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Claigan PFAS Submission #2

PFOA in Articles

Test Data - 2022/2023

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1. Summary

This report is submission #2 of 5 by Claigan Environmental Inc. (Claigan) on behalf of the EU PFAS Restriction Submission Project ("PFAS Submission Project"). The PFAS submission project is made up of dozens of companies from a wide range of industries (consumer, professional, industrial, medical, oil and gas, laboratory equipment, textiles, electronic components, and retail sales).

The PFAS Submission Project is focused primarily on the needs of complex products (articles). Claigan is both a restricted materials consultancy and high volume restricted materials testing laboratory. Each of the PFAS Submission Project submissions is based on contributions from all major sectors of industry and 2023 PFAS testing data of complex products.

This report (#2) is a description of measured forever chemicals in articles based on testing data from 2022 to 2023 (with the exception of fluoroalkylphosphates). Fluoroalkylphosphates were no longer used in products in 2022 and 2023, and reference data from published papers were used instead. Claigan purchased (online) a range of cosmetics in 2022 that listed C9-C15 fluoroalkylphosphate on their ingredients list online, however that ingredient was no longer present when the product arrived. Claigan conducted another survey of cosmetics ingredients in 2023, but was unable to find any that still used fluoroalklylphosphates.

The data presented in this report is generalized from over 200 complex products averaging 20 to 1,000 components per product.

The primary source of perfluorocarboxylates (PFOA family) in products is related to either the cleavage of the weak (low energy of bond dissociation) C-O-C bond in some fluoropolymers or from perfluorocarboxylates created during irradiation of fluoropolymer powders.

The primary source of perfluorosulfonates (PFOS) family in products was related to the degradation of the C6 complex fluorosurfactant used to manufacture fluoroelastomers, perfluoroelastomers, and similar fluoro rubbers.

Important note - contrary to common belief, no perfluorocarboxylates in unirradiated PTFE were detected in products tested in 2022 and 2023 (detection limit of 25 ppb). There is currently no reason to believe that perfluorocarboxylates are present in unirradiated and unexpanded PTFE in modern products.

September 21 2023

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2. Comparison Chart

Comparison	PTFE	Irradiated PTFE	ePTFE	PFA	Fluoro elastomers	Fluoro acrylates	Fluoro Silicone	Fluoro phosphates
Short Chain Perfluorocarboxylates (C4-C7)	Never	Commonly	Commonly	Commonly	Rarely	Commonly	Never	Commonly
Long Chain Perfluorocarboxylates (C8-C14)	Never	Commonly	Commonly	Commonly	Never	Commonly	Never	Commonly
Short Chain Fluorotelomers (C4-C7)	Never	Never	Never	Never	Never	Commonly	Never	Commonly
Long Chain Fluorotelomers (C8-C14)	Never	Never	Never	Never	Never	Commonly	Never	Commonly
Short Chain Fluoroacrylates (C4-C7)	Never	Never	Never	Never	Never	Commonly	Never	Never
Long Chain Fluoroacrylates (C8-C14)	Never	Never	Never	Never	Never	Commonly	Never	Never
Short Chain Fluorosulfonates (C4-C7)	Never	Never	Never	Never	Never	Never	Never	Never
Long Chain Fluorosulfonates (C8-C14)	Never	Never	Never	Never	Never	Never	Never	Never
Short Chain Fluorotelomer sulfonates	Never	Never	Never	Never	Commonly	Never	Never	Never
Long Chain Fluorotelomers sulfonates	Never	Never	Never	Never	Never	Never	Never	Never

3. Definitions

3.1. Description

3.1.1. A general description of each detected (by testing and engineering evaluation) use

3.1.2. Exception - fluorophosphates (C9 to C15 fluoroalkyl phosphates) were no longer available in cosmetics for testing in 2022 and 2023.

3.1.2.1. Fluorophosphate details are from “Risk assessment of fluorinated substances in cosmetic products. Survey of chemical substances in consumer products No. 169 (DEPA - October 2028)”:

3.2. Forever chemical risk

3.2.1. Does the material contain measurable perfluorocarboxylates (PFOA family) or perfluorosulfonates (PFOS family) in the finished article?

