

Sept 20, 2017 DRAFT PFAS CAP – Chemistry Chapter for external review.
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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.

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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 (PFASs) are prized for their effectiveness in reducing surface energy (of solids) and surface tension (of liquids). These properties make PFASs resistant to both oil and water. PFASs can retain these properties at high temperatures and in corrosive environments.

Most PFASs are manufactured by electrochemical fluorination (ECF) or telomerization processes. Both processes produce unintended by-products giving end-mixtures of variable structural shapes (mostly ECF) and lengths (both ECF and telomerization). These product mixtures of target compounds, by-product substances, residuals and contaminants complicate efforts to assess environmental and human health impacts.

Many PFASs degrade to highly persistent and bioaccumulative perfluoroalkyl acids like PFOA and PFOS. Fluorotelomer alcohol substances are volatile and can be transported long distances in the atmosphere before breakdown and washout by rain. Newer replacement PFAS products, like 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 Substances (PFASs)?

[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 1.¹

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
1763-23-1	Perfluorooctane sulfonic acid (PFOS)	C ₈ F ₁₇ SO ₃ H	SO ₃ H
29081-56-9	Perfluorooctane sulfonic acid, ammonium salt	C ₈ H ₄ F ₁₇ NO ₃ S	SO ₃ NH ₄
70225-14-8	Perfluorooctane sulfonic acid, diethanolamine salt	C ₁₂ H ₁₂ F ₁₇ NO ₅ S	C ₄ H ₁₂ NO ₅ S
29457-72-5	Perfluorooctane sulfonic acid, lithium salt	C ₈ F ₁₇ SO ₃ Li	SO ₃ Li
2795-39-3	Perfluorooctane sulfonic acid, potassium salt	C ₈ F ₁₇ SO ₃ K	SO ₃ K

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

¹ "Sulfonates" referred to in the WAC are identified here as "sulfonic acids." This chapter uses the widely-adopted terminology for PFASs described in Buck et al., 2011. Chemical names cited in sources, such as the WAC in this case, are modified without further reference.

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.

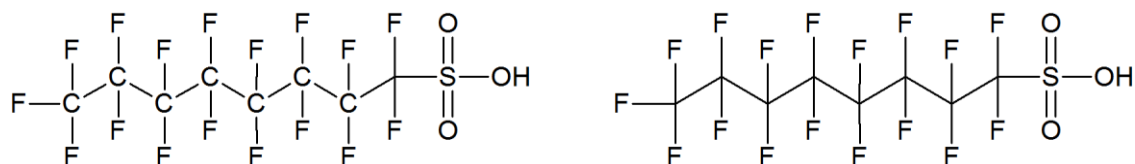


Figure 1 Perfluorooctane sulfonic acid (PFOS) shown with (left) and without (right) the carbon atoms.

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 SO₃H sulfonic acid group. Manufacturers may alter the R-group to achieve desired properties, for example, solubility in a particular solvent.

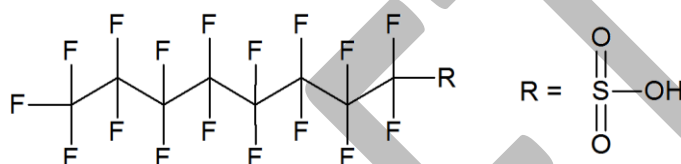


Figure 2 PFOS in which the SO₃H functional group is represented by R.

The remaining substances in Table 1 can be specified by redefining the R-group. For example, perfluorooctane sulfonic acid, potassium salt is represented as C₈H₁₇SO₃K, or by C₈H₁₇R, where R = SO₃K. 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 SO₃H replaced by an OH, indicating an alcohol.

