

Brief History of Perfluorochemical
Production, Products and Environmental
Presence

Michael A. Santoro
Director, Regulatory Affairs
3M Company, St. Paul, MN

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Timeline of Major Milestones

- **Late 1940's – 3M purchase of Simon Electrofluorination Patent**
- **1950's – Development of PFOS substances and PFOA
– Scotchgard Brand**
- **1960 - 1980's – Expanded list of products**
- **Late 1990's – Development of improved analytical capability
– Finding of wide-spread presence (PFOS and PFOA)**
- **2000 – Phase-out announcement of production (PFOS and PFOA)**
- **2002 – Global production cessation (PFOS and PFOA)**
- **2007 – Development of a PFOA substitute**

PROCESS FLOW DIAGRAM

Electro-Chemical Fluorination Cells
(Hydrocarbon Feed Stock + HF + electrical energy)



Perfluorooctane sulfonyl fluoride



Secondary Reactors



**Various commercialized
intermediates and
surfactants**



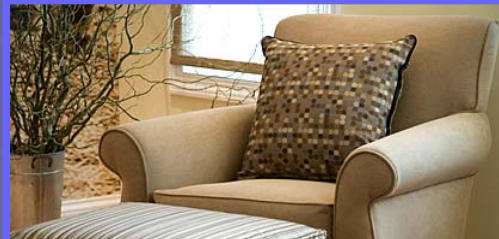
**Acrylate Polymers
Urethane Polymers**

Perfluorocarbon Chemistry

- Fluorine forms the strongest known single bond to carbon (C – F)
- Perfluorocarbons (PFC's) are organic materials that differ markedly from other materials
- Very stable and non-reactive
- Effective in very low concentrations
- Oleophobic and hydrophobic

Product Applications

- The family of PFCs are used to make products that are resistant to water, oil and extreme temperatures.
- Some important applications:
 - Stain repellants
 - Protective coatings for electrical wiring
 - Fire fighting foam
 - Semiconductor manufacturing
 - Aviation hydraulic fluid



Finding of Wide-Spread Presence

- Analytical methodology development by 3M
- Two compounds found in the environment and in humans:

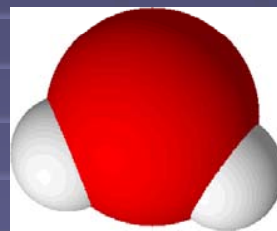
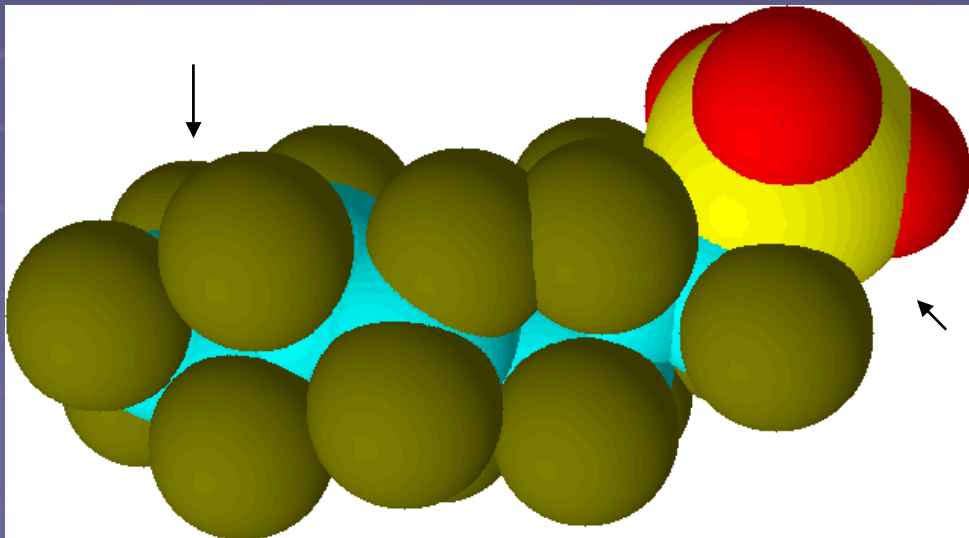
Perfluorooctane Sulfonate: $C_8F_{17}SO_3^-$

Perfluorooctane Carboxylate: $C_7F_{15}COO^-$

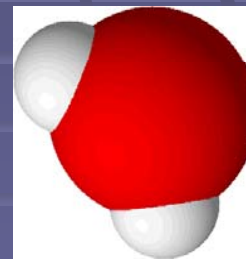
Perfluorooctanesulfonate (PFOS)

- Has two “ends”. One is Hydrophobic (water repelling) and the other is Hydrophilic (water soluble)

