Partnership for Sustainable Textiles

Per- and polyfluorinated chemicals

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Content

1. Identification and classification

The term PFC is sometimes applied just to perfluorinated chemicals and sometimes to both perfluorinated and polyfluorinated substances. In this document the term PFC is used to describe per- and polyfluoroalkyl substances (PFAS) in which all or nearly all the hydrogen atoms in the carbon skeleton are replaced by fluorine atoms. More than 3,000 substances fall into this category (1).
PFASs do not occur naturally but are entirely anthropogenic in origin. Because of their high binding energy, highly fluorinated alkanes are among the most stable organic compounds.

Widely used perfluorinated chemicals include perfluorinated carboxylic acids (such as perfluorooctanoic acid – PFOA) and sulfonic acids (such as perfluorooctanesulfonic acid – PFOS). Polyfluorinated chemicals can break down into persistent perfluorinated substances: they are therefore also termed precursors.

PFCs are obtained either by electrofluorination or by telomerisation. Electrofluorination involves synthesising the perfluoroctanyl side chains of the PFC. PFCs produced by this method were used in the textile industry until about 2002. The market leader has voluntarily stopped manufacturing and using them because PFOS is produced as a decomposition product of perfluoroctanyl. Since 2002, use of PFCs obtained by electrofluorination has virtually ceased, at least in Europe. A new generation of electrofluorinated polymers based on shorter-chain components (C4) has not achieved the same market importance.

Since 2002 the textile industry has used mainly telomer-based PFCs. Telomerisation involves lengthening the molecule from one end in a stepwise process by adding tetrafluoroethylene, thereby producing substances such as fluorotelomer alcohols. These alcohols are incorporated into the polymer skeleton as fluorinated side chains. Production of telomer-based PFCs does not involve either PFOA or PFOS. However, traces of PFOA may be formed as an unintended by-product.
PFCs are subdivided into long-chain and short-chain substances, with different chemical properties (2). Short-chain PFCs include perfluorinated carboxylic acids with fewer than seven perfluorinated carbon atoms. In the case of perfluorinated sulfonic acids, compounds with fewer than six perfluorinated carbon atoms are classed as short-chain. Long-chain PFCs are now being replaced by short-chain PFCs in many applications.

2. Existing regulations

Some PFCs are covered by the CLP Regulation, the European Union chemical regulation REACH and the Stockholm Convention on Persistent Organic Pollutants (POP). Because they are persistent, bioaccumulative and toxic (REACH Article 57 (d)) or very persistent and very bioaccumulative (REACH, Article 57 (e)), the EU has identified these PFCs as giving particular cause for concern and placed them on the REACH Candidate List (3). From July 2020 the manufacture, use, placing on the market and importing of PFOA, its salts and precursor compounds will with a few exceptions be prohibited in the EU (Regulation (EU) 2017/1000).
PFOS has been placed on the lists of POPs in the Stockholm Convention. Other than in a few exceptional circumstances, the manufacture and use of PFOS is restricted worldwide. Preparations for the inclusion of PFOA in the POP list are under way; a decision is expected in 2019.

3. Use in wet textile production processes

In the textile industry PFCs are used in breathable membranes and in treatments to repel dirt, oil and water. Uses include the manufacture of outdoor clothing, shoes, workwear, carpets and home furnishings (e.g. tablecloths, curtains). Impregnating agents for clothing and shoes often contain PFCs.
The membranes (e.g. Goretex) are made of polytetrafluoroethylene (PTFE). PFOA is used as a process auxiliary in the manufacture of PTFE.

Since 2002 most textile treatments have used telomer-based PFCs. PFOS and PFOA, which are particularly hazardous substances, are not used directly in textiles. PFCs are used that break down into PFOS or PFOA.
In recent years there has been a growing trend for these long-chain PFCs to be replaced by short-chain PFCs.

