PFAS and Process-supporting-substances

Focus PFPE / CF4

1 ZVEI association

ZVEI e. V., the German Electro and Digital Industry Association, represents an industry with an annual turnover of about 225 bn. Euro and 906 thousand employees in 2022.

2 Relevance in EU and Germany

The ZVEI represents the electrical and electronic industry in Germany and covers 25 market sectors for E&E products. Nearly every technically advanced product contains E&E components and without E&E modern life is impossible. PFAS are used for many different purposes to make applications safe (fire retardants), energy efficient (friction reduction) or resistant to harsh environments.
Most advanced applications somehow contain PFAS. The unavailability of PFAS would disrupt the supply chain and affect the business in Europe.

3 PFAS in supporting substances

Because of the unique characteristics PFAS are required as processing agents for dedicated advanced processes in industrial applications. The respective tools are developed for very particular processes with high investment requirements. Usually these machines are depreciated over 10 years and longer (AFA-list) and need double the lifetime to make the high investments reasonable. As common characteristic the PFAS are kept in close industrial processes without uncontrolled release into the environment. The PFAS containing liquids are used in closed loops and are internally circulated and refurbished by the manufacturers.

a) Perfluoropolyether (PFPE) in vapor phase solder process

1. Process description

Vapor phase soldering (also condensation soldering) uses the heat of condensation released during the phase change of a heat transfer medium from a gaseous to a liquid state to heat and solder electronic assemblies. Condensation occurs on the surface of the assembly until the entire assembly has reached the vapor temperature. A saturated, chemically inert vapor zone is created at a temperature identical to the boiling point of the liquid. This provides an optimal inert and oxygen-free atmosphere. The heat transfer is fast and independent of the geometry of the assembly. There are no cold zones in the shadow of large components. Due to the clearly defined soldering temperature and the uniform heating, overheating and the resulting damage to the components is physically impossible. As almost no oxidation takes place during the completely soldering process, soldering with low activated fluxes is possible.

2. Function of PFAS content

PFPE are used as heat transfer fluid. They offer excellent process advantages due to the fact that they have an excellent heat transfer coefficient (significantly better than air in convection soldering), a clearly defined boiling point (that prevents heat damages), high thermal stability, no flashpoint, high vapor density, low surface tension that provide excellent wetting properties, no contamination potential and excellent material compatibility (inert).

3. Release in Environment / residues on products

Process control and technical equipment of the vapor phase soldering systems ensure that the process liquid largely remains in the system. Filters are collected and sent for waste treatment. PFPE bound on assemblies get cleaned after soldering and detergents are sent for proper waste treatment. Assemblies without cleaning get sent for proper disposal at end of lifetime (WEEE).

4. Waste Treatment

When operating PFAS containing process fluids in vapor phase soldering systems, no waste is generated except for the regular replacement of filters. Chemical contamination with a deterioration of the material properties is physically impossible. Due to the inert properties of the PFAS-containing process fluids, the materials can therefore be used in the soldering system without any restrictions on service life. Only foreign substances introduced during the soldering process from printed circuit boards, electronic components and solder paste must be mechanically filtered out. The filters and cleaning materials to be disposed of are usually disposed of in accordance with legal regulations at temperatures above 1000°C in approved incineration plants without leaving any PFAS containing residues (1). It is stated that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment (2). PFAS transport containers can be landfilled according to the manufacturer MSDS (1).

5. Lifetime of process machinery

The projected average lifetime of vapor-phase production equipment in the electronic industry is 15 years. PFAS containing process fluids are drained, filtered and then reused in new vapor phase soldering equipment prior to scrapping and recycling of the production equipment. The PFAS containing process fluids are NOT disposed of or destroyed. 100% of the fluids used can be reused. Cleaning agents and filters are thermally disposed of in accordance with legal requirements and incinerated at high temperatures (see also point 4).

6. Exemption Request

Vapor phase soldering is increasingly replacing conventional soldering processes, as the soldering technology requirements of the new product generations can no longer be met with conventional processes. Electronics for the energy sector (production of energy, storage, power electronics), automotive (electromobility, charging infrastructure), medical, aerospace and communication technology (5G, networks, data storage) are just a few examples. Without exemption highly engineered electronics, products such as electric vehicles, aircraft, power converters, satellites, renewable energy, and battery technology can no longer be manufactured. This technology is one of the essential success factors for achieving and successfully implementing the goals of the EU Green Deal as well as the initiatives for environmentally friendly mobility and digitalization.

