PFASs in Carpet and Furniture Applications
DTSC Workshop
January 31, 2017
Sacramento, CA
Overview

- Introduction to FluoroCouncil and PFASs
- Short-chain-based products – safe for their intended use
- Regulatory oversight of short chains
- Status of long chains
- Summary and conclusions
Introduction to FluoroCouncil and PFASs
About the FluoroCouncil

• Represents leading manufacturers of FluoroTechnology products

• Member companies:
  – Archroma Management LLC - Arkema France
  – Asahi Glass Co., Ltd. - Daikin Industries, Ltd.
  – Solvay Specialty Polymers - The Chemours Company LLC
  – Dynax and W.L. Gore and Associates (provisional members)

• Other manufacturers of fluorinated products also serve this market, including manufacturers in other countries and of other technology.
### FluoroTechnology Used in Carpets/Furniture

#### Surface Modifiers
- **Modify material properties:** surface modification & protection, water & oil repellency, soil resistance and release, wetting and spreading
- **Applications:** Textiles, Protective Medical/First Responder Gear, Carpets, Paper, Stone & Tile, AFFF, Surfactants
- **Chemistry:** Fluorinated chains attached to organic polymer backbones.

#### Plastics/Polymer
- **High molecular weight polymers**
- **PTFE, Melt Copolymers, Thermoset Elastomers**
- **Fluorinated “backbone”**
- **Material properties:** chemical resistance, thermal stability, resilience (elastomers)
- **Applications:** Breathable membranes, Aerospace materials, Hydraulic tubing, Chemical processing, Semiconductor manufacture, Transportation

#### Gases and Liquids
- **Refrigerants**
- **Cleaning solvents**
- **Blowing agents**
- **Etching agents**
- **CFC alternatives** (e.g., HFCs)
FluoroTechnology Used in Mill Treatments of Carpets/Furniture

Per- and polyfluoroalkyl substances (PFASs)

- Perfluoroalkyl acids (PFAAs) $\text{CnF}_{2n+1}R$
  - Perfluoroalkyl carboxylic acids (PFCAs)
  - Perfluoroalkane sulfonic acids (PFSA)
  - Perfluoroalkyl phosphoric acids (PFPA)
  - Perfluoroalkyl phosphinic acids (PFPIA)

- Perfluoroalkane sulfonyl fluoride (PASF) $\text{CnF}_{2n+1}SO_2F$
  - PASF-based derivatives $\text{CnF}_{2n+1}SO_2R$, $R = \text{NH, NHCH}_2\text{CH}_2\text{OH}$, etc.

- Perfluoroalkyl iodides (PFIAs) $\text{CnF}_{2n+1}I$
  - Fluorotelomer iodides (FTIs) $\text{CnF}_{2n+1}\text{CH}_2\text{CH}_2I$
  - FT-based derivatives $\text{CnF}_{2n+1}\text{CH}_2\text{CH}_2R$, $R = \text{NH, NHCH}_2\text{CH}_2\text{OH}$, etc.

- Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives
  - Polyfluoroalkyl ether carboxylic acids

- Fluoropolymers
  - Polytetrafluoroethylene (PTFE)
  - Polyvinylidene fluoride (PVDF)
  - Fluorinated ethylene propylene (FEP)
  - Perfluoroalkoxy polymer (PFA), etc.

- Perfluoropolyethers
  - Fluorinated (meth)acrylate polymers
  - Fluorinated urethane polymers
  - Fluorinated oxetane polymers

OECD(2013), OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD.
The key functionality is provided by the fluorinated side-chain
   - $n = 8$ – long chain; $n = 6$ – short chain
The polymer backbone is NOT fluorinated
PFOA is not used in carpets/furniture, but was a byproduct, impurity, and potential degradation product of C8 long-chain fluorinated polymer
Regulatory focus on long-chain fluorinated polymers ($\geq$ C8) or ECF-based sulfonated ($\geq$C6) substances
Defining long chains vs. short chains

- Distinction based on **science and policy**
  - Began at EPA in 2006 in reviews of long chain replacements, recognizing hazard profiles of short chain alternatives were clearly more favorable than long chains


### Short Chains
- Example Product: Fluorinated polymer with C6 side-chain
- Example Degradation Products: PFHxA, PFBS
- Well studied
- Reviewed and approved by regulators as alternatives to long chains
- Products in use for over 30 years and pathway to full conversion over past ~10 years

### Long Chains
- Example Product: Fluorinated polymer with C8 side-chain
- Example Degradation Products: PFOA, PFOS
- Focus of regulatory action
- PFOA/PFOS classified as PBT substances
- Phased out by Stewardship Program* companies
- Production/use/trade continues by non-Stewardship Program companies

