

Alternative Fluorochemistries to PFOS, PFOA & other PFAS with Known Human Health Risks

May 10, 2018



Overview

- About FluoroCouncil
- History of PFAS Manufacturing and Transition to Modern PFAS Products
- PFAS Uses
- Best Practices and Product Stewardship
- Questions/Discussion

About FluoroCouncil

About FluoroCouncil

Represents the world's leading manufacturers of FluoroTechnology products

Our Focus:

- Support end use market access to the unique and critical benefits of FluoroTechnology
- Work with regulators to facilitate global transition from long-chain substances (e.g., PFOA) to more sustainable alternatives
- Support science- and risk-based regulatory outcomes that facilitate this transition

Archroma
Management
LLC

Arkema
France

Asahi Glass
Co., Ltd.

Daikin
Industries,
Ltd.

Solvay
Specialty
Polymers

The Chemours
Company LLC

Dynax
(associate)

Tyco Fire
Products LP
(associate)

History of PFAS Manufacturing and Transition to Modern PFAS Products

Overall Transition to Today's PFAS Products

Shift in Fluoropolymer Polymerization Aids

PFOA/Long-Chain
Polymerization Aids



Today's
Polymerization Aids
(a variety of
solutions)

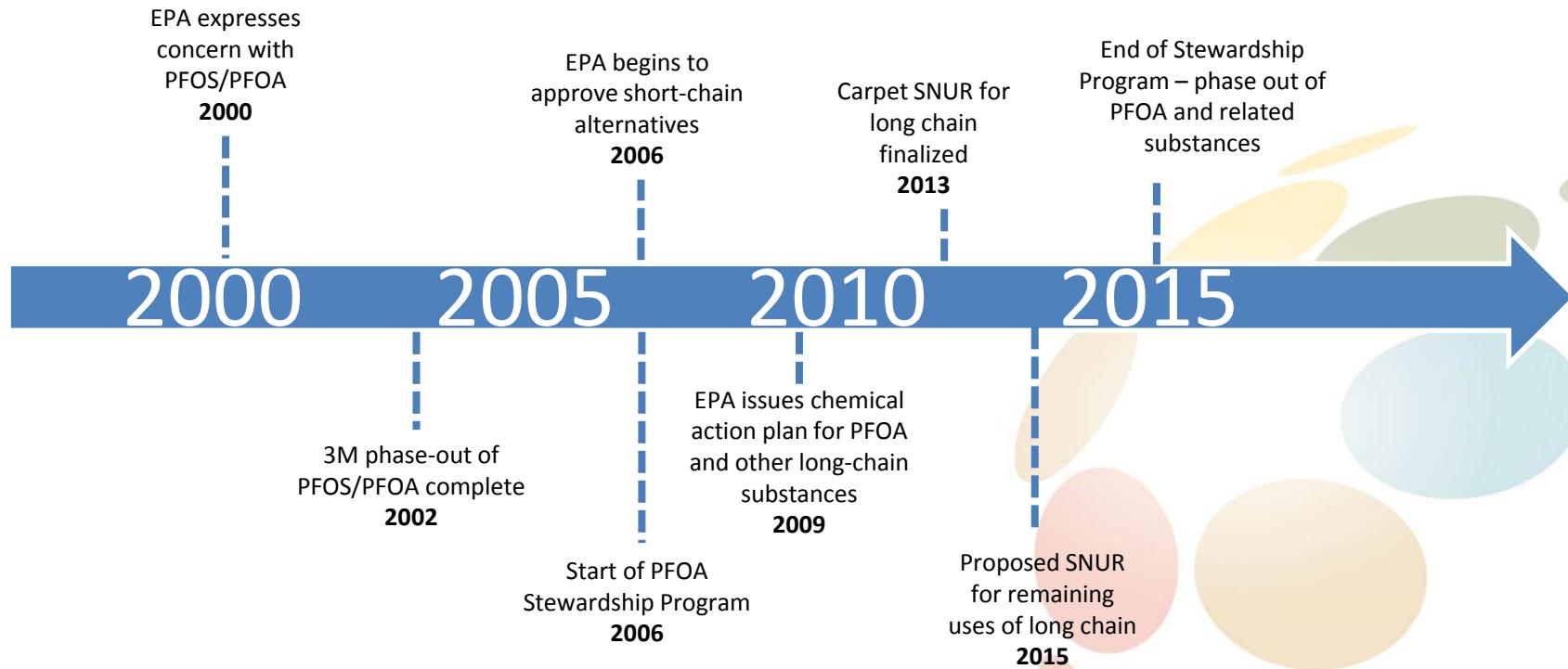
Shift in Fluorotelomer-based Products Manufactured

