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## September 2017 DRAFT Per- and Poly-Fluorinated Alkyl Substances Chemical Action Plan (PFAS CAP)

The Washington State departments of Ecology and Health prepared a draft of several PFAS CAP chapters for external review. This document is one chapter to a planned multi-chapter PFAS CAP. This material may be modified in response to comments and the content re-organized for the final Action Plan.

The September 2017 Draft PFAS CAP includes: Health, Environment, Chemistry, Regulations, Uses/Sources, Intro/Scope. This draft may include cross-references to other sections/chapters in the Draft PFAS CAP or notes where additional information will be provided in a later draft.

An updated draft of the PFAS CAP will be provided in November/December 2017 for additional review and comment. The PFAS CAP Advisory Committee will discuss comments on these draft chapters at the November 1, 2017 meeting.

Ecology and Health are asking interested parties to provide feedback. Comments on these draft documents are due to Ecology by **October 20, 2017**. Submit comments, suggestions, and questions to Kara Steward at [kara.steward@ecy.wa.gov](mailto:kara.steward@ecy.wa.gov).

**Submit comments, suggestions, and questions to Kara Steward at**  
[kara.steward@ecy.wa.gov](mailto:kara.steward@ecy.wa.gov)

The Draft PFAS CAP documents are posted at <https://www.ezview.wa.gov/?alias=1962&pageid=37105> (at the bottom of the webpage).

## General Chemical Information

### Summary

Per- and polyfluorinated alkyl substances (PFAS) are a group of fluorinated substances that are diverse and different. See Figure 15. in their properties. Their unique and valuable properties originate from the strength of the carbon-fluorine bond. Fluorosurfactants are prized for their effectiveness in reducing surface energy (of solids) and surface tension (of liquids). These The surface properties of side-chain fluorinated polymers se properties make surfaces to which they are applied PFAS resistant to both oil and water. Repellent and may also impart soil and grease resistance. Many PFAS substances, such as the high molecular weight fluoropolymers are stable can retain these properties at high temperatures and in extreme corrosive environments.

Most Fluorosurfactants and side-chain polymer PFAS are manufactured from raw materials made by either the electrochemical fluorination (ECF) or the telomerization processes. Both processes produce unintended by products The ECF process givesing end-mixtures of variable structural shapes (mostly branched chains in ECF) and lengths (odd and even) in both ECF and while a homologous mixture of even chain lengths are produced by in telomerization). These product mixtures of target compounds, by-product substances, residuals, and contaminants may complicate efforts to assess environmental and human health impacts. [REFERENCES?]

Many PFAS may degrade to highly persistent and bioaccumulative perfluoroalkyl acids such as PFOA and PFOS. Fluorotelomer alcohol alcohols substances and perfluoroalkane sulfonamido ethanols are volatile and can be transported long distances in the atmosphere before breakdown and washout by rain. [REFERNCE] Newer replacement PFAS products, such as the perfluorinated alkyl ethers and polyethers, have structural elements that are comparatively unexplored in the PFAS technical literature. There are often no analytical standards or methods for newer product substances and their environmental breakdown products. This makes it difficult to track the volume of PFAS emissions and to identify where they end up in the environment.

What are Per- and Polyfluorinated Alkyl Poly fluoroinated Aalkyl Substances (PFAS)?  
“What are the Per- and Poly-fluorinated Alkyl Substances (PFAS) within the Scope of this Chemical Action Plan?”

[The discussion here is based largely on Buck et al., 2011 and Knepper & Lange, 2012. Other references are provided inline as needed.]

The Washington Administrative Code (WAC) 173-333-310 identifies five persistent, bioaccumulative, and toxic (PBT) substances in a perfluorooctane sulfonic acid (PFSA) chemical group, Table 1.<sup>1</sup>

Table 1 Perfluorooctane sulfonic acid and selected salts identified in WAC 173-333-310 (Washington State Legislature, n.d.).

CAS Number	Substance	Formula	R-Group
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<sup>1</sup> “Sulfonates” referred to in the WAC are identified here as “sulfonic acids.” This chapter uses the widely adopted terminology for PFAS described in Buck et al., 2011. Chemical names cited in sources, such as the WAC in this case, are modified without further reference.

**Commented [A1]:** Consider a picture like Buck et al Figure 4 to show the different major classes of PFAS. Or Figure 15 already in this document.

**Commented [A2]:** Need specificity here as the originally written statements are not true for PFAS as a group of substances.

**Commented [A3]:** Fluorinated surfactants and repellents. *Surfactant Science Series, Marcel Dekker, New York, NY 2001, 97, (Fluorinated Surfactants and Repellents (2nd Edition)), 1-615.*

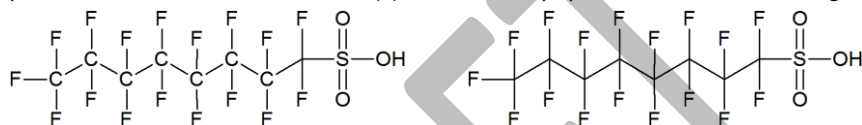
Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management 2011, 7, (4), 513-541.*

**Commented [A4]:** The text in this section doesn't clearly answer the question posed. It could be read as PFAS are the five substances identified in the Washington Administrative Code. Or it could be read as PFAS are the non-polymeric per and poly-fluoroalkyl substances on the left side of Buck Figure 4. Suggest changing the title to something like “What are the Per- and Poly-fluorinated Alkyl Substances (PFAS) within the Scope of this Chemical Action Plan?” Then a clear description of those PFAS should be provided.

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1763-23-1	Perfluorooctane sulfonic acid (PFOS)	$C_8F_{17}SO_3H$	$SO_3H$
29081-56-9	Perfluorooctane sulfonic acid, ammonium salt	$C_8H_4F_{17}NO_3S$	$SO_3NH_4$
70225-14-8	Perfluorooctane sulfonic acid, diethanolamine salt	$C_{12}H_{12}F_{17}NO_5S$	$C_4H_{12}NO_5S$
29457-72-5	Perfluorooctane sulfonic acid, lithium salt	$C_8F_{17}SO_3Li$	$SO_3Li$
2795-39-3	Perfluorooctane sulfonic acid, potassium salt	$C_8F_{17}SO_3K$	$SO_3K$

Figure 1 illustrates the first of these substances, perfluorooctane sulfonic acid (1), also designated as PFOS. The structure on the left shows all of the individual atoms, while the structure on the right shows a simplified version where each carbon atom (C) is indicated only by the intersection of the straight lines



(which represent bonds between the atoms). The style on the right will be used throughout this chapter.

Figure 1 Perfluorooctane sulfonic acid (PFOS) shown with (left) and without (right) the carbon atoms.

For convenience, structures often use R to represent a “functional group” add-on to the main carbon chain. R may represent a single atom or a group of atoms. In Figure 2, R represents the  $SO_3H$  sulfonic acid group. Manufacturers may alter the R-group to achieve desired properties, for example, solubility in a particular solvent.

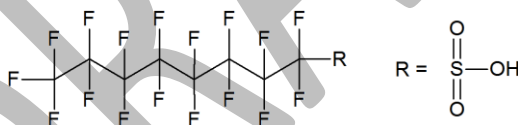


Figure 2 PFOS in which the  $SO_3H$  functional group is represented by R.