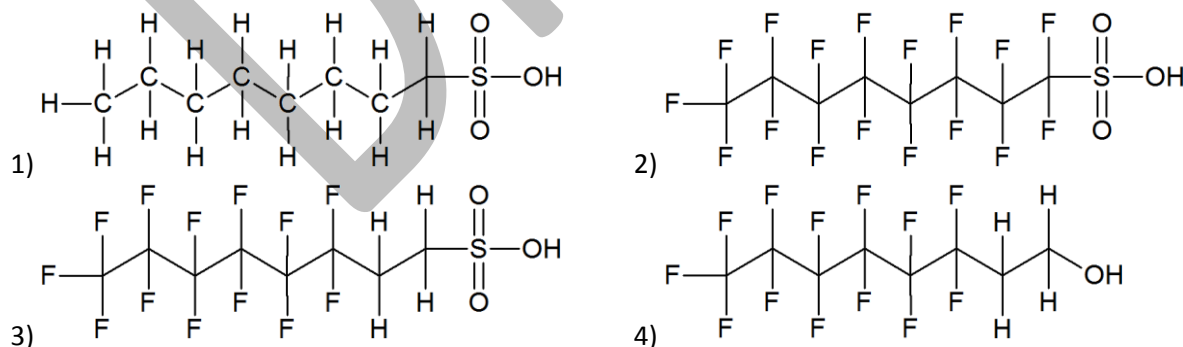


Figure 3 Four related structures: 1) the non-fluorinated octane sulfonic acid (a hydrocarbon with no fluorine), 2) its perfluorinated cousin PFOS, 3) the polyfluorinated 6:2 fluorotelomer sulfonic acid (with hydrogen and fluorine on the backbone carbon chain) and 4) the polyfluorinated 6:2 fluorotelomer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

This chapter focuses primarily on *alkyl* substances, referring to the single-bonded backbone chain of carbon atoms in all four structures of Figure 3. Structures (1), (2) and (3) are *acids* defined by the sulfonic acid end-group, SO₃H. While (1), (2) and (3) are *alkyl acids*, (2) is a *perfluorinated alkyl acids* (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 polyfluorinated alkyl substances (PFASs).

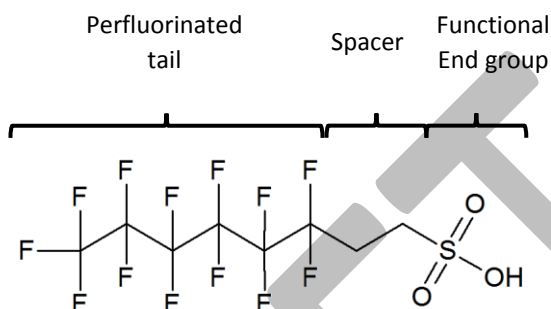


Figure 4. Schematic structure of a typical polyfluorinated surfactant. The 6:2 fluorotelomer sulfonic acid. In this naming convention, there are six perfluorinated carbons and two hydrogenated carbons (Hs not shown except for those in the functional end-group). Generally, the hydrocarbon (H) atoms are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

Perfluorinated chains are often represented in a shorthand form as C_nF_{2n+1}. In Figure 4, the 6 perfluorinated carbons, n = 6 could be represented as C₆F₁₃, the hydrocarbon spacer as C₂H₄, and the end group as SO₃H. The polyfluorinated 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 Alkyl Substances (PFASs)

The Essential Nature of Perfluorinated Substances

Perfluorinated substances 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, fluorocarbons are often preferred for use in extreme environments (high temperatures, strongly reactive conditions, etc.).²

Per- and polyfluorinated substances are also *low surface energy* substances. Fluoropolymers, such as polytetrafluoroethylene³ (PTFE), are un-wettable in that both oil and water will “bead-up” on PTFE surfaces. Polymers derived from PFASs 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.

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

² 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.

³ 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.

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.

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.

