

PFAS-Containing Lubricants Used in Semiconductor Manufacturing

Semiconductor PFAS Consortium Lubricants Working Group

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About the Semiconductor PFAS Consortium

The Semiconductor PFAS Consortium is an international group of semiconductor industry stakeholders formed to collect the technical data needed to formulate an industry approach to perfluoroalkyl and polyfluoroalkyl substances (PFAS).

Consortium membership comprises semiconductor manufacturers and members of the supply chain, including chemical, material and equipment suppliers. The consortium includes technical working groups, each focused on the:

- Identification of PFAS uses, why they are used, and the viability of alternatives.
- Application of the pollution prevention hierarchy to (where possible) reduce PFAS consumption or eliminate use, identify alternatives, and minimize and control emissions.
- Development of socioeconomic impact analysis data.
- Identification of research needs.

This data will better inform public policy and legislation regarding the semiconductor industry's use of PFAS-containing materials and will focus research and development efforts. The Semiconductor PFAS Consortium is organized under the auspices of the Semiconductor Industry Association. For more information, see www.semiconductors.org.

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Executive Summary

In this white paper, we'll identify the applications of lubricants made with perfluoroalkyl and polyfluoroalkyl substances (PFAS) within the semiconductor manufacturing process; specify application-specific performance requirements and discuss the viability of non-PFAS-containing alternatives, along with potential areas of research and development.

High-performance PFAS-containing lubricants are essential within the semiconductor manufacturing process because of their unique ability to meet multiple performance requirements simultaneously, including the need to prevent particle creation and outgassing while providing effective lubrication within the extreme physical environments present in manufacturing processes, and remaining inert to aggressive chemistries used in certain manufacturing process steps.

Currently, non-PFAS-containing alternatives are not viable because they are unable to meet all performance requirements necessary for semiconductor manufacturing. The implications of any requirement to use non-PFAS-containing substitutions would likely result in insufficient lubrication performance and increased mechanical system and seal failures. These substitutions would result in greatly increased costs and an increased potential for worker and environmental exposure.

Current applications of PFAS-containing lubricants require handling during maintenance activities. However, the potential for exposure is negligible because the lubricants have very low volatility, and because the industry's standard safety practice requires appropriate personal protective equipment (PPE) for maintenance/service activities.

There is little potential for lubricants to be released to air or water during normal use within the semiconductor manufacturing process, because of their low volatility.

1.0 Introduction

PFAS-containing lubricants used in the semiconductor manufacturing process are vital to the success of semiconductor technology. Leading-edge semiconductor manufacturing processes build transistors that are 5 nm in dimension or smaller – exact replicates of each other numbering in the billions over the entire surface of a silicon wafer. Thus, semiconductor manufacturing operations require extreme levels of control, as even the smallest amount of contamination, imprecision or impact on reliability can result in product defects and performance losses.

Lubricants ensure the smooth and precise functionality of fabrication and processing equipment. Selecting a lubricant capable of achieving all required performance requirements prevents unscheduled downtime and/or contamination of the process. Each stage in the process must be virtually perfect (with yields above 99%) because there may be hundreds of process steps used to manufacture an advanced semiconductor device. Without these very high yields, semiconductor manufacturing would fail to produce functional and economically viable products.

A lubricant is a material, applied in oil, grease or solid form, designed to reduce friction and wear between surfaces that are in relative motion with each other. Oil and grease lubricants consist of a base oil, with included thickeners or other additives that can modify the inherent properties of the lubricant base or impart new properties. Solid lubricants may come in a pure polymer form, or as an additive in polymers and coatings or surface treatments.

Semiconductor manufacturing requires high-performance lubricants because they help prevent particle creation and outgassing, provide effective lubrication within the extreme physical environments present in manufacturing processes, and remain inert to the aggressive chemistries in some manufacturing process steps. Among all available high-performance lubricants, PFAS-containing lubricants have the unique ability to meet multiple high-priority performance requirements at once.

1.1 Objectives and Scope of This White Paper

Given evolving concerns regarding the high persistence, bioaccumulation potential and potential toxicity of PFAS chemicals, several efforts to develop regulatory restrictions are currently underway that intend to limit the use of PFAS-containing materials to only those deemed essential to the functioning of society. In this white paper, we will focus our discussion on the technical aspects of PFAS-containing lubricants in applications vital to semiconductor manufacturing operations, as well as the viability of potential non-PFAS-containing alternatives. The concept described by Cousins et al. requires the determination of uses that are “necessary for highly important purposes for which alternatives are not yet established.” As such, the primary intent of this white paper is to apply this concept to the use of PFAS-containing lubricants within semiconductor manufacturing (Cousin 2019).

The objectives of this white paper are to identify applications of PFAS-containing lubricants within the semiconductor manufacturing process, specify the application-specific performance requirements, and assess the viability of non-PFAS-containing alternatives, while highlighting potential areas of research and development.

The white paper also explores the potential health and safety concerns associated with the use of PFAS-containing lubricants, the potential for environmental releases, and the controls that are in place to reduce these concerns.

A complicating factor for this technical effort is the lack of a commonly agreed-upon definition for the term PFAS within the multitude of regulatory development activities. Since the noted purpose of this white paper is to document the use of all materials that could potentially meet a regulatory definition of a PFAS-containing material, along with the performance requirements necessary to determine the criticality or essentiality of its use, the Semiconductor PFAS Consortium has defined the scope of materials described in this white paper to include all chemistries and materials that contain molecules with -CF₂- and/or -CF₃.

Since the scope of this white paper is intended to cover common applications across all semiconductor manufacturing processes, it is likely that we have not captured certain highly specialized applications, including uses in analytical laboratory applications that are necessary for supporting manufacturing operations; manufacturing operations at upstream suppliers of products necessary for semiconductor manufacturing; and those within future manufacturing applications, including those currently undergoing research and development.

1.2 PFAS-Containing Lubricants Used in Semiconductor Manufacturing

PFAS-containing lubricants used in semiconductor manufacturing environments and support equipment can be oils, greases or solid materials with low friction coefficients. PFAS-containing lubricants identified as marketed and/or sold for use in semiconductor manufacturing operations include those listed below.

Oils:

- Perfluoropolyether (PFPE).
- Fluorosilicone.
- Poly chlorotrifluoroethylene (PCTFE).

Greases:

- PFPE with polytetrafluoroethylene (PTFE) micropowders and/or thickeners.
- Poly chlorotrifluoroethylene (PCTFE) (both as base fluid and thickener).
- Fluorosilicone with PTFE micropowders.
- Synthetic hydrocarbons with PTFE micropowders as a thickener and friction modifier.
- Multiply-alkylated cyclopentane (MAC)-based greases with PTFE thickener.

Solid lubricants:

- PTFE polymers and polymer plastics with PTFE additives.
- Electroless nickel phosphorous plus PTFE coatings.
- Aluminum anodized surfaces impregnated with PTFE.

1.3 Critical Performance Requirements Met by PFAS-Containing Lubricants in Semiconductor Manufacturing

The lubricants required for use in semiconductor manufacturing operations must have the ability to meet multiple performance requirements, including those necessary to ensure the overall cleanliness of the manufacturing environment through each individual manufacturing step; to maximize the reliability, operating lifetime and ongoing precision of moving parts; and to provide an overall resistance to the

breakdown and degradation of performance within the extreme environments required to accomplish semiconductor manufacturing processes.

