-triethyl-, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonate (1:1)	56773-42-3
1-Decanaminium, N-decyl-N,N-dimethyl- , 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonate (1:1)	251099-16-8
Perfluorooctane sulfon amides	Several
Perfluorooctane sulfonamide	754-91-6
Heptadecafluoro-N-methyloctane sulfonamide	31506-32-8
Perfluorooctane sulfon amidoethanols	Several
Heptadecafluoro-N-methyloctane sulfonamideoethanol	24448-09-7
1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-	4151-50-2
1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-	1691-99-2
Perfluorooctane sulfon halides	Several
1-Octanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-	307-35-7

5. Recommended actions by Manufacturers (Suppliers):

- Contact your raw material (yarns, fabrics, wet blue, trims) suppliers and explain that you require materials that conform to the AFIRM RSL on PFAS.
- Consider performing risk-based testing of raw materials to ensure the current AFIRM RSL limits for PFAS are met.
- Ensure that you purchase chemical formulations that meet the ZDHC MRSL V3.0 requirements for PFAS and are listed on the ZDHC Gateway at appropriate ZDHC MRSL Conformance Levels.
- Request a GHS compliant Safety Data Sheet (SDS) from your chemical vendor.

6. References:

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