Long-chain
Fluorotelomer-
based Products



Short-chain
FluoroTelomer-
based Products

U.S. Long-chain PFAS History Highlights



Phase-out of PFOS

- 3M/EPA announced phase-out plan in May 2000
 - 3M U.S. production of PFOS stopped at end of 2002
- EPA issued TSCA Significant New Use Rules (SNUR) to lock in 3M commitment to phase-out
 - Rules issued in 2002 and 2007 (271 chemicals)
 - Rules did not cover PFOS in imported articles
- Proposed rule (2015) issued to cover PFOS in carpets
 - Gap in coverage for other articles will remain

PFOS: Shifts in Global Market Profile

- Est. global historic emissions (1970 – 2002)*:
 - Raw Material: PFOSF ($\text{F-C}_8\text{F}_{16}\text{-SO}_2\text{F}$): 6,800t – 42,250t
 - PFOS ($\text{F-C}_8\text{F}_{16}\text{-SO}_3^-$) : 450t – 2,700t
- 2003: PFOSF and PFOS production ceased in the U.S.
- 2006: PFOSF production in China** increased to 250t/a
- Today:
 - PFOSF and PFOS production continues outside the U.S.
 - PFOS contains >10% PFOA, ~10% PFHxS, and other short-chain PFSAs and PFCAs as impurities***
 - Potential use of stockpiled PFOS-based firefighting foams

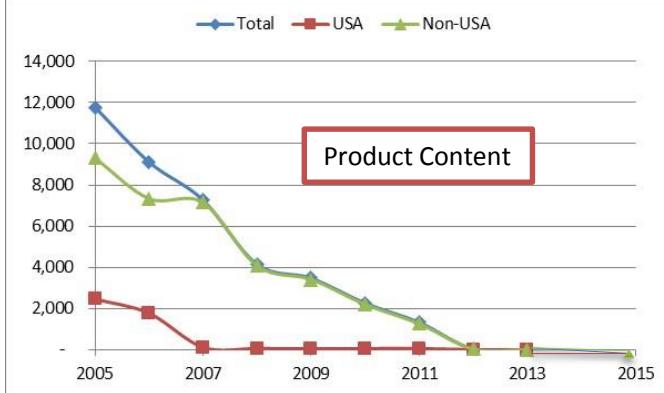
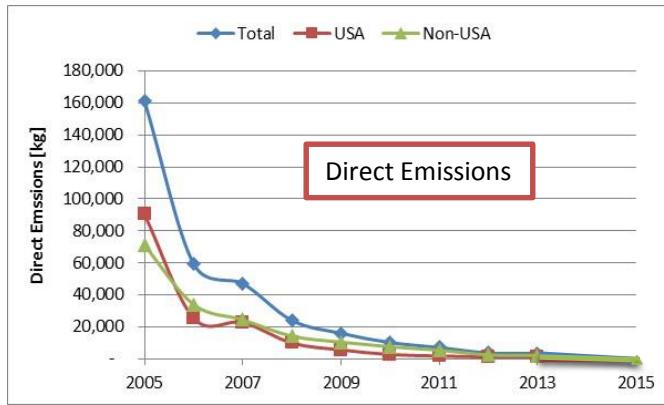
*Paul et al., Environ. Sci. Technol. 2009, **43**, 386-292

** W. Han, 2009. PFOS Related Actions in China. International Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives, p. 12-13 and Xie et al., Environ. Int. 2013, 52, 1-8

*** Jiang et al., Chemosphere 2015, **127**, 180-187

While FluoroCouncil members have never manufactured, sold or used PFOS, this public information is provided for historical context.

