Loureiro

Per- and Polyfluoroalkyl Substances (PFAS) in Consumer Products, Part 2

Historical Uses of PFAS

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Why are the historical uses of PFAS important?

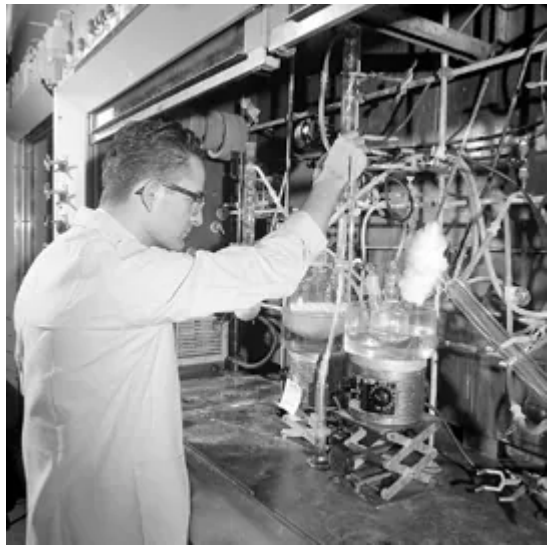
- **PFAS - one of the most dynamic emerging contaminant classes**
  - Sources – many known, more unknown?
  - Fate and Transport - prevalent in the environment including atmospheric deposition
  - Regulatory Status - Federal and State action levels / criteria / wastewater
  - Treatment Technology – proven/mature and experimental/evolving
- **Who, What, When, Where, Why, and How**

General Background

- PFAS – in use since the 1940s, US manufacturing reduction/elimination from 2010 to 2015
- PFAS – China, India and Russia manufacturing replaces US manufacturing
- PFAS - studied since the 1990s, gained significant traction when the EPA published health advisories in 2016
- PFOA/PFOS - in the news in Connecticut and across the US
- Federal – initially slow to act/moving faster now
- States – States take action establishing drinking water and remediation criteria, requiring assessment and remedial action

Where to Begin?

Industrial archaeology is the systematic study of material evidence associated with the industrial past.[1]



The field of industrial archaeology incorporates a range of disciplines including archaeology, architecture, construction, engineering, historic preservation, museology, technology, urban planning and other specialties, in order to piece together the history of past industrial activities.[2]

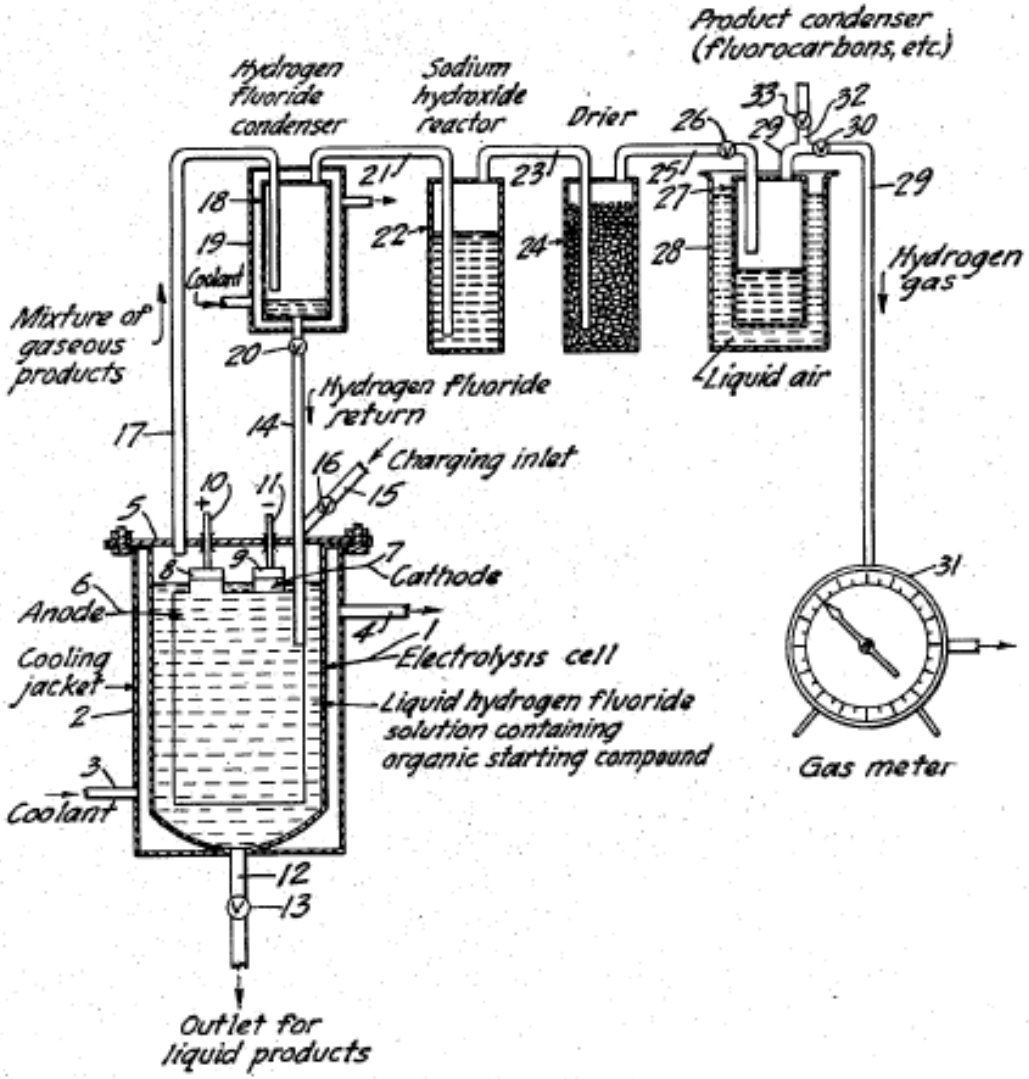
1 - Industrial Archaeology: Principles and Practice, Peter Neaverson and Marilyn Palmer, Routledge, 1998, chapter 1
2 - Society for Industrial Archeology. "About the Society for Industrial Archeology (SIA)". Siahq.org. Retrieved 2014-01-29.
https://www.3m.com/3M/en_US/company-us/about-3m/history/