As of today, there are no alternative liquids to the PFAS containing liquids used for vapor phase soldering in development. Due to the unique chemical properties, it is based on current state of knowledge impossible to develop non PFAS containing alternatives.
Without exemption the aforementioned highly engineered products can no longer be manufactured. This technology is one of the essential success factors for manufacturing these types of products in the EU.
For this reason, we request an unlimited exemption for PFAS in vapor phase soldering process.

Literature:

(1) Solvay, Safety Data Sheet, HS240, P01000018309, Version: 1.06 / EU (EN); Safety Data Sheet, LS230, P01000018315, Version: 1.06 / EU (EN)
(2) Dr. Gehrmann, Hans-Joachim et al, “Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions”.

b) PFPE in Chemical Vacuum Pump

1. Process description

For deposition of thin silicon oxide or silicon nitride layers PECVD or LPCVD processes are commonly used. Chemical Vapor Deposition (CVD) processes are driven at reduced pressure and increased temperature. Reactants are fed under well controlled conditions into the process chamber. The chemical reaction happens either in Plasma phase (PECVD) or at increased temperature with reduced pressure (LPCVD). The processes are strictly controlled with chemical active and corrosive substances.

2. Function of PFAS content

PFPE is required for lubrication of the moving parts in vacuum pumps to reduce friction of the moving parts and prevent abrasion ending in malfunction. The lubrication oil acts as sealant between pump chamber and shutter to achieve pump down. Because of the highly activated process chemicals in the reaction chambers these come into contact with the lubrication oil. Mineral oil based lubricants will be destroyed and fail in their lubricating function.

3. Release in Environment / residues on products

The PFPE oil is encapsulated in the pump chamber with almost no losses. In case of potential PFPE leakage the pump process would be immediately affected and the main process will become instable. The exchanged PFPE pump oil is returned to the oil manufacturer and will be cleaned/recycled and send back for second use. In case of required pump maintenance the pump system will be decommissioned at specialized companies. The cleaning solvents are collected and sent for waste treatment.

4. Waste Treatment

PFPE is a liquid. In case reconditioning is impossible it is collected and sent to waste operators for proper disposal.

5. Lifetime of process machinery

Machines for chemical processing are specialized to dedicated process. Typically, they are in use for several decades. During machine lifetime components like pumps are repaired but the pump system can’t be exchanged by other pumping technologies because of the interaction between the intended chemical processing and the pump system.

6. Exemption Request

We request the unlimited exemption for PFPE as lubrication substance in closed loop application to prevent early depreciation which would result in very high losses for companies invested in these innovative High-Tech processes.

<u>Literature:</u>
https://www.pfeiffer-vacuum.com/de/maerkte/halbleiter/abscheidung/diffusion-lpcvd/
https://www.lesker.com/newweb/fluids/mechpumpoils-inert-solvayspecialtypolymers-fomblin/fomblinx/

c) PFAS as process gas in the plasma etching process in the electronics and semiconductors use sector

1. Process description

In certain sensors flexible films (FF) are used instead of rigid PCBs. The advantage of flexible conductive films compared to rigid PCBs is that the FF can be:

- formed into almost any shape,
- bent and folded and
- be moved / curved several times without breaking or tearing conductive tracks.

In addition, it is possible to structure the display and the evaluation unit on the same level, without additional solder joints, which would represent an additional process step, and could therefore be subject to errors. If the whole process is carried out reel-to-reel, the handling between the process steps is also easier because the FF do not have to be stored in bulky trays.

These flexible printed circuits films (FF) are de facto a copper-coated polyimide film that is further manufactured in several reel-to-reel processes. First, a chemical treatment is carried out, then the circuit is exposed and etched and finally assembled with electronic components using lead-free soldering pastes. The fully assembled FFs are built into the finished products.

Certain finished products require a special through-hole plating in the polyimide. To be able to create a blind hole for this special through-hole, after the wet-chemical opening of the copper, the carrier material polyimide is etched off with the aid of a plasma etching process taking place under vacuum and the addition of a CF4, Nitrogen and Oxygen gas mixture.

2. Function of PFAS content

The CF4 cannot be replaced in this process because there is no alternative gas that etches the plastic out of the blind hole and does not attack the copper. An alternative manufacturing possibility to produce the blind holes or the vias (blind hole) is not possible, as these have a special shape (undercut). Since the FFs in a reel-to-reel process, the through-hole plating process cannot be carried out in any other way due to the special type and shape of the through-hole plating.

