Revisiting Our Fluorinated Surfactant Case: What we have learned so far

April 4th, 2011
Marty Mulvihill, class 19

Second third of the class complete

• Project Updates:
  – Expectations
  – Grading

• Next phase of the class: decision making

• Survey-will be emailed this evening
Relevant data from each discipline

1. Environmental Fate
2. Exposure
3. Toxicity
4. Design for Degradation
5. Efficiency
6. Regulation
7. Voluntary Initiatives
8. Business Case

Major Molecular Players

- PFOA
  - CF₃
  - \( \begin{array}{cccccccc} F & F & F & F & F & F & F & OH \\ F & F & F & F & F & F & F \\ \end{array} \)

- PFOS
  - CF₃
  - \( \begin{array}{cccccccc} F & F & F & F & F & F & F & O \end{array} \)

- FTOH
  - CF₃
  - \( \begin{array}{cccccccc} F & F & F & F & F & F & F & OH \\ F & F & F & F & F & F & F \\ \end{array} \)
Uses

- Polymerization of Fluoropolymers
- Whetting efficiency
- Harsh environments
- Green products which improve process efficiency have included fluorinated surfactants.

Environmental Emissions PFOA

K Prevedouros, et al. EST, 2006, 32-44.
PFOS Emissions

Estimated Global Production volume of PFOS

<table>
<thead>
<tr>
<th>Period</th>
<th># of Years</th>
<th>Global Production (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1957 - 1975</td>
<td>19</td>
<td>3905</td>
</tr>
<tr>
<td>1976 - 1984</td>
<td>9</td>
<td>12859</td>
</tr>
<tr>
<td>1985 - 1990</td>
<td>5</td>
<td>11907</td>
</tr>
<tr>
<td>1990 - 2002</td>
<td>13</td>
<td>36480</td>
</tr>
<tr>
<td>2003 - 2010</td>
<td>8</td>
<td>1460</td>
</tr>
<tr>
<td>TOTAL</td>
<td>54</td>
<td>66021</td>
</tr>
</tbody>
</table>


Environmental Partitioning

\[
\begin{align*}
\text{log } K_{AW} &\quad \text{log } K_{OC} & T_{1/2 \text{ air}} \\
\text{CP}_{3} & & -0.57 & 1.8 & - \\
\text{CP}_{3} & & 0.78 & 3.6 & 20 \\
\text{CP}_{1} & & -8 & 2.5 & - \\
\text{CP}_{2} & & -1 & 5.48 & 28 \\
\end{align*}
\]
Design for Degradation: BAF BCF

Table 6.5: Accumulation of PFAS in fish carcass (Martin et al. 2003).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Half-life (days)</th>
<th>BAF</th>
<th>BCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA C8</td>
<td>3.0±0.4</td>
<td>0.03±0.006</td>
<td>4.0±0.6</td>
</tr>
<tr>
<td>PFDA C10</td>
<td>9.9±1.3</td>
<td>0.23±0.04</td>
<td>450±62</td>
</tr>
<tr>
<td>PFUnA C11</td>
<td>11±1.4</td>
<td>0.38±0.04</td>
<td>2,700±400</td>
</tr>
<tr>
<td>PFDoA C12</td>
<td>15±1.9</td>
<td>0.43±0.06</td>
<td>18,000±2,700</td>
</tr>
<tr>
<td>PFTA C14</td>
<td>35±8.3</td>
<td>1.00±0.25</td>
<td>23,000±5,300</td>
</tr>
<tr>
<td>PFHxS C6</td>
<td>9.1±1.1</td>
<td>0.14±0.02</td>
<td>9.5±1.0</td>
</tr>
<tr>
<td>PFOS C8</td>
<td>12±1.8</td>
<td>0.32±0.05</td>
<td>1,100±100</td>
</tr>
</tbody>
</table>

US EPA
New Chemicals Program
To order testing:
Fish BCF/BAF ≥ 1000
To ban pending testing:
Fish BCF/BAF ≥ 5000

US EPA
Design for Environment
Low concern: BCF < 1000
Moderate concern:
1000 < BCF < 5000
High concern: BCF > 5000

Exposure

Figure 0.1: Human blood levels of PFOS-related substances in various countries
Human Blood concentrations


Telomere Alcohols in the Blood

Mabury et al. *EST*, 2007, 4799-4805
Health Hazards

In animal studies, toxicologists have seen that high doses of both PFOS and PFOA cause cancer, physical development delays, endocrine disruption, and neonatal mortality.

Regulation-Voluntary initiatives

1. Class Action Lawsuit against DuPont re. PFOA in drinking water.
3. EPA organized 8 companies to reduce PFOA by 2010, eliminate by 2015.
4. Canada proposed to eliminate manufacture and import of PFOS.
5. 2010 EU phase out of PFOS as use of alternatives becomes feasible.
Business Trends

Dyneon offers a broad line for fluorothermoplastic products. From the low temperature processability of our THV products to the high temperature resistance of our PFA and FEP products, Dyneon™ Fluorothermoplastics are innovative materials for applications in industries including food packaging, chemical processing and semiconductor manufacturing. Along with innovative products, we have the innovative technical and support teams who work directly with you to ensure your utmost satisfaction.

