HISTORICAL USAGE OF PFAS

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USES ASSOCIATED WITH KNOWN ENVIRONMENTAL CONTAMINATION

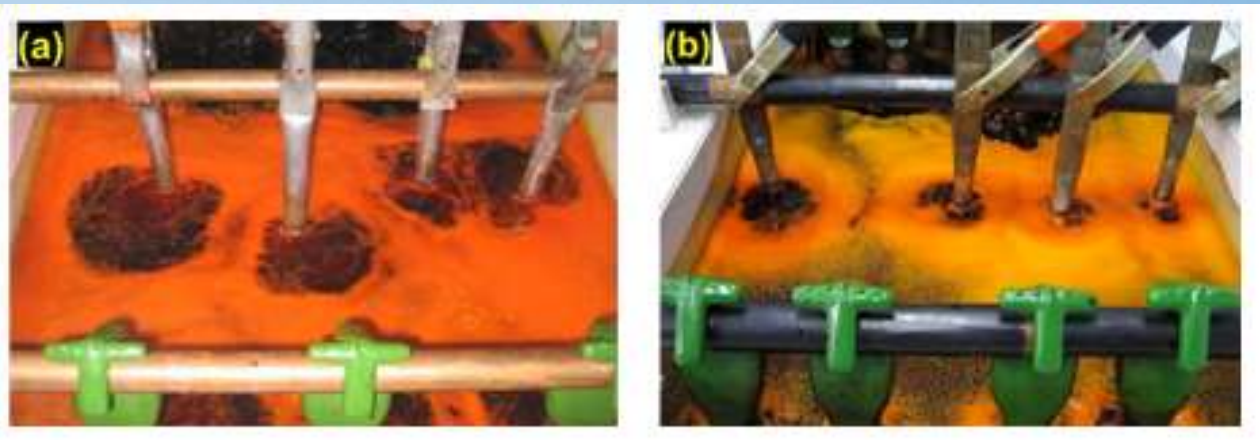
FIRE FIGHTING FOAM

- U.S. Naval Research Laboratory tested PFAS in foam in early 1960s
- PFCAs made by ECF used as components in AFFF from 1965-1975
- POSF-based AFFF became product of choice from 1970s until 2002
- Fluorotelomer-based AFFF was produced from 1975 to 2004 but less market share than POSF-based AFFF
- 2017: DOD edited mil-spec for AFFF to include no more than 800 ppb, the quantitation limit by using DOD Quality Systems Manual (QSM) 5.1, of PFOA and PFOS in the concentrate

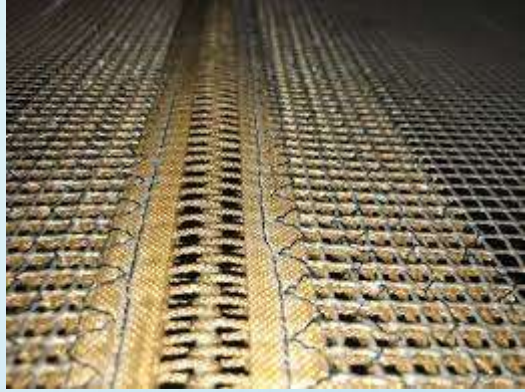
Photo: Batelle

METAL PLATING

- Used as a surfactant, wetting agent, and mist-suppressing agent for metal plating, esp. Cr
- 1954: first reported use for chrome plating
- 2012: EPA phased out PFOS from WA/FS, other PFAS not mentioned
- 2020: Report by MI DEGLE and EPA found only 6:2 FTS of 25 targeted PFAS in current WA/FS
- PFAS associated with Cr, Cu, Ni, and Sn plating
- PFAS used to treat metal surfaces



Photos: Products Finishing, L: PFOS, R: non-PFOS



TEXTILES

- Since 1950s: PFAS used extensively for their ability to repel water, oil, and stains
- All types of clothing, outer wear and accessories (e.g. shoes, umbrellas), household textiles (e.g. carpets), technical textiles for high temp or corrosive environments (e.g. fiberglass or Kevlar), and medical garments are treated pre-market or after market
- Fluoropolymers can be woven to make textiles also (e.g. fire-fighter clothing, sailcloth)