EPA 2010/2015 PFOA Stewardship Program



- Global and voluntary partnership between U.S. EPA and industry aimed to reduce human and environmental exposure to PFOA, its precursors and higher homologues
 - ✓ All companies met the goal in 2015 or earlier:
https://www.epa.gov/sites/production/files/2017-02/documents/2016_pfoa_stewardship_summary_table_0.pdf
 - ✓ Led to virtual elimination of those chemicals from facility emissions to all media and product content
- Similar program in place with Canada
- Participating companies:
 - Archroma
 - Asahi Glass Company
 - DuPont/Chemours
 - BASF Corporation
 - Arkema Inc.
 - Daikin America, Inc.
 - Solvay Solexis, Inc.
 - 3M/Dyneon
- <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass#tab-3>
- Baseline = Year 2000 or other

U.S. EPA New Chemicals Program – Alternative Products

- Industry submitted PMNs for alternatives
- EPA issued TSCA Section 5(e) Orders
 - For fluorotelomers, focus on common degradant (PFHxA)
 - Testing allocated among PMN submitters to assure comprehensive picture
 - For example: testing for cancer, reproductive/developmental, systemic toxicity, bioretention, ecological endpoints, environmental fate and transport
- Alternative products approved for manufacture, sale and use
- Data generated during this process established the value of transitioning from long-chain to short-chain chemistry

Status of PFAS of Concern

- Through the EPA PFOA Stewardship Program, PFOA and related “long chain” PFASs have been voluntarily phased out by major manufacturers in the U.S., Europe, and Japan
 - PFOA no longer used as processing aid in manufacture of fluoroplastics
 - Long-chain fluorotelomer-based products replaced with short-chains
- EPA plan to back up this stewardship with regulation did not occur
 - Proposed EPA SNUR is limited and would not stop import of components made with PFOA
- Manufacture and use of PFOA and long-chain fluorotelomer-based products continues in China/India/Russia under **no existing regulation**
- Import of PFOA in consumer articles is currently permitted in the U.S.

Fluorotelomer Manufacturing: Shift to Short-Chains

1970s - 2015

Historical long-chain product mixtures



2002 - 2015

Manufacturing Innovation and Process Reengineering
Short-chains

2005 - Present

C6

Short-Chain Fluorotelomer Intermediates & Products
 $n = 2$ or 3

Phase-out of long-chain PFAS under Stewardship Program resulted in significant **innovation** and **simplification** in fluorotelomer manufacturing

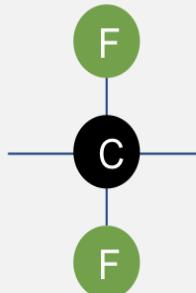
Transition to Alternatives

- Replacing long-chain substances has been a major challenge:
 - Over \$700M invested and ten+ years of research into the development of alternatives
 - Investigated a large universe of options: “short-chain” alternatives represent the most feasible and sustainable of those options.
- Replacement products reflect a careful balance.
 - Meet or approximate performance and current products and manufacturing standards of long-chain technology
 - Extensive toxicological and environmental testing data have been generated
 - Are approved/registered for use in key countries/regions around the world
- Lack of other options that meet all these criteria.
 - Non-fluorinated alternatives have not always met criteria for performance set by downstream industries
 - Lack of human health and environmental data about many non-fluorinated materials