Transportation - Dyneon™ Fluoropolymers are increasingly found in the fuel and powertrain systems of a variety of vehicles because of their effectiveness as barriers against evaporative emissions, their chemical resistance to a broad variety of lubricants and fuels, their temperature resistance and their long-term durability.

CHEMFAB® Non-stick solutions are the result of pioneering work to develop high temperature, chemically resistant, flexible advanced materials. We support our customer with in-house technical capabilities that are unmatched in the industry. Our research staff conduct extensive studies in composites, reinforcements, cast films, coatings, laminates and fabrication techniques. Pilot plant and scale-up facilities are available to prototype your material. The key benefits are best summarized under 4 main groups of properties as follows:

Replacements For PFOA and PFOS

<table>
<thead>
<tr>
<th>Use area</th>
<th>Use of PFOA and related substances</th>
<th>Used alternatives</th>
<th>Other alternatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impregnation of</td>
<td>Largest use area in Denmark (16-80%). PFOS-related substances may have been phased out (at least in</td>
<td>Other highly fluorinated compounds, like fluorotelomer and</td>
<td>Silicone based products.</td>
</tr>
<tr>
<td>textiles, leather</td>
<td>the UK and Sweden).</td>
<td>fluorotelomer and PFBS.</td>
<td></td>
</tr>
<tr>
<td>and carpets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impregnation of</td>
<td>Major use area in Denmark (15-28%). PFOS and other PFAS-related substances may be going out of use</td>
<td>Fluorotelomer-based substances.</td>
<td></td>
</tr>
<tr>
<td>paper and cardboard</td>
<td>(at least in Canada, the UK, Norway and Sweden). However, DuPont states that they sell</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>telomer products for use in this application area.</td>
<td></td>
<td></td>
</tr>
</tbody>
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\text{O} \\
\text{S} \\
\text{CH}_3
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<tr>
<td>Wax and floor polishes</td>
<td>Large use area in Denmark (0.5-5%). PFOA-related substances are still used. Only some substitution has been carried out.</td>
<td>Fluorinated polyesters, Cₓ perfluorinated compounds, Tetramer-based substances.</td>
<td>Acrylates.</td>
</tr>
<tr>
<td>Paint/venetion</td>
<td>Former major use area in Denmark (18-25%). Substitution has been carried out. PFOA-related substances are no longer used, but PFAS-related compounds are used as well as other alternatives.</td>
<td>Other highly fluorinated compounds like PFBS, Propylated aromatics, Aliphatic alcohols, Silicone surfactants, Sulfosuccinates, Tetramer-based substances.</td>
<td>Fluorinated polyesters, Polyether-modified polydimethylsiloxane.</td>
</tr>
<tr>
<td>Fire-fighting foams</td>
<td>Minor use area in Denmark (0.3-1.1%). PFOA-related compounds have been phased out and fluorotetramer alcohols are used instead.</td>
<td>Perfluorooctaneomers based on Cₓ. Fluorine-free alternatives for.</td>
<td>Protein-based foams or synthetic detergent foams (but may not work).</td>
</tr>
</tbody>
</table>

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</thead>
<tbody>
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<td>Photographic industry</td>
<td>Minor use area in Denmark (0.2-1%). A shift to digital techniques has reduced the use drastically.</td>
<td>Tetramer-based surfactants products, based on ClₓFₓOₓ functionality. Hydrocarbon surfactants. Silicone products,</td>
<td>None identified.</td>
</tr>
<tr>
<td>Semiconductors</td>
<td>PFOA-free techniques are not yet ready for commercial use. May take up to 3 years.</td>
<td></td>
<td>None identified.</td>
</tr>
<tr>
<td>Hydraulic oils</td>
<td>PFOA-related compounds are not used, but other PFAS-related compounds are. PFAS-free techniques are not available, as tetramers cannot be used. May take up to 10 years to find replacements.</td>
<td></td>
<td>None identified.</td>
</tr>
<tr>
<td>Metal surface treatment</td>
<td>Large use area in Denmark (0.6-8%). Working on identifying alternatives to Cr (VI) in chromating and hard chromium plating, which will make the use of PFOS-compounds unnecessary. Cr (III) has already replaced Cr (VI) in decorative chromium plating.</td>
<td></td>
<td>None identified.</td>
</tr>
<tr>
<td>Plumbing (flushing agents)</td>
<td>Minor use in Denmark (0.3%). Banning of lead (2006) in electrical and electronic equipment will automatically phase out the need for PFOA-related compounds.</td>
<td></td>
<td>Not necessary.</td>
</tr>
</tbody>
</table>
Alternatives: Polymerization aid to Replace PFOA in H₂O

Which would you choose, and why?

1. 
2. 
3. 
4. 
5. 
6.