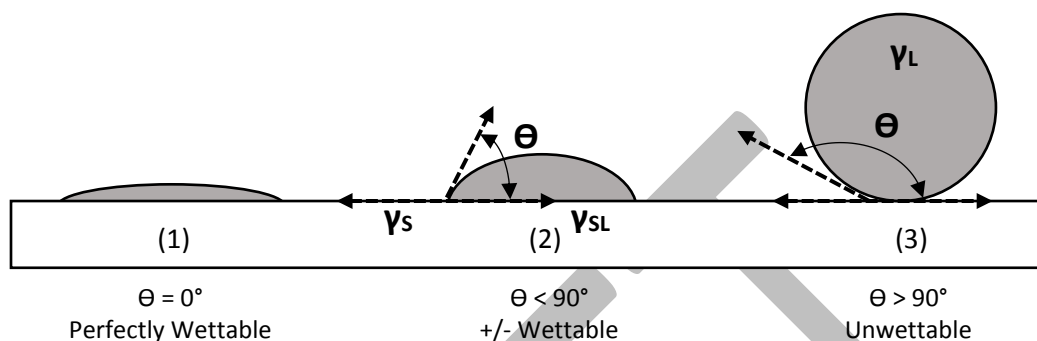


Figure 5 Contact angle and spreading. The three cases illustrate (left) complete wetting, (middle) partial wetting and, (right) no wetting. θ represents the contact angle and γ the surface energy or tension (see Equation 1 below). Water will bead-up on many hydrophobic plastics (3), but oil will more 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, γ_s , is high, and the liquid surface tension, γ_L , is low. [The interfacial tension, γ_{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 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.

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, γ_s (mN/m)	Liquid	Surface tension, γ_L (mN/m)
-CF ₃	6	Water	72
-CF ₂ H	15	n-Octane	22
-CF ₂ -	18	Olive oil	32
-CH ₃	22		
-CH ₂ -	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 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's 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 introduced a hydrocarbon spacer between the perfluorinated tail and the head-group. The hydrocarbon "spacer" extends the combined tail length and is believed to recover some of the functionality lost when using shorter perfluorinated chains, Figure 6 (Renner, 2006).



Figure 6 Schematic of a fluorinated surfactant. The perfluorinated chain is represented by the black bar (left), the non-fluorinated hydrocarbon spacer by the gray portion (center), and the functional R-group (right) by the white portion. The R-group is adjusted to ensure solubility in the solvent of interest or other functional purposes.

Very similar surfactant-like structures are used as monomers for polymeric surface-treatment or impregnation products for textiles and paper. R-groups such as acrylate or methacrylate polymerize to form a non-fluorinated hydrocarbon backbone with fluorinated side-chains, like teeth on 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).

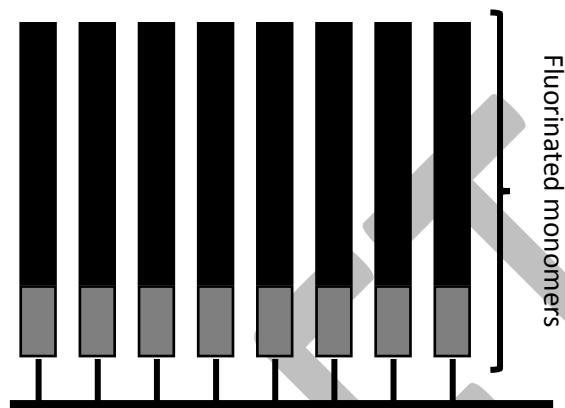


Figure 7 Fluorinated “side-chain polymer” typical of stain-resistant surface treatments for textiles. The solid line at the base represents the main polymer backbone. Fluorinated chains (black bars) are bonded to the backbone through reactions with the hydrocarbon spacer group (gray bar).

Heteroatoms, like oxygen (O), may also be introduced into the fluorinated tail. The resulting perfluoroalkyl ethers are used as 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).

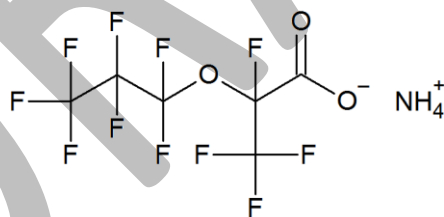


Figure 8 The ammonium salt of PFPrOPrA (GenX) is a processing aid used in the manufacture of fluorinated polymer resins like PTFE. GenX has replaced APFO, which readily dissociates in the environment to highly persistent PFOA.

The know-how to fine-tune these surfactant and monomer molecular structures is highly-valued intellectual property and may be one reason why the details of these structures are often not publically disclosed. The first chapter in Knepper& Lange 2012 contains many examples of fluorinated surfactant structures, their associated applications, and relevant literature citations (Knepper & Lange, 2012).

Manufacturing

[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 PFASs 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 building blocks for most PFASs are manufactured 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 Voigt, 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.