Note that elsewhere in this white paper:

- The Applications for PFAS-Containing Lubricants in Semiconductor Manufacturing section provides more detailed descriptions of performance requirements for individual applications.
- Appendix A contains a table that summarizes performance requirements for each application.
- Appendix B provides the definitions, test methods and applicable thresholds for each individual performance requirement.
- Appendix C contains a summary table for each application and the critical lubricant performance requirements, alongside potential non-PFAS-containing alternatives and the current state of viability.

1.4 The Role of the C-F Bond and the Unique Properties Provided by PFAS-Containing Lubricants

Its compact size and strong electron-withdrawing characteristics make the fluorine atom stand out in the periodic table and give fluorocarbon materials unique properties unmatched by other chemical compounds. In addition, the high C-F bond strength (the bond dissociation energy is approximately 485 kJ mol⁻¹) helps impart special and outstanding characteristics not easily found in other materials (Friesen and Ameduri 2018).

The most common PFAS-containing lubricants chosen for semiconductor manufacturing are those within the family of PFPEs and PTFE used as a thickener to create greases, as well as in solid lubricant applications as pure polymers, additives to other polymers and coatings, or surface treatments. The properties of PFPE and PTFE are known to be unique and valuable in the application of high-quality lubricants that possess high thermal, oxidative and hydrolytic stability, chemical inertness, nonflammability and low volatility. With their exceptional rheological and tribological properties, PFPE and PTFE are useful in application areas such as high-temperature and high-speed applications, as well in aggressive environments and those exposed to radiation (Marchionni, Ajroldi and Giovanni 1989).

The extreme electronegativity of fluorine results in a strongly polarized bond with carbon ($\delta^+C-F\delta^-$), which means a partially ionic character and increased strength of carbon to fluorine (+68 kJ mol⁻¹ higher than the C-H bond). Because of this extreme polarization, the carbon-to-carbon bonds in a perfluorinated molecule are stronger than those found in their nonfluorinated analogues. Thus, perfluorinated organic compounds exhibit outstanding thermal and chemical stability, nonreactivity, low surface energy, stability against ultraviolet (UV) irradiation and a low refractive index (Friesen and Ameduri 2018).

In PFPEs, the presence of the fluorine atoms strengthen the C-O bonds compared to hydrogenated analogs (+84 kJ mol⁻¹), contributing to the stability of the entire perfluoropolyether structure. In addition to the high electronegativity, the fluorine atom possesses very low polarizability, which translates into lower van der Waals interactions between the molecules of perfluorinated compounds compared to hydrogenated analogs (Smart 1994). Considering in particular PFPEs, ether oxygen atoms contribute negligibly to the intermolecular interaction, making the cohesive energy density of PFPEs even lower than that of perfluorocarbons with the same number of atoms in the backbone chain (Marchionni, et al. 1993). This very low intermolecular interaction can explain some important properties of PFPEs, in particular their excellent rheological characteristics (low viscosity at low temperature, low glass transition temperature [T_g] and pour point, high viscosity index), their wide liquid range and their very low surface energy.

The fluorine atom, though relatively compact in size, has nevertheless a bigger van der Waal radius than hydrogen (1.47 Å vs. 1.2 Å) (Kirsch 2004). For this reason, partially negatively charged fluorine atoms

provide effective shielding of the C-C backbone of the perfluoropolyether, contributing to greater chemical stability of PFPE than its hydrogenated counterparts. In addition, the fluorine atom (attached to the backbone) cannot react with radicals (or be abstracted by radicals as hydrogen does), and therefore remains stable when exposed to the radicals typical of oxidations/combustion, which explains the nonflammability of perfluorocarbons and PFPE in aggressive environments.

The chemical stability of PFPE and PTFE is outstanding: they do not react with almost any chemical, including oxygen at high pressure or even liquid oxygen, elemental fluorine, or strong acids and bases. This is one of the reasons for the success of these materials in the semiconductor manufacturing industry, where several applications require stability with aggressive chemicals.

Other interesting properties of PFPE include their optical transparency in a wide range of ultraviolet wavelengths and their immiscibility with practically all hydrogenated oils and fluids. They can be defined as both hydro- and oleophobic. Related to the immiscibility property, PFPEs also have outstanding compatibility with materials commonly used in the construction of mechanical equipment. PFPE can be used with practically any plastics and elastomers since they do not permeate and swell hydrogenated materials.

The fluorine atom imparts a number of unique and beneficial properties to the molecules of PFPE such that no other nonfluorinated fluid can claim a similar set of properties all together in the same material. The first effect of F is to strengthen the C-F, C-C and C-O bonds and to impart excellent thermal, oxidative and chemical stability. The second effect is to shield the carbon skeleton of the molecule, contributing to exceptional chemical stability and nonflammability. The third effect is to reduce at very low levels the intermolecular interactions (minimal dispersion forces), resulting in excellent rheological and tribological properties. Finally, the low polarizability of fluorine explains the extremely low dielectric constant and very low surface tension.

1.5 Physical Environments and Chemistries Encountered in Semiconductor Manufacturing That Drive the Required Performance Characteristics of Lubricants

Semiconductor manufacturing environments must be maintained at the highest levels of cleanliness possible. Controlling contamination to the level required to make nanoscale integrated circuits requires that production take place within clean rooms that must be thousands of times cleaner than those used for manufacturing medical devices. Semiconductor equipment must also maintain highly precise mechanical control for the movement of in-process workpieces.

All moving mechanisms must be lubricated with a material that will not contaminate the environment or workpieces, while reducing frictional forces to the extent required for nanometer-level precision, and through all of the physical conditions and chemistries encountered in the semiconductor manufacturing process.

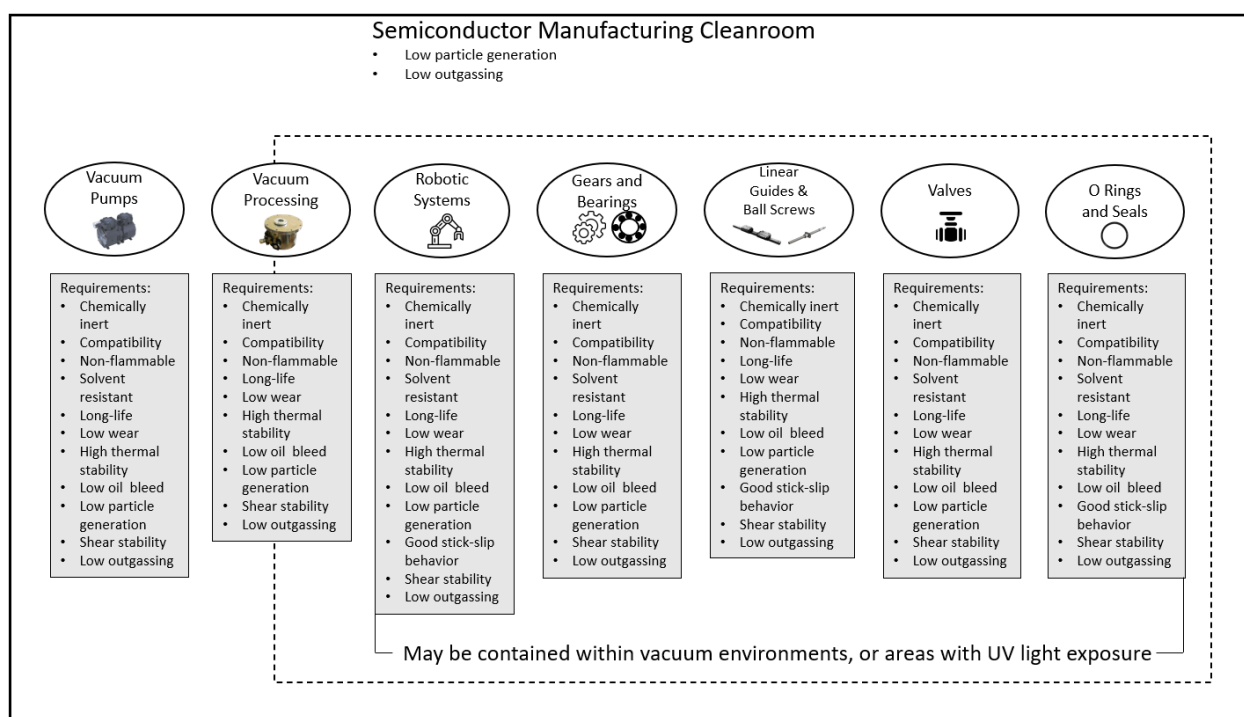
Semiconductor manufacturing and processing equipment must often operate at high temperatures, under UV-light irradiation and vacuum conditions while making use of various chemistries, thus requiring high-performance lubricants that will protect moving parts and seals against wear within extreme physical and chemical environments. The aggressive chemistries used in the semiconductor manufacturing process include strong acids, oxidizers and caustics like sulfuric acid, hydrogen peroxide and tetramethylammonium hydroxide, as well as reactive gas radicals such as ionized chlorine and fluorine gas, pyrophoric gases such as silane, arsine and phosphine, and highly oxidative gases such as pure oxygen.