3. Release in Environment / residues on products

In the plasma etching process itself, 25% of the CF4 used is consumed. What remains is 75% uncracked CF4 in the vacuum exhaust air, which is further treated to reduce CF4 content (see section 4)
Industry is constantly working to improve the process and further reduce CF4 emissions, as well as researching alternative processes, but to date there is no adequate substitute available.

4. Waste Treatment

The gas is combusted/decomposed by a downstream plasma source and cleaned by a wet exhaust air scrubber before being released to the environment. This process converts 80-85% of the 75% CF4 to CO2 and F2 with the addition of oxygen. These exhaust air purification processes ensure that only about 13% of the CF4 used is emitted.

Literature:
Sun, Jong-Woo, et. Al; “CF4 Decomposition by Thermal Plasma Processing”; Korean J. Chem. Eng. ; 2003 p. 476-481

d) PFPE in fluid heating process

1. Process description

The fluid-based heating process uses a heat transfer medium in liquid state to heat products to a required processing temperature and thus prepare the products for further processing at these achieved temperatures. A wide variety of processing operations take place at these process temperatures. Only a few of the most common ones should be mentioned here, such as tempering mechanical products, high voltage treatment for piezo ceramic components, curing of coating materials, liquid soldering of high mass mechanical and electromechanical components etc. To heat the products to the required specific temperature, they are immersed directly into a chemically inert heating liquid. This provides an optimal inert and oxygen-free atmosphere. Negative influences on the products are safely prevented. The heat transfer is fast and independent of the geometry of the specific product. Due to the clearly defined liquid temperature and the uniform heating, overheating and the resulting damage to the products is physically impossible. The very good insulation properties enable high-voltage treatments of heated products such as the production of piezoceramics under the highest quality, safety and performance criteria. After the thermal treatment process, the products are removed from the liquid and dried in a vacuum drying process. The process liquid remains entirely inside the processing machine.

2. Function of PFAS content

PFPE are used as heat transfer fluid. They offer excellent process advantages due to the fact that they have an excellent heat transfer coefficient (significantly better than air), a clearly defined boiling point (that prevents heat damages), high thermal stability, no flashpoint, high vapor density, low surface tension that provide excellent wetting properties, no contamination potential, excellent material compatibility (inert). A decisive technical property is the fact that these heat transfer fluids do not conduct any current, i.e. they are insulating and show a high dielectric strength.

3. Release in Environment / residues on products

The process liquid largely remains in the fluid heating system. Filters that are installed in the fluid heating systems are collected and sent for waste treatment. PFPE bound on products gets cleaned after heating and detergents are sent for proper waste treatment. Products without cleaning are properly disposed at end of lifetime (WEEE).

4. Waste Treatment

When operating PFAS-containing process fluids in liquid heating systems, no waste is generated except for the regular replacement of filters. Due to the unique properties any chemical contamination with a deterioration of the material properties is physically impossible. The PFAS-containing process fluids are inert, so there is an unlimited use of these fluids in the heating system without any restrictions of service life.
Mechanical solids that might be brought into the heat transfer fluid are filtered out by mechanical filtration up to ultra-fine filtration. The solids remain in the filter. The filtered liquid can be reused in the heating system as process fluid.

The filters and cleaning materials to be disposed of are usually disposed of in accordance with legal regulations at temperatures above 1000°C in approved incineration plants without leaving any PFAS containing residues (1).
It is stated that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment (2). PFAS transport containers can be landfilled according to the manufacturer MSDS (1).

5. Lifetime of process machinery

For liquid heating equipment the average lifetime in the electronic industry is projected with 15 years. At equipment end of lifetime PFAS containing process fluids are drained, filtered and then reused in new equipment. The fluids are simply taken out of the equipment before it's scrapping and recycling. The PFAS containing process fluids are NOT disposed of or destroyed. 100% of the fluids used can be reused. Cleaning agents and filters are thermally disposed of in accordance with legal requirements and incinerated at high temperatures (see also point 4).

6. Exemption request

Due to their specific thermal requirements certain products (i.e. piezo ceramics) need a very effective method of heating up to enable further processing at these achieved temperatures. This heating up method can only be granted by PFAS heat transfer liquids.
As of today, there are no alternative liquids to the PFAS containing liquids used for fluid heating existing or in development. Due to the unique chemical properties, it is based on current state of knowledge impossible to develop non PFAS containing alternatives.
Without exemption the aforementioned highly engineered products can no longer be manufactured. This technology is one of the essential success factors for manufacturing these types of products in the EU.
For this reason, we request an unlimited exemption for PFAS in liquid-based heating.

