Why Do I need to worry about PFOA in my equipment?

INTRODUCTION

The presence of the substance ‘PFOA’ in semiconductor manufacturing and related equipment (SMRE) placed on the European Union (EU) market will be restricted to 25 ppb per component (or any part thereof) from 4 July 2022.

Components made from common fluoropolymers such as PTFE, PFA, PVDF and fluoroelastomers such as FKM and FFKM, could contain residues of PFOA in excess of the restriction threshold. Such components include: fluid tubing and fittings, pipe/seal tape, wire and cable insulation filters, valves, tanks, panels, reaction vessels, and o-rings.

PFOA is also being considered for restriction under the UN Stockholm Convention, which could drive restrictions in other countries. Taiwan has already a PFOA restriction.

The SEMI EHS Division hosts PFOA Compliance Working Group, which has been working for several years to understand whether and how PFOA might be present in SMRE components, including spare parts. The following is a summary, in the form of an FAQ, of the working group’s findings to date. It is intended to educate stakeholders in the SMRE supply chain. The working group has also published a SEMI webpage (http://www.semi.org/en/pfoa-info) and a PFOA detailed information document (a ‘Primer’) (see webpage).

Q1: Why should I care about PFOA?

A1: PFOA is a regulated substance that might be present above regulatory thresholds as a residue in the fluoromaterials that make up many of your equipment components. You will be required by the companies that import your products into Europe (such as by customer purchasing specifications or customer requests for you to sign declarations of compliance) to ensure any equipment imported after 2022 contains compliant components.

Q2: What is ‘PFOA’?

A2: The meaning of ‘PFOA’ can depend on context. Specifically ‘PFOA’ refers to Perfluorooctanoic Acid (CAS Number 335-67-1), but the term can also refer to the related compounds and salts, such as ammonium pentadecafluorooctanoate – APFO (CAS Number 3825-26-1, also known as ammonium perfluorooctanoate).
Q3: Is ‘PFOA’ hazardous?
A3: PFOA is internationally recognized as hazardous; specifically as a Persistent Organic Pollutant (POP).

Q4: How is ‘PFOA’ used in the semiconductor industry?
A4: PFOA is an intentional constituent in some process chemicals (e.g., for photolithography) and an unintentional residue in some SMRE components.

Q5: Is the use of PFOA regulated?
A5: Per an amendment of the EU REACH Regulation (Regulation 1907/2006) published June 2017, the presence of PFOA in SMRE components will be restricted in Europe to less than 25 ppb per part as of 4 July 2022. PFOA might soon be restricted to similar levels under the UN Stockholm Convention, which will drive restrictions in other countries. Taiwan has already enacted a PFOA restriction in anticipation of Stockholm Convention changes.
Q6: Why is PFOA thought to be potentially present in certain SMRE components?

A6: Some production processes for fluoroplastics and fluoroelastomers (referred to in this article as fluoromaterials) have used the Ammonium salt of PFOA, APFO, as a surfactant to facilitate efficient polymerization. At the end of the process, both APFO and PFOA can be trapped in the fluoromaterial matrix as an unintended residue, with a concentration dependent on the process conditions. These fluoromaterials can be present in SMRE components.

Q7: How and when can PFOA in SMRE components enter the environment or affect personnel.

A7: Of the three major fluoromaterial-component lifecycle stages: manufacture of raw PFOA, PFOA use in fluoromaterial polymerization and PFOA residue in components made from fluoromaterial, only the first two stages have robust studies indicating there can be significant environmental or worker exposure to PFOA during those two stages.

Q8: Which SMRE components might contain PFOA?

A8: SMRE components made from fluoroplastics such as PTFE, PFA, PVDF; and fluoroelastomers such as FKM and FFKM; could contain residues of PFOA. Examples include: cable ties, spiral wrap, fluid tubing and fittings, pipe/seal tape, wire insulation, coaxial dielectrics, cable jackets, filters, printed circuit board laminates, capacitor electrodes and separation films, valves, gaskets, small mechanical parts, bearings, coatings, paints, tanks, panels, reaction vessels, ducting, battery films and binders, heat-shrink tubing, and o-rings.