To enable the provision of excellent lubrication under these physical and chemical conditions, the lubricants used must be extremely resistant to outgassing and degradation and be nonreactive and chemically inert while maintaining high performance and reliability over time.

2.0 Applications for PFAS-Containing Lubricants in Semiconductor Manufacturing

It is possible to group the many individual applications for lubricants in semiconductor manufacturing into seven distinct uses, as described and shown in Figure 1.

All manufacturing for semiconductors takes place within a clean room, where lubricants must be resistant to low-particle generation and outgassing. Semiconductor manufacturing operations contain many vacuum pumps that require lubrication of the moving parts within them. These vacuum pumps enable all of the manufacturing steps that require vacuum conditions for processing. The many moving parts that require lubrication include those associated with robotic systems, gears and bearings, linear guides and ball screws, valves, and O-rings and seals.



Note: The dashed box indicates that most of these moving parts are located in vacuum processing, where lubricants help meet performance requirements under extreme vacuum conditions and during exposure to aggressive chemicals. The lubricated parts may also be exposed to UV light within photolithography systems.

Figure 1: Lubricant applications and associated performance requirements in semiconductor manufacturing.

Let's look more closely at the applications within the semiconductor manufacturing process that require lubrication.

2.1 Oils and Greases in Vacuum Pumps

Within the process chambers of semiconductor manufacturing equipment, a vacuum provides the appropriate physical environment required for manufacturing steps that include evaporation, sputtering, chemical vapor deposition, dry etching, and implantation. In many semiconductor manufacturing applications, dry vacuum pumps provide these conditions. They have become common because of their

high reliability and design elements, which eliminate contamination in the process chamber if oil were to backstream from the pump. Another advantage provided by a dry vacuum pump is longer intervals between required maintenance, given the absence of oxidation and contamination of pump oil by corrosive gases or reaction products (Nagaoka and Mase 1994).

The moving parts inside dry vacuum pumps such as bearings and gears require lubricants that offer a wide range of performance characteristics, including low viscosity and thermal resistance at operating temperatures as high as 130°C; the ability to lubricate bearings and gears without creating harmful byproducts, consuming excess power, or reducing component reliability; compatibility with metals and other construction materials; low vapor pressure and outgassing; chemical resistance; and nonflammability.

Dry vacuum pump manufacturers specify the use of PFPE-based oil and greases to lubricate bearings, gears and seals. PFPE-based oil and grease lubricants provide a viscous, hydrodynamic film that is sufficient to support the load and separate the ball from the raceway in bearing applications, enabling high-endurance performance.

In addition, PFPE-based lubricants provide a variety of essential functions, including sealing, lubrication, cooling and corrosion protection. Lubricants used in dry vacuum pump systems are exposed to chemically reactive, oxidative process materials and/or corrosive process materials used or generated by the semiconductor manufacturing process. In these chemically aggressive environments, the lubricant oils/greases must be chemically inert (Fowzy 1998); (Walther, Bell and Howell 2013). The ability of PFPE-based oils and greases to provide these performance requirements in turn minimizes any life-shortening contamination of the lubricants, which in turn enables the high reliability that these pumps must achieve (Bell and Howell 2005).

Currently, no non-PFAS-based oils and greases are known to be viable for use in dry vacuum pump applications within semiconductor manufacturing processes, as only PFPE-based oils and greases have demonstrated compatibility with the wide range of process chemistries used in the semiconductor manufacturing process.

2.2 Greases and Solids Used in Vacuum Processing Environments

As mentioned in the Oils and Greases in Vacuum Pumps section, the creation of vacuum environments is vital for providing the appropriate physical environment required for manufacturing steps that require evaporation, sputtering, chemical vapor deposition, vacuum dry etching, implantation and other important processes. Vacuum environments used in semiconductor manufacturing equipment occur in vacuum chambers. These vacuum chambers contain many moving parts that position the wafers for manufacturing steps and deliver chemicals and gases, among other mechanical systems that require lubrication.

PTFE-thickened PFPE grease and solid PTFE lubricants can meet performance requirements even in harsh environments with extremely low pressures, extremely high or low temperatures, or conditions that entail exposure to aggressive chemicals or gases associated with manufacturing steps completed in vacuum chambers.

Another common application of PFAS-containing lubricants is to the ferromagnetic seal that creates ultra-high vacuum environments. These seals allow moving parts to penetrate through the walls of vacuum chambers without creating leakage through the penetration. The creation and tightness of this seal is made possible by the extremely low vapor pressures, chemical inertness and high thermal stability uniquely provided by the use of PFPE oil placed between permanently charged magnetic seals (Apex n.d.).

2.3 Greases and Solids Used to Lubricate Robotic Systems

A typical semiconductor manufacturing facility uses thousands of robotic systems to transport wafer-containing carriers throughout and to move and position wafers inside semiconductor manufacturing equipment. Robots must move at high speeds to enable high throughput and require placement with high precision and repeatability, in order to drive consistency and reduce defects in all manufacturing steps. Robots in manufacturing environments use PFAS-containing lubricants because they do not adversely affect the required cleanliness levels, while providing the immediate and accurate responses without jerkiness required for high precision. Their performance characteristics include excellent stick-slip performance, stability and absence of gum formation, and a very low coefficient of friction (Bell and Howell 2005).

Robotic applications typically use greases that consist of PFPE base oils thickened with PTFE micropowder, and/or PTFE solid lubricants. The application of PTFE micropowder as a thickener is one for which there is no known substitute, as it is a self-lubricating solid that slides against itself with very little friction, without becoming a source of particulate contamination.

2.4 Greases Used in Photolithography Applications

Photolithography is a technology of patterning that is central to the semiconductor manufacturing process, directly enabling the manufacturing of complex integrated circuits. Photolithography is an optical process that requires multiple high-precision lenses and complex fine-tuning mechanisms to direct and appropriately focus light in uniform and consistent doses. All semiconductor manufacturing equipment, including photolithography equipment, contains a multitude of moving parts that require effective lubrication (including those described previously within this section of the white paper).