Literature:
(1) Solvay, Safety Data Sheet, HS240, P01000018309, Version: 1.06 / EU (EN); Safety Data Sheet, LS230, P01000018315, Version: 1.06 / EU (EN)
(2) Dr. Gehrmann, Hans-Joachim et al, "Pilot-Scale Fluoropolymer Incineration Study: Thermal Treatment of a Mixture of Fluoropolymers under Representative European Municipal Waste Combustor Conditions".

4 PFAS waste treatment

Most of the technically used PFAS are long time stable and very resistant to chemicals. PFAS waste treatment technologies are mostly investigated and technically evaluated by energy assisted technologies. In case of polymeric PFAS, incineration technologies were investigated with PTFE waste.

Under test conditions in a waste incineration chamber, with a setup in compliance to the requirements of the 17th BImSchV, it was demonstrated that polytetrafluoroethylene (PTFE) can be almost fully transformed into fluoride (F-) (as hydrofluoric acid (HF)). Samples of the flue gas were analysed for the presence of 31 PFAS and found to be without significant measurable PFAS content.(1)

At temperatures above 750°C PTFE decomposed to C2F4 and C3F6 in a pyrolysis process. During further combustion CF4 will be generated. At combustion temperatures above 1000°C CF4 formation is much reduced.(2)

Based on this result a municipal incineration system according to the requirements according to §8 of the 17.th BImSchV (3) was sufficient to not detect any PFAS in the flue gas with exception of green house gases like CF4 or C2F6 but with low evidence due to weak database. Technologies for CF4 decompositions are in operation and development with focus on semiconductor processes. A system for incineration of hazardous waste operates at about 200°C higher combustion temperature.

A test facility for incineration of production PFAS waste was setup in Cooperation with the “Deutsche Bundesstiftung Umwelt” and company Dyneon. This facility is able to decompose more than 90% into its monomers. (4)

Other test facilities investigated the incineration of PFOA treated fibers and observed decomposition at 1000°C without chromatographically detectable PFAS in the flue gas. (5)

In a literature study PFOA and PFOS decomposition was successfully investigated at 350°C in supercritical water. (6)

Incineration of Perfluoropolyether (PFPE) are less investigated but during development of PFPE fluids was observed that these fluids become instable at temperature above 290°C (7)

Other incineration systems for PFPE operate at 330°C with metallic iron reactants like aluminum powder for binding decomposed PFPE. (8)

For treatment of radioactive PFPE lubricants an incineration system with MnO2-catalyst and N12CO3 immobilizer was successfully tested (9)

Literature:
(1) Krasimir Aleksandrow, et. al; “Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas“; Elsevier Chemosphere 226, p898-906; 2019
(2) Sandra Huber, et. Al.; “Emissions from incineration of fluoropolymer materials”; Researchgate OR 12/2009
(3) 17. BImSchV
(4) Press Release “Pilotprojekt: Recycling von Fluorpolymeren”; Universität Bayreuth; Lehrstuhl für Werkstoffverarbeitung
(5) Takahoro, Yamadam et. Al.; “Thermal degradation of fluorotelomer treated articles and related materials” Elsevier Chemosphere Vol 61, Issue 7 p974-984; 2005
(6) Sanny Verma, et. Al.; “Recent advances on PFAS degradation via thermal and nonthermal methods” Chemical Engineering Journal Advances; Elsevier Marc. 2023
(7) William R. Jones, et. Al.; “Thermal Oxidative Degradation Reactions of Linear Perfluoroalkyl Ethers”; II Symposium on Fluorpolymers; 183rd National Meeting of the American Chemical Society; 1982;
(8) Mimi Y. Keating, et. Al.; “Decomposition of perfluoropolyether lubricants” Journal of Thermal Analysis and Calorimetry 106; p213-220; 2011
(9) XinHang Du, et. Al.; “An efficient approach for the treatment of radioactive waste perfluoropolyether lubricants via a synergistic effect of thermal catalysis and immobilization”; Journal of Environmental Sciences, Vol 136, p512-522; 2024

5 General Exemption Request

We request an unlimited exemption for PFAS containing fluids in applications without intended contact to the environment.

Also, we request an unlimited exemption of PFAS etch gases in controlled ambiance with additional abatement systems for PFAS decomposition.
These substances are only used in combination with other technical machines or tools. These substances have no function on their own.

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