Supply Chain Overview

Side-chain Fluorinated Polymer Manufacturers

short chains (includes all FluoroCouncil members)

long chains

Carpet/Textile Mills

After market treatments

Consumers
Key Benefits of Side-Chain Fluorinated Polymers in Carpet/Furniture Applications

• Combination water repellency, oil repellency, stain resistance and soil release with abrasion resistant finishes

• Durability – Treated products stay cleaner longer, reducing need for washing and use of cleaning products

• Longer useful product life, reducing raw material, energy and water used to manufacture replacements
Short chain-based products – safe for their intended use
Degradation products are focus of risk assessment

• Scientific consensus that fluorinated polymers do not present toxicity concerns
  – Not bioavailable
  – Considered low risk to humans/environment
  – Not a focus of regulators

• Consistent with direction of EPA, studies have focused on degradation products to characterize toxicity profiles of short-chain-based products.

• Studies show short-chain-based products do not present significant adverse impacts.
Short-chain-based products - well studied

• Rich database on short-chain-based products, including data provided by FluoroCouncil member companies.

• Toxicity and environmental data developed and submitted to regulators on:
  – Short-chain products
  – Raw materials used to produce those products
  – Degradation products

• Studies conducted include:
  – testing for cancer
  – reproductive/developmental toxicity
  – systemic toxicity
  – bioaccumulation
  – ecological endpoints
  – environmental fate and transport

• Relevant studies developed by FluoroCouncil and others available at www.fluorocouncil.org/resources/research
PFHxA*: Toxicity Summary

- Does not represent a reproductive, developmental or neurobehavioral hazard
- Not carcinogenic
- Not mutagenic
- Does not bioaccumulate in fish
- Quickly eliminated from living organisms
- Not an endocrine disruptor

* PFHxA is an impurity/degradation product
PFHx Toxicity Profile

Impurity/Degradation product - Perfluorohexanoate (PFHx)*

Repeated-Dose Mammalian (Oral)
- 2-year chronic (rat)
  - NOAEL M 15 mg/kg/day; F 30 mg/kg/day
  - Not carcinogenic
- 90-day sub chronic (rat)
  - NOAEL 100 mg/kg/day
  - Target: liver, body weight
- One-Generation Reproduction (rat)
  - NOAEL 100 mg/kg/day
  - No effects on reproductive parameters
- Repro/Development (mouse)
  - NOAEL 100 mg/kg/day
- Development (rat)
  - NOAEL 100 mg/kg/day
- Pharmacokinetics (rat, mouse, monkey)
  - Single and repeated dose studies completed: rapid elimination for both genders in all species

Summary
- Not damaging to DNA, not genotoxic or mutagenic
- Not a selective developmental or reproductive toxicant
- Not carcinogenic^ 
- Rapid bioelimination, not bioaccumulative¥
- Not expected to be harmful to human health or the environment at environmentally relevant concentrations

* Loveless et al., *Toxicology*, 2009, 264(1-2), 32-44
Chengelis et al., *Repro Tox*, 2009, 24(3-4), 342-351

## Very Different Toxicological Profiles for PFCAs

<table>
<thead>
<tr>
<th>Study Type</th>
<th>PFOA</th>
<th>PFHxA</th>
<th>PFHxA</th>
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</thead>
<tbody>
<tr>
<td>Repro-Developmental F1 NOAEL</td>
<td>Rat</td>
<td>Rat</td>
<td>Mouse</td>
</tr>
<tr>
<td></td>
<td>3 mg/kg/d M</td>
<td>100 mg/kg/d M &amp; F</td>
<td>100 mg/kg/d M &amp; F</td>
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<td>10 mg/kg/d F</td>
<td>(Loveless, 2009)</td>
<td>(Iwai, 2014)</td>
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<tr>
<td>2 yr Chronic Toxicity</td>
<td>1.3 mg/kg/d M</td>
<td>15 mg/kg/d M</td>
<td>-</td>
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<tr>
<td></td>
<td>1.6 mg/kg/d F</td>
<td>30 mg/kg/d F</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Butenhoff, 2012)</td>
<td>(WIL Research Labs, 2010)</td>
<td></td>
</tr>
<tr>
<td>Carcinogenicity</td>
<td>Leydig cell tumor, liver adenoma, pancreatic tumor 300ppm diet 14.2 mg/kg M 16.1 mg/kg F (Butenhoff, 2012)</td>
<td>No carcinogenicity at maximum tolerated doses 100 mg/kg/d M 200 mg/kg/d F (Klaunig, 2015)</td>
<td>-</td>
</tr>
</tbody>
</table>