Optical lithographic equipment that makes use of light at UV wavelengths, such as steppers and scanners, have proven to be vulnerable to airborne molecular contamination (AMC) in several different ways (Otto 2015). Any AMC generated from exposure to UV light will contaminate the lens during exposure, causing transmission loss, image distortion and subsequent yield loss. AMC lowers product performance, yield and leads to increased cost of ownership.

Semiconductor industry experience obtained during experiments conducted while using non-PFAS-containing alternatives such as silicone oils for use in manufacturing demonstrated these effects in photolithography equipment. When using silicones, the Si-C-bond cracks upon UV light irradiation for wavelengths <354 nm. This cracking of the Si-C-bond leads to a buildup of a thermodynamically stable silicon dioxide layer on top of the optical lens elements, detuning the optical performance. In the extreme case, this optical detuning will prevent UV light (operation wavelengths of 248 nm and 193 nm used in photolithographic steps) from passing through the optical systems and reaching the wafers being photolithographically processed; in other words, the optical system encounters a massive loss in transmissivity.

PFAS-containing lubricants remain stable even in the presence of the deep UV light wavelengths currently in use. Requiring non-PFAS-containing alternatives in manufacturing would likely necessitate a significant effort to redesign the overall photolithographic manufacturing system in order to accommodate the additional AMC load. Such a redesign would require several years and significant expense to complete fundamental research; qualify new designs; and implement the use of lesser performing, non-PFAS-containing lubricants.

2.5 Greases Used to Lubricate Gears and Bearings

The semiconductor manufacturing process makes extensive use of high-performance gears and bearings that are capable of meeting high-precision requirements. The ability to provide for high precision over

time requires effective lubrication to enable low wear and long lifetimes, meeting requirements to maintain cleanliness and resist corrosion while working within extreme physical environments that often contain aggressive chemistries.

Greases used for the lubrication of gears and bearings most commonly use PFPE base oils and PTFE micropowder thickeners. The greases used for lubricating gears and bearings do not change consistency significantly while in service (shear stability), do not separate (bleed) oil, prevent wear and seizure, and are of the correct consistency to stay put, having the correct base-oil viscosity to ensure proper oil film thickness and to reduce friction between moving parts.

Many gears and bearings used in the semiconductor manufacturing process are used in vacuum processing environments that have extreme vacuum pressures, extreme temperatures, and exposure to harsh chemicals and corrosive and oxidative gases. To be suitable for use in these environments, lubricants must have extremely low particle generation and outgassing characteristics, be chemically inert and thermally stable, and maintain long life and low wear characteristics.

2.6 Greases and Solids Used to Lubricate Linear Guides, Slides and Ball Screws

Semiconductor automation, robotic and wafer positioning systems make extensive use of linear guides, slides and ball screws to enable highly precise movements.

PTFE-thickened PFPE grease and solid PTFE lubricants can meet performance requirements for linear guides, slides and ball screws, as they are often associated with vacuum processing and robotic systems, often during exposure to aggressive chemistries in clean-room environments.

The performance requirements for greases used to lubricate these linear guides, slides and ball screws are similar to those used for the lubrication of gears and bearings, and most commonly use PFPE base oils and PTFE micropowder thickeners. These lubricants must have all of the properties described in the Greases Used to Lubricate Gears and Bearings section, along with good stick-slip performance.

2.7 Greases and Solids Used to Lubricate Valves

In semiconductor manufacturing, high-performance valves control the flow rate and pressure of fluids. In order to achieve the high levels of precision and repeatability required for manufacturing, valves must be dependable, have fast response times, and provide accurate control. Maintaining the high precision, repeatability and accuracy of the valves requires high-performance lubricants.

Greases for lubricating valves are similar to those used for lubricating gears and bearings, and most commonly use PFPE base oils and PTFE micropowder thickeners. These greases must have all of the properties described in the Greases Used to Lubricate Gears and Bearings section, with the additional requirement to stay put under high differential pressures, which may require a stiffer consistency formulation.

PTFE-thickened PFPE grease and solid PTFE lubricants meet the performance requirements of valves used in the semiconductor manufacturing process, including within vacuum processing environments that have extreme vacuum pressures, high and low temperatures, and exposure to harsh chemicals and corrosive and oxidative gases. To be suitable for use in these environments, lubricants must have extremely low particle generation and outgassing characteristics, be chemically inert and thermally stable, and maintain long life and low wear characteristics.

2.8 Greases and Solids Used to Lubricate O-Rings and Seals

The use of O-rings and seals in the semiconductor manufacturing process is important, as an aid in containing chemistries and gases within varying physical environments. The proper lubrication of O-rings

and seals is essential for the proper function and full-service life of the seal through the minimization of frictional forces. Because O-rings and seals contain highly aggressive chemistries throughout a variety of challenging physical environments, including extremes of pressure and temperature, the O-ring/seal and its lubricant system must be robust. The consequences of the failure of O-rings and seals can result in significant safety concerns, as well as costly impacts to the manufacturing process.

Lubricants used in O-rings and seal applications in the semiconductor manufacturing environment must demonstrate low outgassing and low particle generation. They must be chemically inert, nonflammable and solvent-resistant, with high thermal stability, low friction, good shear stability and low oil bleed. Lubricants must also be compatible with synthetic elastomeric polymers such as fluoropolymer elastomers (FKM), perfluoroelastomers, PTFE and fluorosilicones, which are most often used to make O-rings and seals.

Seals in reciprocating as well as rotary applications use PTFE-based solid lubricants because they enable a combination of high contact pressures required for sealing performance and the high sliding velocities imposed by the design. PTFE's low surface energy provides low friction and reduces heat generation and thereby wear.

To meet all of the performance requirements, lubrication for O-rings and seals are most commonly PFAS-based, with no known viable non-PFAS-containing alternatives.

3.0 Potential Non-PFAS-Containing Lubricant Alternatives

The most common PFAS-containing lubricants used in semiconductor manufacturing are PFPEs and PTFE used as a thickener to create greases, as well as PTFE used in solid lubricant applications as pure polymers, additives to other polymers and coatings, or surface treatments.

Non-PFAS-containing alternative base oils include mineral oils, ester-based oils, synthetic hydrocarbons, silicone, MAC, and polyalphaolefins (PAOs). In terms of performance, PFPE-based lubricants used in semiconductor manufacturing applications typically outperform non-PFAS-containing alternatives across multiple important performance characteristics. Among all of the performance characteristics required for use in semiconductor manufacturing, the most distinguishing characteristics differentiating PFPE from available non-PFAS-containing alternatives include its very low outgassing and chemical and oxidative inertness over a wide range of physical conditions, and a very wide temperature operating range (–90°C to 250°C) (Marchionni, Ajroldi and Pezzin 1996) (Chemours n.d.).

In comparison to PFPE, let's review the known limitations of non-PFAS-containing alternatives.

- Mineral oil has detrimental outgassing characteristics, and a limited useful temperature range of –38°C to 180°C.
- Ester-based oil lubricants have detrimental outgassing characteristics, and a limited useful temperature range of –20°C to 155°C. The ester group (O-C=O) is prone to chemical attack by corrosives, like strong acids and bases.
- Synthetic PAOs will outgas less than mineral-based lubricants, but can still be considered reactive. PAOs' temperature range is –30°C to 110°C.
- Silicone oil (with a vapor pressure of 5 mmHg at 20°C and a boiling point greater than 140°C) is used as a hydraulic oil in aircraft. It is compatible with many plastics and elastomers, including FKM. Silicone lubricants are prone to migration and may adversely affect the electrical conductivity of electrical contacts (Fowzy 1998). Its temperature range is –20°C to 160°C. It is not stable against irradiation for wavelengths at less than 345 nm.