3.2.1.1. **Never** - Not expected to contain perfluorocarboxylates (PFOA family) or perfluorosulfonates (PFOS family).

3.2.1.2. **Rarely** - Rarely contains perfluorocarboxylates (PFOA family) or perfluorosulfonates (PFOS family). Not the standard case.

3.2.1.3. **Commonly** - Normally (the majority) contains perfluorocarboxylates (PFOA family) or perfluorosulfonates (PFOS family).

3.2.1.4. Note - additional details to be provided in the case that presence is possible.

4. Related documents

4.1. Claigan PFAS Submission #1 - PFAS in Articles

4.1.1. Comprehensive 2023 test data regarding locations and uses of PFAS in articles.

4.2. Claigan PFAS Submission #3 - PFAS in Drinking Water

4.2.1. Evaluation of recent news articles and related science papers on PFAS in drinking water and in human blood.

4.3. Claigan PFAS Submission #4 - PFAS Substitutes and Alternatives

1.1.1. A review of pros and cons of fluoropolymers and their potential substitutes.

4.4. Claigan PFAS Submission #5 - PFAS Derogations and Justifications

1.1.2. Requested derogations and related justifications for necessary uses of PFAS.

5. Polytetrafluoroethylene (PTFE)

CAS # - 9002-84-0

5.1. Summary

5.1.1. PTFE is the most common fluoropolymer with a wide range of applications. This listing is for the unirradiated and unexpanded PTFE polymer. Irradiated PTFE and ePTFE have separate summaries in this document even though they share the same CAS number. The additional processing of irradiation or expansion changes the chemical characteristics of PTFE sufficiently so that separate listings were necessary.

5.2. Forever Chemicals (initial)

5.2.1. **None expected.** Unirradiated and unexpanded PTFE does not contain any PFOA or PFOS family of chemicals. PFOA related substances may have been used decades ago for the manufacture of PTFE, but testing of hundreds of PTFE parts by Claigan has not shown any PFOA or PFOS related chemicals in unirradiated and unexpanded PTFE.

5.3. Forever Chemicals (over time)

5.3.1. **None expected.** PTFE does not degrade into forever chemicals such as PFOA or PFOS. PTFE does not have the ether bond (C-O-C) that leads to degradation into PFOA related chemicals that can occur in other fluoropolymers (such as fluoroacrylate coatings or PFA polymers).

6. Irradiated Polytetrafluoroethylene (PTFE)

CAS # - 9002-84-0 (Irradiated - Same as PTFE)

6.1. Summary

6.1.1. PTFE in its normal state is fairly rigid. For use in situations requiring flexibility, PTFE is often irradiated with either gamma or e-beam radiation. The radiation fractures the long polymer chains. Most of the chains reconnect randomly with other fractured chains (called crosslinking) to create a rubberized form of PTFE.

6.1.2. However, some chain fractures react with oxygen and form different lengths of perfluorocarboxylates (PFOA family).

6.1.3. Applications for irradiated PTFE include heat shrinkable tubing and plumber's (pool) tape. PTFE tape in medical devices is commonly made from irradiated PTFE.

6.2. Forever Chemicals (initial)

6.2.1. **Commonly present.** Irradiated PTFE usually contains 100s of ppb of each of the perfluorocarboxylate (PFOA family). The perfluorocarboxylates are randomly formed from chains fractured from the original long PTFE polymer chains with gamma (or e-beam) radiation that react with air instead of crosslinking with other chain fractures.

6.3. Forever Chemicals (over time)

6.3.1. **None expected.** Irradiated PTFE does not further degrade into further forever chemicals such as PFOA or PFOS. Irradiated PTFE does not have the ether bond (C-O-C) that leads to degradation into PFOA related chemicals that can occur in other fluoropolymers (such as fluoroacrylate coatings or PFA polymers). Irradiated PTFE has no natural degradation path into the PFOA family unless it is further irradiated.

7. Expanded Polytetrafluoroethylene (ePTFE)

CAS # - 9002-84-0 (Same as PTFE)

7.1. Summary

7.1.1. ePTFE, or expanded polytetrafluoroethylene, is a woven version of PTFE which is soft, flexible, microporous, air permeable, and fluid impermeable. ePTFE is made from the same polymer as PTFE but expanded to create a porous structure.