The remaining substances in Table 1 can be specified by redefining the R-group. For example, perfluorooctane sulfonic acid, potassium salt is represented  $C_8H_{17}SO_3K$ , or by  $C_8H_{17}R$ , where  $R = SO_3K$ . When the H associated with the sulfonic acid group is replaced by any of a number of single atoms, for example, potassium, the name reflects this substitution: *perfluorooctane sulfonic acid, potassium salt*.

Ordinary *hydrocarbons* contain mostly hydrogen (H) and carbon (C) atoms, however, when the H are totally replaced by fluorine (F) atoms, the substance is described as *perfluorinated*. Figure 3 includes a non-fluorinated hydrocarbon, octane sulfonic acid (1), and its perfluorinated cousin, perfluorooctane sulfonic acid (PFOS) (2). The third and fourth structures in Figure 3 are *poly*-fluorinated substances, where the C atoms have a mix of both F and H atoms attached. The end-group is also different in (4), with the  $SO_3H$  replaced by an OH, indicating an alcohol.

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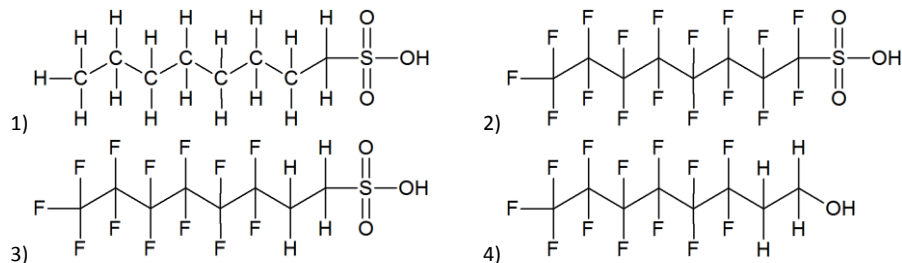


Figure 3 Four *example-related* structures: 1) the non-fluorinated octane sulfonic acid (a hydrocarbon with no fluorine), 2) its perfluorinated cousin PFOS, 3) the polyfluorinated 6:2 fluorotelomer sulfonic acid (with hydrogen and fluorine on the backbone carbon chain) and 4) the polyfluorinated 6:2 fluorotelomer alcohol.

This chapter focuses primarily on *alkyl* substances, referring to the single-bonded *backbone* *perfluoroalkyl* chain of carbon *bearing fluorine* atoms in *three of the all* four structures of Figure 3. Structures (1), (2) and (3) are *acids* defined by the sulfonic acid end-group,  $\text{SO}_3\text{H}$ . While (1), (2) and (3) are *alkyl acids*, (2) is a *perfluorinated alkyl acid* (PFAA). Substances like (2), (3), and (4), but also many others of varying lengths and types of substituent R-groups are together referred to as per- and

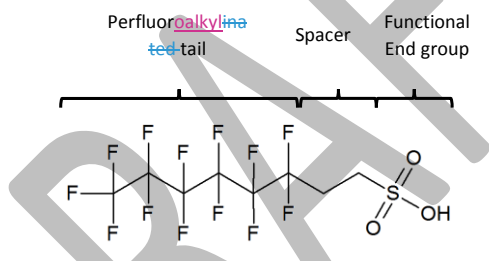


Figure 4. Schematic structure of a *typical* polyfluorinated surfactant. The 6:2 fluorotelomer sulfonic acid. In this naming convention, there are six perfluorinated carbons and two hydrogenated carbons (Hs not shown except for those in the functional end-group). Generally, the hydrocarbon (H) atoms are not shown on the carbon backbone. The hydrocarbon portion of the carbon backbone is sometimes described as a spacer.

*polyfluorinated polyfluoroalkylated alkyl* substances (PFAS).

*Perfluorinated Perfluoroalkylated* chains are often represented in a shorthand form as  $\text{C}_n\text{F}_{2n+1}$ . In Figure 4, the 6 perfluorinated carbons,  $n = 6$  could be represented as  $\text{C}_6\text{F}_{13}$ , the hydrocarbon spacer as  $\text{C}_2\text{H}_4$ , and the end group as  $\text{SO}_3\text{H}$ . The *polyfluorinated polyfluoroalkyl* structures have a numerical prefix based on these structural elements to indicate the number of *perfluorinated* versus *non-fluorinated* C atoms. Figure 4 illustrates the 6:2 fluorotelomer sulfonic acid.

## Physical and Chemical Properties of *Perfluorinated Per- and Poly-fluoroalkylated Alkyl* Substances (PFAS)

### *The Essential Nature of Perfluorinated Substances*

#### *“Relationship between certain PFAS properties and Commercial Uses”*

**Commented [A5]:** It appears this section is supposed to cover both per- and poly-fluorinated alkyl substances. Suggest changing the title to reflect this.

**Commented [A6]:** It's very difficult to describe the “essential nature” of such a wide variety of chemical substances. Suggest using a subtitle that is more reflective of the text, which is something like “Relationship between certain PFAS properties and Commercial Uses”

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~~Perfluorinated substances~~ ~~Per- and Poly-fluoroalkylinated substances, such as those shown in Figure 15 (or in Buck et al, 2011) (give a specific substance example here),~~ have some unique and valuable properties when compared with non-fluorinated hydrocarbon chemicals of similar structure (Krafft & Riess, 2015). Fluorine forms an extraordinarily strong bond with carbon, and when fluorine completely replaces hydrogen in an alkyl chain of carbons, the resulting substance is much more resistant to thermal or chemical attack than a similar fluorine-free hydrocarbon. As a result, ~~the per- and poly-fluoroalkyl substances~~ ~~fluorocarbons~~ are often preferred for use in extreme environments (high temperatures, strongly reactive conditions, etc.).<sup>2</sup>

#### Fluoropolymers

~~Per- and polyfluorinated polyfluoroalkylated substances are also low surface energy substances. Fluoropolymers, such as polytetrafluoroethylene (PTFE), are un-wettable in that both oil and water will “bead up” on PTFE surfaces. Polymers derived from PFAS can be used to coat surfaces on a molecular scale, imparting oil and water (i.e., stain) resistance at the individual fiber level in textiles, fabrics, or carpets. Fluoropolymers are primarily characterized by having a fluorinated backbone. They are high molecular weight polymers such as PTFE (polytetrafluoroethylene), melt co-polymers and thermoset fluoroelastomers. They are known largely for their chemical resistance, thermal stability and resilience (elastomers). Common applications include breathable membranes, hydraulic tubing, plenums, chemical and pharmaceutical processing, semiconductor manufacture and automotive and other transportation applications.~~

#### How and Why Fluorosurfactants Function ~~Surfactants~~

~~Hydrocarbon surfactants are often described as having a head and a tail. The tail is often a long alkyl chain and relatively insoluble in water (hydrophobic). In contrast to the tail, the head is typically more compact, and often hydrophilic, or water-loving. Most surfactants for water-based applications orient at the surface of the liquid, with the tail portion extending out and over the surface at the molecular level and the head-only immersed in liquid. The head is equivalent to the R-group described in the previous section.~~

~~Wetting~~ is controlled by the interplay of solid surface energy and liquid surface tension, Figure 5. Droplets of water, which normally has high surface tension, will bead-up on low-energy hydrocarbon surfaces like polyethylene, reflecting the *hydrophobic* (water-hating) nature of many hydrocarbons. On the other hand, oil, itself a hydrocarbon, has a much lower surface tension. Oil droplets will spread on polyethylene, Figure 5-2, and polyethylene is described as *oleophilic* or oil-loving.

**Commented [A7]:** This section is on perfluoroalkyl substances. This is not the correct wording to start this paragraph?