Q9: What have the companies that make fluoromaterials done to remove PFOA from their processes?

A9: In 2010, recognizing the potential hazards of PFOA, and in cooperation with the United States Environmental Protection Agency (EPA) under a ‘PFOA Stewardship Program’, several major fluoromaterial producers agreed to stop using PFOA in the production of their fluoromaterials globally (see the working group primer for details). Many achieved this goal as early as 2013 and all of them achieved it by 2015. Other global companies have also been successful in removing PFOA from their processes.

Q10: Do any fluoromaterial producing companies still use PFOA?

A10: Fluoropolymer producers/exporters, primarily in China, Russia and India, who are not EPA Stewardship Program signatories and who may still use PFOA pose some risk to the world wide SMRE supply chain. China is the world’s largest producer of PTFE (53% of W/W production) and produces large volumes of PVDF, FEP and FKM, (38% of W/W production). Approximately 25% of the volume of fluoropolymers produced in China is exported worldwide, primarily to USA, Japan, EU and India with additional exports in finished goods. It is estimated that 75%-85% of Chinese Fluoropolymer is manufactured using PFOA some of which could be used in the manufacturing of the common SMRE components noted above1.

Q11: Can one test for PFOA in a component or fluoromaterial?

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A11: Analysis of residual PFOA in an SMRE component requires detection of the APFO or PFOA entrained in the solid fluoromaterial matrix. For this scenario, there are currently no nationally recognized analytical standards relevant to regulatory thresholds. Laboratories offering PFOA testing services use confidential, customized versions of test methods developed in-house, based on methods originally intended for detecting a similar chemical, PFOS, in a solid matrix, or for detecting PFOA in water, soil or blood. Cryogenic grinding and sonication of the sample are important features of these methods, but the accuracy of their results is not known.

Q12: If testing is not practical, how else could I learn if PFOA is present in the components I buy?
A12: As an alternate to testing, you could use supplier declarations. Supplier declarations rely on transfer of information through the supply chain from the original fluoromaterial producer to the final SMRE manufacturer. This can be a very long chain.

Q13: Won’t PFOA be declared in SDSs for the original fluoromaterials used in the components?
A13: Because of the low PFOA residue concentration, it is unlikely it would trigger any standard reporting obligations, such as in a safety data sheet. Therefore, any communication of PFOA presence would be dependent on the knowledge and discretion of each actor in the supply chain, and would have no standardized format.

Q14: Is this a practical concern for our industry? Has anyone found that PFOA is actually present in components?
A14: Some SMRE manufacturers have tested suspect materials and engaged in supply chain inquiries at the 25 ppb level. Both show instances of PFOA above 25 ppb, particularly in fluoromaterial components in storage that were manufactured before 2015, but we don’t know if these isolated cases or not.

Q15: Fluoromaterials go through various heating cycles as they are processed into end-use materials and components. Doesn’t this break-down the PFOA or APFO molecules that might remain?

A15: The APFO molecule is known to decompose in minutes at temperatures around 200°C, and in milliseconds around 350°C. The PFOA molecule is more robust. In addition to decomposition, elevated temperatures increase the mobility of APFO and PFOA in the fluoromaterial, and this allows for greater evaporation of the substances. Many fluoromaterials are subject to temperatures near these critical temperatures when formed into the parts expected to be supplied for SMRE. However, it is not certain how much will decompose or evaporate, or what starting concentrations might be. These facts are often considered proprietary information. Therefore, no definitive statement can be made as to whether the heat history of a fluoromaterial component will bring any PFOA/APFO levels it might have below regulatory threshold.

Q16: Doesn’t the SMRE supply chain know if PFOA is being used?

A16: The supply chain immediately downstream of fluoromaterial production has had no need to be aware of the presence of PFOA at ppb levels unless they are EU importers, and so, generally speaking, the supply chain immediately upstream of SMRE manufacturing has no understanding of whether their components contain PFOA, or if so, at what levels.

