Lessons for Safer Chemicals in Products - PFAS

14 March 2017
Webinar Aims

This webinar will explore the substitution of perfluoroalkyl substances, specifically:

• Issue and regulatory responses, including EU/international/UN/OECD initiative and the scientific background.

• How Chemours has transitioned from making PFAS to short chain alternatives and developing non-fluorinated alternatives for some uses.

• The challenges for shifting to non-fluorinated alternatives for many elements of their footwear.
Dr. Eeva Leinala – a principal administrator in the Environment Health and Safety Division of the Organization for Economic Co-operation and Development (OECD) where she collaborates with OECD member countries and stakeholders to advance projects related to risk assessment and risk reduction of chemicals.

Ronald Bock – Prior to his current responsibilities as EMEA Risk Management Manager within Chemours International Fluoroproducts, Ronald held the position of Registration Manager for DuPont’s biocide products and EMEA Product Stewardship Manager for the Surface Protection Solution business in the EMEA region.

Chris Enlow – with a background in the non-profit sector, Chris began working for KEEN Footwear in the areas of philanthropy and sustainability in 2006. In the role, Chris pursues his passion for protecting public lands, disaster relief support, and supply chain responsibility.
Questions

- Please submit questions during the webinar using your chat box.
- Any unanswered questions can be raised in the Chemical Watch LinkedIn group following the webinar:

www.chemicalwatch.com/CRM-LI
PFASS – OVERVIEW OF CONCERNS AND RISK REDUCTION APPROACHES TO TRANSITION TO SAFER ALTERNATIVES

Eeva Leinala, Principal Administrator, OECD Chemical Watch – March 2017
The main objectives of the Programme are to:

• Assist OECD Member countries' efforts to protect human health and the environment through improving chemical safety and biosafety

• Make chemical control policies more transparent and efficient and save resources for government and industry; and

• Prevent unnecessary distortions in the trade of chemicals, chemical products and products of modern biotechnology.

35 Member countries, many partner countries and other stakeholders work together to develop and co-ordinate activities on chemical safety and biosafety on an international basis. One of the core aspects of the work relates to the Mutual Acceptance of Data.

http://www.oecd.org/env/ehs/
Terminology
Per- and Polyfluoroalkyl Substances (PFASs)

Fully or partially fluorinated carbon chain connected to a functional group

\[
\begin{align*}
\text{Perfluorocarboxylic acids (PFCAs):} & & \text{Perfluoroalkyl sulfonates (PFSAs):} \\
\text{Perfluorooctanoic acid (PFOA):} & & \text{Perfluorohexane sulfonic acid (PFHxS):} \\
\text{Perfluorooctane sulfonate (PFOS):} & & \text{Perfluorooctane sulfonate (PFOS):}
\end{align*}
\]

Short chain & long chain

Long-chain PFAS refers to:

- Perfluorocarboxylic acids (PFCAs) with carbon chain lengths C8 and higher, including perfluorooctanoic acid (PFOA);
- Perfluoroalkyl sulfonates (PFSAs) with carbon chain lengths C6 and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS);

Precursors of e.g. PFCAs and PFSAs

Fluorinated polymers: Polymers with fluorinated side-chains
Fluoropolymers: Polymers with fluorinated backbone
PFASs

Per- and polyfluoroalkyl substances (PFASs)

- perfluoroalkyl carboxylic acids (PFCAs), \( \text{C}_n\text{F}_{2n+1}\text{-COOH} \)
- perfluoralkane sulfonic acids (PFASs), \( \text{C}_n\text{F}_{2n+1}\text{-SO}_2\text{H} \)
- perfluoroalkyl phosphonic acids (PFPAAs), \( \text{C}_n\text{F}_{2n+1}\text{-PO}_3\text{H}_2 \)
- perfluoroalkyl phosphonic acids (PFPAAs), \( \text{C}_n\text{F}_{2n+1}(\text{C}_m\text{F}_{2m+1})\text{-PO}_2\text{H} \)

non-polymers

- perfluorooalkyl iodides (PFAIs)
- perfluorooalkyl sulfonfyl fluoride (PASF)

PASF-based substances

- \( \text{C}_n\text{F}_{2n+1}\text{-SO}_2\text{R}, \text{R} = \text{NH}, \text{NHCH}_2\text{CH}_2\text{OH}, \text{etc.} \)

polymers

- fluoropolymers (FPs) — fluoroalkene, ethylene propylene (FEP), perfluoroalkyl polymer (PFA), polyvinyl fluoride (PVF), etc.
- side-chain fluorinated polymers
- perfluoropolyethers (PFPEs) — e.g., \( \text{HOCH}_2\text{O\text{[C}_m\text{F}_{2m+1}\text{-CH}_2\text{OH}} \)

From OECD 2015

Swedish Chemical’s Agency (KEMI) identified >3000 PFASs (June 2015)

* These polymers are based on monomers derived from PASFs or fluorotelomer-based raw materials.
History & Characteristics

• First manufactured in the 1930s
• In use since the late 1940s
• Unique physicochemical properties
  – surfactants
  – water, oil and stain resistance
  – durability & strength

• Wide range of applications & sectors – surface protectors, fire fighting, electronics, construction, textiles, automotive, aerospace, medical devices ... etc ...