PFAS Uses

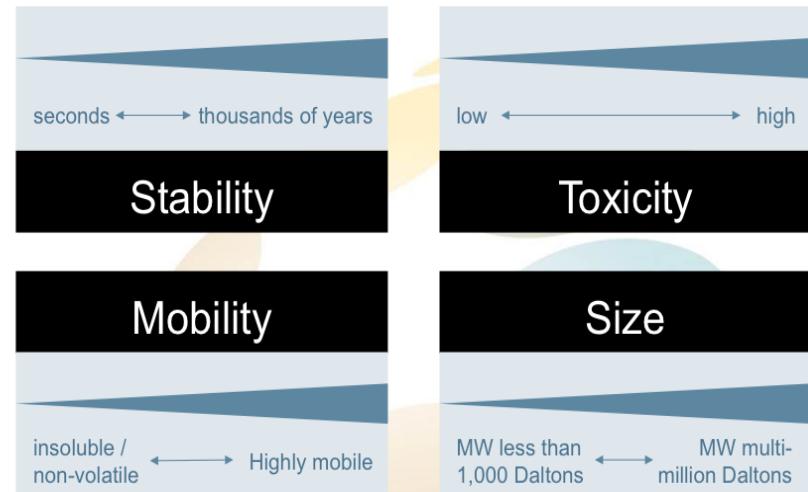
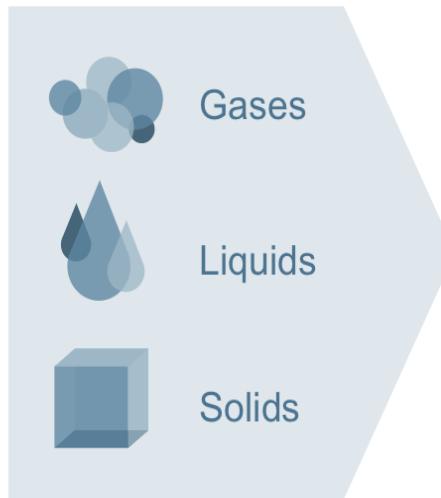
Overview: PFAS includes thousands of substances with very different properties

