Primer on PFOA use within the Fluoropolymer and Fluoroelastomer Industry

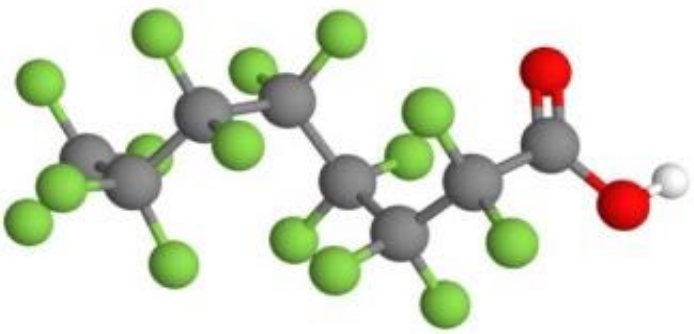
by the SEMI "PFOA Compliance" Working Group

Version 1.3, September 2017

Introduction

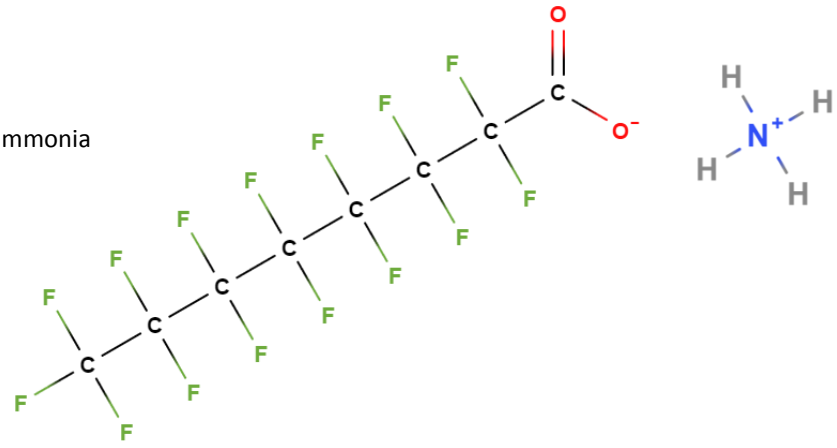
This primer was developed by the SEMI EHS Division "PFOA Compliance" working group, which was primarily comprised of semiconductor equipment manufacturers and members of the FluoroCouncil. It is intended to give an introductory overview of how PFOA has been, and can be, used in the production of fluoropolymers and fluoroelastomers, with a focus on relevance to equipment used in the semiconductor industry and regulatory restrictions on PFOA.

Although this primer does discuss some aspects of the equipment supply chain with regard to PFOA, it is not intended to answer the question of whether or not PFOA is, or could be, present above regulatory thresholds. The working group currently has insufficient data to answer that question.



The PFOA molecule

8	Carbon (black)
17	Fluorine (green)
2	Oxygen (red)
1	Hydrogen (white)



Schematic of the ammonia salt of PFOA

Content:

Definitions

C4, C6, C8 etc. – for the purpose of this document, fluorinated substances with a chain of four, six, eight, etc., fluorinated carbon atoms.

Fluoropolymer – a polymer that contains molecules with a carbon backbone having fluorine atoms bonded to it. They are plastic materials used in harsh chemical and high-temperature environments, primarily where a critical performance specification must be met. Fluoropolymers are also commonly referred to as fluoroplastics. A well-known fluoropolymer example is PTFE, and Teflon[1] is a commonly known brand name of PTFE.

Fluoroelastomer – a class of synthetic rubbers with a high ratio of fluorine to hydrogen which provides extraordinary levels of resistance to chemicals, oil and heat, while providing useful service life above 200°C. A well-known fluoroelastomer example is FKM and FKKM (per ASTM D1418), and Viton[2] is a commonly known brand name of FKM.

Fluoropolymer semi-finished good – an intermediary stock form of a fluoropolymer such as blocks, sheets, rods, tubes.

Fluorotelomers – fluorinated chains that can be attached to other organic polymer backbones. Typically used for modifying and protecting surfaces to provide oil, water and soil repellency. Also used in firefighting foams. Lower molecular weight than fluoropolymers and fluoroelastomers. Fluorotelomers are not usually used in semiconductor equipment industry.

Fluoropolymer/Fluoroelastomer Manufacturer (FPEM) – a company that manufactures a fluoroelastomer and/or a fluoropolymer.