- MAC oils have a limited temperature range of –50°C to 125°C.

PTFE-thickened PFPE base oils create greases that have low outgassing and low particle-generating properties, which make them ideal for use in semiconductor manufacturing applications. Another advantage to PTFE/PFPE greases is that they have excellent material compatibility with plastics and elastomers. A drawback to PTFE is that it is an inefficient thickener, and typically can require up to 50% thickener depending upon the required stiffness of the resulting grease.

PTFE can also be used to thicken non-PFAS-containing base oil chemistries such as PAOs and silicones, which are used in automotive and damping applications (Nye Lubricants Inc n.d.). Using a fluorinated thickener ensures that the resulting grease possesses similar temperature and chemical stability to PFPE base oils, allowing their use in the most harsh and demanding conditions (IKV Tribology Ltd n.d.). Mineral oils and MAC oils lack this degree of compatibility with PTFE micropowders, which leads to increased oil bleed resulting from separation of the base fluid from the PTFE micropowder thickener. This oil bleed can lead to increased particle contamination.

Non-PFAS-containing solid lubricants include graphite and the family of dichalcogenides, such as molybdenum disulfide (MoS₂). The performance of non-PFAS-containing solid lubricants is highly dependent on environmental conditions such as temperature and humidity. Graphite, for example, does not perform well under dry conditions such as those encountered under vacuum or a nitrogen purge, while MoS₂ does not perform well when exposed to ambient humidity. PTFE in solid lubricant applications functions as required, independent of temperature and humidity.

It is for these reasons that we conclude that there are currently no viable substitutes for PFAS-containing lubricants within the semiconductor manufacturing applications described in this white paper.

3.1 Potential Implications of Substitution

Given the lack of known viable alternatives to PFAS-containing lubricants, it is difficult to definitively ascertain what the implication of substitution with non-PFAS-containing alternatives will be. Nonetheless, we will discuss several plausible implications for the purpose of generating awareness of potential impacts.

Assuming a restriction of the supply of PFAS-containing lubricants to the point that only non-PFAS-containing alternatives were available to use in existing semiconductor manufacturing equipment, the potential impacts would be numerous. The most significant examples are:

- The need for an extensive redesign and retrofit of all semiconductor manufacturing equipment to an extent that would be cost-prohibitive for semiconductor manufacturers.
- Decreased product throughput through the manufacturing process, and increased product defects.
- An increased likelihood of the failure of lubricated O-rings and seals that would compromise the ability to contain process chemistries to an extent resulting in significant safety concerns for manufacturing employees and potential releases to the environment.
- Increased mechanical failures of moving parts, resulting in an increased need for maintenance and shorter lifetimes of semiconductor manufacturing equipment, and a need to update semiconductor manufacturing equipment designs to incorporate additional redundancy and allow access to removable parts.
- The need to complete a thorough cleaning of all parts currently lubricated with PFAS-containing lubricants, as any non-PFAS-containing lubricant would not be effective unless all residues of PFAS-containing lubricants were removed. This removal would require the application of special cleaning solvents that would likely require full rebuilds of all semiconductor manufacturing equipment, an

activity would result in extensive downtime and place a significant strain on the supply of semiconductors.

- Additional energy consumption resulting from increased friction, and the need to remove increased waste heat that will likely be generated from mechanical systems.
- Thermal decomposition that may occur with the use of most current non-PFAS-containing alternatives beyond their temperature limits, resulting in the formation and outgassing of products of incomplete combustion, including formaldehyde (Filsinger 1995).
- Decomposition by UV light that may occur with the use of the most current non-PFAS-containing alternatives.

3.2 Case Studies

In most semiconductor applications that require lubrication, PFAS-containing lubricants are the only lubricants known to provide the low particle generation and outgassing performance characteristics required for use within a semiconductor clean room, as well as the ability to maintain the required long-life and low wear characteristics within challenging high and low temperature and pressure environments, and to withstand exposure to extremely aggressive chemical and oxidative conditions. Because PFAS-containing lubricants meet these performance requirements, and because of the known liabilities of non-PFAS-containing alternatives, there are relatively few evaluations of non-PFAS-containing lubricants that have taken place to date.

One completed case study involved the use of silicone-based sealing materials in photolithography equipment, which were outgassing siloxanes. These outgassing siloxanes were converted to thermodynamically stable silicon dioxide during UV irradiation. This silicon dioxide layer was deposited on the optical surfaces of sensitive lens elements, leading to a detuning of the optical performance (that is, a lower transmission of the optical column). Furthermore, the deposits could not be effectively removed through attempted cleaning activities and resulted in the need to replace and scrap all contaminated components. From this experience, the case study authors concluded that only PFAS-based sealing and PFAS-based lubrication materials are viable for photolithography applications. Pure hydrocarbon-based materials are not considered viable because of their poor outgassing behavior.

Other relevant case studies, such as the semiconductor industry's voluntary phaseouts of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (World Semiconductor Council 2006) (World Semiconductor Council 2011) (World Semiconductor Council 2018), have demonstrated that the industry requires time to find and implement alternatives. Moreover, the broader PFAS definitions adopted in recent years that bring in scope any fully fluorinated carbon mean shorter chain fluorocarbon alternatives would now be considered PFAS and could require new alternatives. Nonfluorinated alternatives require invention with no guarantee an equivalent alternative will be found. If alternatives are found, they will take multiple years to demonstrate, qualify, and implement. A fundamental reason for this extended timeline is the need for the semiconductor manufacturers to both maintain and improve performance of their processes and products over time. Given these critical needs, the industry follows a standard method of identifying, developing and implementing promising alternative chemicals, materials and technologies, in stages that include the:

- Identification of promising chemistries and technologies as potential alternatives.
- Development of potential alternatives into proven manufacturing solutions.
- Integration of new manufacturing solutions into new and existing manufacturing processes.
- Qualification of new processes to ensure appropriate matching to performance requirements for each manufacturing step.

- Demonstration of device performance in end applications to meet minimum requirements in end-product applications.

3.3 Potential Areas of Research and Development

Current manufacturing processes rely on the performance requirements provided by PFAS-containing lubricants to an extent that drop-in replacements with non-PFAS-containing lubricants are not currently available. It is possible, however, that investigations could begin to work toward the development of non-PFAS-containing lubricant solutions that may become viable in the future.

Enabling the future use of non-PFAS-containing lubricants in the semiconductor manufacturing process would require an extended amount of time, along with very significant pools of financial and human resources. The effort could begin with the completion of evaluations of non-PFAS-containing lubricants in semiconductor applications, with an aim to develop any new non-PFAS-containing lubricants that may be required and/or to redesign semiconductor manufacturing equipment to accommodate lubricants of lesser performance.

The actual needs required to enable a full substitution of PFAS-containing lubricants at some point in the future would be numerous. For example, the types of research include:

- An evaluation of current PFAS-containing lubricants in common semiconductor manufacturing applications against the best available high-performance non-PFAS-containing alternatives, with the intent to complete side-by-side evaluations that would be useful for further determinations of the potential impacts of substitutions, and whether any future semiconductor equipment designs can accommodate differences in performance.
- Focused development of novel base oils, additives, thickeners and solids that may be able to perform at a higher level in semiconductor applications than current high-performance non-PFAS-containing lubricants.