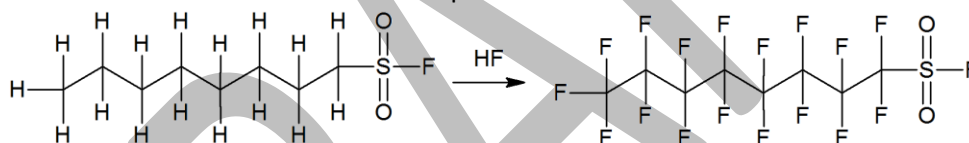


Figure 9 A schematic of the ECF reaction that forms POSF.

Telomerization

Following 3M's phase-out of PFOS and PFOA production by ECF, DuPont began large-scale manufacture of PFOA using telomerization. Telomerization typically results in products with even-numbered carbon chain lengths with an iodide (I) functional end-group. If the process is continued with the *hydrocarbon* ethylene instead of *fluorocarbon* reactants, 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.

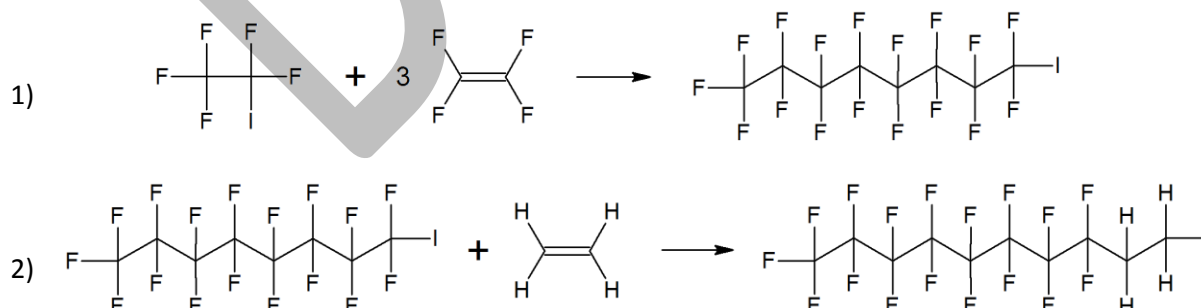


Figure 10 Reaction 1 shows the telogen (perfluoroethyl iodide) reacting with three taxogen units (tetrafluoroethene) to form a perfluorinated product, perfluorooctyl iodide (PFI). PFI can be further reacted (reaction 2) with the hydrocarbon ethene to form the polyfluorinated 8:2 fluorotelomer iodide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

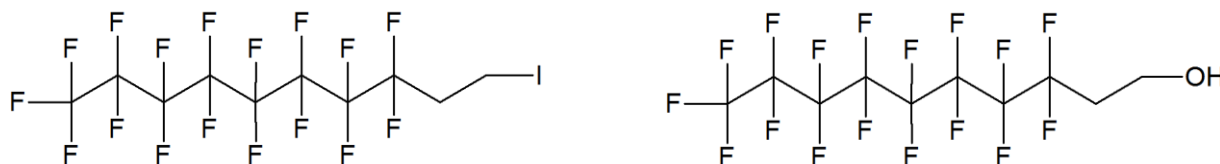


Figure 11 An 8:2 fluorotelomer iodide (left) can be converted to an 8:2 fluorotelomer alcohol (right). The “8” refers to the eight perfluorinated carbons. The “2” refers to the two hydrogenated carbons (Hs not shown) adjacent to the end group.

Technical Quality and Implications for Environmental Impacts

While we often describe discrete substances, like PFOS or PFOA, ECF and telomerization produce complex *mixtures* of substances rather than pure one-component products. The harsh conditions of the ECF process lead to a variety of unwanted side-reactions resulting in complicated mixtures of perfluorinated 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).