PFCs are usually applied in combination with other auxiliaries using the Foulard process. They are often applied in combination with extenders, which may contain hydrocarbons (e.g. waxes) or crosslinking agents (e.g. melamine and isocyanate or blocked isocyanates) (4).
PFCs can be emitted into the environment throughout the life cycle, i.e. during manufacture of the chemicals, when the PFC is used in textile finishing, during usage of the textiles (washing processes) or during disposal (5).

Various manufacturers of outdoor clothing have already stopped using PFCs in their products. Gore plans to replace PFCs in the pre-products (laminates) of 85% of the outdoor products manufactured therefrom by the end of 2020; by the end of 2023, it will replace PFCs in all pre-products for outdoor clothing.
GOTS and the Blue Angel for textiles prohibit the use of PFCs. The EU Ecolabel for textiles prohibits treatment with PFCs but not membranes that contain PFCs.

4. Hazard potential

Harmonised classifications and labels of perfluorinated carboxylic acids (PFCA) and sulfonic acids (PFSA) under the CLP Regulation.

Substance	Index number	CAS number	Classification
Perfluorosulfonic acid (C8-PFSA, PFOS) [1], and sodium salt [2], diethanolamine salt [3], ammonium salt [4] and lithium salt [5]	607-624-00-8	1763-23-1 [1] 2795-39-3 [2] 70225-14-8 [3] 29081-56-9 [4] 29457-72-5 [5]	Carc. 2 (H351) Repr. 1B (H360 D) STOT RE 1 (H372) Acute Tox. 4. (H302) Acute Tox. 4. (H332) Lact. (H362) Aquatic Chronic 2 (H411)
Perfluorooctanoic acid (C8-PFCA, PFOA) [1] and ammonium salt [2]	607-704-00-2 [1] 607-703-00-7 [2]	335-67-1 [1] 3825-26-1 [2]	Carc. 2 (H351) Repr. 1B (H360 D) STOT RE 1 (H372) (liver) Acute Tox. 4. (H302) Acute Tox. 4. (H332) Lact. (H362) Eye Dam. 1 (H318)
Perfluorononanoic acid (C9-PFCA, PFNA)[1] and sodium salt [2] and ammonium salt [3]	607-718-00-9	375-95-1 [1] 21049-39-8 [2] 4149-60-4 [3]	Carc. 2 (H351) Repr. 1B (H360 Df) STOT RE 1 (H372) (liver, thymus, spleen) Acute Tox. 4. (H302) Acute Tox. 4. (H332) Lact. (H362) Eye Dam. 1 (H318)
Perfluordecanoic acid (C10-PFCA, PFDA) [1] and sodium [2] and ammonium salt [3]	607-720-00-X (entry effected with the 10th ATP)	335-76-2 [1] 3830-45-3 [2] 3108-42-7 [3]	Carc. 2 (H351) Repr. 1B (H360 Df) Lact. (H362)

Perfluorinated carboxylic acids (PFCA) and perfluorinated sulfonic acids and their salts in the REACH Candidate List (European Chemicals Agency, 2017a)

Substance	**CAS number**	**REACH Candidate List**
Perfluorooctanoic acid (C8-PFCA, PFOA) [1] and ammonium salt [2]	335-67-1 [1] 3825-26-1 [2]	Placed on the Candidate List in June 2013: ▪ toxic for reproduction (Article 57 (c)) ▪ persistent, bioaccumulative and toxic (Article 57 (d))
Perfluorononanoic acid (C9-PFCA) [1] and sodium [2] und ammonium salt [3]	375-95-1 [1] 21049-39-8 [2] 4149-60-4 [3]	Placed on the Candidate List in December 2015: ▪ toxic for reproduction (Article 57 (c)) ▪ persistent, bioaccumulative and toxic (Article 57 (d))
Perfluorodecanoic acid (C10-PFCA) [1] and sodium [2] and ammonium salt [3]	335-76-2 [1] 3830-45-3 [2] 3108-42-7 [3]	Placed on the Candidate List in December 2016: ▪ toxic for reproduction (Article 57 (c)) ▪ persistent, bioaccumulative and toxic (Article 57 (d))

Perfluoroundecanoic acid (C11-PFCA)	2058-94-8	Placed on the Candidate List in December 2012: ▪ very persistent, very bioaccumulative (Article 57 (e))
Perfluorododecanoic acid (C12-PFCA)	307-55-1	Placed on the Candidate List in December 2012: ▪ very persistent, very bioaccumulative (Article 57 (e))
Perfluorotridecanoic acid (C13-PFCA)	72629-94-8	Placed on the Candidate List in December 2012: ▪ very persistent, very bioaccumulative (Article 57(e))
Perfluorotetradecanoic acid (C14-PFCA)	376-06-7	Placed on the Candidate List in December 2012: ▪ very persistent, very bioaccumulative (Article 57 (e))
Perfluorohexane sulfonic acid and ammonium and potassium salt (PFHxS, C6-PFSA)	355-46-4	Placed on the Candidate List in June 2017: ▪ very persistent, very bioaccumulative (Article 57 (e))

5. Environmental behaviour

In general, polyfluorinated chemicals in the environment can be transformed into perfluorinated chemicals both biotically and abiotically. However, the perfluorinated chemicals are persistent. Once PFCs are released into the environment, they remain there for a very long time (5).

In particular, PFCs with a long carbon chain tend to accumulate in the organism and along the food chain. In addition, it is known that some PFCs have toxic effects, and there are indications that some affect the endocrine system.
According to the information currently available, PFCs with a short carbon chain are less bioaccumulative, but they are found in edible parts of plants (6).They are very mobile and can therefore pollute groundwater and raw water. There is a lack of toxicological information on short-chain PFCs with regard to issues such as reproductive toxicity or endocrine effects.

PFCs are transported over long distances by rivers and ocean currents and through the formation of marine aerosols, so that they become distributed worldwide. These compounds are found even in remote regions such as the Arctic and in the animals that live there (5).

6. Possible substitutes

For water-repellent purposes there are already alternatives to PFCs in the form of substances such as paraffin formulations, polysiloxanes, modified melamine resins and polyurethanes (7)(8).
The alternatives should have less hazardous properties than the PFCs. This is being investigated in the ongoing project ‘Outdoor textiles – waterproof, breathable and green’, a comparative risk assessment of short-chain polyfluorinated/perfluorinated alkyl compounds and fluorine-free alternatives funded by the German Federal Environmental Foundation (DBU). The project is due to be completed by the end of 2017 (9).

For oil- and dirt-repellent purposes, no comparably effective alternatives are at present available. In many cases the amount of PFC that is needed can be reduced by using additional extenders, which may be based on highly branched and radially branched polyurethanes (7).

7. Summary

PFCs are used in textiles on account of their water-repellent, oil-repellent and dirt-resistant properties. They are often used in outdoor clothing.
The particularly hazardous substances perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are not used directly in textiles. Instead, PFCs are used that may contain PFOS or PFOA as impurities or break down into PFOS or PFOA.

In recent years there has been a growing trend for these long-chain PFCs to be replaced by short-chain PFCs (PFCs with a carbon chain of up to six carbon atoms).
If PFCs enter the environment, they remain there for a long time, because they cannot be broken down either abiotically or biotically. They are widespread in the environment worldwide. Organisms ingest PFC via air, water and food. PFCs with a long carbon chain accumulate in organisms. Short-chain PFCs, by contrast, are very mobile, which means that they can enter groundwater and drinking water. Some PFCs have toxic effects and are harmful to reproduction.
Other than in a few exceptional circumstances, the manufacture and use of PFOS is restricted worldwide. From July 2020 the manufacture, use, placing on the market and importing of PFOA, its salts and precursor compounds will with a few exceptions be prohibited in the EU.

It is now possible to produce textiles with water-repellent properties without using PFCs – for example, by using paraffin formulations, polysiloxanes, modified melamine resins or polyurethanes.

8. References

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