7.1.2. Either part of the expansion process creates similar polymer bond fracturing as irradiation or the powder size is reduced by irradiation before expansion - creating a low concentration of perfluorocarboxylates (PFOA family) normally in ePTFE (which is not normally found in unirradiated, and unexpanded PTFE).

7.1.3. Applications for ePTFE are generally applications requiring the passage of air or gas, but the blocking of water or other chemicals.

7.2. Forever Chemicals (initial)

7.2.1. **Commonly present.** ePTFE usually contains 100s of ppb of each of the perfluorocarboxylate (PFOA family). The perfluorocarboxylates are randomly formed from chains fractured from the original long PTFE polymer chains from either the expanding process or from gamma (or e-beam) radiation used to rubberize the micropowder feedstock of the ePTFE.

7.3. Forever Chemicals (over time)

7.3.1. **None expected.** ePTFE does not further degrade into further forever chemicals such as PFOA or PFOS. ePTFE does not have the ether bond (C-O-C) that leads to degradation into PFOA related chemicals that can occur in other fluoropolymers (such as fluoroacrylate coatings or PFA polymers). ePTFE has no natural degradation path into the PFOA family unless it is further irradiated.

8. Perfluoroalkoxy alkane (PFA)

CAS # - 26655-00-5

8.1. Summary

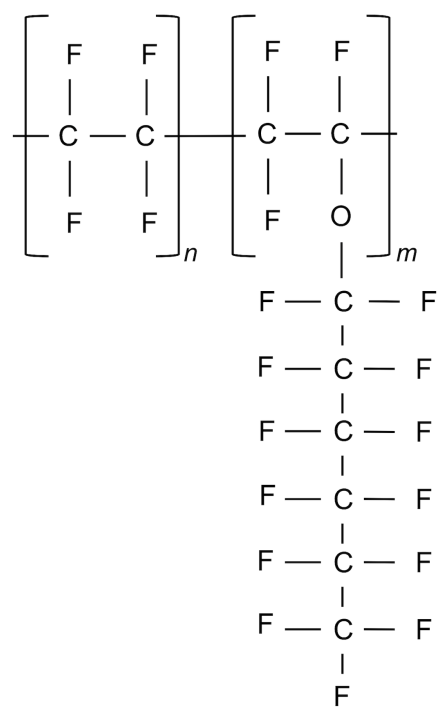
8.1.1. Perfluoroalkoxy alkanes (PFA) are fluoropolymers. They are copolymers of tetrafluoroethylene (C_2F_4) and perfluoroethers ($C_2F_3OR_f$, where R_f is a perfluorinated group such as trifluoromethyl (CF_3) or longer). The properties of these polymers are similar to those of polytetrafluoroethylene (PTFE). Compared to PTFE, PFA has better flexibility, equivalent low friction, and higher chemical resistance.

8.1.2. PFA is commonly used in applications where superior flexibility is needed compared to PTFE such as internal wiring in dense electronics or in medical devices.

8.2. Forever Chemicals (initial)

8.2.1. **Commonly present.** The ether bond in PFA commonly breaks during manufacturing (due to the low energy of bond dissociation of the ether bond), releasing random lengths of PFAS chains that become the range of C2 to C14 perfluorocarboxylates (ie. the PFOA family). PFA normally (but not always) has 100 to 300 ppb of each length of the PFOA family.

8.2.2. Example PFA polymer. Note the side chain can be various lengths.



8.2.3. Note - the majority of PFA in products contains a full range of short and long chain perfluorocarboxylates, however, this is not true in all cases. PFA can be made and is widely available without perfluorocarbyxylates.

8.2.3.1. Due to the widespread use of PFA with perfluorocarboxylates and no simple way (without testing) to distinguish between perfluorocarboxylate containing and non-containing PFA - it will take time and effort to identify and replace perfluorocarboxylate containing PFA.