Green End: Hydrophobic
or Water Repelling



Water



Yellow/Red End: Hydrophilic
or Water Soluble

Characteristics of PFOS

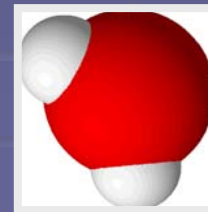
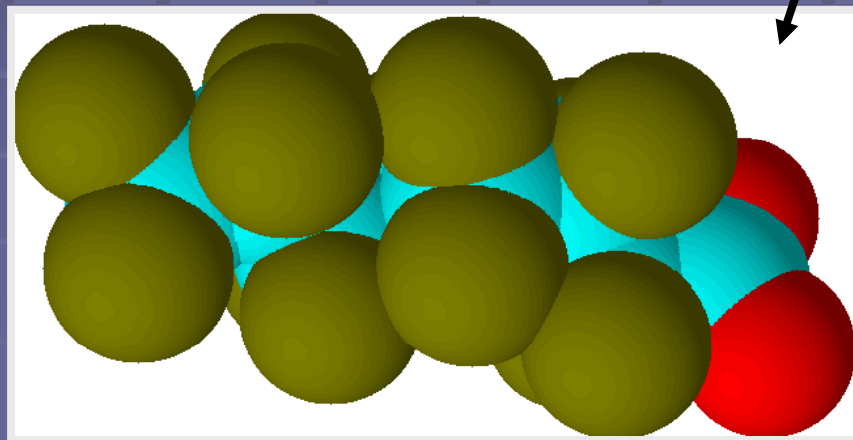
- **Man-made substance**
- **Persistent, not-biodegradable and potential to bio-accumulate**
- **Long half-life in humans**
- **Breakdown product of POSF-based chemistry**
- **3M was the major global producer of POSF-based products and the only producer in the US**

Perfluorooctanoic Acid (PFOA)

- Like PFOS, PFOA has two “ends”. One is Hydrophobic (water repelling) and the other is Hydrophilic (water soluble)

Green End: Hydrophobic
or Water Repellant

Red End: Hydrophilic
or Water Soluble



Characteristics of PFOA

- **Similar to PFOS, with differences in toxicology**
- **3M the former major producer (now produced by other companies)**
- **Essential for production of fluoropolymers**
- **Persistent, not-biodegradable and potential to bio-accumulate**
- **Can form through the degradation of telomer chemistry**

3M Actions

- **Understand the science (hazard, exposure, risk)**
- **Improve process understanding**
- **Enhance waste and emissions controls**
- **Inform customers**
- **Engage regulatory bodies globally**
- **Develop alternative chemistry**

Conclusion of Scientific Research

- **No adverse effects from either PFOS or PFOA at the levels found in people and the environment**
- **Difficult to determine source of exposure and distribution of PFC in the environment**
- **Phase-out announcement of May 2000**

Reasons for the Phase-out Decision

- PFOS is widespread in the environment, and 3M did not want to add to its presence
- 3M committed to responsible environmental management and sound business practices
- Desire to direct energies to other business opportunities
- Voluntary business decision to phase-out of production of perfluorooctanyl chemistry, included:
 - PFOS-based production
 - PFHS-based production
 - PFOA-based production

Phase-out of PFOS-related Substances

- Focus on “production”
- Voluntary action
- Submission of Phase-out plan to US EPA
- Customer interactions
- Two target dates – end of 2000, end of 2002
- Accounted for critical use applications
 - Specific products having safety benefits
 - No technically acceptable substitute
 - Government specified products

Status of 3M Phase-Out Implementation

- End of 2000: 90% PFOS production cessation
Protective chemicals, surfactants, consumer products
- End of 2002: 100% PFOS global production cessation
Substances for SEMI-conductor industry, aviation hydraulic fluid, photolithography, fire-fighting foams
- End of 2002: 100% PFOA production cessation
- Continuing internal “use” of PFOA for fluoropolymer production at a facility outside the US
- Levels of PFOS have decreased by 50% in humans and the environment

3M Activities Related to PFOA

- Developed recycle/reuse technology in Germany
 - Product content and emissions of PFOA reduced
- Technology licensed to other companies
- Participation in EPA Stewardship Program
- PFOA substitute developed – 2007

Ongoing Global PFOS Production/Use

- Some production in Italy, Japan and China by other companies
- SNUR exemptions allow for importation and use in the U.S.
- Inventory use allowed in the U.S.
- In the EU inventories can be used now but will be impacted by the Marketing Use Directive

Ongoing Global PFOA Production/Use

- Presently produced by another company in the US
- Some production in Japan and China
- Continued use globally as an essential processing aid in fluoropolymer production
- Degradant of telomer-based products used in protective treatments and surfactants

3M Ongoing Research and Activities

- Inform the scientific discourse through additional studies and publications
- Evaluate former production and disposal sites
- Implement appropriate management steps at these sites
- Work closely and cooperatively with state agencies
- Overall goal: to demonstrate that potential exposure to these compounds is minimized

Summary

- PFOS, PFOS-related substances, and PFOA production at 3M has ceased globally
- “Levels of PFOS have decreased by 50% in humans and the environment”
- US EPA SNUR regulates manufacturing and importation of many of these substances – some exemptions allowed
- EU Marketing and Use Directive will control future manufacturing and use in those countries – some exemptions allowed
- Production continues in some Asian countries (may be impacted by global treaties)