**Commented [A8]:** Please do not use trade or brand names

**Commented [A9]:** Note: the substances used to coat surfaces are POLYfluoroalkyl substances, not perfluoroalkyl substances.

**Commented [A10]:** References on fluorosurfactants that may be useful:

Fluorinated surfactants and repellents. *Surfactant Science Series, Marcel Dekker, New York, NY 2001, 97*, (Fluorinated Surfactants and Repellents (2nd Edition)), 1-615.

Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management 2011, 7*, (4), 513-541.

Chemistry, Properties and Uses of Commercial Fluorinated Surfactants. In *Handbook of Environmental Chemistry, Volume 17, Polyfluorinated Chemicals and Transformation Products*, Knepper, T. P.; Lange, F. T., Eds. Springer: New York, 2012; pp 1-24.

Fluorinated surfactants in practice. *Annual Surfactants Review 1999, 2*, (Design and Selection of Performance Surfactants), 271-316.

**Commented [A11]:** This is a discussion about Fluorosurfactants. A header would be helpful.

<sup>2</sup> These same characteristics are responsible for the extreme environmental persistence of perfluorinated substances as they are completely resistant to naturally occurring breakdown mechanisms, see X below.

<sup>2</sup> May be referred to as Teflon™, originally developed by Chemours™ (formerly the Performance Chemicals business of DuPont). The Teflon® brand may also cover products that do not contain fluorinated substances.

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When a surfactant is added to water, the normally high surface tension is reduced and droplets behave more like oil droplets, spreading on the polyethylene surface. Fluorinated surfactants are effective at reducing surface tension in both oil- and water-based products to promote wetting and spreading.

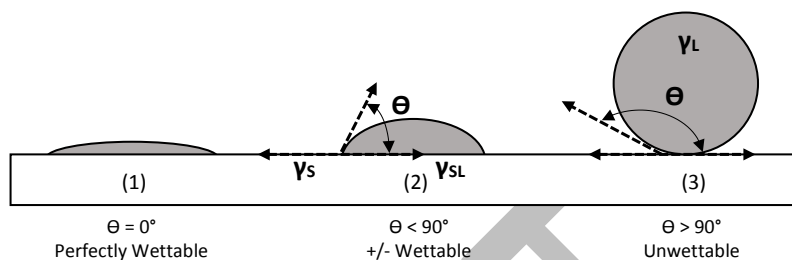


Figure 5 Contact angle and spreading. The three cases illustrate (left) complete wetting, (middle) partial wetting and, (right) no wetting.  $\theta$  represents the contact angle and  $\gamma$  the surface energy or tension (see Equation 1 below). Water will bead-up on many hydrophobic plastics (3), but oil will more likely wet and spread (2). Both oil and water behave like (3) when the solid is a fluorinated-polymer surface.

Wetting and spreading are critical for a great many commercial processes: paints must cover surfaces uniformly and completely, with tolerance for surface defects like roughness or sporadic contamination; inks need to achieve full coverage on printing plates; etc. A spreading formula is often used to describe this behavior:

Equation 1

$$S = \gamma_s - \gamma_L - \gamma_{SL}$$

where  $S$  is termed the *spreading coefficient*. In simplest terms,  $S$  must be positive for good wetting and spreading, and is favored when the solid surface energy,  $\gamma_s$ , is high, and the liquid surface tension,  $\gamma_L$ , is low. [The interfacial tension,  $\gamma_{SL}$ , a property of the interface between the liquid and the solid, is ignored here.] Table 2 contains some typical values for surface energy and surface tension of various solids and liquids. While the spreading formula provides some *qualitative* understanding, dynamic spreading is far more complex and depends on many properties beyond surface energy and surface tension (Kovalchuk et al., 2014).

The principle uses of [fluorinated chemicals](#) [fluorosurfactants](#) reflect their unique surface energy properties and their ability to modify wetting and spreading behavior. When these requirements are combined with a need for chemical inertness or resistance to high temperature, PFAS can have distinct advantages over traditional hydrocarbon surfactants or materials. Krafft & Riess, 2015 contains an excellent discussion of the physical chemistry behind these properties and other unique characteristics of fluorinated substances.

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Table 2 Adapted from Posner in Knepper & Lange, 2012. Due to water's high surface tension, water-based coatings will not readily spread onto low-energy hydrocarbon or fluorocarbon polymers. Surface-active additives (surfactants) can reduce the coating surface tension and help facilitate spreading.

Solid	Surface energy, $\gamma_s$ (mN/m)	Liquid	Surface tension, $\gamma_L$ (mN/m)
-CF <sub>3</sub>	6	Water	72
-CF <sub>2</sub> H	15	n-Octane	22
-CF <sub>2</sub> -	18	Olive oil	32
-CH <sub>3</sub>	22		
-CH <sub>2</sub> -	31		
Polyester	42		

### Modifications for PFAS Chemical Function

Hydrocarbon surfactants are often described as having a head and a tail. The tail is often a long alkyl chain and relatively insoluble in water (hydrophobic). In contrast to the tail, the head is typically more compact, and often hydrophilic, or water-loving. Most surfactants for water-based applications orient at the surface of the liquid, with the tail portion extending out and over the surface at the molecular level and the head only immersed in liquid. The head is equivalent to the R-group described in the previous section.

Many perfluorinated surfactants fluorosurfactants have a similar design, but the fluorocarbon tail is insoluble in both oil and water (oleophobic and hydrophobic). Most often, the tail is relatively fixed to a long perfluorinated chain. The head varies more widely and is chosen so that surfactants will perform certain functions in each product application. For example, a fluorinated surfactant for a water-based paint application often has an R-group that is hydrophilic (water-loving). Sulfonic acid or carboxylic acid R-groups work well in these applications, so both PFOS and PFOA were used in water-based applications.

It is important to understand that formulating mixtures of chemicals and a solvent is itself a complex art. A surfactant may play multiple roles and need to meet other functional requirements (color, temperature stability, etc.). In a floor polish, the surfactant improves wetting and spreading, but also helps achieve a smooth, glossy finish through its effect on surface tension as the polish dries. Several surfactants may be used in a single product, with hydrocarbon surfactants used to keep ingredients dispersed and fluorinated surfactants to promote wetting. The individual constituents must work well in the whole system of ingredients for the product to function as intended.

The basic head/tail concept is a bit different in polyfluorinated surfactant design. Due to the need to reduce perfluorinated chain length, manufacturers have included introduced a hydrocarbon spacer between the perfluorinated tail and the head-group. The hydrocarbon "spacer" does extends the

Figure 6 Schematic of a fluorinated surfactant. The perfluorinated chain is represented by the black bar (left), the non-fluorinated hydrocarbon spacer (middle), and the head group (right) by the white portion. The R-group



**Commented [A12]:** The point of this subsection is not clear. The paragraphs seem to be focused mostly but not exclusively on surfactants. Some kind of introductory paragraph might be helpful.

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combined tail length, and in particular allows a significant number of derivatives to be prepared from an otherwise less functional perfluorinated intermediate. For example if the spacer is an ethyl group and R is iodide, one can react the perfluoroalkyl iodide directly to make acrylates and methacrylates or convert the ethyl iodide to an ethyl alcohol group (see Fig 10 step 2. And Figure 11) and then derivatized, extends the combined tail length and is believed to recover some of the functionality lost when using shorter perfluorinated chains, Figure 6.6 (Renner, 2006).

Very similar surfactant-like structures are used. Fluoroalkyl acrylates and methacrylates are often used as co-monomers with other non-fluorinated/hydrocarbon monomers. The resulting polymeric materials, often aqueous dispersions, are used for polymeric surface treatments and/or impregnation products for textiles, carpets, upholstery, and paper products and other end-use applications. R-groups, as shown in Figure 6, such as hydrocarbon acrylates or methacrylates are polymerized to form the non-fluorinated hydrocarbon backbone with the fluorinated side-chains

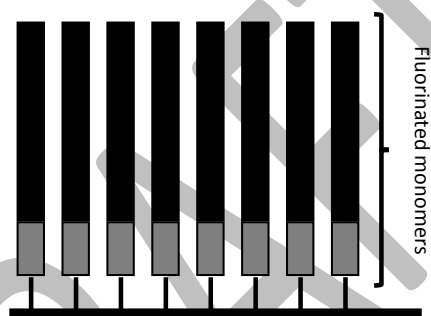


Figure 7 Fluorinated “side-chain polymer” typical of stain-resistant surface treatments for textiles. The solid line at the base represents the main polymer backbone. Fluorinated chains (black bars) are bonded to the backbone through reactions with the hydrocarbon spacer group (gray bar).

orienting as shown at the air interface, like teeth/tines of a comb. These “side-chain polymer” teeth, Figure 7, can be mixtures of per-, poly- and non-fluorinated monomers. In some cases, fluoroethoxylates, which contain repeating ethoxylate units ( $\text{CH}_2\text{CH}_2\text{O}$ ), are used to connect a perfluorinated chain to hydrocarbon-based plastics (Trier et al., 2011). This is not a correct use and/or application for most fluoroethoxylates.

Heteroatoms, like oxygen (O), may also be introduced into the fluorinated tail. The resulting perfluoroalkyl ether surfactants are currently used as polymer polymerization processing aids in emulsion polymerization, where they replace legacy processing aids like APFO, the ammonium salt of perfluorinated octanoic acid (PFOA). One example is the ammonium salt of perfluoro-2-propoxypropanoic acid (PFPrOPrA), known by the tradename GenX, Figure 8. Perfluoroalkyl ether carboxylic acids (PFECAs) contain ether O-atoms interspersed among short perfluorinated chains (Sun et al., 2016).

**Commented [A13]:** It is REALLY important to know that typical side-chain polymers made from fluorotelomer and ECF raw materials have NO surfactant properties as all. There are some ECF-based polymeric products that are used as surfactants.

Oil and water repellency are not surfactant properties. They are surface properties manifest using side-chain fluorinate polymers by the orientation of the perfluoroalkyl chain at the air interface, perpendicular to the surface. Fluoropolymers are different still. They have oil and water repellency as a bulk property of the material itself.

**Commented [A14]:** While this may be accurate text from this reference, it is not a true statement.





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## Manufacturing Via the ECF and Telomerization Processes

[The material in this section is based on two recent publications that review PFAS manufacturing processes: Buck et al., 2011 and Knepper & Lange, 2012. Statements supported by other references are noted inline.]

Complex chemicals like PFAS generally require a number of sequential manufacturing steps and utilize multiple chemical raw materials, catalysts, and other additives too numerous to detail here. However, the principle ~~perfluorinated~~ ~~perfluoroalkyl~~ ~~fluorinated~~ building blocks used for making fluorosurfactants and side-chain fluorinated polymers for most PFAS are briefly explained below for manufacture using two main processes: 1) electrochemical fluorination (ECF) and 2) telomerization.

### Electrochemical Fluorination (ECF)

When a hydrocarbon raw material is combined with hydrofluoric acid (HF), application of a strong electric current can break the H – F bond and create reactive fluoride species. These reactive species replace the hydrogens in the hydrocarbon one-by-one with fluorine resulting in a perfluorinated molecule. ECF was the dominant global method of production (principally by the 3M Company) for both PFOS and PFOA from the late 1940s until their phase-out beginning around the year 2000 (De Voogt, 2010). ECF is still used in both the U.S. and abroad, especially China, India, and Russia (OECD, 2015).

Perfluorooctane sulfonyl fluoride (POSF), Figure 9, from the ECF process was the basic building block for a wide variety of surfactant and polymer products, including PFOS. In spite of the phase-out, PFOS derivatives are still manufactured and used in imported articles.

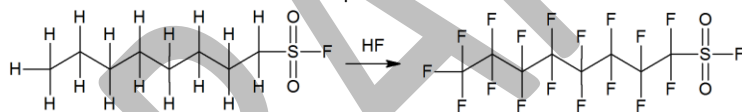


Figure 9 A schematic of the ECF reaction that forms POSF.

### Telomerization

Following 3M's phase-out of PFOS and PFOA production by ECF, DuPont began large-scale manufacture of PFOA from a pure telomer intermediate called perfluorooctyl iodide, using telomerization.

Telomerization typically results in products with even-numbered carbon chain lengths with an iodide (I) functional end-group. Figure 10, 1). If the process is continued with the hydrocarbon insertion of ethylene instead of fluorocarbon reactants, converts a per-fluorinated molecule is converted to a linear poly-fluorinated alkyl chain, such as the 8:2 fluorotelomer iodide (8:2 FTI), Figure 10, 2).

**Commented [A15]:** These processes are used to manufacture non-polymeric per and poly-fluorinated alkyl substances, and fluorinated side chain polymers. They are not the processes used to manufacture other PFAS, such as fluoropolymers. Non-polymeric PFAS, fluoropolymers, and side-chain fluorinated polymers seem to be equated in this section, and they should not be. They are distinct classes of PFAS with different properties and uses.

**Commented [A16]:** This is a very strange sentence to begin this section. It belongs elsewhere after the general description of telomerization.

Moreover, PFOA was made from a fluorotelomer raw material, it was not made by telomerization.

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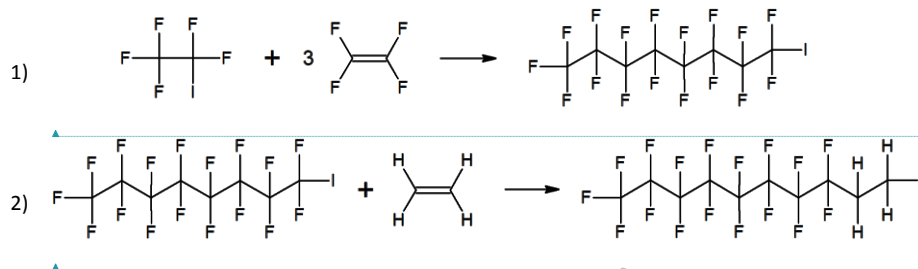


Figure 10 Reaction 1 shows the telogen (perfluoroethyl iodide) reacting with three taxogen units (tetrafluoroethene) to form a perfluorinated product, perfluorooctyl iodide (PFI). PFI can be further reacted (reaction 2) with the hydrocarbon ethene to form the polyfluorinated 8:2 fluorotelomer iodide (FTI).

Fluorotelomer iodides can be converted to alcohols (FTOHs) and further functionalized for use as fluorotelomer surfactants. A significant share of the fluorotelomer market is for side-chain fluorinated polymers (USEPA 2009), made from monomers like the fluorotelomer acrylates (FTACs). [See Figure 11.](#)

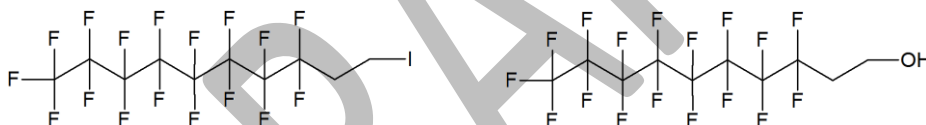


Figure 11 An 8:2 fluorotelomer iodide (left) can be converted to an 8:2 fluorotelomer alcohol (right). The “8” refers to the eight perfluorinated carbons. The “2” refers to the two hydrogenated carbons (Hs not shown) adjacent to the end group.

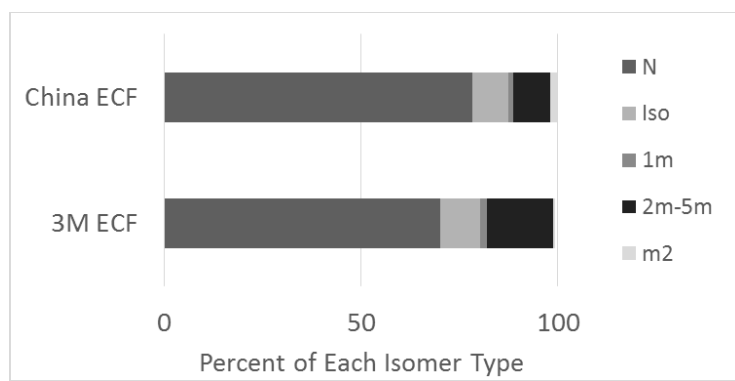
#### Technical Quality and Implications for Environmental Impacts

While we often describe discrete substances, like PFOS or PFOA, [the ECF<sub>7</sub>](#), and telomerization processes [may produce a complex mixtures](#) of substances rather than pure one-component products. [For example, the harsh conditions of the ECF process lead to a variety of unwanted side-reactions \(linear vs branched; odd and even chains\) often](#) resulting in complicated mixtures of perfluorinated [products variants](#). ECF production targeting PFOA (C8) includes 70-80% linear substances (of differing carbon chain lengths) with 20-30% branched substances, including even cyclic compounds (De Voogt, 2010).

While ECF mixtures randomly vary, they are sufficiently consistent for forensic application. PFAS environmental contaminants collected in China matched the chain-length profile expected for ECF products, suggesting that nearby manufacturing facilities employ the ECF process, Figure X (Jiang, 2015).

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Figure 12 The bars represent the isomer composition of two ECF products reported in Jiang 2015. “N” represents the “normal” straight-chain product, while the other legend items represent various branched isomers. The China ECF bar represents Chinese ECF production (Defu PFOSK, China). The isomer distribution is reminiscent of the “average” ECF isomer proportions for the 2000-era 3M PFOS. ECF products can contain 20 to 30% branched isomers. (Legend items colors from top-to-bottom match bar colors from left-to-right.)



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~~The telomerization process produces a series of homologous iodides~~

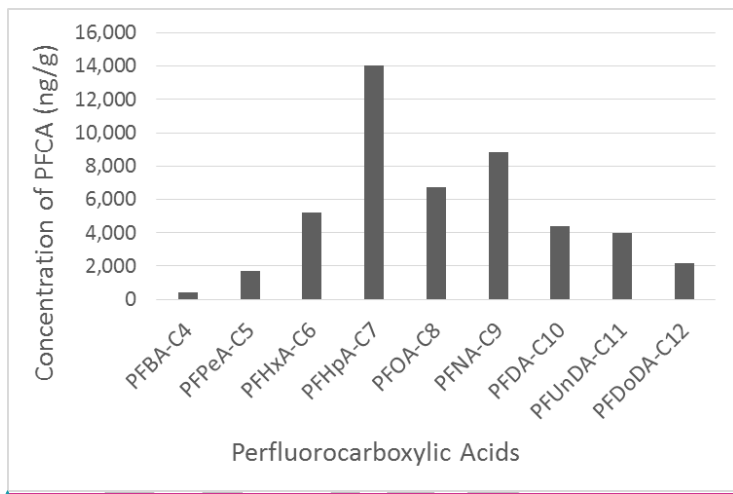
~~Telomerization also produces unintentional by-products, with chain lengths varying by even numbers. For example, production targeting the 6:2 FTI may include minor quantities of 8:2 and 4:2 chain lengths. The two carbon tetrafluoroethene taxogen (shown in Figure 10, reaction 1) adds about 100 g/mol in each addition step. As some FTIs have sufficient relative volatility, the change in properties between the  $C_n$  to  $C_{n+2}$  homologue<sup>4</sup> allows for purification by distillation (Krafft & Riess, 2015). The extent to which manufacturers purify their products is not well understood, albeit relative pure C6 telomer iodide is readily available on the market.~~

~~Products historically are sometimes marketed as contained mixtures of PFAS isomers or homologues (KEMI, 2015). Surflon® S-111, a surfactant produced by further reactions on a specific fluorotelomerization intermediate and essentially presumably discontinued, contained primarily the intended 9-C perfluorononanoic acid (PFNA). The product but also appeared to contain also significant quantities of other linear homologues, the 11-C PFUnDA (205 – not sure what this is?) and the 13-C PFTTrDA (5%) (Prevedouros, 2006). Chemical analysis of “articles of commerce” (from 10 years ago) shows that many formulated products were are complex PFAS mixtures, Figure 13 (Liu et al., 2012).~~

<sup>4</sup> A compound belonging to a series of compounds that differ only by a repeating unit.

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Figure 13 Analytical chemistry data for the PFCA content (C4-C12) of a U.S. carpet/upholstery protector concentrate (designated B-1) (Liu, 2012). The sample, purchased in 2007, contains a wide-distribution of chain lengths.



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Products can also be contaminated with residual raw materials, ~~or polymer polymerization processing aids and unintended manufacturing byproducts.~~ PFOA, higher homologues, and PFOA precursors have been found in historical fluorotelomer and fluoropolymer products. Similarly, FTOHs and fluorotelomer olefins (FTOs) have been identified in fluorotelomer acrylate and methacrylate products (Lassen et al., 2013).

~~The following discussion of PFAS chemical classes describes a very few “characteristic” substances. In most cases, final products or treated articles will contain a mix of related structures, impurities, residual raw materials, and other contaminants. Some of these substances are known and well characterized, but many are unknown. While much of the discussion of PFAS chemicals focuses on well known substances like PFOA, PFOS and PFHxA, the potential environmental and human health impacts of the many other known and unknown constituents of PFAS products should not be ignored.~~

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## PFAS Chemical Classes

*[The discussion in this section is based on Buck et al., 2011, Knepper & Lange, 2012, OECD, 2015 and Poulsen, 2005. Other references are provided inline.]*

The following discussion of PFAS chemical classes describes a very few “characteristic” substances. In most cases, final products or treated articles will contain a mixture of related structures, impurities, residual raw materials, and other contaminants. Some of these substances are known and well-characterized, but many are unknown. While much of the discussion of PFAS chemicals focuses on well-known substances like PFOA and PFOS and PFHxA, the potential environmental and human health impacts of the many other known and unknown constituents of PFAS products should be further studied, not be ignored.

Given the endless variety of possible R-groups, heteroatoms, and alkyl chain lengths, manufacturers have a large chemical-design space available for innovation. A recent survey by the Swedish Chemical Agency suggests that there may be more than 3,000 PFAS in existence on the world market (KEMI, 2015). Table X highlights some important PFAS classes, the associated R-groups that define each class, class abbreviations, and representative substances. Figure 15 contains a simplified PFAS classification organizational map for most of these classes.

### Trends in Per- and Polyfluorinated Substance Design

PFOS and PFOA, both with long perfluorinated alkyl chains, dominate the literature on PFAS due to their well-established PBT properties. These substances are associated with workhorse technologies of the historical first decades of PFAS development and use. PFOS is both a directly manufactured product and

is a highly stable degradation product of many legacy POSF-based surfactants and can also occur as an impurity in derivative products. PFOA was widely used as a polymer polymerization processing aid in fluorinated polymer manufacture. PFOA emissions have historically been linked to releases from these manufacturing operations (Prevedouros et al., 2006), but also occur as breakdown products of PFOA-precursors like the longer chain fluorotelomer alcohols. Production of PFOS and PFOA-associated chemistries has continued in China, India, and Russia, Figure 14. Articles treated with long-chain PFAS are still imported from these countries to the U.S.

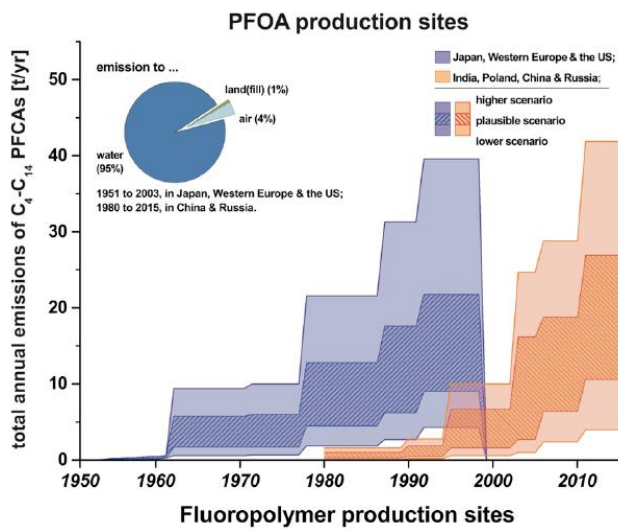
**Commented [A17]:** It could be very useful to the reader to introduce Figure 15 earlier – perhaps along with a diagram similar to Buck Figure 4 up in Section 2. Then the specific PFAS classes that are the subject of this CAP could be highlighted, and any specific PFAS discussed could be related to its class. For example, PFOA is a long-chain perfluoroalkyl carboxylic acid, and PFOS is a long-chain perfluoroalkane sulfonic acid.

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Figure 14 Manufacturing emissions estimates from the OECD. While most developed economies eliminated PFOA and PFOS production, production has moved to developing and transitional economies in recent years. Figure reproduced from "Working towards a Global Emission Inventory of PFAS: Focus on PFCAs - Status Quo and the Way Forward," © OECD, 2015, p. 39 (OECD/UNEP 2015).



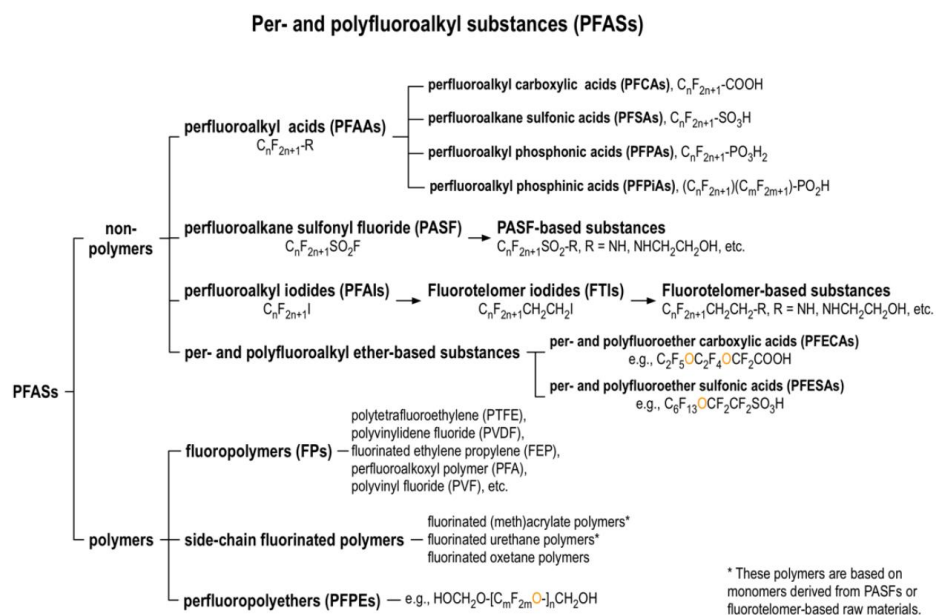


Figure 15 Classification of per- and polyfluoroalkyl substances (PFAS) based on the terminology found in Buck et al. 2011. Figure reproduced from "Working towards a Global Emission Inventory of PFAS: Focus on PFCAs - Status Quo and the Way Forward," © OECD, 2015, p. 39 (OECD/UNEP 2015).

Due to regulatory restrictions and voluntary withdrawal campaigns, manufacturers in the US, Western Europe and Japan have shifted manufacture primarily to shorter-chain PFAS products. Alternatives include (OECD, 2013):

- Perfluorobutane sulfonyl fluoride (PBSF)-based derivatives.
- Shorter-chain (i.e., 6:2) fluorotelomer-based chemicals.
- Mono- and polyfluorinated-ether compounds.
- Fluorinated oxetanes.
- Other fluorinated polymers.

Both *legacy* products, which are responsible for much of current-day emissions, but also the newer chemistries of so-called *alternative* products are included in the discussion of classes below. ~~It's~~ **important to remember that PFOS and PFOA often do may be present as an unintended very low level manufacturing impurity occur as by-products** of shorter-chain manufacture **in the by either ECF or telomerization process.** ~~es.~~ If non-target isomers and homologues are not removed by further processing, they **may well** end up in the final product formulation or treated articles.

#### Characteristic PFAS Substances by Use

[Poulsen, 2005 has a good discussion of legacy product designs. Information on both legacy and current-use products is taken from OECD, 2013, Buck et al., 2011, and Knepper & Lange, 2012.]



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The primary uses for PFAS products with commercial uses include fluorotelomer-based surfactants and side-chain fluoropolymers, perfluoropolyethers and oxetane derivatives, fluoroplastics (classic fluoropolymers) and fluoroelastomers. In addition there is another complete set of chemistries currently used based on PFBS manufactured by the ECF process. ~~are commercial surfactants and polymers.~~ While fluoroplastics (i.e. fluoro polymers) dominate the commercial market for fluorinated materials, this section will limit the overall polymer discussion primarily to side-chain fluorinated polymers used as surface treatments. Example chemicals for both legacy and current-use PFAS products in some selected use categories are presented in Table 3. Substances identified in these characteristic uses will be carried forward to the discussion of environmental fate and analytical chemistry. The substances identified should not be thought of as comprehensive, but rather more widely-known substances, or those with more readily-available data. Additional detail on the relative volumes of product types by use will be presented in the Uses chapter.

Table 3 ~~Typical~~ Examples of legacy and current-use products for selected use categories. *Non-exhaustive list*

Use Category	Example Legacy Products	Example Current-Use Product <sup>1</sup>
Carpet, <del>and</del> Textile, <del>Leather, Stone &amp; Tile, Paints and Coatings Additives and Surface Treatments</del>	EtFOSE <sup>5</sup> -based acrylate, <del>adipate</del> and FTOH-based acrylate, methacrylate and urethane side-chain polymers	FTI/FTOH-based <del>and PBSF-based</del> acrylate, methacrylate and urethane side-chain polymers
Paper and Packaging Treatment	EtFFOSE phosphate esters, MeFOSE acrylate polymers	FTOH-based PAPs, Perfluoropolyethers, <del>Side-chain fluoropolymers</del>
Specialty Chemicals	potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (PFOS-based surfactant)	FTOH-based <del>and PBSF-based</del> surfactants, Perfluoropolyethers
Fire-Fighting Chemicals	perfluoroalkyl sulfonamido amine derivatives and <del>other PFOS-based products</del>	6:2 FTAB (FTalkyliodideOH-based surfactant) <del>and 6:2 thiol derivatives (6:2-SH)</del>
Polymer Processing Aids	PFOA, PFNA	<del>GenX, ADONA, Others?</del> per- and poly-fluoroalkyl ether carboxylates

<sup>1</sup> It must be noted that legacy products are still manufactured and used globally by those that were not part of the US EPA VSP

#### Carpet and Textile Surface Treatment

Surface treatment for carpets, upholstery, leather, apparel, and other textiles are the largest market for fluorinated ~~ted~~ surfactants and side-chain polymers. Carpeting and upholstery involve large treated areas and stain-resistance treatment is a frequent specification among institutional purchasers (DTSC, 2017).

Perfluoroalkane sulfonyl fluoride (POSF) is a manufacturing precursor for the perfluoroalkane sulfonamido alcohols. These alcohols are converted to acrylates and methacrylates used as monomers in the production of polymeric surface protection products. Acrylates of N-methyl or N-ethyl perfluorooctane sulfonamido ethanol (MeFOSE and EtFOSE) and related precursors have been phased-

**Commented [A18]:** Why is the intention to limit the discussion to uses of side-chain polymers? Also, the discussion actually is not limited to uses of side-chain polymers because it discusses PPAs, which are unrelated to side-chain polymers. As previously noted in comments, this list is far from exhaustive when it comes to uses of the side-chain polymers.

**Commented [A19]:** This does not acknowledge that fact that the legacy products are still used in these applications in some parts of the world.

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<sup>5</sup> Table 4 below identifies the chemical formulas associated with the structure acronyms in Table 3.

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out among U.S., [EU and Japanese](#) manufacturers over the last decade. Current-use alternatives are made using shorter-chain precursors, such as the 4-C PBSF.

Similarly, fluorotelomer alcohols [and ethyl iodides](#) are the basis for acrylate, methacrylate, or urethane substances that are polymerized to the fluorinated side-chain polymers [partly](#) illustrated in Figure 7 above. Fluorotelomers offer [products longer chain lengths](#) based on polyfluorinated 4:2 or 6:2 products without the [intended use of longer 8-C](#) perfluorinated chains [of the FOSE legacy products](#).

#### **Paper and Packaging Treatment**

Surface treatment and impregnation products provide water, oil, and grease resistance, and non-stick performance for paper and packaging. These include both food-contact materials such as popcorn bags, pizza boxes, and fast-food wrappers, but also non-food applications, such as masking papers and folding cartons.

Legacy products include variants of perfluorooctane sulfonamido alcohols (like EtFOSE) in mono-, di-, and triphosphate ester products (monoPAPs, diPAPs, and triPAPs). These polyfluoroalkyl phosphoric acid (PAP) products are also called SAMPAPs (D'eon et al., 2009; Geueke, 2016). MeFOSE-based acrylate polymers similar to those used in textiles were also used for paper protection. [PFCA and PFOS-based and other long chain](#) chemistries are still used for food-contact materials in Thailand and China (Geueke, 2016; Yuan et al., 2016).

[As with carpets and textile products,](#) [C](#)urrent-use alternatives in food-contact materials may be based on:

- Short-chain replacements for the FOSE-like products, e.g., N-ethyl perfluorobutane sulfonamidoethanol (EtFBSE) (Geueke, 2016)
- Fluorotelomer acrylate and methacrylate side-chain polymers [made with short-chain fluorotelomer intermeidates](#)
- [Fluorotelomer alcohol versions of the mono-, di-, and triPAPs](#)
- Perfluoropolyethers (Wang et al., 2013)

It's difficult to find data on the extent of perfluoropolyether (PFPE) use, but they are reportedly used as surface treatments for a wide-range of materials.

#### **Specialty Chemicals**

Fluorinated surfactants are used in innumerable industrial and consumer products, where they provide advantages both during application, but also in the final product performance. Paints, coatings, and sealants need to wet the solid substrate and penetrate into crevices or other imperfections. The final finish should be smooth and level. These performance characteristics are all facilitated by the very low surface tension obtained using fluorosurfactants. The same or related surfactants [when formulated appropriately](#) can impart water, oil, and dirt resistance to painted walls, sealed grout, or polished floors.

Liquid-applied products vary substantially by type, and the specialty chemical market requires a broad range of surfactant designs. Knepper & Lange, 2012 provides a number of examples with supporting literature references. A study of commercial products purchased around 2010, such as, the carpet



Figure 16 Typical POSF-based surfactant used in liquid-applied products. [Wrong Structure with H present](#)

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protector in Figure 13 (above), often contained a mix of PFAA chain-lengths (4-C to 12-C PFAAs were quantified) (Liu et al., 2012). The potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (CASRN<sup>6</sup> 2991-51-7, also marketed as Fluorad 129, presumably discontinued) is a typical legacy POSF-based substance used in cleaning agents and polish products (Poulsen et al., 2004), Figure 16. [Need to fix structure.](#)

Product brochures from major manufacturers [like 3M Company and Chemours \(formally a DuPont set of businesses\) DuPont](#) identify 4-C (PFBS) and 6-C (6:2 FTOH) chemistries for a wide-range of product types (3M, 2016; DuPont, 2008). More example structures and classes can be found in the patent literature and product safety data sheets (SDSs).<sup>7</sup>

#### **Fire-Fighting Chemicals**

PFAS-based AFFF (aqueous film forming foams) were developed in the 1960s to extinguish [high-hazard Class B](#) flammable liquid fuel fires. After extinguishing the fire, the foam-surfactant film acts as a radiation barrier and vapor-sealant to prevent re-ignition or “burnback.” AFFFs are not a large use category, but they [were are often used in uncontrolled circumstances and historically used widely](#) in training exercises with little or no barrier to direct environmental release. They have been implicated in a great many cases of groundwater contamination (Hu et al., 2016).

While PFCAs were used [only](#) in the earliest AFFF formulations, POSF-based products dominated the market in the 1970s and later (Prevedouros et al., 2006). Many [1970-2000-era](#) AFFF products [were appear to be](#) PFSA-based, with derivatives of perfluoroalkylsulfamido amines and PFOS as “major presence[s]” (Favreau et al., 2017). Formulations for the military produced in the [1980s early to mid to early 2000s](#) contain perfluorinated chains up to 8-, 9-, and 10-C in some cases (Place & Field, 2012).

