PFC Substitution in textile supply chain –
Finishing of textile articles with fluorinated polymers

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- Fluorochemicals in textiles – Background and Status
- Consumer Risks?
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PFC in textiles

Differentiation I:

- **Fluoropolymers**: in membranes of breathable clothings
- **Fluorinated Polymers = Fluorocarbon Resins**: Used for water, oil and stain repellent finishing, inter alia textiles
  - Electro Fluorination
  - Telomerization process

Differentiation II:

- “Long chain” (C8) Fluorochemistry → substituted by TEGEWA members in their formulations by short-chain fluorochemistry and, if technically achievable, by non-fluorinated alternatives. Implementation well underway.
- “Short chain” (C6) Fluorotelomer chemistry → better toxicological and exotoxicological profile

⇒ e.g. polytetrafluoroethylene (PTFE)
⇒ e.g. poly-acrylate
⇒ officially since January 2016
Risks for consumers and environment?

- Potential consumer risk is connected with occurrence of traces of PFOA in consumer articles.
- PFOA occurs as unintended by-product within production of fluorocarbon resins (C8, long chain chemistry).
- PFOA is not being used for water and stain repellent finishing of consumer articles such as textiles, leather or paper.

Different risk potential of C6 and C8 chemistry:

- **C8** / long chain fluorochemistry: Acc. to an RA there is no consumer risk from potential exposure to traces of PFOA in water and stain repellent finished textiles.
- **C6** / short chain fluorochemistry: No consumer risk, better exotoxicological profile.
- But: negative environmental impact – release into the environment has to be avoided.
Industry works on sustainable solutions

Since 2006:

- Optimization of conventional fluorocarbon products
  - Reduction of PFOA and PFOA precursors by process optimization

- Prevention of building of PFOA and precursors by:
  - Development of alternative fluorotechnology („short chain fluorochemistry, C6 and C4“)
  - Development of fluorine-free alternatives
Fluorine-free alternatives

- There are fluorine-free alternatives for textiles with a water repellent effect only
  
  → This means without stain repellency

- Dependent on specific requirements the following chemical groups can be used:
  
  → Paraffine formulations
  
  → Polysiloxanes
  
  → Modified melamine resins
  
  → Polyurethane
  
  → So called dendrimers

→ Intense research work on alternatives by producers; development of further products on different basis available
Possibilities and limitations of fluorine-free chemistry

- Fluorine-free water repellent finishing agents are suitable, provided that
- Oil and stain repellency is not requested at the same time
- Fluorine-free water repellent finishing agents are only partially suitable
- They are in most cases not suitable, if customers ask for combination of effects such as:
  - Very high water repellency
  - Abrasion resistance
  - Suitability for lanimation
  - High wash durability (high number of wash cycles, high temperatures)
  - High effect level in dryer or drying system
- All such requirements can currently only be met with use of fluorinated polymers
Possibilities and limitations of fluorine-free chemistry (II)

- There is no possibility to use fluorine-free chemistry for technical textiles with a sufficient repellent (especially for oil, stain and chemicals) effect which is requested e.g. for personal protective equipment

- Bullet-proof vests for police and armed forces
- Apparel for fire fighters
- Protective work wear against chemicals in chemical and other industries
- Certain textiles used in clinics with requests for repellence of blood
- Automotive textiles
- Insulation products for vehicles
- Specific products for coating textiles (e.g. tents)
Conclusion, Outlook

- **Fluorinated Polymers** are being used for the water, oil and stain repellency of textiles.
- There are no risks for the consumer, especially regarding textiles being finished with short-chain fluorochemistry.
- C6 fluortelomeric chemistry shows a significant better tox- and exotox-profile.
- There are alternatives without fluor regarding water repellent finishing – but they cannot meet every customer requirement yet.
- Global fashion brands and out-door textil brands are tending to ban fluorocarbon resins from their products.
- Regarding technical textiles, e. g. personal protective equipment fluorocarbon resins can currently not be replaced.
Thank you very much for your attention!