Article (made from a fluoropolymer or fluoroelastomer) – Essentially the smallest item or part that is formed from a fluoropolymer or fluoroelastomer such as an o-ring, tank, wafer carrier etc. that cannot be disassembled or separated into other parts. 'Article' is a term established in the EU REACH regulation, but its exact meaning is somewhat complicated to interpret for real life manufacturing scenarios. The European Chemicals Agency (ECHA) has published a related guidance document[3].

Background Information on PFOA

[1] Teflon™ is a registered trademark of the Chemours Company.
[2] Viton™ is a registered trademark of the Chemours Company.
[3] see https://echa.europa.eu/guidance-documents/guidance-on-reach

PFOA (pentadecafluoro-octanoic acid, $C_8HF_{15}O_2$, commonly referred to as 'C8') has been described as a persistent organic pollutant (POP) that does not readily degrade and has a tendency to accumulate in ecosystem food chains and within living organisms, leading to potential cancers and birth abnormalities in animals and humans. PFOA is a very stable substance that will persist within the environment and was reported to be found in the blood of more than 98% of the general US population[4].

The Stockholm Convention and regional regulatory authorities such as the US EPA are working to eliminate or restrict the use of PFOA and substances that may degrade to PFOA. There are regulations already in place to do this such as the EU REACH regulation[5], which limits PFOA in articles to less than 25 ppb[6].

PFOA is used as a processing aid during the manufacture of certain fluoropolymers and fluoroelastomers for consumer and industrial applications. Trace amounts can remain in the final product. Uses of fluoropolymers for consumer products include non-stick coatings for cookware, fabric for high performance outdoor apparel, and thread seal (pipe) tapes. Due to their mechanical properties and chemical stability, fluoropolymers are also widely used within the Semiconductor Industry in insulators, chemical baths, tubing, tanks, wiring, and filters. Fluoroelastomers are also widely used in the Semiconductor Industry in seals, o-rings, and hoses where elastomeric properties are needed along with excellent chemical resistance.

Fluorotelomers are used in consumer products such as food wrappers and stain resistant carpets, but they are not known to be used in semiconductor manufacturing equipment or processes. PFOA is not used in fluorotelomer production, but it is sometimes an unintended byproduct, or a degradation product, of some fluorotelomers under certain conditions.

Until recently, there has not been much regulatory (e.g. EPA) interest in articles made from fluoropolymers and fluoroelastomers used in industrial applications because there is such a small chance of significant-risk-exposure (e.g. ingestion) as compared to consumer products. Studies of PFOA in articles made from fluoropolymers conducted and published by EPA, Norway, and Sweden have mainly been focused on consumer articles; however the studies do not reach a conclusion about the impact of articles with low levels of PFOA on the PFOA levels that have been found in blood.

The Fluoropolymer and Fluoroelastomer Industry

The fluoropolymer and fluoroelastomer industry essentially consists of three parts:

[4] reference https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2072821/
[5] Regulation 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals
[6] See REACH Annex XVII entry 68

- Manufacturers producing a variety of fluoropolymers and fluoroelastomers. Fluoropolymers are typically supplied as dispersions (polymer particles dispersed in an aqueous media), fine powders, and pellets. Fluoroelastomers are typically supplied as pellets or sheets. Some FPEMs also produce fluoropolymer filled compounds, formulated coatings, and films (e.g., thin sheets).
- Manufacturers producing fluoropolymer and fluoroelastomer semi-finished goods/articles such as sheets, films, tubing, stock shapes, etc.
- Manufacturers producing fluoropolymer and fluoroelastomer end-use goods/articles such as seal tapes, o-rings, tubing, fittings, and other machined and molded parts.

The FluoroCouncil[7] is the industry association that represents many of the major FPEMs and their subsidiaries worldwide. Some FPEMs are members of the Fluoropolymer Group of the Plastics Industry Association (formerly the Society for the Plastics Industry, SPI).

FPEMs produce a wide range of products, including the fluoropolymers PTFE, ETFE, PFA, PVDF, PCTFE and FEP and the fluoroelastomers FKM and FFKM.

Within the semiconductor industry: tubing and fittings are typically made from PFA or PTFE; filter membranes are typically made from PTFE; tanks and wafer carriers are PFA or PTFE; some wire insulation can be PTFE, FEP, PFA , or PVDF; and DI water systems are typically made of PVDF components. Fluorinated lubricants, typically used in vacuum pumps, are very different from fluoropolymers and fluoroelastomers, and are not known to be made with surfactants such as PFOA. Fluoroelastomers are typically used in sealing applications such as o-rings and packings.

