PFAS in Non-Stick Coatings: a Life Cycle Perspective

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PFAS i nonstick-beläggningar – en fara för människa och miljö
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Ongoing in the European Union

- Authorities of Denmark, Germany, Netherlands, Norway and Sweden are preparing a REACH restriction proposal for a wide range of PFAS
  - Unclear which of the PFAS will be included
    - All substances that contain -CF$_2$- or CF$_3$- fragments (OECD definition)
    - 6330 PFAS (US EPA dashboard)
  - Derogations or exemptions granted according to essentiality
The PFAS Universe

Interstate Technology & Regulatory Council (ITRC) (https://pfas-1.itrcweb.org/)
Diversity of structures of PFAS

Perfluorooctanesulfonic acid (PFOS), a PFSA

Perfluorocyclohexanecarbonyl fluoride

Perfluorooctanoic acid (PFOA), a PFCA

Perfluorosuccinic anhydride

Perfluoro-(2,5,8-trimethyl-3,6,9-trioxadodecanoic) acid

Trifluoroacetic acid

1-Bromoheptfluoropropane

Perfluamine
Diversity of PFAS

- Many thousands of **structurally diverse** PFAS in use in society
  - polymers & non-polymers; neutral, anionic, cationic & zwitterionic; solids, liquids & gases; reactive & inert; soluble & insoluble; volatile & involatile; mobile & immobile; bioaccumulative & non-bioaccumulative; highly toxic and relatively non-toxic
  - We don't know much about most of them
Are all PFAS of concern?

- **All PFAS are highly persistent** (EU REACH)
  - they are either non-degradable or transform ultimately into stable terminal transformation products
- Continual release of high P chemicals results in increasing levels and increasing probabilities of known and unknown effects. Exposure poorly reversible
- Fluoropolymers – need to consider lifecycle
Fluoropolymers

Dominated by:
- polytetrafluoroethylene (PTFE)
- fluorinated ethylene propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- tetrafluoroethylene-copolymers
- polyvinylidene fluoride (PVDF)
- polyvinyl fluoride (PVF) and fluoroelastomers

• ~ 320 300 t in 2018, and production steadily increasing
Uses of PFAS?

More than 200 uses identified for more than 1400 PFAS
Some definitions

- Fluoropolymer substances (PTFE, FEP, PVDF) - material of known chemical structure

- Fluoropolymer product
  - actual material produced/sold by manufacturer (e.g. Chemours, Solvay, Daikin, Asahi Glass, multiple Chinese companies, etc.)
  - in different grades (e.g. granular PTFE, fine powder PTFE)
  - contain impurities

- Fluoropolymers in finished articles
  - PTFE tape, GoreTex jacket, PTFE cookware

- Many different processes of making fluoropolymer products
  - some fluoropolymer products do not require PFAS-based processing aids (e.g. granular PTFE, fine powder PVDF)
  - other fluoropolymers (e.g. fine powder PTFE) are manufactured using PFAS-based processing aids (e.g. salts of PFOA or GenX chemicals) during emulsion polymerization
Phasing out Uses of PFAS

• Impractical to ban all uses in one step
  – Some may serve a critical role for which alternatives do not exist (essential)
  – However, some uses of PFAS are non-essential and for others there are alternatives (substitutable)
  – Concept of essentiality originated in the Montreal Protocol
Defining essentiality: 3 categories

<table>
<thead>
<tr>
<th>Category</th>
<th>Definition</th>
<th>PFAS examples</th>
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<tbody>
<tr>
<td>1</td>
<td>&quot;Non-essential&quot;</td>
<td>Uses that are not essential for health and safety, and the functioning of society. The use of substances is driven primarily by market opportunity.</td>
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<tr>
<td>2</td>
<td>&quot;Substitutable&quot;</td>
<td>Uses that have come to be regarded as essential by society because they perform important functions, but where alternatives to the substances have now been developed that have equivalent functionality and adequate performance, which makes those uses of the substances no longer essential.</td>
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<tr>
<td>3</td>
<td>&quot;Essential&quot;</td>
<td>Uses considered essential by society because they are necessary for health or safety or other highly important purposes and for which alternatives are not yet established.*</td>
</tr>
</tbody>
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* This essentiality should not be considered permanent; rather, a constant pressure is needed to search for alternatives in order to move these uses into Category 2 above.
Is use of PTFE in non-stick coatings an essential use?

- Is the use of PTFE in non-stick coatings essential for health and safety and the functioning of society?
  - No, but it is very convenient
  - Chemicals of concern should not be used to provide convenient technical functions
  - Is PTFE a chemical of concern?

- Are there alternatives?
  - Yes the non-stick functionality can be provided by enamelled iron-, ceramic, and anodized aluminium coatings are available
    - Are they really PFAS-free?
    - Do they provide sufficient technical performance?
    - Do they have lower environmental impact during their lifecycle?
What about PTFE in non-stick cookware?

- Is it toxic/a risk?
  - Toxic impurities in PTFE coatings?
    - Very low...removed during manufacture
    - PFCAs (e.g. PFOA) be produced if heated to >250°C
    - PFOA etc. are in our uncooked foods!

- Is PTFE a Polymer of Low Concern (PLC)?
Lifecycle Considerations

- But PLC only focuses on the use phase
- Lifecycle considerations important
PFAS Processing Aids Used to Manufacture PTFE

- In US, Europe and Japan, historically ammonium salt of PFOA used in PTFE fine power manufacture
  - PFOA everywhere in environment, wildlife and humans
- PFOA still used in large quantities in China
- Manufacturers in US, Europe and Japan now use fluorinated alternatives (also PFAS)

HFPO-DA

ADONA
Percent of total historical (1950-2004) global PFCA emissions by source

- 79% Fluoropolymer Manufacture
- 5% PFOA Manufacture
- 4% PFNA Manufacture
- 4% POSF Products
- 3% Fluoropolymer Dispersion - PFOA
- 3% Fluoropolymer Dispersion - PFNA
- 1% POSF Degradation
- 1% Fluorotelomer Degradation
- 0.2% POSF AFFF
- 0.1% Fluorotelomer Products
New Problems (vPvM and T?)!

HFPO-DA: high contamination around Dordrecht, NL and Fayetteville, NC, US. Substance of Very High Concern (SVHC)

Perfluoropolyether (Solvay): high contamination in Bormida River (Italy) and New Jersey

Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (CAS No 1190931-27-1) (cC604) now observed in ground- and surface water in the Veneto region (Italy)

Ammonium 4,8-dioxa-3H-perfluorononanoate (CAS 958445-44-8) (ADONA) detected in the Rhine River and serum samples
Fluoropolymers in the media!

Dordrecht teflon plant is emitting cancer-causing chemicals: Volkskrant

GenX is used to make teflon. Photo: Depositphotos.com

AG’s PFAS lawsuit welcome news for advocates as it joins litany of litigation
The last few weeks have seen continued developments in the exploration of GenX and other PFAS.
By Emily Featherston

The Intercept

UNDER DUPONT BRIDGE
The Teflon Toxin Goes to China

THE DEVIL WE KNOW

DARK WATERS
One of the Darkest Cover-Ups in American History

18
Releases during manufacturing

- Polymerization “processing” aids
  - PFOA, GenX chemicals etc.
- Volatile fluorinated by-products with global warming potential
- Oligomers (McCord et al., 2019, in stack)
- Multiple other unknown PFAS
  - E.g. Chemours listed 250 unknown PFAS at Fayetteville Plant in North Carolina
  - US EPA also identified multiple PFAS in soils

RESEARCH

ANALYTICAL CHEMISTRY

Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils

John W. Washington¹, Charlita G. Rosal², James P. McCord², Mark J. Strynar², Andrew B. Lindstrom², Erica L. Bergman², Sandra M. Goodrow², Haile K. Tadesse², Andrew N. Pilant², Benjamin J. Washington³, Mary J. Davis¹, Brittany G. Stuart⁵, Thomas M. Jenkins⁷
Safe Disposal of Fluoropolymers?

- Recycling of PTFE?
  - Not industrialized
- Waste disposal of PTFE coated cookware?
- Release of micro- and nano-plastics
  - Penetrate cell membranes/effects?
  - PTFE particles found in Mediterranean fish and Arctic sediments
- Incineration effective to destroy PFAS?
  - requires at least 800 °C and maybe 1100 °C
  - formation of fluorinated organic by-products?
  - ongoing research
PTFE coatings used in commercial baking in Sweden

- Commercial bakeries remove PTFE after 12-24 months and PTFE is recoated
- In Sweden alone, for example, every year ca. 20,000 baking pans are “recoated” with a total baking surface of 500,000 m²
- Stripping the old coating is performed by
  - “burning off” at 450 °C for 4–5 h to “break down” the coating followed by grit blasting
  - water blasting at 1500 bar
- Unknown emissions of PFAS

Info provided by: https://www.runex.com/
Can PTFE be made without fluorinated processing aids?

- Arkema and Solvay now make fine powder PVDF (polyvinylidene – another fluoropolymer) without fluorinated processing aids
  - Use to use ammonium salt of perfluorononanoic acid (PFNA) or PFOA
  - required 20 years of R&D to develop alternatives
- Patents available for making fine powder PTFE without fluorinated processing aids
  - Not been operationalized
  - But certainly possible
Conclusions/Way Forward

- PTFE does not provide an “essential” function and there are alternatives is convenience desired
- Is PTFE a Polymer of Low Concern?
  - inert in the use phase
- Environmental release of PFAS occur during PTFE lifecycle
  - Release of PFAS during manufacture and waste disposal
  - Manufacturing remains a big problem!
  - Is the release of PTFE particles problematic?
- Alternatives exist so use them
  - Are they definitely safe?
- Improve PTFE manufacturing and waste management?
Thank you for your Attention!