8.3. Forever Chemicals (over time)

8.3.1. **Commonly degrades.** PFA does degrade further overtime into additional lengths of perfluorocarboxylates (PFOA family) due to the cleavage of the remaining ether (C-O-C) bonds.

8.3.2. Note - this is only true of PFA that contains perfluorocarboxylates initially. PFA without initial perfluorocarboxylates will not have a chemical structure that degrades into perfluorocarboxylates.

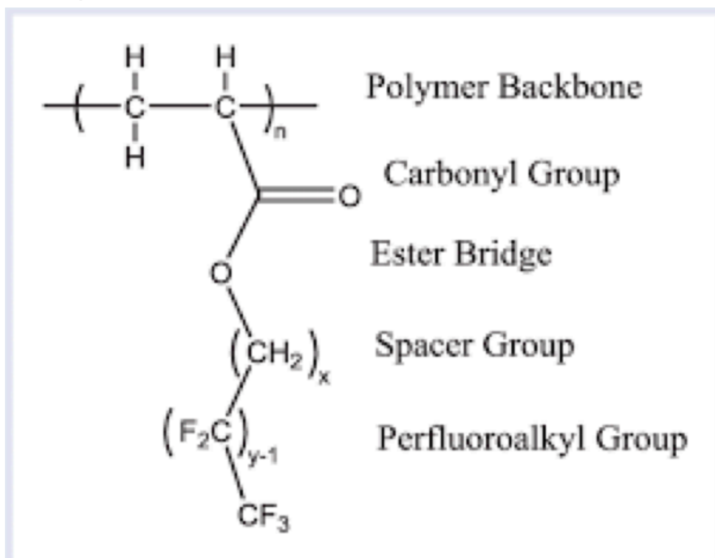
9. Polyfluoroacrylates

CAS # - Multiple (Example - 25087-17-6)

9.1. Summary

9.1.1. Polyfluoroacrylates are a group of polymers primarily formed from an acrylic (non-fluorinated) polymer backbone with side chain fluorotelomers connected by an ester bridge.

9.1.2. Example -



9.1.3.

9.1.4. Polyfluoroacrylates are used as coatings, primarily on fabric, to provide water repellency. The ester bridge has a similar weak (low bond dissociation energy) C-O-C bond as polyfluoroxy alkane (PFA) polymer resulting in fracturing of the fluorinated side chain from the main polymer creating moderate concentrations of perfluorocarboxylates (PFOA family).

9.1.5. A common usage of polyfluoroacrylates, outside of outerwear, is on the washing instructions or country of origin fabric tags in most clothing to maintain the quality of the written instructions over time.

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9.2. Forever Chemicals (initial)

9.2.1. **Commonly contains.** Polyfluoroacrylates usually contain up to 1 ppm of each of the perfluorocarboxylate (PFOA family). The perfluorocarboxylates are randomly formed from side chains fracturing during manufacturing and application.

9.3. Forever Chemicals (over time)

9.3.1. **Commonly degrades**. Polyfluoroacrylates do further degrade into forever chemicals such as PFOA or PFOS as more of the side chain fluorochains fracture at the C-O-C bond. The material would also be expected to lose some of its water and oil repellency over time as side chain fluorochains fracture from the acrylic polymer backbone.

10. Fluoroelastomers (FKM)

CAS # - multiple (example - 9011-17-0)

10.1. Summary

10.1.1. A fluoroelastomer is a fluorocarbon-based synthetic rubber. Fluorine Kautschuk Material (FKM) fluoroelastomer all contain a fluorovinyldiene monomer as a base material and do not contain the side chains ether (C-O-C) fluoro chain of perfluoroelastomers (FFKM).

10.1.2. FKM can have variations in chemical structure. This listing is to include all non-silicone, non-side chain fluoro vinyldiene based fluoro rubbers including phosphorus and nitrogen based fluoroelastomers (PNF).

10.2. Forever Chemicals (initial)

10.2.1. **Commonly contains.** FKM is normally manufactured with an emulsion process that involves a C6 fluorosulfonate surfactant such as the Capstone family by Chemours. These complex surfactants degrade into 6:2 fluorotelomer sulfonate (6:2 FTS) up to 100 ppm in the FKM, and to small concentrations (<100 ppb) of C4-C7 short chain fluorocarboxylates (PFHpA and smaller).

