Phase out of PFAS on the international regulatory agenda

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What are highly fluorinated compounds/ polymers?

- Surfactants
  - extremely low surface tension

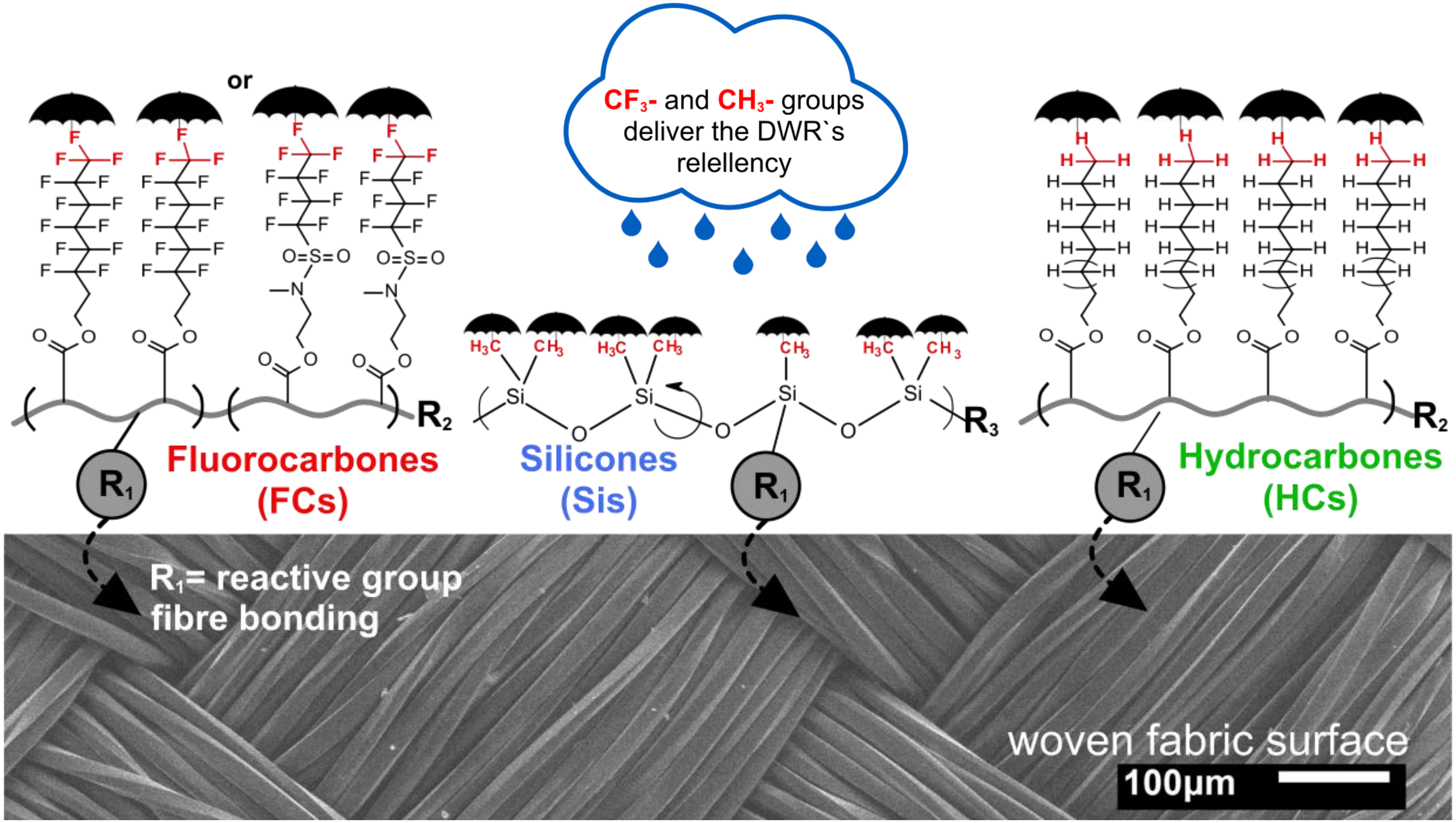
Fluorinated ”tail”	Spacer	Hydrofilic group

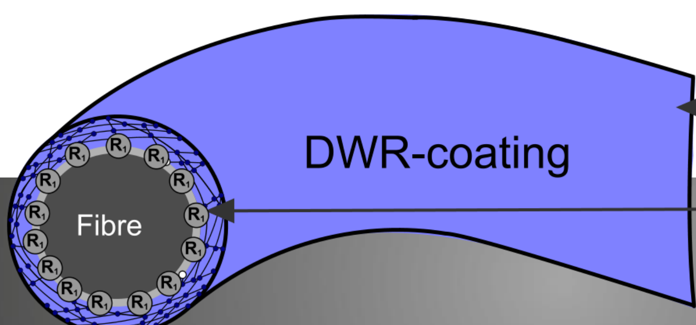
- Side chain fluorinated polymers
  - extremely low surface energy

- Fluoropolymers e.g PTFE - *another chemistry*

Perfluorinated polymer chain (extremely long chains)

DWR chemistry – side chain “polymers”





- DWR-coating (nm-range) consists out of a crosslinked polymer network
- Covalent bonding to the fibre surface in case of a lack of reactive groups on the DWR-polymersform a “crosslinked shell”

Terminology
Per and polyfluorinated substances

PFAS; chemicals that contain one or more perfluoroalkyl moieties, –C_nF_{2n+1}.

In the past, PFASs were often referred to as “PFCs” (per- and polyfluorinated chemicals)

The family of PFAS

- PFAA; Perfluoroalkyl acids
- PFCA; Perfluoroalkyl carboxylic acid
- PFSA; Perfluoroalkane sulfonic acids
- Compounds derived from perfluoroalkane sulfonyl fluoride (PASF)
- Fluorotelomer (FT)-based compounds
- Per- and polyfluoroalkyl ether (PFPE)-based compounds

Electrochemical fluorination - ECF

Input PFAS

$H(CH_2)_nSO_2F$ (n = 4, 6, **8** , 10)

$e^- + HF$ ECF

$F(CF_2)_nSO_2F$

Perfluoroalkyl sulfonyl

$F(CF_2)_nSO_2N$

Perfluoroalkyl sulfonamide

Perfluoroalkyl sulfonamide

R = H, Me, Et, Bu

$F(CF_2)_nSO_2N(R)CH_2CH_2OH$

N-Alkyl Perfluoroalkyl sulfonamido alcohol

R = H, CH_3

$F(CF_2)_nSO_2N(R)CH_2CH_2OC(O)CR{=}CH_2$

(Meth)acrylate monomer

$F(CF_2)_nSO_2N(R)CH_2CH_2CH_2N(CH_3)_2$

n > =6 so called long chain

n < 6 so called short chain

Surfactants
- **Adipate**
- **Fatty acid ester**
- **Phosphate**

Oligomeric Surfactants

Surfactants
- **Betaine**
- **Sulfobetaine**
- **Cationic**

T r m a t i o n

Output PFAS

...ation products
...nated
...cids (PFSA)

n = 4 formation to PFBS
n = 6 formation to PFHxS
n = 8 formation to PFOS
n = 10 formation to PFDS

Telomerization

Input PFAS

$CF_3CF_2\text{-}I$ + $CF_2{=}CF_2$

$F(CF_2)_nI$ = 4, 6, 8, 10, …) → $F(CF_2)_{n-1}CO_2M$

Perfluoroalkyl iodide

M = H, NH_4, K, Na, …

$F(CF_2)_nCH_2CH$…

F(CF…

$F(CF_2)_nCH_2CH_2SO_2N(R)CH_2CH_2CH_2N(CH_3)_2$ $F(CF_2)_nCH_2CH_2OC(O)CR{=}CH_2$

(Meth)acrylate
monomer

Surfactants
- Betaine
- Sulfobetaine
- Cationic

Oligomeric Surfactants

Surfactants
- Ethoxylate
- Phosphate
- Sulfate

n > =7 so called long chain
n < 7 so called short chain

T r a … a t i o n

Output PFAS

Final degradation products … perfluorinated …ylic acids (PFCA)

… formation to PFBA
… = 6 formation to PFHxA
n = 8 formation to PFOA
n = 10 formation to PFDA

The international regulatory agenda of PFAS

PFOS and r d substances

PFOA and rel ted substances

Higher hom ges to PFOA

PFHxS (so called long chain) *pending*

So ca d short ain PFAS

Under OA) in EU

Of concern in the ckholm Convention

Stockholm Convention (SC)
Global action on persistent organic pollutants (POP)

Legal measures to reduce or eliminate releases from

- Intentional production and use (art. 3)
- Unintentional production (art. 5)
- Stockpiles and wastes (art. 6)

Binding commitments

- Implementation plans (art 7)
- Information exchange (art. 9)
  - *Facilitate or undertake the exchange of information of alternatives to POPs, relating to their risks as well as to their economic and social costs.*
- Public information, awareness and education (art. 10)
- Research, development and monitoring (art. 11)
- Reporting (art. 15)

Alternatives to POPs and candidate POPs in SC.

- Should not exhibit POP charateristics (annex D in SC)
- Should not have hazardous properties that raise serious concern about
  - mutagenicity, carcinogenicity or adverse effects on the reproductive, developmental, endocrine, immune or nervous systems.
- Assessment of risks related to alternatives
  - Attention should be paid to the potential for harm under actual conditions.
- Should represent equivalent uses as for POPs and candidate POPs.
- Exhibit availability, technical feasibility, accessibility and efficacy
- Stimulation of innovation in the development of new and safer alternatives
- Social and economic assessment of alternatives

- **Publicly available scientific data are the basis for <u>all</u> evaluations.**

Source: General guidance on alternatives in SC, UNEP/POPS/POPRC.5/10/Add.1

SC conclusion
Perfluorohexanoic acid (PFHxA), CAS: 307-24-4

- Potential degradation product from shorter chain (C_6) fluorotelomer-based surfactants.

Toxicology: Toxicological data for PFHxA is extensive.

- Potential endocrine toxicity.
- Distinct binding sites were identified by NMR in human albumin.
- Raising questions about possible interferences with the pharmacokinetics of fatty acids and drugs.
- Changed the secondary structure of the protein
- Studied on rats and mice indicate that PFHxA is faster eliminated than PFOA and PFOS

Environment:

- Contaminant with increased production, shorter-F-chain substances, such as PFHxA, are now increasingly often detected in the environment.
- PFHxA levels were substantial in drinking water downstream of a fluoropolymer manufacturing plant and from fire fighting foam sources.
- It cannot be excluded that PFHxA bioconcentrate, bioaccumulate or biomagnify

SC conclusion:
6:2-Fluorotelomer sulfonate (6:2 FTS). CAS: 27619-97-2

Toxicology:

- Acute and repeated-dose mammalian and aquatic toxicity

Degradation in the environment:

- Degradation of fluoroalkylthioamido- sulfonates into 6:2 FTS is susceptible under sulphur-limiting and aerobic conditions.

Emissions:

- Emission to the environment may be expected from chemically driven oil production and in manufacturing.
- Emission from STP effluents is found.
- Can be expected in the aqueous environment.
- Has been shown to degrade to the persistent perfluorohexane acid (PFHxA) in the environment.

- **Monitoring data:**
  - Has been detected in environmental samples including water, soil, air particulates and biota.
  - Observations has been done in the Arctic. More publically available data is needed to determine its origin and whether it is a LRT substance or not.

SC conclusion:
Fluorotelomer alcohols (FTOH),
CAS: 2043-47-2 (4:2 FTOH) and 647-42-7 (6:2 FTOH) (1/2)

- Precursors for fluorotelomer-based polymers.

- **Toxicology:** 4:2 FTOH is poorly characterized. 6:2 FTOH is well characterized.
  - Acute and repeated-dose mammalian toxicity, pharma- and toxicokinetics studies have been conducted.
  - Recent research shows that 4:2 FTOH is more potent than 6:2 and 8:2 for cytotoxicity.

- **Degradation in the environment**:
  - The oxidation of fluorotelomer alcohols in the atmosphere by OH-radicals leads to the corresponding polyfluorinated aldehydes, being further degraded to perfluorinated carboxylic acids (PFCA).