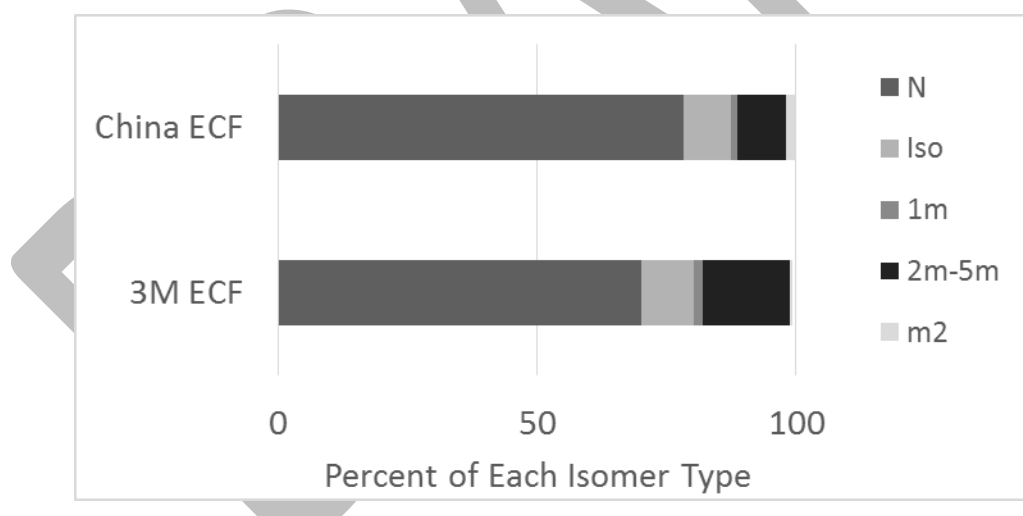


Figure 12 The bars represent the isomer composition of two ECF products reported in Jiang 2015. “N” represents the “normal” straight-chain product, while the other legend items represent various branched isomers. The China ECF bar represents Chinese ECF production (Defu PFOSK, China). The isomer distribution 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.)

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 FTIs are relatively volatile, the change in properties between the C_n to C_{n+2}

homologue⁴ allows for purification by distillation (Krafft & Riess, 2015). The extent to which manufacturers purify their products is not well understood.

Products are sometimes marketed as mixtures of PFAS isomers or homologues (KEMI, 2015). Surflon® S-111, a surfactant produced by telomerization and presumably discontinued, contained primarily 9-C perfluorononanoic acid (PFNA), but also significant quantities of linear homologues, the 11-C PFUnDA (205) and the 13-C PFTTrDA (5%) (Prevedouros, 2006). Chemical analysis of “articles of commerce” shows that many formulated products are complex PFAS mixtures, Figure 13 (Liu et al., 2012).

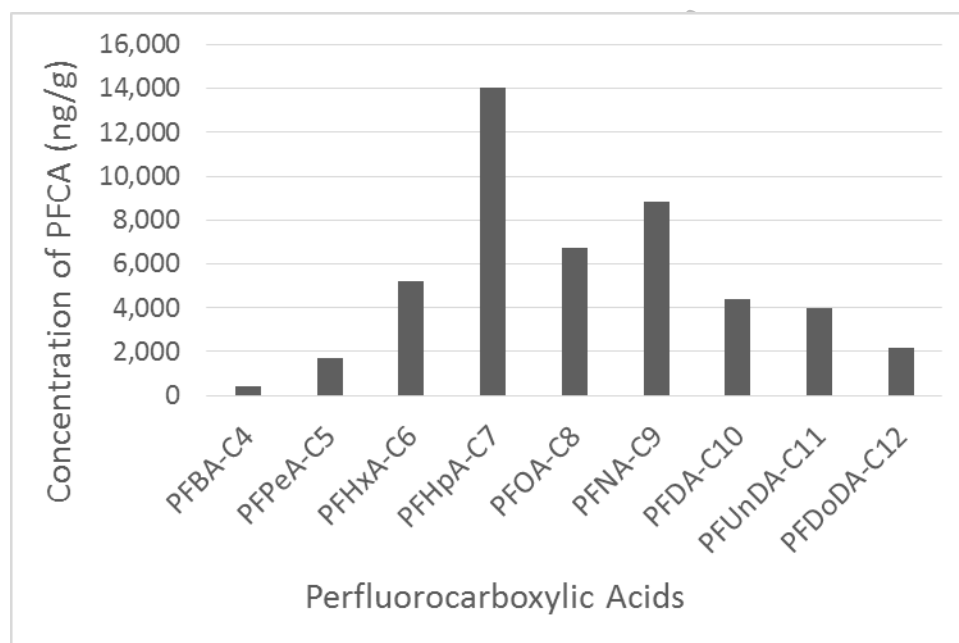


Figure 13 Analytical chemistry data for the PFCA content (C4-C12) of a U.S. carpet/upholstery protector concentrate (designated B-1) (Liu, 2012). The sample, purchased in 2007, contains a wide-distribution of chain lengths.