10.2.2. Technically, these are not currently classified as PBT or vPvB in the EU, but are very similar to substances that meet that classification and would be regulated under the proposed EU PFAS restrictions.

10.2.3. The C6 fluorosurfactants used in FKM manufacturing could likely be phased out, but it would take time and validation.

10.3. Forever Chemicals (over time)

10.3.1. **Does not degrade.** FKM does not degrade significantly further into forever chemicals. Further amounts of the 6:2 FTS fluorotelomer sulfonate would be expected to further degrade into shorter chain perfluorocarboxylates but that would only change the concentrations of the fluoro salts in the FKM materials.

11. Perfluoroelastomers (FFKM)

CAS # - multiple (example - 26425-79-6)

11.1. Summary

11.1.1. Perfluoroelastomeric compounds contain a higher amount of fluorine than FKM fluoroelastomers. FFKM perfluoroelastomers all contain fluorovinyldiene monomer as a base material but, unlike FKM, do contain a side chain ether (C-O-C) connected to an additional fluorochain. Perfluoroelastomers generally exhibit higher compression set values and are the most expensive of all elastomers.

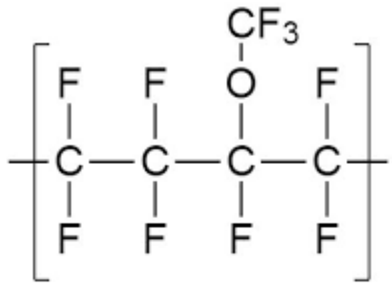
11.1.2. FFKM can have variations in chemical structure similar to variations in FKM.

11.2. Forever Chemicals (initial)

11.2.1. **Commonly contains.** FFKM is normally manufactured with an emulsion process that involves a C6 fluorosulfonate surfactant such as the Capstone family by Chemours. These complex surfactants degrade into 6:2 fluorotelomer sulfonate (6:2 FTS) up to 100 ppm in the FKM, and to small concentrations (<100 ppb) of C4-C7 short chain fluorocarboxylates (PFHpA and smaller).

11.2.2. The C6 fluorosurfactants used in FKM manufacturing could likely be phased out, but it would take time and validation.

11.2.3. FFKM commonly has a side change fluorochain connected by a C-O-C ether bond. This bond will fracture contributing additional short chain fluorocarboxylates (shorter versions of PFOA family).



Perfluoroelastomer (FFKM)

11.3. Forever Chemicals (over time)

11.3.1. **Rarely degrades.** FFKM has C-O-C side chains that could degrade into shorter chain perfluorocarboxylates (shorter version of PFOA family), however these are expected to be very short chain and only contribute marginally to the short chain perfluorocarboxylates that are present initially from the degradation of the C6 surfactant commonly used in manufacturing of FFKM. Further amounts of the 6:2 FTS fluorotelomer sulfonate would be expected to further degrade into shorter chain perfluorocarboxylates but that would only change the concentrations of the fluoro salts in the FKM materials.

12. Polyvinyldienefluoride (PVDF)

CAS # - 24937-79-9

12.1. Summary

12.1.1. Polyvinylidene fluoride or polyvinylidene difluoride (PVDF) is a non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride.

12.1.2. PVDF is commonly used as a specialty plastic for piping, sheet, tubing, and films. PVDF powder is common in outdoor paints. PVDF is also used as the cathode binder in lithium batteries and supercapacitors.

12.1.3. Note - irradiated PVDF is a more flexible version of PVDF caused by gamma or e-beam radiation of a PVDF polymer. Irradiated PVDF does not have a separate listing in this document, but does undergo the same formation of perfluorocarboxylates (PFOA family) as irradiated PTFE.

12.2. Forever Chemicals (initial)

12.2.1. **None expected.** Unirradiated PVDF does not initially contain any PFOA or PFOS family of chemicals. Irradiated PVDF contains similar perfluorocarboxylate (PFOA family) concentrations (100 of ppb of each) as irradiated PTFE.