• But ... some of the unique physicochemical properties of PFASs that popularised their widespread use are also associated with environmental and human health concerns.
Characteristics of concern
Long Chain PFASs

• Persistent
• Bioaccumulative
• Long range transport properties
• Toxicity
  – e.g. concerns for reproductive toxicity & aquatic toxicity)
Release to the Environment

- Production, use & waste streams
- Products (manufacture, use & disposal)

Detection of PFASs in the Environment

Footprints in the Snow Greenpeace 2015


Snapshot of risk reduction activities for PFASs in a number of countries (2015)

Analysis can inform countries about options for risk reduction of PFASs

Information from:
- Australia, Canada, Denmark, the European Union, Finland, Germany, Japan, the Netherlands, Norway, the People’s Republic of China, Poland, Republic of Korea, Russia, Sweden, the United Kingdom and the United States
- Industry provided input on voluntary approaches within sectors

Main findings

• Drivers for development of risk reduction approaches
  – growing scientific knowledge on the risk of certain PFASs
  – increasing number of international initiative supporting transition towards safer alternatives

• Risk reduction approaches for PFASs
  – combination of voluntary and regulatory approaches
  – under existing national and/or regional regulatory frameworks
  – principally long chains PFASs and their precursors and salts
  – approaches aimed at gathering new knowledge and at awareness-raising tend to include broader categories of PFASs
Risk Reduction – Some Examples

2000 - Following negotiations between the US EPA and 3M, 3M announced its voluntary manufacturing phase out of PFOS

2006 - The United States Environmental Protection Agency Voluntary Stewardship Program - reduce and eventually eliminate use of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals by 2015 globally

2009 - PFOS and related compounds were listed under Annex B of the Stockholm Convention for Persistent Organic Pollutants (POPs)

2009 - Strategic Approach to International Chemicals Management - ICCM2 Resolution II/5

2012 - Strategic Approach to International Chemicals Management (SAICM) ICCM3 Resolution III/3

2017 – PFOA and PFOA related salts – proposal for listing

OECD/UNEP Global PFC Group supports
EU– Long Chain PFASs

- **REACH Candidate List for substances of very high concern**
  - long-chain PFCAs (C8 - 14 PFCAs),
    - Persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB)
  - Proposal for listing: Perfluorohexane-1-sulphonic acid and its salts (PFHxS)

- **REACH restrictions**
  - C8PFCA/PFOA its salts and PFOA-related substances – decision pending
  - Perfluorinated silanes: On-going process: restriction covering use of a combination of perfluorinated silanes and one or more organic solvents in sprays used for the general public
  - Completed call for information: PFCAs (C9-C20) and other fluorinated substances

- **POPS Regulation**
  - PFOS
• Work towards establishing a global emission inventory for per- and polyfluoroalkyl substances (PFASs)

• Uses perfluoroalkyl carboxylic acids (PFCAs) as a reference to present an overall picture of global and regional emissions of PFASs and other related fluorinated substances

Main sources responsible for the majority of C7–C9 and C11 PFCAs in the global environment are relatively well understood.

Geographic shift

- these new sources may more than offset the reductions obtained by the former major global manufactures

Understanding of (potential) sources of some other PFCA homologues, particularly C4, C5, C10, C12–C14 PFCAs, is still incomplete.
Detection of PFASs in the Environment

Footprints in the Snow Greenpeace 2015


Areas to be strengthened - identified by the OECD/UNEP Global PFC Group

- Enhance information and knowledge sharing on alternatives to PFASs
  - Webinars on sharing of information on shifting to alternatives

- Increase understanding on uses of PFASs and product content

- Develop estimates of PFASs production and release, particularly in relation to use and exposure potential

- Engage in capacity building activities, in particular with emerging and in-transition economies.