Products can also be contaminated with residual raw material or processing aids. PFOA, higher homologues, and PFOA precursors have been found in 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.

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

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.]

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 PFASs 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 organizational map for most of these classes.

Trends in Per- and Polyfluorinated Substance Design

PFOA and PFOS, both with long perfluorinated alkyl chains, dominate the literature on PFASs due to their well-established PBT properties. These substances are associated with workhorse technologies of the first decades of PFAS development and use. PFOA 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 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 fluorotelomer alcohols. Production of PFOA and PFOA-associated chemistries has continued in China, India and Russia, Figure 14. Articles treated with long-chain PFASs are still imported from these countries to the U.S.

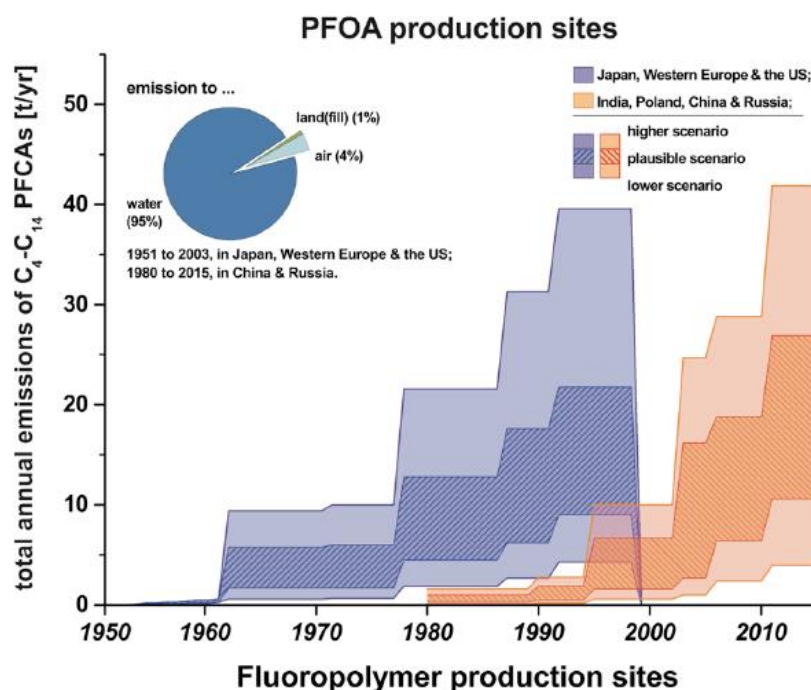


Figure 14 Manufacturing emissions estimates from the OECD. While most developed economies eliminated PFOA and PFOS production, production has moved to developing and transitional economies in recent years. Figure reproduced from "Working towards a Global Emission Inventory of PFASs: Focus on PFCAs -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

Per- and polyfluoroalkyl substances (PFASs)

