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Linde plc comments to ANNEX XV RESTRICTION REPORT – Per- and polyfluoroalkyl substances (PFASs)

Introduction

Linde plc welcomes the opportunity to provide comments and feedback to the proposal for a restriction of Per- and polyfluoroalkyl substances (PFASs) as set out in the "Annex XV restriction report" of March 22, 2023.

Linde is a leading global industrial gases and engineering company with 2022 sales of $33 billion, approximately 86 percent of Linde's 2022 sales were generated from industrial gases operations across three geographic segments of which 25 percent is within our EMEA (Europe, Middle East & Africa) operating segment. The remaining 14 percent is related to other operations including our engineering and coating businesses.

The below comments relate to Linde's industrial and medical gases business. Please note that separate comments have been submitted also from our coating technology and hydrogen fuelling business entities (cf. submissions from "Praxair srl" and "Linde Hydrogen Fueltech GmbH").

In this context, Linde would also like to draw attention to the separate statements submitted by our European sector association, the European Industrial Gases Association (EIGA), as well as various national sector associations, including the British Compressed Gases Association (BCGA), which we also endorse.

Linde supports the overall intent of the restriction proposal in reducing emissions of PFAS and their degradation products into the environment and that certain exemptions have been proposed by the report. However, not all safety critical uses of Polymeric PFAS components and materials have been adequately considered.

Linde therefore requests maximum derogations for use of Polymeric PFAS in the industrial and medical gases industry, in particular for harsh and extreme conditions in manufacture, handling, transport, and use, with the opportunity for further review if safe alternatives don't become available and proven to meet all requirements in that time.

Moreover, Linde also provides information related to the proposed derogation to allow further time to replace existing refrigeration units containing Fluorinated Gases with alternative refrigerants.

Further information and details on specific uses of Polymeric PFAS in the industrial gases industry, emissions during use and end of life as well as about the use of fluorinated gases in existing refrigeration equipment can be found on the following pages.

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Use of Polymeric PFAS in the industrial and medical gases industry not adequately reflected.

The submitted restriction proposal considers some Sectors and Sub-uses of PFAS in detail but has clearly omitted many uses within the chemical industry and the industrial and medical gases industry as a whole.

The production, delivery and use of industrial and medical gases occurs within many harsh and extreme environments, and components made from Polymeric PFAS are often the only available option to allow safe operation. Materials and components made from Polymeric PFAS are at higher cost than alternatives but are chosen due to their enhanced and reliable safety performance. At this point in time no alternatives are available for the specific uses identified and described further below.

Our products and applications serve multiple end markets, for example Healthcare, Manufacturing, Chemicals & Energy, Metals & Mining, Electronics, Food & Beverage.

Many of Linde's applications bring environmental, economic and social benefits to our customers, communities and the planet. For example, use of Oxygen supports more energy efficient industrial production, provides cleaner drinking water and is used in medical applications; Nitrogen is used for freezing and preserving food and medical samples; Noble gases support breathing applications, energy efficiency and laser eye treatments; and Hydrogen is used both directly and as a feedstock in ammonia production, to provide clean energy sources to reduce GHG emissions and for desulfurisation of hydrocarbon fuels to reduce SO2 emissions from downstream combustion.

Continued safe production, delivery and use of these products is therefore critical.

Safety Considerations

Safe production, delivery and use of industrial and medical gases requires components that can withstand some or all of the following harsh and extreme conditions:

- Wide range of temperatures. Processes can operate between -269DegC and 50DegC, consistent material properties and characteristics are required across the range of temperatures.
- Vacuum to high pressures. Cylinder filling operations can require components to withstand > 450Barg pressures and vacuum to 10^{-3}mbar to minimise contamination.
- Oxygen Enrichment. O2 enriched atmospheres can allow materials that do not burn in air to auto ignite with very intense fires.[1]
- Chemical compatibility. Multiple different gases are included in the industrial and medical gas portfolio and the use of components that have wider compatibility, prevents unintended uses of incompatible materials.[2]

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Key functionalities

Across the range of harsh and extreme conditions listed above, the components chosen need to consistently maintain the following functionality:

- Flexibility across temperature range (-269DegC to 50DegC). Many of the PFAS substances are used in sealing such as PTFE tape and paste, gaskets and valve seats, in order to maintain a gas tight seal. Many materials become rigid and inflexible at low temperatures that would allow leaks and breakages.
- Low permeability. Hydrogen possesses high buoyancy and greater diffusivity than other gases. The small size of the hydrogen molecule gives it diffusivity greater than that of helium and approximately 3 times that of nitrogen in air at ambient conditions. Gaseous hydrogen also readily diffuses into solids.[3]
- Low friction coefficient and wear resistance. Moving parts in pumps and valves need to be able to operate for multiple cycles without degradation.
- Oxygen Compatibility. Components in use in Oxygen enriched atmospheres, including lubricants, seals such as tapes and o-rings, high pressure flexible hoses, etc., need to be able safely operate without igniting or enhancing fires. Mandatory material characteristics have been defined as:
    - Resistance to ignition – an autoignition temperature >400DegC (ASTM G-72 and ISO 21010)
    - High Oxygen Index - O2 purity required to burn as high as possible (ASTM D-2863 and G-125)
    - Low Heat of Combustion <4200J/g - Low heat energy (should an ignition take place) will prevent fire propagation (ASTM D-4809)
    - Liquid Oxygen Impact Rating >98J - A high LOX impact rating will prevent components from igniting in liquid oxygen under impact (ASTM D-2512, ASTM G-86, and ISO 21010)
- Food compatibility. Many gases go onto uses in the Food industry. All non metallic materials must comply with Regulation 10/2011 which defines maximum migration values.[4]
- Approved for use in medical applications. All products and components used in medical applications need to be assessed and controlled to the principles of Good Manufacturing Practice. Any manufacturer of medicines intended for the EU market, no matter where in the world it is located, must comply with GMP [5]