The Beginning

Application US2519983

1948-11-29 Application 3M

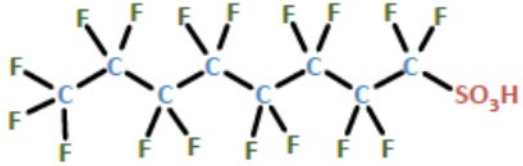
"electrolyzing a liquid hydrogen fluoride (HF) solution containing a fluorinatable organic starting compound, at an electrolyzing potential which is insufficient to generate free fluorine under the existing conditions, but which is sufficient to cause the production of fluorine-containing carbon compound products at a useful rate



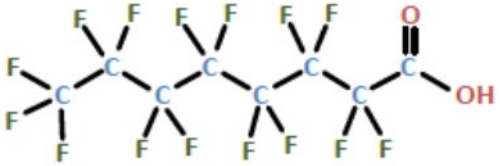
Unique Chemistry

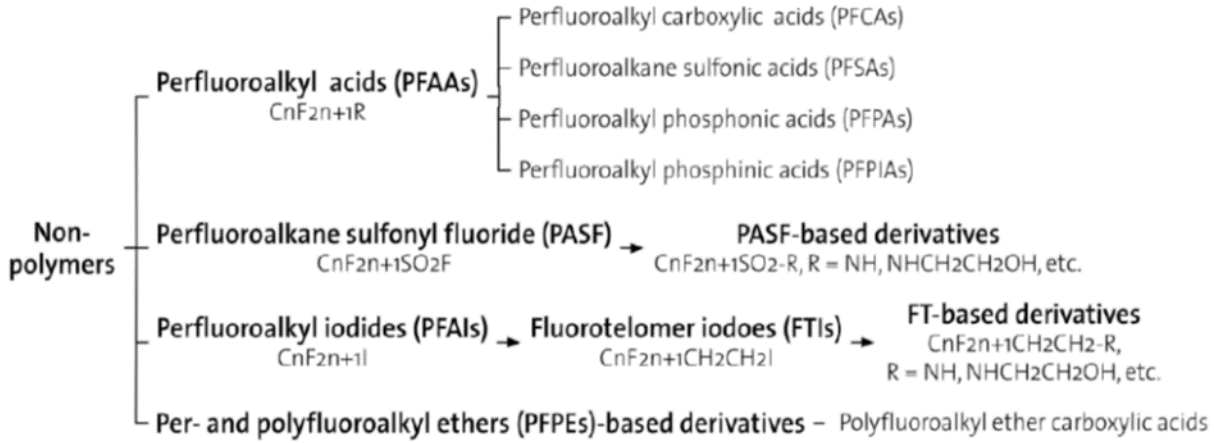
The highly stable carbon-fluorine bond and the unique physicochemical properties of PFASs make these substances valuable ingredients for products with high versatility, strength, resilience and durability, which provide benefits to manufacturers and consumers.