[The current generation fluorotelomer-based products](#) [Newer products are fluorotelomer-based with generally shorter perfluorinated chains, such as, the 6:2 fluorotelomer sulfonamide alkylbetaine \[6:2 FTAB, C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>SO<sub>2</sub>NHC<sub>3</sub>H<sub>6</sub>N<sup>+</sup>\(CH<sub>3</sub>\)<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup>\] \(Wang et al., 2013\). It is important to note that short chain fluorotelomer-based AFFF surfactants have been in use since the 1970s. These can also carry a three-digit prefix indicating three types of carbons: X:Y:Z \(perfluorinated-polyfluorinated-non-fluorinated\) carbons \(Place & Field, 2012\).](#)

[Polymer Processing Aids](#) [This chapter/section is largely not about PPAs so this has been deleted as not relevant to the overall discussion.](#)

[Fluorinated surfactants are used as emulsifiers in aqueous reaction systems, for example, the emulsion polymerization of PTFE. Sodium and ammonium salts of PFOA and perfluorononanoic acid \(PFNA\) were widely used in the U.S. and Europe and their use continues in developing and transitional economies.](#)

<sup>6</sup> Chemical Abstract Services Registration Number, a widely used identifier for chemical substances. The CASRN is most often unique, but there are at times multiple numbers for a single substance and some newly developed or non-commercial substances may not have an assigned CASRN.

<sup>7</sup> For example, SDSs can be found for specific Chemours fluorosurfactant products at <https://www.3eonline.com/EeeOnlinePortal/DesktopDefault.aspx?tabid=90> using the product identifier.

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Newer processing aids identified in the literature are functionalized perfluoroethers or perfluoropolyethers (PFPEs) which contain ether O atoms. Among these are, Figure X (Wang et al., 2013):

- Ammonium 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid] (ADONA from 3M/Dyneon)
- Ammonium perfluoro-2-propoxypropanoic acid (PFPrOPrA, or GenX from Chemours).



*Figure 17 Polyether processing aids ADONA (left) and GenX (right).*

While there is no evidence of fluoropolymer manufacture in Washington State, these PFAS ether-structures are some of the very few examples for which any literature data is available. Other ether-based PFAS are likely in use in products in Washington State, but the extent of their use is not known.

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Table 4 Should this include application information? Buck does. Not much room here.

Group	Subgroup	Abbreviation	Functional group $C_nF_{2n+1}R$ , where R =	Examples
Perfluoroalkyl acids (PFAAs)	Perfluoroalkyl carboxylic acids	PFCAs	-COOH	Perfluorooctanoic acid (PFOA) Perfluorononanoic acid (PFNA) Perfluorohexanoic acid (PFHxA)
	Perfluoroalkyl carboxylates	PFCAs	-COO-	Sodium perfluorooctanoate (Na-PFOA) Ammonium perfluorooctanoate (APFO) Ammonium perfluorononanoate (APFN)
	Perfluoroalkane sulfonic acids	PFSAs	-SO <sub>3</sub> H	Perfluorooctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorobutane sulfonic acid (PFBS)
	Perfluoroalkane sulfonates	PFSAs	-SO <sub>3</sub> -	Tetraethylammonium perfluorooctane sulfonate (NEt <sub>4</sub> -PFOS)
	Perfluoroalkyl phosphonic acids	PFPAs	-P(=O)(OH) <sub>2</sub>	Perfluorooctyl phosphonic acid (C8-PFPA)
	Perfluoroalkyl phosphinic acids	PFPIAs	P(=O)(OH)(C <sub>m</sub> F <sub>2m+1</sub> )	Bis(perfluorohexyl) phosphinic acid (C6/C6-PFPIA)
Perfluoroalkane sulfonyl fluorides		PASFs	-SO <sub>2</sub> F	Perfluorooctane sulfonyl fluoride (POSF) Perfluorobutane sulfonyl fluoride (PBSF)
Perfluoroalkane sulfonamides		FASAs	-SO <sub>2</sub> NH <sub>2</sub>	Perfluorooctane sulfonamide (FOSA)
Perfluoroalkanoyl fluorides		PAFs	-COF	Perfluorooctanoyl fluoride (POF)
Perfluoroalkyl iodides (Telomer A)		PFAls	-I	Perfluorohexyl iodide (PFHxI) <a href="#">Perfluorooctyl iodide (PFOI)</a>
Perfluoroalkane sulfonamido substances	N-Alkyl perfluoroalkane sulfonamides	MeFASAs, EtFASAs, BuFASAs	-SO <sub>2</sub> NH(R') where R' = C <sub>m</sub> H <sub>2m+1</sub> (m = 1,2,4)	N-Methyl perfluorooctane sulfonamidoethanol (MeFOSE), N-Ethyl perfluorooctane sulfonamidoethanol (EtFOSE)
	Perfluoroalkane sulfonamidoethanols and N-alkylperfluoroalkane sulfonamidoethanols	FASEs, MeASEs, EtFASEs, BuFASEs,	-SO <sub>2</sub> N(R')CH <sub>2</sub> CH <sub>2</sub> OH where R' = C <sub>m</sub> H <sub>2m+1</sub> (m = 1,2,4)	N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE) Perfluorooctane sulfonamidoethanol (FOSE)

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Group	Subgroup	Abbreviation	Functional group $C_nF_{2n+1}R$ , where R =	Examples
	N-Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates	MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs	$-SO_2N(R')CH_2CH_2OC(O)CH=CH_2$ and $SO_2N(R')CH_2CH_2OC(O)C(CH_3)=CH_2$ where $R' = C_mH_{2m+1}$ ( $m=1,2,4$ )	N-Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC)
Fluorotelomer substances	Semifluorinated n-alkanes and alkenes	SFAs SFAenes	$-(CH_2)_mH$ and $-CH=CH(CH_2)_{m-2}H$ , with $m = 2-16$ and $n = 6-16$	(Perfluorooctyl)ethane ( $F_8H_2$ )
	n:2 Fluorotelomer iodides	n:2 FTIs	$-CH_2CH_2I$	8:2 Fluorotelomer iodide (8:2 FTI)
	n:2 Fluorotelomer olefins	n:2 FTOs	$-CH=CH_2$	6:2 Fluorotelomer olefin (6:2 FTO)
	n:2 Fluorotelomer alcohols	n:2 FTOHs	$-CH_2CH_2OH$	4:2 Fluorotelomer alcohol (4:2 FTOH)
	n:2 Fluorotelomer acrylates and methacrylates	n:2 FTACs  n:2 FTMACs	$-H_2CH_2OC(O)CH=CH_2$ and $-CH_2CH_2OC(O)C(CH_3)=CH_2$	6:2 Fluorotelomer acrylate (6:2 FTAC) 6:2 Fluorotelomer methacrylate (6:2 FTMAC)
	n:2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates	PAPs	$(-CH_2CH_2O)_x-$ $P(=O)(OH)_{3-x}$ where $x = 1$ or $2$	10:2 Fluorotelomer phosphate monoester (10:2 monoPAP)
	n:2 Fluorotelomer sulfonic acids	n:2 FTSAAs	$-CH_2CH_2SO_3H$	6:2 Fluorotelomer sulfonic acid (6:2 FTSA)
	n:2 Fluorotelomer sulfonic acid chlorides	n:2 FTSAcs	$-CH_2CH_2SO_2Cl$	6:2 Fluorotelomer sulfonyl chloride
Miscellaneous	Polyfluoroalkyl ether carboxylic acids & others		e.g., $-O(C_mF_{2m})-OCHF(C_pF_{2p})COOH$	4,8-Dioxa-3H-perfluoro-nonanoate 3H-perfluoro-3-[[3-methoxypropoxy]propanoic acid] (ADONA) perfluoro-2-propoxypropanoic acid (GenX)
	Perfluoropolyethers			

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