Lower photos: Wikipedia; miprcorp; ugg; mutiflon.com

PAPER AND CARDBOARD

- PFAS used to provide water and oil resistance to paper products for both food and non-food use
- Plaster board, coated raw paper, wood-containing paper, general liner and flute, neutral white role paper, neutral liner, anti-corrosion liner, paper combined with metal, and kraft paper
- Generally added to pulp at papermaking stage
- Major types of PFAS used:
  - Side-chain fluorinated polymers in which the perfluoroalkane sulfonyl fluoride- or fluorotelomer-based alcohols, their acrylate or methacrylate esters are attached on side chains
  - Phosphate ester salts made through the esterification of perfluoroalkane sulfonyl fluoride- or fluorotelomer-based alcohols with phosphoric acid
  - Perfluoropolyethers

Photos: (L) Archroma (R) Daikinchemicals.com

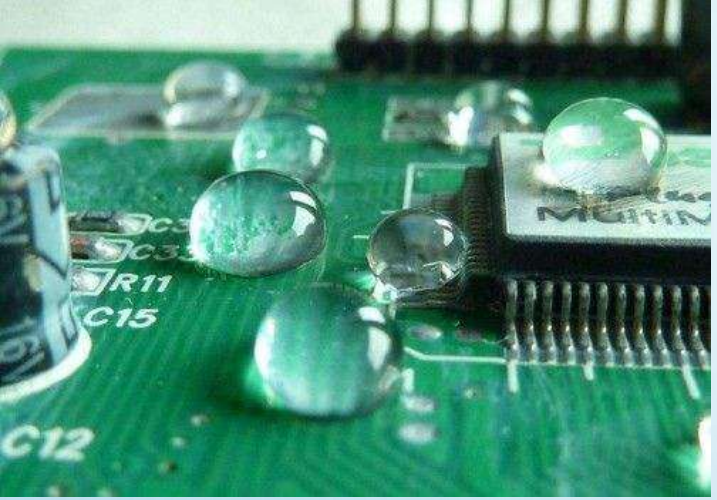
PLASTICS

- PFAS have been used as processing aids, raw material, or a manufacturing intermediate in fluoropolymer production
- Fluoropolymers have many uses in consumer and industrial products, such as textile, medical industry, cookware, electrical cable insulation, handling chemicals, building material, etc.
- Since 1960s: Perfluorinated membranes used in fuel cells, chlor-alkali cells, and water, caustic soda, and caustic potash electrolyzers
- Perfluoroelastomers used in high temperatures and harsh environments

Photos: (L) BorsodChem - PVC (R) ptfe-machinery.com

POLL QUESTION

USES UNKNOWN IF ASSOCIATED WITH ENVIRONMENTAL CONTAMINATION



ELECTRONICS

- Used as lubricants for magnetic tapes and disks
- Fluoropolymers used in cables and wires
- Used for coating inside and outside of electronic devices to protect from moisture and corrosion and for easy cleaning; used for cleaning components
- Patents from 1950s: PFAS used in battery electrolytes and dielectric and heat-exchanging fluids
- Used in the semiconductor industry to reduce surface tension and reflectivity of etching solutions
- For cleaning or polishing Si or GaAs, Si or GaAs wafers coated with thin films of various compositions including metals, conductive polymers, insulating materials, and Cu-containing substrates, such as Cu interconnects

Photos: (L) fluorochemie.com (R) IEEE Spectrum: Fujitsu

PHOTOGRAPHY AND LITHOGRAPHY

- Used in manufacturing film, paper, and plates as both dirt rejecters and friction control agents as well as to reduce surface tension and static electricity; improve in wetting, penetration, and leveling properties
- Added to photothermographic material used for medical diagnostics to stabilize the material in storage
- Used in the photolithography process for anti-reflective coatings
- PFCAs and PFSAs noted as being used with fluorotelomers noted as possible replacements

CLEANING PRODUCTS

- Many industrial and consumer cleaning products: carpet spot cleaners, alkaline cleaners, denture cleaners, shampoos, floor polish, dishwashing liquids, car wash products, and automobile waxes
- Used in cleaners containing strong acids and bases, including those used for cleaning concrete, masonry, and metal surfaces
- Dry cleaning textiles: used in PCE replacement systems