OECD group updating list of PFAS (2017)
Webinar series within OECD/UNEP Global PFC Group:

Presentations from:

• Regulators
• Academics
• Industry, downstream users
Observations from Webinars

• Types of alternatives
  – short chain PFASs
  – other fluorinated
  – non-fluorinated
  – functional

• Challenge: efficacy of the alternative for particular use
  e.g. firefighting foams, water proofing
Observations from Webinars

Concern with detection of short chain PFASs in the environment, including potential for long-range transport
• Concern for persistence in the environment and mobility
• No indications of ecotoxicity

REACH substance evaluation
• Evaluation of some short-chain PFASs
Retailer & Downstream Supply Chain Expectations (some examples related to textiles)
NEW OECD Portal on PFASs (to be released April 2017)

Why this Portal?
This Portal serves to facilitate the exchange of information on per and polyfluorinated chemicals, focusing specifically on per- and polyfluoroalkyl substances (PFASs). In order to support a global transition towards safer alternatives, the Portal provides information on the following areas:

1. What are PFASs?
2. Risk reduction approaches

What’s new
In 2017, the OECD will be updating its Lists of Perfluorooctane sulfonate (PFOS), Perfluorooctyl sulfonate (PFOSA), Perfluorononanoic acid (PFNA), Perfluorocarboxylic Acid (PFCA), related Compounds and Chemicals that may degrade to PFCA, which was last reviewed in 2007.

Read our latest reports
OECD Global PFC Group Documents

(portal will link from this site in April 2017)

Contact:
• eeva.leinala@oecd.org
• marie-ange.baucher@oecd.org
Lessons for Safer Chemicals in Products - PFAS
Use of PFASs in the Textile Industry: Past, Present and Future

Ronald Bock – Product Stewardship Manager
Chemical Watch – March 2017
Agenda

• Stain and durable water repellency, how does it work?
• From long-chain products to short-chain alternatives
• Assessment of short-chain alternatives
• Is the future of textile treatment non-fluorinated?
Stain and durable water repellency (DWR), how does it work?
Stain, oil and DWR

Fabrics fight off dry soil and nasty, unpredictable spills and splashes.

Liquid spills roll off or can easily be wiped away. Dry soil easily brushed off.
Fluorinated Polymers

\[ CF_3 | (CF_2)_n | CF_3 | (CF_2)_n | CF_3 | (CF_2)_n | CF_3 \]

Polymer

Fiber

Fiber and Fabric bulk properties are unaffected

- Long-chain (C8): \( n = 7 \)
- Short-chain (C6): \( n = 5 \)

Definition of long vs. short – chain PFASs:
https://www.oecd.org/ehs/pfc/

Chemours

Use of PFASs in the Textile Industry: Past, Present and Future

March 14, 2017
Consumers want performance

Performances that consumers want:
- Textiles looking new longer
- Repellency, water and/or oil
- Keeps fabrics dry
- Stain Management
- Durability: laundering, light exposure, abrasion, dry cleaning, etc…

→ Product life cycle benefits are significant but

Performance is specific to a product and its intended use
Performance = Sustainability

• **Protection** - water, oil & soil repellent and release

• **Life-cycle Benefits**
  – Water and carbon footprint
  – Durability = Life of garment

• **Design Benefits**
  – Aesthetics
  – Color
From long-chain products to short-chain alternatives
US EPA Product Stewardship Program

- Global partnership between the U.S. EPA and the major fluorotechnology manufacturers in the US, Europe and Japan
- Launched in 2006 to eliminate long-chain products from facility emissions and product content
  - The major global producers have ceased manufacture of long-chain fluorinated technology
  - Led to the elimination of long-chain PFCAs by the end of 2015 and to the development of the short-chain PFCAs

More info on EPA PS Program:
https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program#meet
Alternative requirements

Careful balance taking into account:

• **Performance** required for the end-use applications
• More favorable **environmental, health and safety (EHS) profile**
• **Approval for use** in key countries/regions around the world

Major challenge to replace long-chain PFAS technology:

• **Decade of research** and substantial investments
• Companies investigated a **large universe of options**
Short-chain fluorinated alternatives

Short-chain fluorinated DWR products

• Are **commercially available and approved** by regulators
• Can deliver required **full stain management** performance
• Have a **more favorable** human health and environmental profile
• **Extensive environmental, health and safety data**
Assessment of short-chain alternatives
Assessment requirements

• Composition and impurities
• PBT assessment
  – Physical-chemical properties
  – Toxicology (aka hazards)
    • Mammals
    • Environment - Aquatic
• Exposure & Risk assessment
• Fate
Available Data

**Extensive dataset on short-chain products is available:**
- Chronic and acute toxicity data on mammalian species
- Elimination half-life of major degradation product
- Aquatic toxicity in fish and algae
- Environmental fate (aerobic and anaerobic degradation pathways)

**Current available data demonstrate:**
- No CMR or bioaccumulation properties
- Rapid elimination from living organisms
- Not broadly found in humans

*References available upon request*
Is the future of textile treatment non-fluorinated?
Technologies & Performance

- Paraffin Waxes
- Dendrimers
- Acrylic polymers
- Urethane polymers
- Melamine resins
- Particles
- Silicones
- Fluorinated polymers

- Water repellency
- Oil repellency
- Stain release
- Soft handle
- Abrasion resistance
- Air-dry performance
- Laundry durability
Repellency and stain management

Requirements....