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Eager.
Gorgeous.
Experienced.
Watchful.

Association No.1: TEGEWA
(and very modest)

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Back up
Typische Struktur eines fluortelomerbasierten wasser- und schmutzabweisenden Mittels

- MW > 20000 Dalton
- Enthält fluorierte und nichtfluorierte Seitenketten
- Typische wasserbasierte Formulierung enthält 20 - 30 % aktive Polymerverbindung
- Typischer Fluorgehalt im Polymer 20 - 50%
Das Polymer wird an die Faseroberfläche gebunden
Und bleibt auch nach vielen Wäschen gebunden.
Polymer wird typischerweise 0.2% - 0.5%ig eingesetzt.
Mögliche Verunreinigungen
– Perfluorcarbonsäuren,
– Fluortelomeralkohole
Fluorotelomer Intermediates Product Tree

CF$_2$=CF$_2$ (TFE)

\[ F(CF_2CF_2)_nI \] (Perfluoroalkyl Iodide)

n = 2 - 8 Straight Chain Alkyl

\[ F(CF_2CF_2)_nCH_2CH_2I \] (Fluorotelomer Iodide)

\[ F(CF_2CF_2)_nCH_2CH_2OH \] (Fluorotelomer Alcohol)

e.g. C$_8$F$_{17}$C$_2$H$_4$OH = 8:2 FTOH
C$_6$F$_{13}$C$_2$H$_4$OH = 6:2 FTOH

\[ F(CF_2CF_2)_nCH_2CH_2OCOCR=CH_2 \] (Fluorotelomer (Meth)Acrylate)

Polymeric Textile Finishing Products

Built up of the Perfluoroalkyl Chain

Modifying with functional groups

Reacting to final polymer
Textile Finishing Process

In the Textile Industry, *Foulard Application* is the most common way to apply a Fluorotelomer-based Polymer Formulation.

Concentration depends on:
- material
- weight pick up (wpu)
- coapplication of further additives
- desired effects

20 - 100 g/l

**Stenter**

120°C ... 150-180°C

or 150°C-180°C

This is normally the last step in the preparation of a textile fabric.
Wege zur nachhaltigeren Oleo- und Hydrophobierung

„C8-Chemie“

Produkte auf „C8-Basis“:

perfluorierte Seitenketten unterschiedlicher Kettenlänge (C4, C6, C8, C10 …) mit Verteilungsschwerpunkt bei C8
Wege zur nachhaltigeren Oleo- und Hydrophobierung

Neue Fluortechnologie („C6-Chemie“)

Produkte auf „C6-Basis“:

perfluorierte Seitenketten
basierend auf 6 C-Atomen
(keine längerkettigen Anteile)

% F

0 20 40 60 80 100

C4 F9 C6 F13 C8 F17 C10 F21 C12 F25 C14 F29

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Health and safety profile of C6 based fluorotelomers

- C-6 based fluorocarbon resins do almost have no long chain parts

- Superior toxicological profile of perfluorooctanoic acid (PFHxA) compared to PFOA:
  - PFHxA is not producing tumors in long-term studies: not cancerogen
  - PFHxA not genotoxic
  - PFHxA is not toxic for reproduction
  - PFHxA has a lower tox-profile after repeated exposure
  - PFHxA is being excreted quickly (within a few hours)
TEGEWA: Association of producers of …

- Textile auxiliaries and colourants,
- Paper auxiliaries and colourants
- Leather/Fur auxiliaries and colourants
- Surfactants,
- Complexing agents,
- Antimicrobial agents,
- Polymeric flocculants,
- Cosmetic raw ingredients and pharmaceutical excipients
- and allied products

Process and performance chemicals for industrial users

- Substances,
- Formulations,
- Polymers,
- Reaction Mixtures