Lack of key functionalities can have severe consequences.

Linde is concerned that failures of the above functionalities can lead to sudden or slow loss of containment with the potential for the following severe consequences.

- Build up of gas concentrations in public areas or confined spaces (and therefore depletion of Oxygen levels) leading to asphyxiation and death[6]
- Cold burns from sudden release of cryogenic liquids between -80 to -269DegC
- Build up of O2 enriched atmosphere leading to intense fires.
- Rapid fires or explosions due to O2 incompatibility of materials within the process
- Explosions, or fires from uncontrolled flammable gas releases

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Our industry has extensive experience in preventing such risks. The European Gases Association provides detailed examples of potential risks and how to ensure safe operations.[7]

In accordance with that, materials, and components for use in the above conditions and environments have been selected following decades of experience and delivered improvements in safety and performance.[2]

To approve alternative new materials for use (assuming they become available in the required timeframe) will require hundreds of hours of testing time plus additional surveillance to ensure they meet all requirements in use. Relevant international standards must also be updated with new material information.

For those new materials that will be used in medical gas production or equipment, further risk assessments will be required to the Principles of Good manufacturing Practice (GMP). Any change within the GMP process must be reflected in the marketing authorisation dossier of the respective product (Module I). [5]

To safely implement a change of material, from availability of alternative material to decision to change, would require several years to decades; to change production process; complete stability testing; risk assess finished product; and filing for safety variation and exchange of material in the market.

Requested derogation for use of polymeric PFAS in the industrial gases industry.

The Annex XV report already includes proposals for two derogations that have parallels to the use of Polymeric PFAS in the industrial and medical gases industry:

1. A 12 year derogation for all Fluoropolymer applications in the Petroleum and mining industry. The Annex XV report stated "because manufacturers and suppliers have indicated that it could take a relatively long time (several years to several decades) to transition towards using alternatives that can achieve the same level of performance. Furthermore, given the relatively large (up to hundreds or thousands) number of individual products supplied in this sector, all with different specific formulations, this would be a complex undertaking needing sufficient time [sufficiently strong evidence base]. Continued R&D increases the chance that alternatives for the relevant applications will be identified.""
2. A 12 year derogation for Lubricants where the use takes place under harsh conditions or use is for safe functioning and safety of equipment

Considering the aforementioned information, Linde therefore requests maximum derogations for use of Polymeric PFAS in the industrial and medical gases industry, in particular for harsh and extreme conditions in manufacture, handling, transport, and use, with the opportunity for further review if safe alternatives don't become available and proven to meet all requirements in that time.

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Industrial Gases use of Polymeric PFAS as sealing compounds, lubricants, rotating parts, flexible hoses

The following specific uses of Polymeric PFAS have been identified as having no approved alternative at the current time.

PTFE Sealant Paste, Tape and Gaskets

PTFE sealant paste or tape is applied to threaded joints that will be expected to require disconnection, such as between the cylinder and its valve and on hose connections.

PTFE based paste and gaskets are also applied to flanged connections to ensure no scoring or imperfection in the flange surface will lead to a pathway for a gas to escape.

The sealant ensures that the required torque can be applied to the joint to ensure pressure tightness and it can be disconnected when required. PTFE has been selected based on many years of experience due to its high compatibility with Oxygen, suitability with light gases (He and H_2) and corrosive gases and consistent properties across a wide temperature range. The use of one product that is compatible for all uses prevents accidental application in the wrong service and the potential consequences listed above.

Connections are required to be disconnected and reconnected at the maintenance frequency of the hose or cylinder ranging from every 3 to 10 years.

For Linde in the EU this use is estimated to be of the order of tens of millions of cylinders and tens of thousands of hose and flange connections on our sites and mobile units

Lubricants in O2 service

Fluorinated Oils and greases such as PFPE and PCTFE are used as a lubricant in valves in high pressure O2 service or vacuum pumps in O2 service. The lubricants ensure the longevity of wear components (e.g. valve spindles) to reduce mechanical friction (that can generate heat and ignitions) or cause the break down and deterioration of seals that can generate particles in the system leading to contamination and/or ignition.

The lubricants are selected due to their excellent O2 compatibility. PFPE and PCTFE have an AIT>500DegC, HoC of 3300-4200J/g and Oxygen Index >100%.

Alternatives include dry lubricants such as graphite or MoS2, however, their HoC is significantly higher at 10,000 to 14,000J/g, meaning any ignition is likely to propagate further due to heating of other localised components. