PFAS – Substances, Applications and Environmental Impacts

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Short about Stefan Posner and Swerea IVF

Stefan Posner

Polymer and textile chemist with over 30 years experience in research on chemicals in textiles and polymeric materials in cooperation with international companies, authorities and academia in several international projects over the years. Stefan is since many years working with legal preparatory work on chemicals for UNEP Stockholm Convention, EU Commission and several National Authorities and is deeply involved in research to substitute hazardous chemicals with a recent certain focus on highly fluorinated substances and flame retardants but other groups of hazardous chemicals have been in focus in the past.

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What are highly fluorinated compounds/ polymers?

- Surfactants
  - extremely low surface tension

- Side chain fluorinated polymers
  - extremely low surface energy

- Fluoropolymers e.g PTFE - *another chemistry*

Terminology

PFAS; chemicals that contain one or more perfluoroalkyl moieties, – $CnF2_{n+1}$.

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 fluoride

Perfluoroalkyl sulfonamide

$F(CF_2)_nSO_2NH_2$

Perfluoroalkyl sulfonate

$F(CF_2)_nSO_3M$ M = H, NH_4, K, Na, …

$F(CF_2)_nSO_2NH_2$

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

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

Surfactants
- **Amide**
- **Ethoxylate**
- **Oxazolidinone**
- **Phosphate**
- **Silane**
- **Sulfate**