Similarities



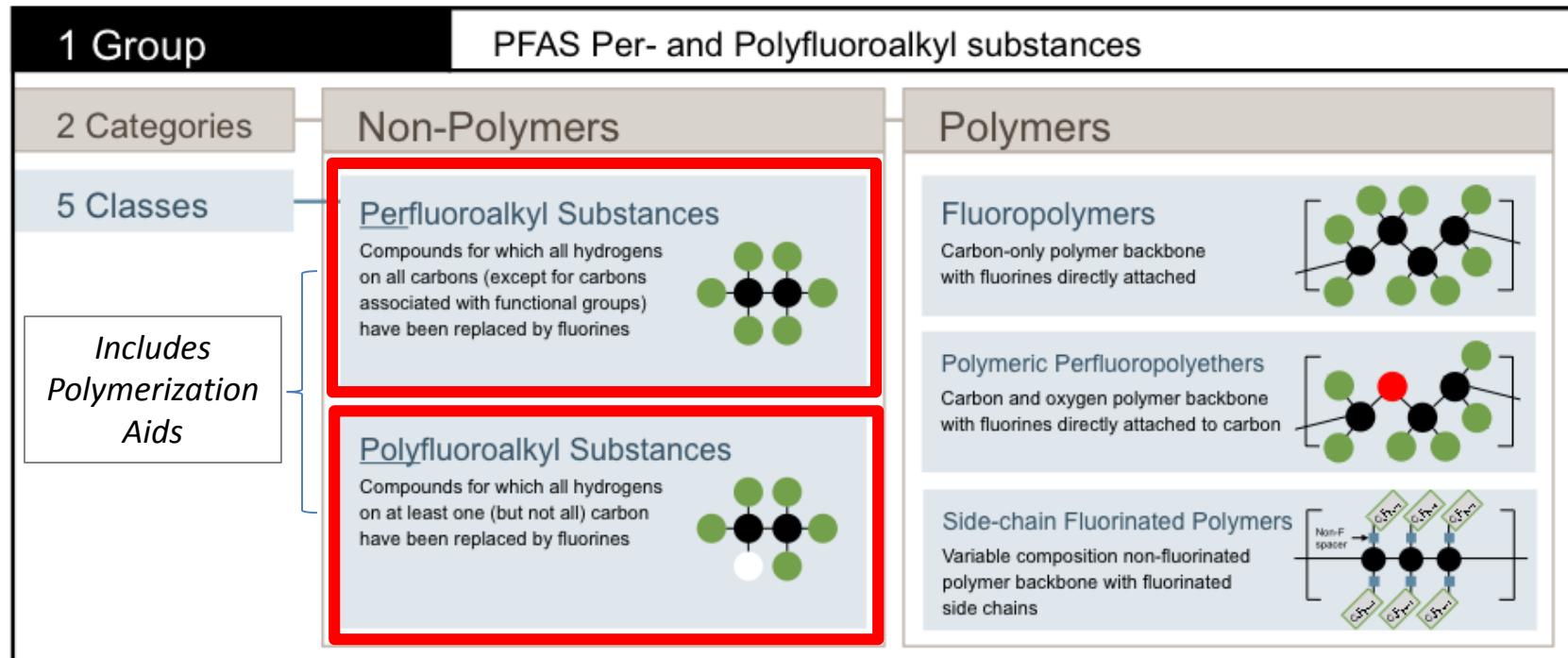
1 fully fluorinated carbon

Differences



PFAS - Categories and Classes: Polymerization Aids

● Fluorine
● Carbon
● Oxygen
○ Hydrogen



Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins.

Integrated Environmental Assessment and Management 2011, 7, (4), 513-541.

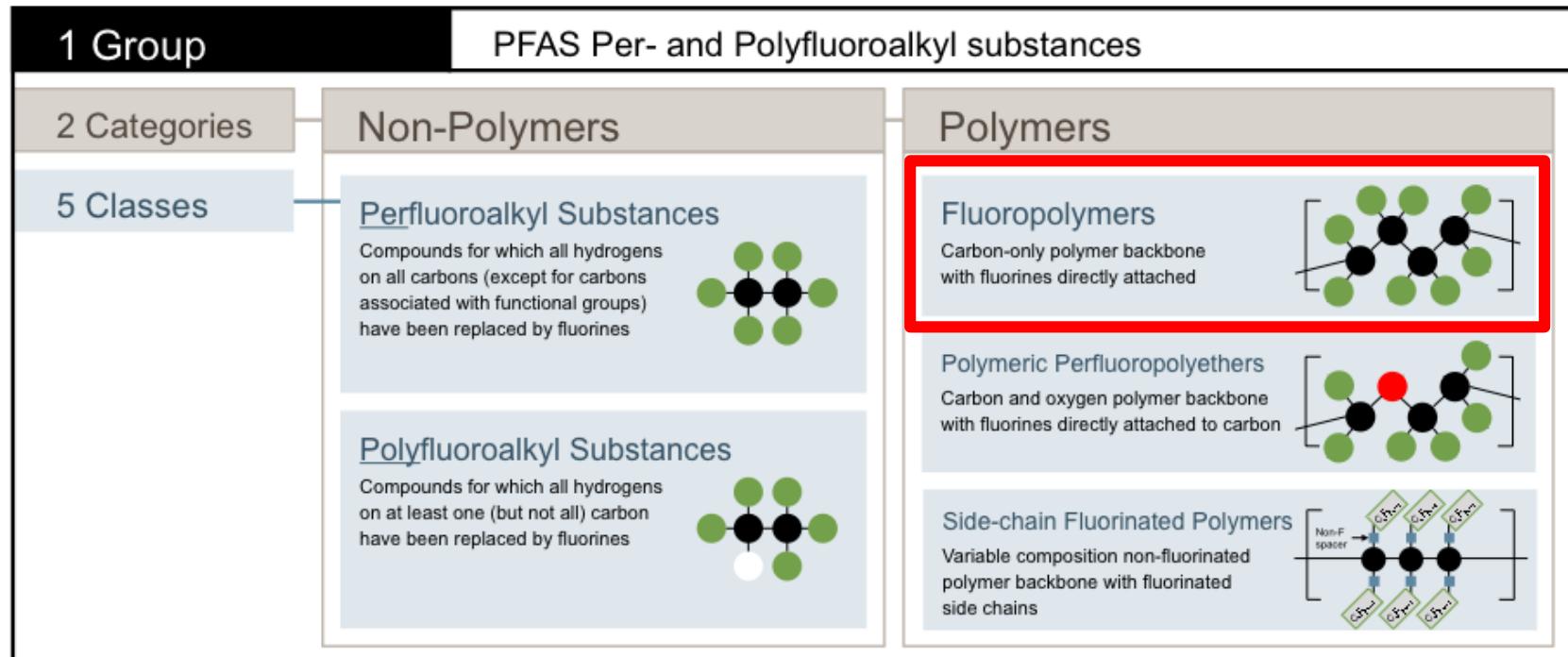
<http://dx.doi.org/10.1002/eam.258>

Polymerization Aids Used in the U.S. Today

- Have been reviewed by EPA's new chemicals program,
 - Subject to administrative orders under TSCA Section 5(e)
 - Supported by health and safety data
- Working to develop and implement a polymerization aid stewardship program
 - Minimizing emissions
 - Reducing product content (in fluoropolymer products)