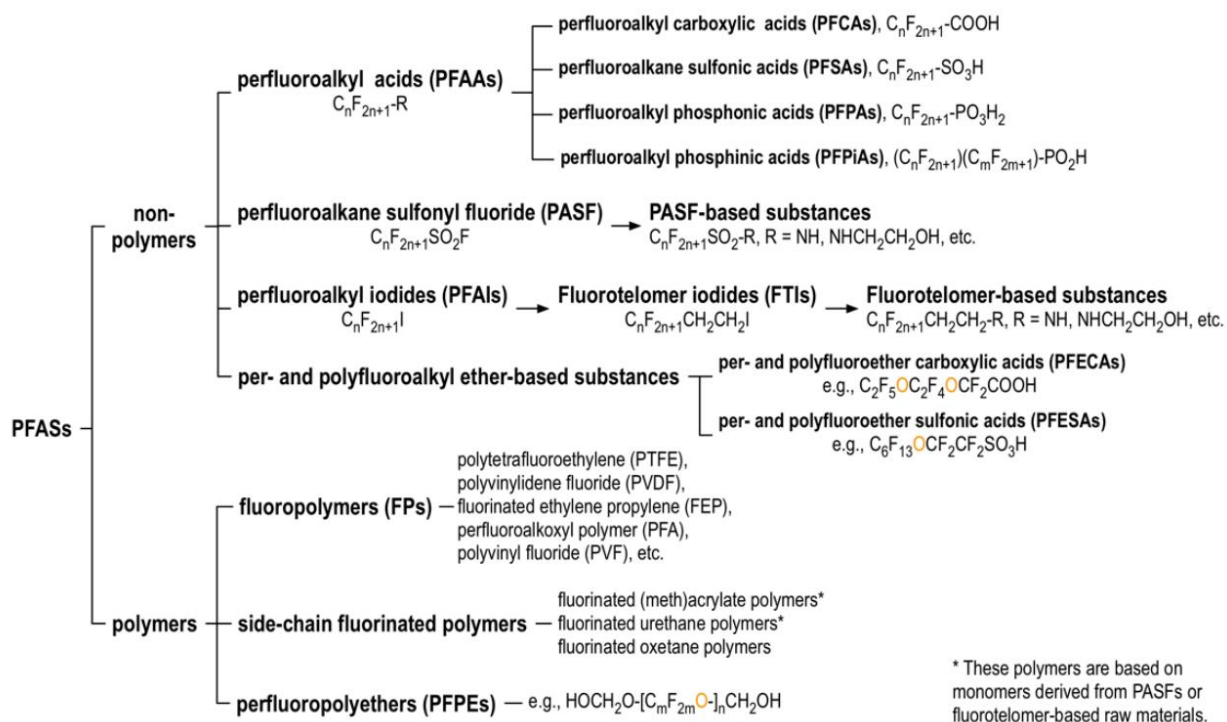


Figure 15 Classification of per- and polyfluoroalkyl substances (PFASs) based on the terminology found in Buck et al. 2011. Figure reproduced from "Working towards a Global Emission Inventory of PFASs: Focus on PFCAs - Status Quo and the Way Forward," © OECD, 2015, p. 39 (OECD/UNEP 2015).

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 do occur as by-products of shorter-chain manufacture by either ECF or telomerization processes. If non-target isomers and homologues are not removed by further processing, they will 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.]

The primary uses for PFASs are commercial surfactants and polymers. While polymers dominate the market for fluorinated materials, this section will limit the *polymer discussion* primarily to side-chain 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.

Use Category	Example Legacy Products	Example Current-Use Product
Carpet and Textile Surface Treatment	EtFOSE ⁵ -based acrylate, adipate and urethane side-chain polymers	FTOH-based acrylate, methacrylate and urethane side-chain polymers
Paper and Packaging Treatment	EtFFOSE phosphate esters, MeFOSE acrylate polymers	FTOH-based PAPs, Perfluoropolyethers
Specialty Chemicals	potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (PFOS-based surfactant)	FTOH-based surfactants, Perfluoropolyethers
Fire-Fighting Chemicals	perfluoroalkyl sulfonamido amine derivatives and PFOS	6:2 FTAB (FTOH-based surfactant)
Polymer Processing Aids	PFOA, PFNA	GenX, ADONA

Carpet and Textile Surface Treatment

Surface treatment for carpets, upholstery, leather, apparel and other textiles are the largest market for fluorinated 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-out among U.S. manufacturers over the last decade. Current-use alternatives are made using shorter-chain precursors, such as the 4-C PBSF.

Similarly, fluorotelomer alcohols are the basis for acrylate, methacrylate or urethane substances that are polymerized to the fluorinated side-chain polymers illustrated in Figure 7 above. Fluorotelomers offer longer-chain lengths based on polyfluorinated 4:2 or 6:2 products without the 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 like popcorn bags,

⁵ Table 4 below identifies the chemical formulas associated with the structure acronyms in Table 3.

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. PFOA- and PFOS-based chemistries are still used for food-contact materials in Thailand and China (Geueke, 2016; Yuan et al., 2016).