Fluoropolymers and fluoroelastomers are supplied in different grades. The grades are essentially differentiated by the molecular weight of the material and its purity. Different grades are supplied to support the extrusion and molding processes of the semi-finished goods and article suppliers. The molecular weight is controlled by so-called "chain transfer agents" and not by PFOA. Each FPEM will have a different method for identifying the grade of their products, but they are usually classified per ASTM standards, which include composition, temperature and melt flow rate (MFR) range, (sometimes referred to as the 'melt index').

The Fluoropolymer and Fluoroelastomer Production Process and the use of PFOA

The first stage of the fluoropolymer and fluoroelastomer production process is polymerization. Fluoropolymers and fluoroelastomers are generally produced by one of two polymerization processes: emulsion polymerization or suspension polymerization. Emulsion polymerization typically requires the use of a surfactant as a process aid. The suspension polymerization does

[7] FluoroCouncil membership includes: Archroma Management LLC, Arkema, Asahi Glass Co., Ltd., Daikin Industries, Ltd., Solvay Specialty Polymers, The Chemours Company LLC (a spin off of Dupont – which includes the former fluoropolymers business of DuPont).

not. Fluoropolymers and fluoroelastomers typically used within the semiconductor industry can be produced by either process.

PFOA is a surfactant that was commonly used as a processing aid for emulsion polymerization by all FPEM's for many years. When used, it is usually added in the form of the ammonium salt, ammonium perfluorooctanoate (APFO). It is used in the main process reactor vessels and allows the ingredients (monomers) to mix and the polymer to grow in molecular weight. PFOA never becomes part of the polymer chain and conveys no specific properties to the polymer, it simply aids in the mixing of the monomers in the reactor. At the end of the polymerization reaction, the aqueous part of the mixture, including most of the PFOA, gets removed.

Following polymerization, the fluoropolymer products are concentrated to form an aqueous dispersion, or are isolated and finished to form fine powders, molding granules, or pellets. Fluoroelastomer products are supplied as pellets or sheets.

A dispersion is a mixture where fluoropolymer particles are suspended in an aqueous media. In some dispersions, both the liquid part and the particles can contain residual PFOA.

Fluoropolymers can be extruded. Some processing aids are used in the extrusion process by semi-finished goods manufacturers, but they are typically additives which are themselves fluoropolymers such as low molecular weight PTFE.

Newly developed fluorotelomers, used in fire-fighting foams, grease-resistant food packaging, leather protectants and stain-resistant carpeting and textiles are based on C4 and C6 chemistries, but these do not degrade to C8. However, under certain conditions, telomers that have greater than 8 carbons can degrade to form PFOA. Regulatory bodies have made a distinction between short carbon chains and long carbon chain perfluoroalkylsubstanses (PFASs) and the 8 carbon chain is the demarcation. Studies have shown that PFOA is not generated during thermal degradation of fluoropolymers.

Studies on the thermal decomposition of the ammonium salt[8] of PFOA show that full degradation occurs in a matter of minutes at ~230^{o}C and in 200ms at 350^{o}C - 400^{o}C. Fluoropolymer semi-finished goods produced by sintering or extrusion typically require processing temperatures of 300^{o}C - 400^{o}C. Fluoroelastomers require a vulcanization process typically up to 250^{o}C for 10hrs-15hrs.

It is expected that the level of PFOA remaining following these thermal treatments would be very low, but testing has not been done to confirm whether remaining PFOA would meet the 25ppb threshold level set by the EU REACH regulation.

[8] "Gas-Phase NMR Technique for Studying the Thermolysis of Materials: Thermal Decomposition of Ammonium Perfluorooctanoate", Krusic and Roe, Anal. Chem., volume 76, pp 3800–3803; and "Gas-phase NMR studies of the Thermolysis of Perfluorooctanoic Acid", Krusic , Marchione, and Roe, Journal of Fluorine Chemistry, volume 126, pp 1510-1516.