PFAS - Categories and Classes: Fluoropolymers

● Fluorine
● Carbon
● Oxygen
○ Hydrogen



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<http://dx.doi.org/10.1002/ieam.258>

About Fluoropolymers

- High molecular weight polymers
 - e.g., PTFE, ETFE, PVDF, FEP, fluoroelastomers (FKM)
- Too large to be bioavailable: 0.5-1MM MW
 - Not toxic, Not bioaccumulative
- Highly stable under all types of environmental conditions
 - Therefore cannot break down to PFAS of concern
- Do not present a significant risk to human health or the environment

Fluoropolymers - Key Properties



Durability



Inertness



Mechanical
strength



Thermal stability



Resistance to
degradation

Example Fluoropolymer Applications



Electronics: High frequency signal transmission; smudge-resistant touch screens



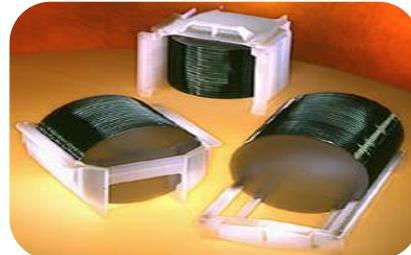
Membranes in outdoor apparel, providing a breathable barrier against wind and rain



Medical Devices: High dielectric insulators in medical equipment that relies on high frequency signals



Aerospace/Auto: Weight reducing fuel lines; heat/chemical resistant wire coatings



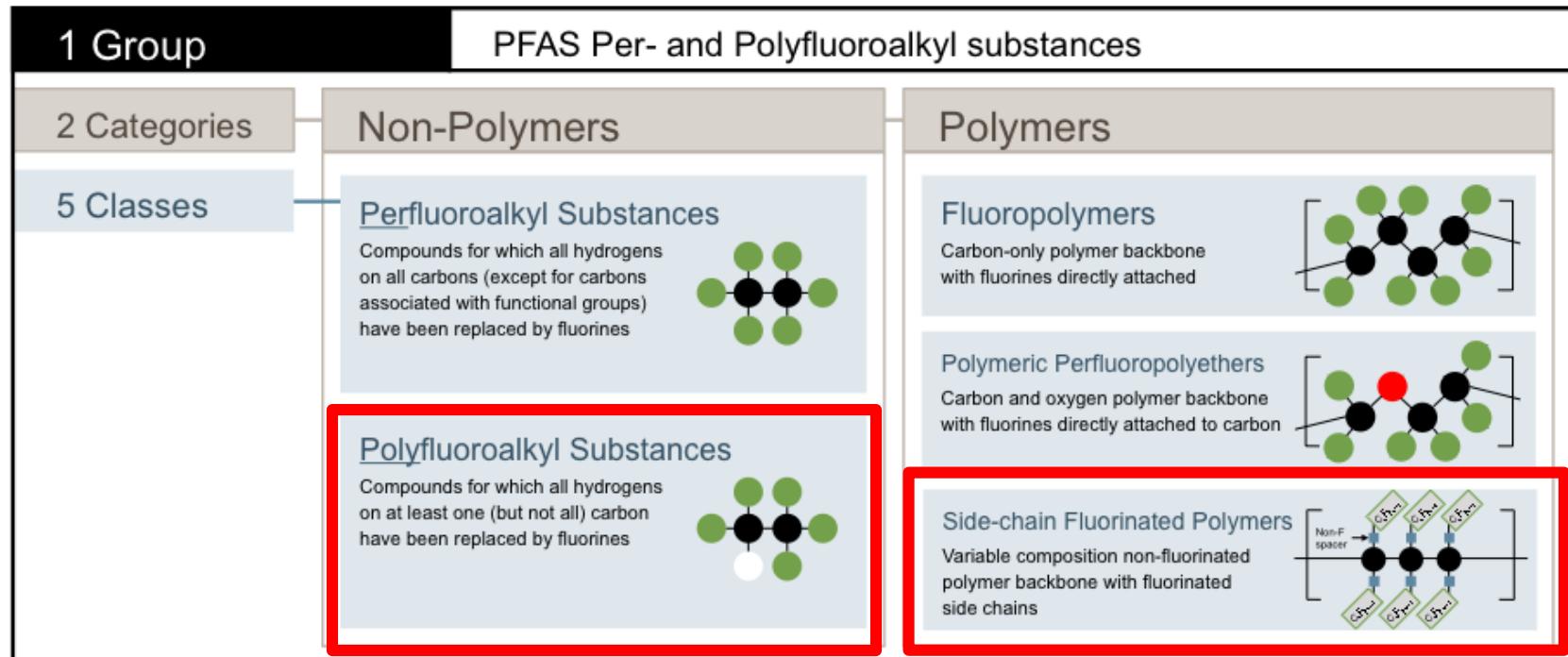
Semiconductor manufacturing: Providing pure environments to transport/store harsh chemicals