4.0 Health and Safety Concerns Resulting from PFAS-Containing Lubricants in the Workplace

PFAS-containing lubricants currently in use are believed to be of very low toxicity, based on information disclosed in safety data sheets that contain basic hazard statements and toxicological information. The observed inactivity of PFPEs in acute toxicity, primary and repeated applications, irritancy and sensitization tests, and the bacterial mutagenicity test have resulted in conclusions that PFPE base oils have a high margin of safety (Malinverno, Pantini and Bootman 1996). Available non-PFAS-containing lubricant alternatives often contain performance-enhancing additives associated with concerning health effects, such as reproductive toxicity, that could represent potentially regrettable substitutions.

Handling of lubricants are routine maintenance tasks of short duration. During the performance of these maintenance tasks, workers wear chemical-resistant gloves as a control to prevent dermal exposure. The potential for inhalation exposure is negligible based on the negligible volatility of PFAS base oils and thickeners.

The potential for manufacturing workers to have direct contact with lubricants is minimal. Most semiconductor manufacturers make use of manufacturing equipment that is designed and certified to comply with SEMI safety guidelines, that require minimization of chemical emissions to the workplace during normal equipment operation and during performance of maintenance activities (SEMI S2 - Environmental, Health, and Safety Guideline for Semiconductor Manufacturing Equipment).

5.0 Environmental Releases and Controls

During conditions of normal use within the semiconductor manufacturing process, which involve PFAS-containing oils and greases with very low volatility, there is little potential for lubricants to be released to air or water.

The most significant volume of PFAS lubricants used in semiconductor manufacturing are in vacuum pumps, which can hold as much as 200 ml per pump, with as many as 10,000 pumps installed per factory. Generally, pumps require refurbishment once every two years or so and are sent offsite where pump refurbishers drain and collect the fluids and send offsite for recycling using particulate and acid filtration reclamation processes (Dams and Hintzer 2016).

Lubricant grease consumption is typically associated with the routine maintenance of moving parts within manufacturing equipment. During these maintenance activities, a quantity of a few grams is most often applied, with the excess wiped off with a clean-room wipe. Used wipes are then disposed of as solvent trash, which is typically managed via incineration.

The highest potential for the release of lubricants would occur from accidents that could result in damage to original packaging during transit, spills during repackaging or spills during application. Noting that greases are immobile and that oils are shipped either within vacuum pumps or in containers of a few liters, and that reasonable action would likely be taken to clean up any spill, the potential for any significant quantity release to the environment from accidents like these is likely negligible (OECD 2004).

The Semiconductor PFAS Consortium is working to more fully map PFAS uses and releases in 2023.

6.0 Conclusions

The characteristics of fluorine, the performance characteristics brought about in PFAS-containing lubricants through its impact on bonds with carbon, and influences on adjacent carbon-to-carbon bonds and carbon-to-oxygen bonds are truly unique and help explain their ability to meet the multiple performance requirements essential for use within the semiconductor manufacturing process.

Lubricants used in the semiconductor manufacturing process must provide several critical performance requirements all at once in order to be suitable for use, including those required to maintain the cleanliness of the manufacturing process and to remain functional under conditions common in semiconductor manufacturing operations such as very low and high pressures, low and high temperatures, and exposure to extremely aggressive chemistries.

PFAS-containing lubricants meet the performance requirements critical to the semiconductor manufacturing process, including low particle generation and outgassing necessary to maintain cleanliness, chemical inertness, and the ability to provide for long life and low wear throughout all environmental conditions.

Currently, no non-PFAS-containing lubricants are not viable for drop-in replacement, and the effort to develop new lubricants and/or new substitute technologies will take many years, require very significant financial and human resources, and a successful outcome is not guaranteed. Such efforts could begin with the evaluation of current PFAS-containing lubricants in common semiconductor manufacturing applications, and/or the focused development of novel base oils, additives and thickeners that could better match the current performance characteristics of PFAS-containing lubricants.

The current applications of PFAS-containing lubricants do require handling during maintenance activities and PPE are used, but formulations have such low volatility that exposure potential is negligible. PFAS-containing lubricants also remain contained during normal equipment operation.

Pumps are sent offsite for refurbishment and waste pump fluids are collected for reclaim. Waste generated from onsite maintenance activities is managed through incineration.

7.0 References

- Apex. n.d. *Ferrofluid Rotary Vacuum Feedthroughs*. Accessed February 26, 2023.
<https://apexvacuum.com/ferrofluid-rotary-seal-vacuum-feedthroughs/>.
- Bell, Gregory A, and Jon L Howell. 2005. "Perfluoroalkylpolyethers." In *Synthetics, Mineral Oils, and Bio-Based Lubricants*, by Ed Leslie R. Rudnick. Boca Raton: CRC Press.
- Chemours. n.d. *Krytox LVP and VPF Lubricants*. Accessed February 26, 2023.
<https://www.krytox.com/en/products/vacuum-lubricant>.
- Cousin, Ian T., Greta Goldenman, Dorte Herzke, Ranier Lohman, Mark Miller, Carla A Ng, Sharlye Patton et al. 2019. "The Concept of Essential Use for Determining when Uses of PFASs Can Be Phased Out." *Published Environmental Science: Processes & Impacts* 1803-1815.
- Dams, Rudy, and Klaus Hintzer. 2016. "Industrial Aspects of Fluorinated Oligomers and Polymers." In *Fluorinated Polymers: Volume 2*, by Bruno Ameduri and Hideo Ed., Sawada, 3-31. Oxford: Royal Society of Chemistry.
- ExxonMobil Industrial Lubricants. 2014. "Slide Ways Lubrication Stick Slip Effect."
www.MobilIndustrial.com. February 21-24.
<https://www.exxonmobil.com/~media/Files/global/us/industrial/tech-topics/slide-ways-lubrication-stick-slip-effect.pdf>.
- Filsinger, D.H. 1995. "Formaldehyde Levels Based on Bulk and Elevated Temperature Evolution Rate Measurements of Silicone Materials." *American Industrial Hygiene Association Journal* 56, no. 12 1201-1207.
- Fowzy, Mahmoud A. 1998. "PFPE, A Unique Lubricant for a Unique Application." discover.dtic.mil.
<https://apps.dtic.mil/sti/pdfs/ADA347666.pdf>.
- Friesen, C.M., and B., Ameduri. 2018. "Outstanding telechelic perfluoropolyalkylethers and applications therefrom." *Progress in Polymer Science*, 81 238-280.
- Galary, Jason. 2017. "Investigation into the Dynamic Particle Generation of Lubricating Greases Used in Space Mechanisms." *ESMATS*. September 20-22.
<https://www.esmats.eu/esmatspapers/pastpapers/pdfs/2017/galary.pdf>.
- IKV Tribology Ltd. n.d. *Fluorinated lubricants for EXTREME conditions*. Accessed February 26, 2023.
<https://www.triboflon.co.uk/>.
- Kirsch, Peer. 2004. *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
- Malinverno, G, G Pantini, and J Bootman. 1996. "Safety Evaluation of Perfluoropolyethers, Liquid Polymers Used in Barrier Creams and Other Skin-Care Products." *Food and Chemical Toxicology* 34, no. 7 693-650.
- Marchionni, Ajroldi, Pezzin, and Righetti. 1993. "Molecular Interactions in Perfluorinated and Hydrogenated Compounds: Linear Paraffins and Ethers." *Macromolecules* 26, no. 7, March 1: 1751-1757.
- Marchionni, Giuseppe, Giuseppe Ajroldi, and Pezzin Giovanni. 1989. *Structure-Property Relationships in Perfluoropolyethers: A Family of Polymeric Oils*. Amsterdam: Pergamon.