As with carpets and textile products, current-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.
- 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 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 protector in Figure 13 (above), often contained a mix of PFAA chain-lengths (4-C to 12-C PFAAs were

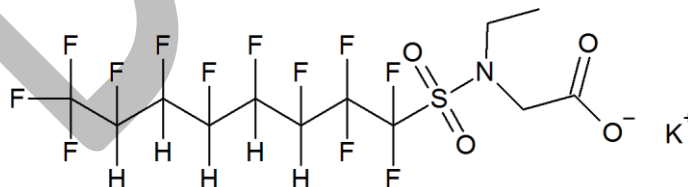


Figure 16 Typical POSF-based surfactant used in liquid-applied products.

quantified) (Liu et al., 2012). The potassium salt of glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl] (CASRN⁶ 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.

⁶ 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.

Product brochures from major manufacturers like 3M Company and 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).⁷

Fire-Fighting Chemicals

PFAS-based AFFF (aqueous film forming foams) were developed in the 1960s to extinguish 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 are often used in uncontrolled circumstances and 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 in the earliest AFFF formulations, POSF-based products dominated the market in the 1970s and later (Prevedouros et al., 2006). Many 2000-era AFFF products 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 early-to-mid-2000s contain perfluorinated chains up to 8-, 9-, and 10-C in some cases (Place & Field, 2012).

Newer products are fluorotelomer-based with generally shorter perfluorinated chains, such as, the 6:2 fluorotelomer sulfonamide alkylbetaine [6:2 FTAB, $C_6F_{13}C_2H_4SO_2NHC_3H_6N^+(CH_3)_2CH_2COO^-$] (Wang et al., 2013). 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

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.

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).

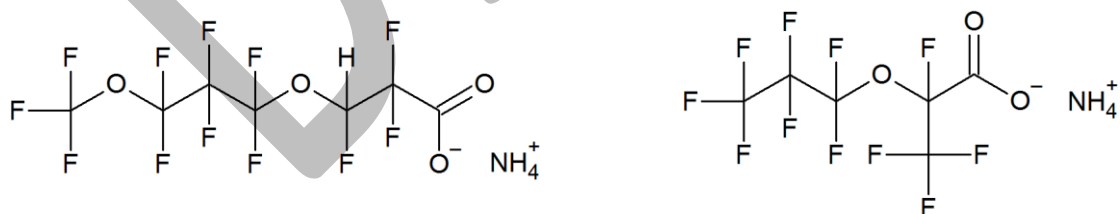


Figure 17 Polyether processing aids ADONA (left) and GenX (right).

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.

⁷ 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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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 ₃ H	Perfluorooctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorobutane sulfonic acid (PFBS)
	Perfluoroalkane sulfonates	PFSAs	-SO ₃ ⁻	Tetraethylammonium perfluorooctane sulfonate (NEt ₄ -PFOS)
	Perfluoroalkyl phosphonic acids	PFPA	-P(=O)(OH) ₂	Perfluorooctyl phosphonic acid (C8-PFPA)
	Perfluoroalkyl phosphinic acids	PFPIAs	P(=O)(OH)(C _m F _{2m+1})	Bis(perfluorohexyl) phosphinic acid (C6/C6-PFPIA)
Perfluoroalkane sulfonyl fluorides		PASFs	-SO ₂ F	Perfluorooctane sulfonyl fluoride (POSF) Perfluorobutane sulfonyl fluoride (PBSF)
Perfluoroalkane sulfonamides		FASAs	-SO ₂ NH ₂	Perfluorooctane sulfonamide (FOSA)
Perfluoroalkanoyl fluorides		PAFs	-COF	Perfluorooctanoyl fluoride (POF)
Perfluoroalkyl iodides (Telomer A)		PFAls	-I	Perfluorohexyl iodide (PFHxI)
Perfluoroalkane sulfonamido substances	N-Alkyl perfluoroalkane sulfonamides	MeFASA, EtFASAs, BuFASAs	-SO ₂ NH(R') where R' = C _m H _{2m+1} (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 ₂ N(R')CH ₂ CH ₂ OH where R' = C _m H _{2m+1} (m = 1,2,4)	N-Ethyl perfluorobutane sulfonamidoethanol (EtFBSE) Perfluorooctane sulfonamidoethanol (FOSE)

Do not cite or quote.

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 salts	n:2 FTSAAs		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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