PTFE seal tape does not undergo a high temperature process such as sintering. If PFOA is used as a surfactant in the manufacturing of seal tape then significant levels of PFOA might remain in the final product. Various published tests on PTFE seal tape indicate that PFOA or related compounds can exceed the 25 ppb threshold. In 2009 the US EPA analyzed 116 commercial articles purchased from retail outlets in the United States between March 2008 and May 2008 to determine the extractable content of C5 to C12 PFCAs. Of interest to the semiconductor equipment industry, PTFE seal tapes and pastes contained 40.6 ppb of these PFOA related compounds. In other studies conducted in 2005 PFOA was detected up to 140 ppb in extracts of PTFE resins, obtained after applying pressure and increased temperatures to the material, and in PTFE film and sealant tape at 1800 ppb. {insert Footnote: http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-NIP-GUID-ArticlePaperPFOSInv-1.En.pdf, pages 12-13}

More recent testing reported levels of 11 and13 ppb in a single brand of seal tape from two tests done for a semiconductor equipment manufacturer[9]. These results indicate that further investigation and testing is likely warranted.

The US EPA PFOA Stewardship Program

PFOA is a molecule with 8 carbon atoms commonly referred to as 'C8'. Higher homologues include C8 thru C20. The higher homologues can potentially degrade to C8. C8 and C9 molecules were commonly used in fluoropolymer and fluoroelastomer manufacture. In 2006 the US EPA, working with many of the major FPEMs, initiated a PFOA Stewardship Program directed at reducing the environmental and human exposure to PFOA, its precursors, and higher homologues and to commit to working toward the elimination of these chemicals from emissions and products by 2015[10]. The Stewardship Program was a global and voluntary partnership between EPA and various FPEMs , which included FluoroCouncil members as well as BASF and 3M/Dyneon. The program has led to the elimination of PFOA from the manufacturing processes of the participating/signatory companies.

Signatory companies (including their various global subsidiaries) to the EPA Stewardship Program were: Archroma (divestiture from Clariant), Arkema, Asahi Glass Company, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont (now Chemours), Solvay Solexis. The Stewardship Program commitment was global in scope. If a signatory company had manufacturing facilities in China, those facilities also manufactured fluoropolymers without the use of PFOA.

[9] Presentation by Tokyo Electron (Lauren Crane) at SEMI EHS SEMICON West 'PFOA' program the afternoon of July 10th, 2017.

[10] See EPA "Fact Sheet: 2010/2015 PFOA Stewardship Program" at https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program

The primary goal of the Stewardship Program was the elimination of PFOA from both facility emissions and products produced by participating companies.

During the fluoropolymer and fluoroelastomer manufacturing process, even if PFOA is used, careful rinsing can remove all residual PFOA. Likewise, PFOA residue can be degraded into other substances by heat applied during the article production process. Therefore, aiming to use only articles or materials stated to be "PFOA free" does not necessarily reduce the demand for PFOA or its related environmental impacts. To indicate their more beneficial approach of eliminating the use and demand for PFOA, some signatories to the Stewardship Program use phrases such as "produced without PFOA" and "PFOA not intentionally added". However, it is not yet certain if such materials will meet regulatory thresholds. It is feasible that PFOA might be present in end use articles in extremely small quantities because of legacy process equipment contamination, degradation and/or recombination of other process substances, cross contamination from shipping infrastructure, and so on.

The Stewardship Program target to eliminate PFOA from manufacturing processes was set for 2015, but was achieved by some members as early as 2013. FPEMs still require the use of surfactant processing aids but no longer use C8 or C9 chemistries. Each company has found their own solution.

There are FPEMs that are not part of the EPA Stewardship Program that have not made a commitment to eliminate PFOA. We are aware of about fifteen such companies in China, at least one in India, and at least one in Russia. These companies are also not members of the FluoroCouncil. They produce a range of fluoropolymers and fluoroelastomers, although a majority of their production is PTFE. Appendix 1 contains a list of some FPEMs operating in China. A few are subsidiaries of FluoroCouncil members.

Neither the FluoroCouncil nor the Stewardship Program signatories have developed a certification program to identify 'PFOA not intentionally added' or 'Produced without PFOA' materials, as this was thought to be too difficult to administer. Tracking the potential of PFOA being in finished goods therefore relies on tracking the supply chain back to the FPEM and determining if they are a signatory of the EPA Stewardship Program, or they otherwise manufacturer without using PFOA.