- Marchionni, Giuseppe, Guisepppe Ajroldi, and Giovanni Pezzin. 1996. "Structure-property Relationships in Perfluoropolyethers: A Family of Polymeric Oils." In *Comprehensive Polymer Science, Second Supplement*, by SL Ed. Aggerwal and S Russo, 383. London: Pergamon.
- Nagaoka, T, and M Mase. 1994. "Application of a Dry Turbo Vacuum Pump to Semiconductor Manufacturing Processes." *Journal of Vacuum Science and Technology* 12, no. 4 2830.
- Nye Lubricants Inc. n.d. *Damping*. Accessed February 26, 2023. <https://www.nyelubricants.com/damping/>.
- OECD. 2004. "Emission Scenario Document on Lubricant Additives." Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides, and Biotechnology.
- Otto, Michael. 2015. "Airborne Molecular Contamination: Quality Criterion for Laser and Optical Components." *Published in Proceedings of SPIE: Components and Packaging for Laser Systems* 9346.
- Scheirs, John. 1997. "Perfluoropolyethers (Synthesis, Characterization and Applications)." In *Modern Fluoropolymers: High Performance Polymers for Diverse Applications*, by John Scheirs, 435-485. New York: Wiley Interscience.
- Smart, Bruce E. 1994. "Characteristics of C-F Systems." In *Organofluorine Chemistry: Principles and Commercial Applications*, by Bruce E Smart, R.E. Banks and J.C. Tatlow, 57-88. New York: Plenum Press.
- Solvay. n.d. *Fomblin PFPE Lubricants Properties*. Accessed February 26, 2023. <https://www.solvay.com/en/brands/fomblin-pfpe-lubricants/properties>.
- . n.d. *Semiconductors*. Accessed February 26, 2023. <https://www.solvay.com/en/chemical-categories/specialty-polymers/electrical-and-electronics/semiconductors>.
- Walther, H Carl, Gregory A Bell, and Jon L Howell. 2013. "Polychlorotrifluoroethylene." In *Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, Second Edition*, by Ed. Leslie R. Rudnick, 185-202. Boca Raton: CRC Press.
- World Semiconductor Council. 2006. "Joint Statement of the 10th Anniversary Meeting of the World Semiconductor Council (WSC)." San Francisco.
- World Semiconductor Council. 2011. "Joint Statement of the 15th Meeting of the World Semiconductor Council." Fukoka, 25-26.
- World Semiconductor Council. 2018. "Joint Statement of the 22nd Meeting of the World Semiconductor Council (WSC)." San Diego.

Appendix A: Critical Performance Requirements Met by PFAS-Containing Lubricants in Semiconductor Manufacturing

Property	Oils and Greases in Vacuum Pumps	Greases and Solids Used in Vacuum Processing Environments	Greases and Solids Used to Lubricate Robotic Systems	Greases Used in Photolithography Applications	Greases Used to Lubricate Gears and Bearings	Greases and Solids Used to Lubricate Linear Guides, Slides and Ball Screws	Greases and Solids Used to Lubricate Valves	Greases and Solids Used to Lubricate O-Rings and Seals
Chemically Inert	X	X	X	X	X	X	X	X
Compatibility	X	X	X	X	X	X	X	X
End-User Safety	X	X	X	X	X	X	X	X
Nonflammable	X	X	X	X	X	X	X	X
Nonhazardous	X	X	X	X	X	X	X	X
Nonreactive	X	X	X		X	X	X	X
Solvent-Resistant	X	X	X	X		X	X	X
Long Life	X	X	X	X	X	X	X	X
Low Wear	X	X	X		X	X	X	X
High Thermal Stability	X	X	X		X	X	X	X
Low Oil Bleed	X	X	X	X	X	X	X	X
Low Particle Generation	X	X	X		X	X	X	
Low Stick-Slip Behavior			X			X		X
Shear Stability	X	X	X		X	X	X	X
Low Outgassing Properties	X	X	X	X	X	X	X	X
UV Stability				X				

Appendix B: Performance Requirements Terminology

This appendix defines some of the terms used throughout this white paper.

Chemically inert

A chemistry term to describe a substance that is not chemically reactive. A lubricant used in industrial applications like semiconductor manufacturing needs to ideally be inert to the aggressive chemistries used in the manufacturing process, such as inorganic and organic bases and acids, halogens, which can be an important safety consideration where alternatives might be subject to ignition/explosion, react to form gummy deposits, act as fuel for fires, or create other unsafe conditions.

Six parameters important to the chemically inert performance characteristic are:

- **Compatibility:** PFAS-containing lubricants are compatible with many materials of construction important to semiconductor manufacturing, including metals and elastomers (Bell and Howell 2005). Materials manufacturers often publish material compatibility charts (Solvay n.d.). Applicable test methods include the grease copper corrosion test (American Society of Testing and Materials [ASTM] D4048; rust prevention (steel) ASTM D1743; compatibility with elastomers and plastics ASTM D4289).
- **End-user safety:** In general, safety data sheets (SDSs) for PFAS greases show no particular end-user safety issues. Example first-aid measures are:
 - Skin contact: Wash off with soap and plenty of water.
 - Eye contact: Rinse with plenty of water. If eye irritation persists, consult a specialist.
 - Inhalation: Move to fresh air in case of accidental inhalation of fumes from overheating or combustion.
 - Ingestion: Never give anything by mouth to an unconscious person. Do not induce vomiting unless directed to do so by a physician or poison control center.
 - General advice: When symptoms persist or in all cases of doubt, seek medical advice.
- **Nonflammable:** PFAS-containing lubricants are generally not flammable within any conditions likely to be encountered in semiconductor manufacturing, as they show no autogenous ignition, flash or fire points in standard ASTM tests. Applicable test methods include flash and fire points of lubricants (of base oils), ASTM D92. Factory Mutual (FM) 6930 can determine the flammability classification of industrial fluids, including lubricants.
- **Nonhazardous:** In general, SDSs indicate that PFAS greases are nonhazardous. Nonhazardous SDS reporting includes:
 - Emergency overview: The product as such is not hazardous. The thermal decomposition vapors of fluorinated polymers may cause polymer fume fever with flu-like symptoms in humans, especially when smoking contaminated tobacco.
 - Potential health effects: May cause eye irritation.
 - Carcinogenicity: None of the components present in this material at concentrations equal to or greater than 0.1% are listed by the International Agency for Research on Cancer, the National Toxicology Program, or Occupational Safety and Health Administration as a carcinogen.
- **Nonreactive:** The chemistries used in semiconductor manufacturing include strong oxidizers and other aggressive and corrosive chemicals. The ability for lubricants to be stable under conditions of exposure to oxygen is important, and can be measured by the [Bundesanstalt für Materialforschung und-prüfung](#) (BAM) and Wendell Hull & Associates liquid and/or gaseous oxygen test. Stability with aggressive and corrosive chemicals is important as well, and can be measured through services such

as those provided by the Chlorine Institute through tests of compatibility of lubricants with chlorine and/or 50% sodium hydroxide.

- Solvent-resistant: PFAS-containing lubricants are typically not soluble in common solvents, acids and bases (Bell and Howell 2005). It is possible to customize certain specialized tests, such as the U.S. Military Standard Performance Specification (MIL PFR) 27617, to applications of solvents used in the semiconductor industry.

Long life

A long-lasting grease helps maximize uptime and the time between service intervals. Lubricants can be tested to specific application cycle requirements; for example, a spiral orbit tribometer produces relative lifetime calculations based on the number of orbits made below a normalized friction level. Applicable test methods include ASTM D3336, Fischer's Automatische Gusstahlkugelfabrik FE9 and the Svenska Kullagerfabriken R0F+ test for grease life.