Rain Management
Water Repellency

Full Stain Management
Water, Oil and Soil

Waxes, Silicones, etc.

Short-chain fluorinated
DWR

Active Protection
Water and oil repellency

Active & Passive Protection
Dual Action

Passive Protection
Stain and soil release

Active Protection
Water and oil repellency

Active & Passive Protection
Dual Action

Use of PFASs in the Textile Industry: Past, Present, and Future

Chemours
Assessment requirements (bis)

Non-fluorinated alternatives need to be assessed as well

- Composition and impurities
- PBT assessment
  - Physical-chemical properties
  - Toxicology (aka hazards)
    - Mammals
    - Environment - Aquatic
- Exposure & Risk assessment
- Fate
Non-fluorinated technology

Zelan™ R3

• Water repellency
• Oil repellency
• Stain release
• Soft handle
• Abrasion resistance
• Air-dry performance
• Laundry durability
In a nutshell…

• No single, all-encompassing, high performance DWR solution is available, as yet.

• Active / Outdoor products are moving to non-fluorinated alternatives where performance requirements can be achieved.

• Technical products are using short-chain fluorinated alternatives to meet high performance requirements.

The future demand is clearly multiple types of products.
Thank you

Contact: ronald.p.bock@chemours.com
Lessons for Safer Chemicals in Products - PFAS
PFC-FREE JOURNEY
Safe, Effective & Affordable

Presenter: Chris Enlow
Chemical Watch
Webinar: Lessons for Safer Chemicals in Products - PFAS's
Tuesday, March 14, 2017
About Me
About KEEN
We strive to reduce our impact on the environment, protect the places where we play and give back to communities in need.
Giving Back
Taking Action

#LiveMonumental
Reducing Impact
Guiding Principle

Reducing Impact

SAFE
EFFECTIVE
AFFORDABLE
Effective
Affordable
101 BOMs  Bill of Materials
Project Timeline

Socialization / Alignment

Hard Work / Slow Process

Get Rid of "low hanging" PFCs

Where is it?

Why?

Phase Out

Performance Testing

Precautionary Principle

101 BOMs

SVHC Research & DWR Survey

Project Kick-Off

2017

2016

2015

2014

2013
Benchmarking Exercise

FOAM

FABRIC

LEATHER

PLASTIC

CHEMICAL AGENTS

PU SYNTHETIC
Alternatives

SAFE

DETOX

EFFECTIVE

AFFORDABLE
# 32 PFCs

![Image showing samples with labels](image)

**Test Item(s)**

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<tr>
<td>PFBS</td>
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<td>PFHpS</td>
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Working with Suppliers

Spray rating 100

FC has much higher efficiency in lower amount. FC free will always need higher dosage which may impact to

- Coating adhesion
- Lamination bonding strength
- Color fastness (also subject to dye’s property)
- Handle
- Cost, etc
Field Testing

SAFE  DETOX  EFFECTIVE

AFFORDABLE
Do we need it?

67% REDUCTION

Precautionary Principle
My Hypothesis

If we apply the precautionary principle Brand-wide, then it should be cost neutral.

Waterproof Shoes → Margin Hit

Non-Waterproof Shoes → Margin Savings
CHALLENGES
PFCs Are Everywhere
Unexpected Places
Unintended Consequences
Socialize
CONCLUSIONS
<table>
<thead>
<tr>
<th>CATEGORY</th>
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*=Waterproof Styles*
100% PFC-FREE FOOTWEAR
Spring 2019

Reducing Impact

SAFE
EFFECTIVE
AFFORDABLE
THANK YOU!

Chris Enlow, Corporate Responsibility Director
chris.enlow@keenfootwear.com
Lessons for Safer Chemicals in Products - PFAS
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Thank you for attending

What did you think about the webinar? Please take part in our email survey (in your inbox now)

A downloadable recording of this presentation (with slides) will be available shortly.

If you have any questions, please contact Jacob - Jacob.ward@chemicalwatch.com

▪ Global Business Summit 2017 – Amsterdam – 20-22 March
▪ Safer Chemicals in Products 2017 – San Francisco – 27-28 March