PFOS - Perfluorooctanesulfonic Acid



PFOA - Perfluorooctanoic Acid





Sources: Discovery / Manufacturing

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production		Protective Coatings				
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

Approach

- **Who: Businesses Identification**
  - Identifying Industries – SIC/NAICS Industry Operations/Processes - Source Identification
- **What: Source Identification**
  - Identifying Past and Present Operations/Processes – SDSs
- **When: Source Evaluation**
  - Understanding Site/Facility History
- **Where: Source Investigation**
  - Site/Facility Site Considerations

Sources

- **Aqueous Film Forming Foam (AFFF)**
  - Class B Foams: high-hazard flammable liquid fires
- **Metal Plating and Finishing**
  - Surfactant, Wetting Agent and Mist Suppressant
- **Industrial Products**
  - Paints/Coatings, Plastics, Resins, Adhesives, Antifogging
- **Oil and Water Repellant Products**
  - Textiles, Paper and Cardboard Packaging
- **Consumer Products**
  - Cleaning Products, Cosmetics and Personal Care

Aqueous Film Forming Foam (AFFF):

- Class A and B foams
- Class A foams are for normal combustibles causes water penetration by reducing surface tension
- Class B foams are for high-hazard flammable liquid fires and often contain PFAS
- Class B foams are synthetic foams – AFFF, alcohol-resistant aqueous film-forming foam (AR-AFFF) or protein foams

Aqueous Film Forming Foam (AFFF) Class B Foams:

- **Legacy PFOS Foams**
  - Long-carbon-chain fluorinated compounds (C8), PFOS/PFOA
  - Manufactured prior to 2003 by 3M, brand name “Lightwater”
- **Legacy Fluorotelomer Foams**
  - Contain some long-chain PFAS
  - Manufactured from the 1970s until 2016 and include all other brands of AFFF.
  - Contain polyfluorinated precursors that break down to PFOA/PFAS and by-products
- **Modern Fluorotelomer Foams**
  - Short-chain (C6) fluorotelomers or short-carbon-chain fluorinated compounds
  - Manufactured from around 2010 to present
  - May still have trace levels of PFOA and PFOA precursors
- **Flourine Free Foams**

PFAS Fact Sheet Aqueous Film-Forming Foam, *Interstate Technology Regulatory Council* **October 2018**.

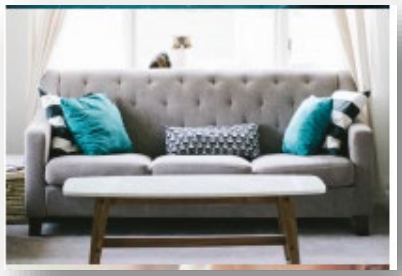
Metal Plating and Finishing:

- **Surfactant, wetting agent and mist suppressant – primarily chromium**
  - US2846380, Patented August 5 1958
  - Regulatory Requirement from 1988 CA/1995 EPA to 2015
    - Benchmark Benchbrite STX AB (custom-made), Benchmark Benchbrite STX, Benchmark CFS, MacDermid Proquel B, MacDermid Macuplex STR, Plating Process Systems PMS-R, Fumetrol-140, Fumetrol 210, Brite Guard AF-1 fume control, Fluorotenside-248, SurTec 960
- **Electroless plating of copper**
- **Depositing nickel-boron layers**
- **Electroplating of copper, nickel, and tin**
- **Zinc electrodeposition**
- **Others**

History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* November 2017. Capsule Report Hard Chrome Suppressants and Control Technologies. USEPA December 2018. PFOS Chromium Electroplater Study EPA Region 5 September 2009

Oil and Water Repellant Products:

- **Textiles**
  - jackets, shoes, and umbrellas
  - carpets, upholstery, and leather
  - tents and sails
    - Scotchgard (3M) and Zonyl, Foraperle, and Capstone (DuPont), fluorochemical (3M FC-808)
- **Paper and Cardboard Packaging**
  - plates, popcorn bags, pizza boxes, and food containers and wraps
    - Scotchban (3M), Baysize S (Bayer), Lodyne (Ciba, BASF), Cartafluor (Clariant), and Zonyl (DuPont)



History and Use of Per- and Polyfluoroalkyl Substances (PFAS). *Interstate Technology Regulatory Council* November 2017.

Industrial/Consumer Products:

- **Paints and Coating**
  - reduce surface tension for substrate wetting, levelling, dispersing agents, and improving gloss and antistatic properties
- **Plastics, resins, and rubbers**
  - polytetrafluoroethylene (PTFE) and polyvinylidine fluoride (PVDF)
- **Adhesives, Antifogging**

Consumer Products:

- **Cleaning Products**
  - carpet spot cleaners, alkaline cleaners, denture cleaners and shampoos, floor polish, and dishwashing liquids
  - car wash products and automobile waxes
  - Novec (3M) and PolyFox (OMNOVA Solutions)
- **Cosmetics and Personal Care**
  - emulsifiers, lubricants, or oleophobic agents
  - hair-conditioning formulations and hair creams
  - toothpastes, sunscreen, dental floss