PFHxA NOEL is at least 10x higher and non-carcinogenic

**References**

- **WIL Research Laboratories** (2010) Study No. WIL-534009
Elimination Half-life Studies in Plasma - Perfluoroalkyl acids (PFAAs)

<table>
<thead>
<tr>
<th>Elimination $t_{1/2}$ (Days)</th>
<th>short-chain</th>
<th>long-chain</th>
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<tbody>
<tr>
<td></td>
<td>PFBA</td>
<td>PFBS</td>
</tr>
<tr>
<td>Rat</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Monkey</td>
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# Fluorinated Carbons

<table>
<thead>
<tr>
<th># Fluorinated Carbons</th>
<th>short-chain</th>
<th>long-chain</th>
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<tr>
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<td>3</td>
<td>6</td>
</tr>
<tr>
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<td>7</td>
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<td></td>
<td>5</td>
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</table>

- BIG difference between “long” and “short” chain PFAAs
- Short chain PFAAs eliminate rapidly and significantly less toxic

Chengelis et al., *Repro Tox* (27), 400-406.
Grouping and read-across for PFASs are inappropriate

- Data demonstrate short chains have distinct hazard profiles from long chains.
- Chemical risk management decisions should be based on chemical-specific data whenever available, not on unsubstantiated references to other chemicals.
- Grouping and read-across, which are useful when data are unavailable, are inappropriate here and unnecessary because data on short chains are available.
Persistence of Short-chain-based Fluorinated Polymers

- Common recognition that short chains products are persistent.
- Persistent properties are linked to their technological strengths as durable materials, the very performance properties relied on by users.
- No evidence of bioaccumulation or sufficient toxicity to warrant regulation – *Not PBTs.*
- Persistence of a substance alone is not a sufficient basis for regulation.
Regulatory Oversight of Short Chains
Regulatory Review of Short Chains

• Short-chain-based fluorinated polymers are accepted for use in carpet/furniture applications by EPA, Environment and Health Canada, Europe and Japan.

• Approvals supported by a robust body of data and recognition that these substances meet relevant regulatory standards for the protection of human health and the environment.
• EPA issued TSCA Section 5(e) Orders
  – Allows for continued oversight (testing and controls) of short-chain-based fluorinated polymers
  – Allows EPA to unilaterally impose restrictions (including an outright ban) on products if determined they will or may present an unreasonable risk to health or the environment
  – Requires performance of safety studies and allows EPA to provide adequate protections based on new data as they become available
Status of Long Chains
Status of Regulation of Long-Chains

- PFOA and related long-chains are no longer produced or used by major manufacturers in the U.S., Europe, Japan
- Long-chains have been under significant regulatory pressure globally but there are important gaps in coverage
  - Exemptions, long timelines in REACH Restriction
  - PFOA listing under Stockholm Convention is moving slowly at best and is likely to include multiple exemptions
- Manufacturing in China/India/Russia under no existing regulation
  - 2012: PFOA production in China* increased to 90t/a
  - Production, use, and global trade of PFOA and long-chain fluorotelomer-based products continues by non-FluoroCouncil companies

* Li et al., Chemosphere 2015, 129, 100-109
Regulation of Long-Chains in CA, U.S.

- Voluntary stewardship by industry accounts for most aspects of long-chain phase-out in California
  - EPA plan to back up this stewardship with regulation did not occur
  - Example: EPA planned SNUR on long-chains was not completed; not clear whether Trump Administration will act in light of other priorities
  - Even as proposed, EPA SNUR was limited and would not have stopped, for example, import of furniture fabric containing long-chains
- Import of PFOA in consumer articles is currently permitted in the state
- DTSC could address the regulatory gaps on long-chains
  - Many stakeholders, including the FluoroCouncil, would support such an approach; the job is not yet done on PFOA
Summary & Conclusions
Key Messages

• Only side-chain fluorinated polymers - a small subset of PFASs - are used in mill treatment of carpet and textiles.
• Short-chain-based fluorinated polymers provide unmatched functionality in carpet and furniture applications.
• Data indicate these short-chain fluorinated polymers are safe for their intended use.
• Short-chain fluorinated polymers have been recognized as meeting relevant regulatory standards by regulators around the world; in the U.S., EPA has ongoing authority to assure adequate protections through TSCA Orders, if needed, in response to new data.
• There are no legal restrictions on long-chain PFAS in California; DTSC should address this situation.
• Regulatory and policy approaches to addressing PFASs should be based on science and risk; grouping and read-across are inappropriate when data are available.
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