Low wear

A lubricant's lubricity is its ability to protect components against friction and wear under specific loads, speeds and geometries (Scheirs 1997). PFAS-containing lubricants often provide excellent performance under conditions applicable to semiconductor manufacturing. Specialized instruments such as the Schwingung, Reibung, Verschleiß (SRV) tribometer can measure coefficients of friction and wear over varying loads, speeds and temperature ranges.

Many common standards describe test procedures, including ASTM E2789, International Organization for Standardization (ISO) 19291, ASTM D6425, ASTM D7421, ASTM D5707, ASTM D5706, ASTM D7594, Deutsches Institut für Normung (DIN) 51834-2, DIN 51834-3, DIN 51834-4 and ASTM D2266. Acceptable thresholds based on National Lubricating Grease Institute (NLGI) high-performance multiuse (HPM) and high-load specifications are ASTM D2266 upper limit (wear scar), 0.5-mm max; ASTM D2596 lower limit (weld point), 400 kgf; ASTM D5706 lower limit (extreme pressure), 800 N; ASTM D4170 upper limit (fretting wear), 5.0 mg; and ASTM D7594 upper limit (wear scar), 0.500 mm.

High thermal stability

A lubricant must be able to protect the mechanical components of semiconductor manufacturing equipment at high temperatures without evaporating. Outgassing is more likely to occur at high temperatures as vapor pressure increases. PFAS-containing lubricants provide outstanding thermal stability because they preserve their properties at low and high temperatures (Friesen and Ameduri 2018). Several lubricant manufacturers have performance charts (Solvay n.d.); (Solvay n.d.).

Low oil bleed

Resistance of the grease to the separation of oil. Applicable test methods and thresholds include ASTM D1742, 5.0% max; and ASTM D6184, 7.0% max, based on the NLGI HPM core specification.

Low dynamic particle generation

What happens when particle contaminants are created by being forced or expelled from a lubricated ball screw, bearing or other mechanical device where dynamic conditions are present. These contaminants could include base-oil constituents, thickener particles and additives, and are freed from the grease through dynamic mechanical actions such as rolling, sliding or a combination.

ISO 14644 covers the classification of air cleanliness in clean rooms and associated controlled environments, along with specifications for testing and monitoring. Dynamic particle generation can be tested through custom methods, such as that developed by Nye (Galary 2017).

Low stick-slip behavior

The Cincinnati lamb friction test, SKC tribometer and Darmstadt rig test are used for slideway lubrication evaluations (ExxonMobil Industrial Lubricants 2014).

Shear stability

PFAS-containing lubricants typically do not break down when subjected to shear, as measured by methods like ASTM D1831 (roll stability of grease), -10% to $+10\%$ based on the NLGI HPM core specification.

Vacuum outgassing properties

When a lubricant outgasses, it releases condensable material that can contaminate wafers, processing equipment and other sensitive components. Vapor pressure is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases at a given temperature in a closed system.

It is essential that all materials used in semiconductor, in-vacuum and aerospace applications possess low vapor pressures to ensure that they can endure low-pressure environments without outgassing and contaminating the surrounding surfaces and environment.

Lubricant outgassing is measured in total mass loss (TML) and collected volatile condensable materials (CVCM) per ASTM E595. Acceptable outgassing limits determined by the semiconductor industry are 1% or less for TML and 0.10% or less for CVCM, at test conditions of 7×10^{-3} Pa at 125°C for 24 hours.

Appendix C: Critical Purpose Provided by PFAS-Containing Lubricants in Semiconductor Manufacturing Applications, and Viability of Non-PFAS-Containing Alternatives

Application for PFAS-Containing Lubricants	Critical Purpose Served	PFAS-Containing Materials in Use/Unique Properties Provided	Known or Potential Non-PFAS-Containing Alternatives	Current Viability of Non-PFAS-Containing Alternatives
Oils and greases in vacuum pumps	Effective lubrication of bearings, gears and seals	PFPE oil, greases containing PFPE base oils with PTFE thickener/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, stability under high shear forces, low aggression to metals and elastomers	Silicone-based oils MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases	Viability is believed to be low, based on the lesser performance in terms of chemical inertness and usable ranges across the temperature and pressure ranges used in the semiconductor manufacturing process
Greases and solids used in vacuum processing environments	Lubrication within low-pressure and high-temperature environments that require high purity for low wafer contamination	Greases containing PFPE base oils with PTFE thickener, greases containing MAC base oils with PTFE thickener, PTFE in solid lubricants/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, complete oxidation resistance, good stick-slip behavior	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases and PTFE solids	Unknown, with expected limitations related to chemical inertness and usable ranges across temperatures
Greases and solids used to lubricate robotic systems	Effective lubrication of mechanical parts that move at high speeds within environments that require high purity for low wafer contamination	Greases containing PFPE base oils with PTFE thickener, PTFE in solid lubricants/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, good stick-slip behavior	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases and PTFE solids	Unknown, with expected limitation with high temperatures encountered at contact surfaces moving at high speeds

Application for PFAS-Containing Lubricants	Critical Purpose Served	PFAS-Containing Materials in Use/Unique Properties Provided	Known or Potential Non-PFAS-Containing Alternatives	Current Viability of Non-PFAS-Containing Alternatives
Greases used in photolithography applications	Effective lubrication of moving parts within environments exposed to UV light	Greases containing PFPE base oils with PTFE thickener/low outgassing, UV stability	MAC fluids, silicone oils, synthetic hydrocarbon oils No known viable alternative for PTFE-thickened greases	The viability of MAC fluids is currently unknown. Silicone and synthetic hydrocarbon oils are known to be nonviable, based on results showing airborne molecular contamination resulting in performance reduction and failure of optical elements
Greases used to lubricate gears and bearings	Effective lubrication	Greases containing PFPE base oils with PTFE thickener/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, stability under high shear forces, low aggression to metals and elastomers	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases	Unknown, with expected limitations related to chemical inertness and usable ranges across temperatures
Greases and solids used to lubricate linear guides, slides and ball screws	Effective lubrication of mechanical parts that move at high speeds within environments that require high purity for low wafer contamination	Greases containing PFPE base oils with PTFE thickener, PTFE in solid lubricants/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, good stick-slip behavior	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases and PTFE solids	Unknown, with expected limitation with high temperatures encountered at contact surfaces moving at high speeds
Greases and solids used to lubricate valves	Effective lubrication of mechanical parts that move at high speeds within environments that require high purity	Greases containing PFPE base oils with PTFE thickener, PTFE in solid lubricants/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-	Unknown, with expected limitations related to chemical inertness and usable ranges across temperatures

Application for PFAS-Containing Lubricants	Critical Purpose Served	PFAS-Containing Materials in Use/Unique Properties Provided	Known or Potential Non-PFAS-Containing Alternatives	Current Viability of Non-PFAS-Containing Alternatives
	for low wafer contamination	operating temperatures and low pressures, good stick-slip behavior	thickened greases and PTFE solids	
Greases and solids used to lubricate O-rings and seals	Effective lubrication and sealing within low-pressure and high-temperature environments that require high purity for low wafer contamination	Greases containing PFPE base oils with PTFE thickener, PTFE in solid lubricants/thermal resistance, inertness toward aggressive chemicals, nonflammability, low vapor pressure and outgassing at high operating temperatures and low pressures, complete oxidation resistance, good stick-slip behavior	MAC fluids where vacuum and temperature levels permit No known viable alternative for PTFE-thickened greases and PTFE solids	Unknown, with expected limitations related to chemical inertness and usable ranges across temperatures