Nonstick surfaces in cookware and small appliances

PFAS - Categories and Classes: Fluorotelomer-based Substances

● Fluorine
● Carbon
● Oxygen
○ Hydrogen



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Fluorotelomer-based Products: Short-chain PFAS

- Chemistry:
 - C6 fluorinated chains attached to organic polymer backbones (e.g., side-chain fluorinated polymers).
 - For polymers with C6 fluorinated side-chains, any degradation is likely to take a very long time (i.e., 1,000+ years). Recently completed 15-month OECD 307 aerobic soil study* on this type of polymer reported:
 - “The study revealed a very low potential for aerobic biological transformation processes of the test item.”
 - The calculated half-lives ($t_{1/2}$) of the polymer were between 3,000 to 5,500 years depending on soil type
- Hazard Profile of Polymeric Products:
 - Widely understood not to present toxicity concerns
 - Not bioavailable
 - Hazard is characterized by their degradation products (example: PFHxA)
- Properties:
 - Polymers: Surface modification & protection, water & oil repellency, grease resistance as well as soil resistance and release
 - Surfactants: Wetting and leveling

* Nuva RP2116 GA 39/13-1 - Aerobic Transformation in Soil study conducted under OECD 307 by Noack Laboratory GmbH (November 1, 2017). Submitted to U.S. EPA by Archroma U.S. Inc. on November 11, 2017.

Example Fluorotelomer-based Product Applications



Healthcare: Garments/Drapes that Protect Against Disease Transmission



First Responder Gear Treatments and Bulletproof Vests that Maintain Performance in Extreme Conditions



Oil/Grease Resistant Food Packaging that is Recyclable, Increases Shelf-Life, Reduces Packaging



Textiles/Carpet with Water/Oil Repellency, Stain Resistance and Soil Release and Longer Useful Life



Class B (Flammable Liquid) Fire Fighting Foam with Shorter Extinguishing Time and Burnback Resistance

Industry Best Practices - Reduces Environmental Release and Potential For Exposure



**Fire
Fighting
Foam
Coalition**

**Best Practice
Guidance for
Use of Class B
Fire Fighting Foams**

March 2016

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1. Use the product only when necessary
2. Use only what you need
3. Reuse/recycle residual liquids if possible
4. Minimize waste and emissions
5. Dispose of all chemicals properly



FluoroCouncil
Global Industry Council
for FluoroTechnology

**Guidance for Best Environmental
Practices (BEP) for the
Global Apparel Industry**
Including Focus on Fluorinated Repellent Products



May 2014

Thank You

Please contact Jessica Bowman of FluoroCouncil for further information at jessica_bowman@fluorocouncil.org or 202-249-6737 or visit <https://fluorocouncil.org/>