12.3. Forever Chemicals (over time)

12.3.1. **Does not degrade.** PVDF does not degrade into forever chemicals such as PFOA or PFOS. PVDF does not have the ether bond (C-O-C) that leads to degradation into PFOA related chemicals that can occur in other fluoropolymers (such as fluoroacrylate coatings or PFA polymers).

13. Fluorosilicone Rubber

CAS # - 63148-56-1

13.1. Summary

13.1.1. Fluorosilicone rubber (also known as fluorinated silicone rubber or FVMQ) is a widely used synthetic elastomer that can be used in a wide range of applications. The mechanical and physical properties of fluorosilicone are very similar to that of silicone rubber, but fluorosilicone rubber offers improved resistance to fuel and mineral oils, while possessing poorer resistance to heated air and gases.

13.1.2. Fluorosilicone rubber can have a varying range of fluorine concentration.

13.2. Forever Chemicals (initial)

13.2.1. **Does not contain.** Fluorocarboxylates or fluorosulfonates.

13.2.2. **Commonly contains silicone forever chemicals.** Fluorosilicone rubber commonly has high concentrations of classified D4, D5, and D6 chemicals.

13.2.3. D6 is also scheduled for restriction under the UN Stockholm Convention on Persistent Organic Pollutant, making silicone a poor potential replacement for fluoropolymers.

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13.3. Forever Chemicals (over time)

13.3.1. **Does not contain.** Fluorocarboxylates or fluorosulfonates.

13.3.2. **Degrades into silicone forever chemicals.** Fluorosilicone rubber does degrade further over time (slowly) in D4, D5, and D6 siloxanes (forever chemicals).

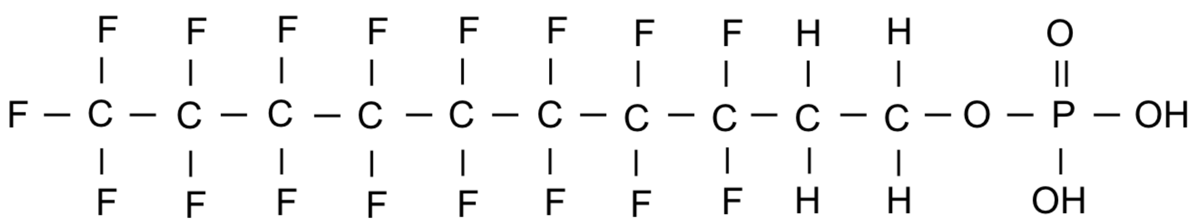
14. Fluoroalkyl phosphates

CAS # - Multiple (Examples - C9-C15 fluoroalkyl phosphate)

14.1. Summary

14.1.1. Fluoroalkyl phosphates are a single or pair of fluorochains connected by a C-O-C ether bond.

14.1.2. Example - 8:2 monoPAP is a member of the C9-C15 fluoroalkyl phosphate family.



14.1.3. Fluoroalkyl phosphates historically had widespread use in cosmetics such as foundation or underlayer. Until recently, the majority of cosmetics of these types contained fluoroalkyl phosphates.

14.1.4. Likely with the increase in PFOA regulation in the EU and North America, C9-C15 fluoroalkyl phosphates were not found in products. Claigan conducted a detailed testing of cosmetics that formerly contained fluoroalkyl phosphates in 2022 (and listed on their ingredients list online) with none found. Of the products that listed C9-C15 fluoroallkyl phosphate in their ingredients online, the delivered version of the product no longer contained fluoroalkyl phosphates on its ingredients list. A subsequent review of cosmetics ingredients in 2023, did not show any continued use of fluoroalkylphophates.

14.2. Forever Chemicals (initial)

14.2.1. **Commonly contains.** Fluoroalkyl phosphates commonly contain >1 ppm of each chain length of perfluorocarboxylates due to degradation of the C-O-C bond connected to the phosphate. C9-C15 fluoroalkyl phosphates is a significant source of PFOA, PFNA, and PFDA.

14.3. Forever Chemicals (over time)

14.3.1. **Commonly degrades**. Fluoroalkyl phosphates rapidly degrade into perfluorocarboxylates from the cleavage of the C-O-C bond connecting the fluorochain to the phosphate.