Conclusion

FluoroCouncil members and members of the EPA Stewardship Program produce a majority of fluoropolymers and fluoroelastomers worldwide with the exception of PTFE. PTFE produced in China, India and Russia by companies that did not participate in the Stewardship Program and that are not part of the FluoroCouncil might still use PFOA as a surfactant, which could remain as a residue in related finished goods, particularly in PTFE seal tape.

Due to the possible[11] continued production of fluoropolymers and fluoroelastomers with PFOA in China, Russia and India, it cannot be assumed that the supply chain is not intentionally adding PFOA unless it can be tracked back to the FPEM and it can be shown that they were a signatory to the EPA Stewardship program, or some other means of verification.

When articles are produced, post polymerization thermal treatments such a sintering, extrusion, and vulcanization are expected to significantly reduce the level of any PFOA residue in materials produced by FPEMs that were not EPA Stewardship Program members, but testing would be required to determine if this meets the 25ppb threshold set by the EU REACH regulation.

Analyzing finished products for PFOA content at a 25ppb threshold is difficult. It is important that analytical tests are carried out by laboratories that have experience in the required methods. As of July 2017 there is no nationally recognized test standard for PFOA in solid fluoropolymer and fluoroelastomer matrices to reporting limits relevant to regulatory thresholds (i.e., about 1 ppb). There are nationally recognized test methods for soil, blood and water matrices, or test methods for materials similar to PFOA (such as PFOS) in solid matrices, and these are being used for PFOA testing in solid matrices with some modifications developed by the test laboratories.

EPA Stewardship Program members have been manufacturing without the use of PFOA for more than 2 years. It is unlikely that there will be large inventories of warehoused fluoropolymers or fluoroelastomers that were made prior to the change away from PFOA due to their high cost. However there may be semi-finished/finished goods still in stock in various supply chain locations that were manufactured prior to 2013.

It is highly likely that fluoropolymers and fluoroelastomers produced with PFOA substitutes and other C8 substitutes are already in the supply chain and in use at semiconductor manufacturing sites. Such materials have most likely been assessed regarding their mechano-chemical-physical properties and have the same performance. However they may not have been fully requalified by the users (i.e., semiconductor manufacturers).

[11] This is based on the observation that PFOA is still produced in China and there are no known exports of PFOA from China. One feasible conclusion is that it is still being used by FPEMs in China (reference Li et al., Chemosphere 2015, 129, 100-109).

Appendix 1 – A List of some FPEMs Operating In China[12]

Note that a few of these companies are subsidiaries of FluoroCouncil members.

- 山东华氟化工科技 (Shandong Huafu) [PTFE, FEP]
- 山东东岳 [PTFE, FEP, PVDF, FKM] (Dongyue)
- 鲁西化工 [PTFE, FEP] (Luxi Chemical)
- 山东德宜 [PVDF] (DeYi)
- 内蒙古奥拓普 (Inner Mongolar Otop) [FKM, PCTFE]
- 内蒙古万豪 WANHAO FLUORUM CHEMICAL LIMITED COMPANY INNER MONGOLAR, 3F JV [PVDF]
- 重庆新氟 (Chongqing Xinfu) [FEP]
- 中昊晨光化工研究院 [PTFE, FKM] (Chengguang)
- 江西理文 [PTFE] Jiangxi Leeman Chemical
- 福建三农 (Fujian Sannong) [PTFE]
- 河北龙星 [PVDF] (HeBei Long Xing)
- 阜新恒通 (Fuxin Hengtong) [PTFE]
- 上海三爱富常熟分厂 (3F Changshu) [PTFE]
- 江苏梅兰化工 (Meilan) [PTFE, FKM]
- 江苏华奥 [PTFE] Jiangsu Huaao
- 常熟新华化工 [PCTFE] (Changshu Xinhua）
- 大金 [PTFE, FKM] (Daikin)
- 杜邦 [PTFE] (Chemours)
- 阿科玛［PVDF] (Arkema)
- 吴羽 [PVDF] (Kureha）
- 上海三爱富 (SH 3F) [PTFE, FEP, FKM]
- GORE 3F [PTFE]
- 巨化集团公司 (Juhua) [PTFE, FEP, PVDF]
- 中化蓝天 (Sinochem Lantian) [PVF, PVDF]
- 浙江永和化工 (Zhejiang Yonghe) [FEP, PTFE]
- 浙江氟诺林 (Zhejiang Fluorine Chemical) [PVDF, FKM]

[12] Derived from a slide provided by M.Cardona (Chemours) June, 2017