Consumer Product Example

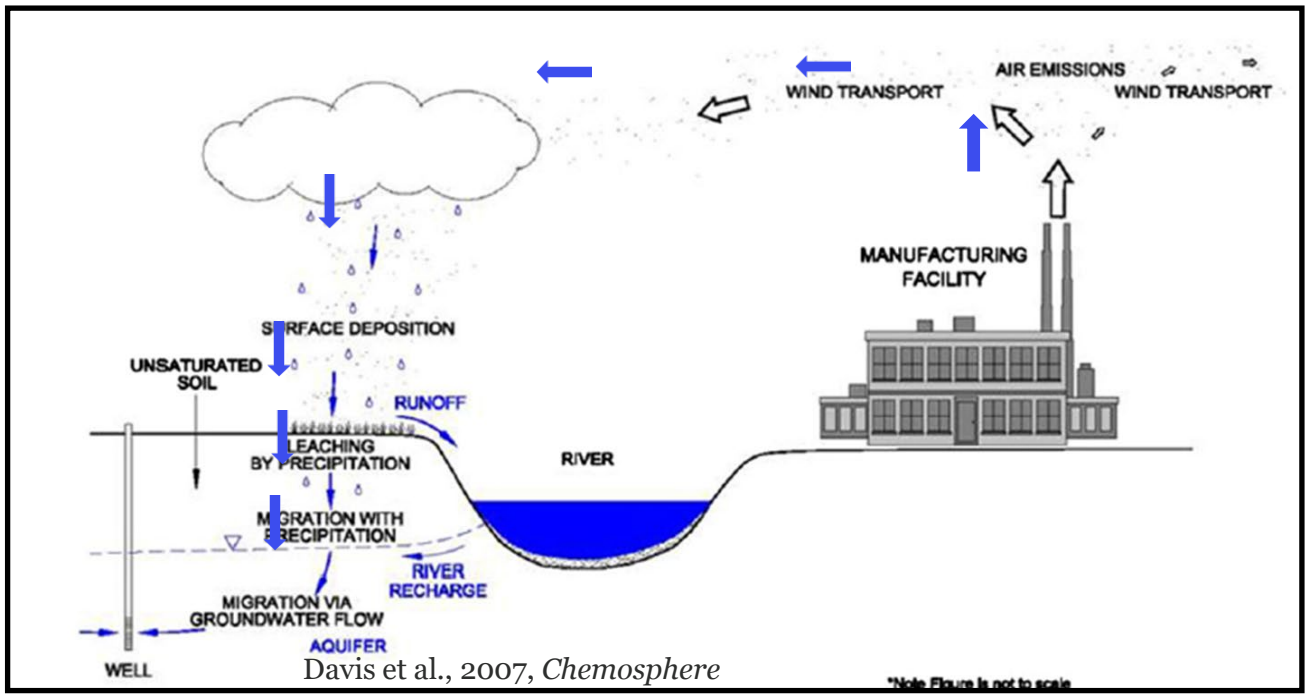
- **BLANK COMPANY LIQUID POLISHING COMPOSITION DRIABLE TO A BRIGHT COATING**
- **US2937098 Patented May 17, 1960**
  - Company came into being as the first American car wax company in 1911. Its formation was made possible by the founder, who developed a cleaner and a carnauba wax product for car finishes.
  - It was during 1957 that a “One-Step Cleaner” entered the market. Combining a cleaner and wax in one product,
  - An Institutional Division organized in 1954. This division offered a complete line of floor waxes, finishes, polishes, cleaners and sponges that were formulated and packaged expressly for business and public large-volume users.

Conceptual Site Model

- **Purpose**
  - Identify and investigate the potential sources and evaluate the soil and groundwater potentially impacted
- **Site: Central CT Manufacturing Facilities**
  - Where and When to look?
  - And not look everywhere
  - Site Operations/Activities/Timeframes

Fate and Transport

- **Example:**
  - Manufacturing Facilities in central CT– potential impacts to soil and groundwater
    - Metal Finishing Areas
    - Wastewater Management Areas
    - Wastewater Treatment Areas
    - Process Tank Vent Areas
    - Stormwater Management Areas
    - Spills/Release Areas
    - Discharge Dilute Wastewaters
    - Surface Impoundments
    - Stormwater Detention Basins
    - Onsite Sanitary Waste Discharges



Davis et al., 2007, *Chemosphere*

Summary

- Businesses Identification
- Source Identification - Past and Present Operations/Processes
- Source Evaluation - Site/Facility History
- Source Investigation - Site/Facility Site Considerations

What's Next?

Minimize and Eliminate Risk

Develop and implement safer replacements

Questions

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