Q17: If everyone put in a reasonable effort, couldn’t we get the information we need from the supply chain?

A17: Given the depth, complexity and fluidity (i.e. design changes and company failures and mergers) of the full supply chain for any given SMRE it is impossible to have an accurate understanding of the PFOA content of all relevant parts at any given time, except, perhaps, for the case where an SMRE manufacturer directly specifies the use of a fluoromaterial in a custom fabricated SMRE component. Confounding this need for clear information transfer in the supply chain, is the fact that PFOA is also the focus of other regulations with actions thresholds many orders of magnitude higher than the 25 part per billion (ppb) of the REACH Restriction action threshold. Many SMRE-relevant suppliers have followed EU REACH Candidate List substance requirements and have familiarity with PFOA being added to that list with a 0.1%-per-part threshold and confuse inquiries into the new PFOA restriction with inquiries into the old Candidate List issue and mistakenly report that they comply.

Q18: If PFOA is present in a component that is, for example, in contact with the SMRE process, doesn’t PFOA removal require careful studies and management?

A18: The removal of PFOA might not always be a significant issue in SMRE processes. PFOA has already been removed from many materials starting in about 2013 with no noticeable effects in the semiconductor industry (this can be called ‘silent substitution’). However if PFOA is present in process-contact components at high levels (several hundred parts per million), the transition to a substitute should be reviewed where feasible. Generally speaking the working group believes the broad functionality and characteristics of components with and without PFOA is the same.
Q19: What about the importation of equipment, such as used equipment, or spare parts into the EU that were manufactured prior to 2013 (when many fluoromaterial manufacturers began phasing out PFOA)?

A19: The concentration of residual PFOA in fluoromaterial components manufactured prior to the phasing out of PFOA use by many fluoromaterial manufacturers is uncertain but it is expected to be at levels above the EU restriction threshold (refer also to Q13 and Q14).

There is currently no accepted test method for determining the residual PFOA concentration. The FluoroCouncil is currently engaged with the European Chemicals Agency (ECHA) to define and agree on a PFOA testing strategy, but until there is an agreed test method and more accurate data becomes available, it is not possible to give a definitive answer.

If data about older components is still uncertain when the exemption expires in 2022, a risk based approach could be adopted. For example, based on Q13 and Q14, one might assume that the residual PFOA concentration is expected to be very low and, given that the PFOA does not easily leach out of fluoromaterials, the risk to the environment and to equipment users handling the fluoromaterial components is extremely low.

This risk based approach will be reviewed as new testing information becomes available.

Note that the above considerations are relevant to individual equipment units and spare part units and not product-lines/model-lines. The EU REACH restriction also applies to the any secondary sales within the EU. There is no ‘grandfather’ clause.

Q20: What is the SEMI PFOA working group focusing on in the near term?

A20: The priority issue for the working group is probably the used equipment issue (see Q19). The working group is also focusing on gathering more information about PFOA use in SMRE components and in fluoromaterials process where it might still be an ingredient (e.g., in the Chinese market). We are also working to monitor and influence the PFOA restriction proposed for the Stockholm Convention that could have an impact on restriction legislation in other countries. We are aware that some of the substitutes for PFOA currently in use are themselves targeted for restrictions. Given the importance of fluoromaterials to the processes and safety of SMRE, in general the working group will probably evolve to have a broader focus on the fluoromaterial supply chain and related regulations.

Q21: My company supplies SMRE or components for SMRE, what should I do about PFOA?

A21: Read the REACH regulation – particularly related to Annex XVII restrictions. Understand if your products are in scope. Learn where components containing fluoromaterials might be in your products. Determine what equipment might be sold into EU and to other regions with PFOA regulations. Identify a potential stakeholder in your organization such as a supply chain director, product EHS lead, Engineering manager, Quality engineer, to join the SEMI working group.

For more information about SEMI or the PFOA Working Group, contact the SEMI EHS Division.