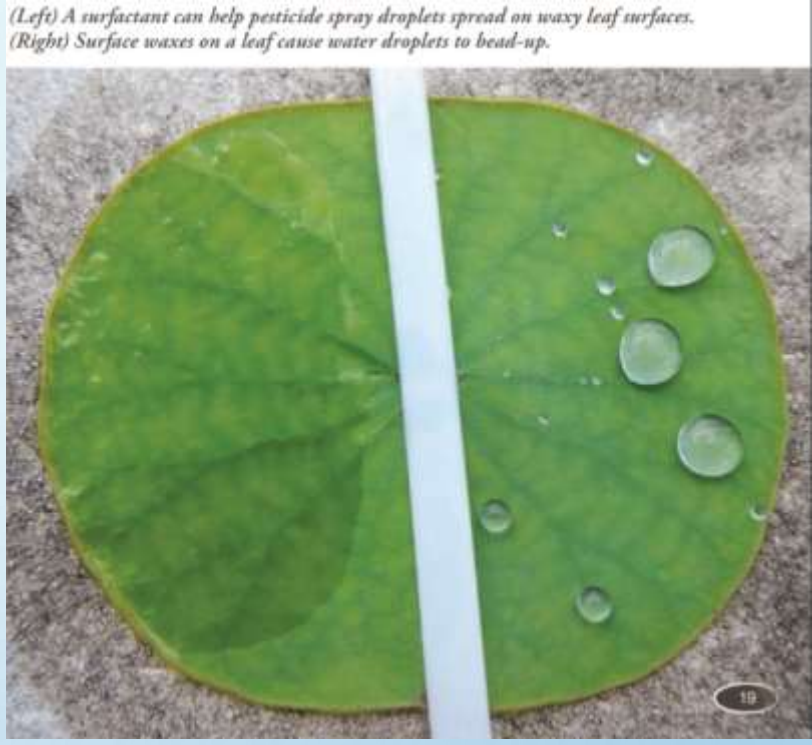
Photos: (clockwise) primereviews.org; autogruide.com; concretesealerreviews.com; goldeagle.com

COATINGS: WAXES, PAINTS, INKS, VARNISH

- PFAS reduce surface tension for substrate wetting, leveling, dispersing agents, and improving gloss and antistatic properties
- Paints, resins, adhesives, inks, clearcoats, floor coverings, ink jet ink, wood stains, graphic arts, caulks, waxes (including ski wax), and polishes
- Used on glass, metal, or plastic surfaces as an anti-mist film to prevent surface fogging in humid environments, such as bathrooms, automobile windshields, and eyeglass lenses; glass and plastic cover sheets used in agriculture

Photos:inkjetwholesale.com.au; biocote

PESTICIDES


(Left) A surfactant can help pesticide spray droplets spread on waxy leaf surfaces. (Right) Surface waxes on a leaf cause water droplets to bead-up.

- Have been used as active and inert (or inactive) pesticide ingredients
- Registered pesticide active ingredient
  - N-Ethylperfluorooctanesulfonamide (EtFOSA, sulfluramid) 1987 – 2008
  - Li-PFOS 1999 – 2002
  - Flubendiamide 2008 - 2016; current import tolerance on dried tea leaves
  - Pyrifluquinazon 2013 – current
- Perfluoroalkyl phosphonic acids and perfluoroalkyl phosphinic acids have been used as inactive pesticide ingredients for foam-breaking agents, proper wetting

Photo: https://ppp.purdue.edu/wp-content/uploads/2016/08/PPP-107.pdf

MEDICINE

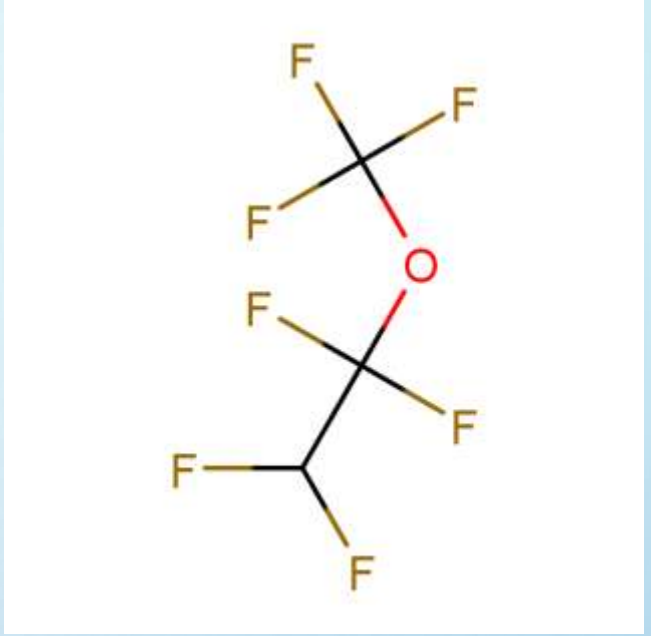
- 1966: Clark and Gollan's experiment of animals breathing PFC emulsion
- Emulsions examined as substitute blood due to their O_2-carrying ability
- 1978-1994: Fluosol 20% intravascular perfluorchemical emulsion
- PFAS used in medical diagnostics, including imaging
- FDA Orange Book
  - Fulvestrant: intramuscular injectable, estrogen receptor antagonist
  - Perflexane: no-longer marketed intravenous injectable, ultrasound contrast activity
  - Perflubron: discontinued oral liquid
  - Perflutren: intravenous injectable, ultrasound contrast activity, diagnose left ventricular dysfunction
- Used in the manufacturing of implantable material and devices; contact lenses

From Zhang and Barralet 2017: mouse breathing oxygenated PFC emulsion

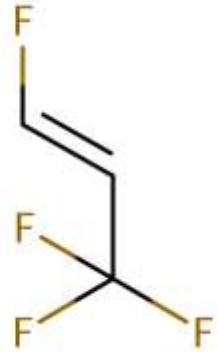
PERSONAL CARE PRODUCTS

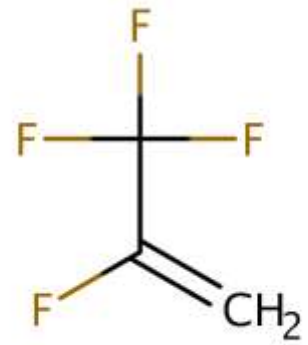
- Used in cosmetics as emulsifiers, lubricants, or oleophobic agents
- Used widely in personal care products, such as sunscreen and cosmetics, for oil and water resistance
- PFCAs and FTSs found
- Patents for use in oral care products such as toothpaste, lozenges, chewing gum, etc.
- Spun into dental floss

REFRIGERANTS



- Generally associated with PFCs, but other PFAS are also used
- Several small fluorinated ethers used
- Montreal Protocol (1987) phased out ozone-depleting substances (ODS)
  - chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs)
- Kigali Amendment (2016) phase down hydrofluorocarbons (HFCs), which are alternatives to CFCs and HCFCs, and are powerful greenhouse gases





BUILDING & CONSTRUCTION

- Reduce shrinkage and stabilize foam in concrete mixtures
- Fluoropolymer coating on marine structures can prevent biofouling
- Woven into fabrics to use for building structures
- Use as coating for building, roof fabrics, and films

Photos: fabricarchitect.com; Materials Performance; bnproducts.com

Fig. 8. Model for MTV flare combustion (a) with real photo-image for MTV flame (b

MUNITIONS

- 1950s: pyrotechnic oxidizer and use in infrared tracking flares
- MTV: Magnesium, Teflon™ (PTFE), and Viton™ composition, used for energetic material
  - Infrared flares, including those used for aircraft countermeasures, target augmentation, and tracking
  - Incendiaries, document destruction, and agent defeat warheads, which are designed to neutralize biological and chemical warfare agents
- Warheads that require improved mechanical properties and stability at high temperatures will have the wax replaced with thermoplastics, which can include a fluorinated polymer
- Energetic material itself can also be fluorinated
- Fluoropolymers used in Pb replacement waterfowl shot

Photos: (L) Elsaidy et al. 2017 (R) airpowerworld.info

OIL & GAS INDUSTRY

- Used as surfactants to enhance recovery in oil or gas recovery wells; improve subterranean wetting, increase foam stability, and modify the reservoir formation's surface properties by lowering surface tension and foaming properties of well-stimulation additives
- Used as evaporation inhibitors for gasoline
- Used in hydraulic oils to prevent evaporation, fires, and corrosion
- Some references to their use helping with oil spills

MINING INDUSTRY

- Used as surfactants to enhance metal recovery from ores in copper and gold mines
- Used in the ore flotation process to separate metal salts from soil and in electrowinning of metals
- References to use with Cu, Au, Ag, Al, V, U
- Used as a mist suppressing agent

CONCLUSIONS

- PFAS has been used in a large variety of industries and in industrial and consumer products.
- In some cases, the specific PFAS that were used in specific applications are known, but in some cases only the general type of PFAS (e.g. fluorinated carboxylic acid) is known. In many cases, the PFAS used seems to be more performance based than specific composition.
- In some cases, estimates of the percentage of PFAS in the total composition is known, but in many cases it is unknown. However, in many cases, available information indicates PFAS was added in minor amounts such as 1% of the total composition.
- This information will be useful when considering what types of sites might have PFAS contamination or from where contamination might originate.

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