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

Oligomeric Surfactants

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

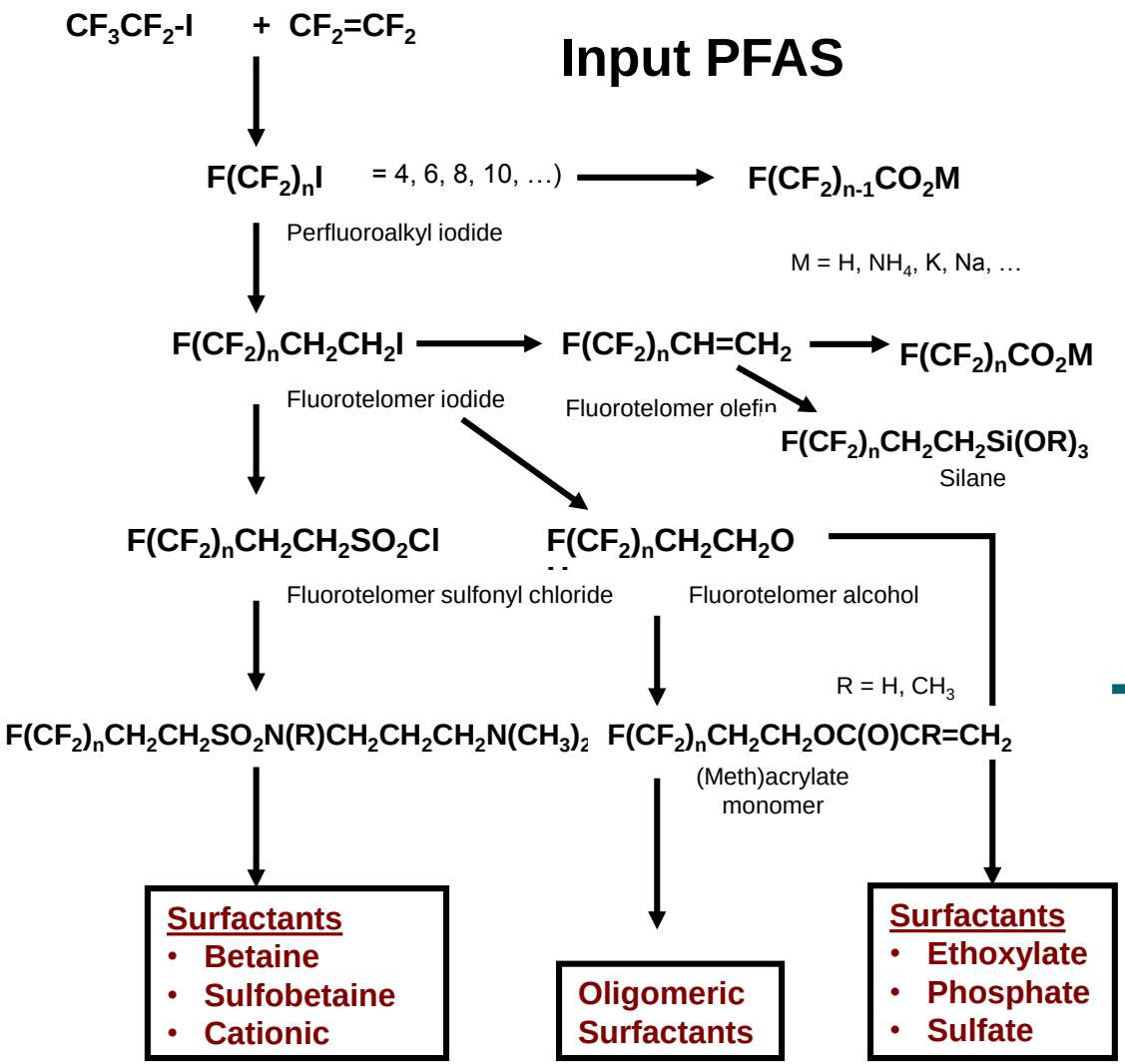
Transformation

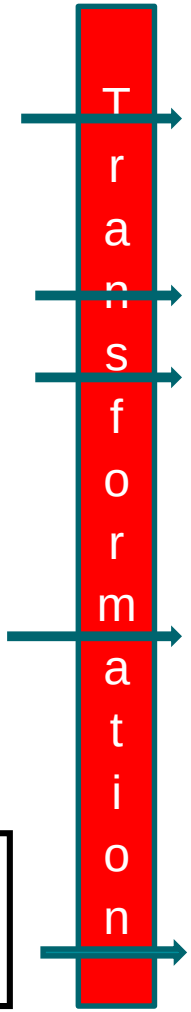
Output PFAS

Final degradation products are perfluorinated sulfonic acids (PFSA)

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

Telomerization





Output PFAS

Final degradation products are perfluorinated carboxylic acids (PFCA)

n = 4 formation to PFBA
n = 6 formation to PFHxA
n = 8 formation to PFOA
n = 10 formation to PFDA

The fluorinated surfactant

- The fluorinated ”tail” is both hydrofobic and oleofobic – unique.

- Long chain PFAS – the fluorinated ”tail” contain
  - More than or equal to 7 perfluorinated carbons if a PFCA
  - More than or equal to 5 perfluorinated carbons if a PFSA
  - Precursors that can degrade to the above compounds.

- PFAS with shorter fluorinated ”tails” than above are called short chain.

Categories and applications of PFAS

Category	Subcategory	Some applications
Salts	K^+, Li^+, NH_4^+	Surfactant in fire-fighting foam, surfactant for alkaline cleaners, emulsifier in floor polish mist, suppressant for metal plating baths, surfactant for etching acids for circuit boards, inks. Photoresist
	Amines	Mist suppressant for metal plating baths
	Ammonium Salts	Mist suppressant for metal plating baths
	Amphoterics	Water/solvent repellence for leather/paper. Oil recovery

Categories and applications of PFAS

Category	Subcategory	Some applications
	Carboxylates	Antistatic agent in photographic paper. Optical elements
	Amides	Pesticide active ingredient
	Oxazolidinones	Waterproofing casts
Polymers	Alcohols, silanes, alkoxylates, fatty acid esters, adipates, urethanes, polyesters, acrylates	Soil/water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass
	Copolymers, phosphate esters	Soil/water repellence for carpet, fabric/upholstery, apparel, leather, metal/glass. Oil/water repellence for plates, food containers, bags, wraps, folding cartons, containers, carbonless forms, masking papers

Emissions of PFAS

Subcategory	Emissions
K^+, Li^+, NH_4^+	Direct emissions as ingredients/processing aids
Amines	
Ammonium Salts	
Amphoterics	

Emissions of PFAS

Subcategory	Environmental source
Carboxylates	Transformation/degradation products
Amides	
Oxazolidinones	
Alcohols, silanes, alkoxylates, fatty acid esters, adipates, urethanes, polyesters, acrylates	Transformation/degradation products Impurities/residual
Copolymers, phosphate esters	

PFAS hazards

- Persistent (P)
  - PFAS do not occur in nature – no natural system that have the ability to degrade PFAS
  - F- C bond is very strong, meaning that all PFAS are extremely persistent.
- Bioaccumulation (B)
  - PFAS are hydrofobic and oleofobic meaning that these substances do not really bioaccumulate in the same way as other organic substances.
  - Some PFAS have a high biomagnification potential
- Toxicity (T)
  - Some have shown human and environmental toxicity

Global market information on PFAS

- Information on how the substance is used (about 3000 substances), had about half unknown use.
- The market information found for most PFAS was often short.
- Information on functionality such as "surfactant" could be linked to 20% of the PFAS substances.
- PFAS that were called “surfactants” had a wide range of applications often briefly described.
- For a third of all the substances that were identified (approximately 1000 PFAS), a bit more detailed market information was available.

A report from the Swedish Chemicals Agency (2015) Occurrence and use of PFAS and alternatives

Global market information on PFAS

- Identified applications based on market information, in descending order are:
  - Synthesis Chemicals
  - Electronics Products
  - Printing Products
  - Cosmetic Products
  - Textile / leather impregnation
  - Pharmaceuticals
  - Plant protection
  - biocides
  - Paints
  - Adhesive raw materials
  - Paper impregnation
  - Foam-based fire extinguishing agents

Summary
Major challenges and opportunities

- PFAS - a huge group of subjects in which we are far from know all about these compounds
- Still considerable datagaps for many of these PFAS.
- More transparancy and consistent PFAS information along the whole value chain is required, where all stakeholder shall contribute with essential chemicals information that prevent real risks to humans and environment.

Thanks for your attention

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