SC conclusion: Fluorotelomer alcohols (FTOH), CAS: 2043-47-2 (4:2 FTOH) and 647-42-7 (6:2 FTOH), (2/2)

Emissions:

- On the basis of their volatility, polyfluorinated telomer alcohols are expected to occur predominantly in the atmospheric gas phase.
- Given their low solubility in water and high sorptivity to organic solvent or sorbent, the fluorotelomer alcohol is expected to partition to the air compartment only under conditions where no sorptive medium is present.

Monitoring data:

- Found in the North American atmosphere.
- Present modelling results show that with current estimates of chemistry and fluxes the atmospheric oxidation of FTOH can provide a quantitative explanation for the presence of PFCAs in remote regions.
- Present in the highest concentrations in a study of office air monitoring which also correlated PFOA levels in the serum of office workers with air levels of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH.

SC conclusion:
Perfluorobutane sulfonate (PFBS), CAS: 29420-49-3

- The principal terminal degradation product of N-methyl perfluorobutane sulphonamidoethanol and PFBS-based products.

Toxicology: The substance is well characterized.

- Possible neurotoxicity.

Monitoring data:

- Widely detected in water and has very low sorption.
- Found in municipal landfill leachates.
- Found in indoor dust from homes and offices.
- Monitoring near a manufacturing facility found PFBS in groundwater, river water, and in human serum
- Observations in the Arctic may qualify PFBS as a LRT substance.

Emissions:

- Emission to the environment may be expected from chemically driven oil production and PFBS manufacturing

Stockholm Convention 2016
The battle of siloxanes

D4	Octamethyl cyclotetrasiloxane	556-67-2

→ **Polysiloxanes (DWR)**

- Alternatives to PFOS and PFOA were vividly discussed, especially D4.
- The cyclic siloxane D4 is in a critical position since this substance possibly is a POP according to the criteria of the Stockholm Convention.
- The silicon industry demonstrated that without D4 the whole silicon industry will be gone.

Siloxanes are manufactured from silicons
(Source: Global Silicon Council)

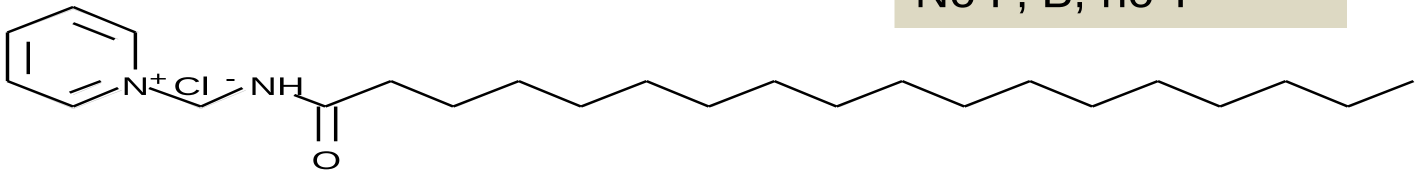
Process:

- Highly integrated manufacturing
- Recycling of side streams
- Recycling of waste streams where possible, via manufacturing of chlorosilanes
- Further reaction to
- **D4 is a critical building block silicones**
- **D4 is always present as an**
- **D4 total ban = no silicone**

Water repellent cotton and cotton/PET blends

- A classic cationic textile surfactant is 1-(stearamidomethyl) pyridinium chloride

SC assessment:
No P, B, no T



- The substance reacts with cellulose at elevated temperatures to form a durable water-repellent finish on cotton

- There are also other similar resins used to water repellent cotton

- Sometimes these treatments are adressed as paraffin wax treatments

Conclusions, recommendations and future developments Stockholm Convention

Low surface tension is a key function

- Physical stability
- Low surface tension / surface energy

Substitutes for PFOS (and PFOA) are available.

- Global market shift to shorter-chain PFAS.
- There are concerns about their current known hazard and environmental properties.
- More data is needed to perform comprehensive risk assessments

Need for improved information from industry on the alternatives and actions parties can take to deploy alternatives safely.

- Trade secrets and lack of transparency from industry
- More publically available independent scientific data

Need for incentives

- Develop safe, affordable and technologically feasible alternative substances and processes and to identify the driving forces for their development.
- Don't postpone the development of national law until perfect alternatives are available, since manufacturers may not develop alternatives if they are not forced to do so.

Thanks for your attention!

Questions?

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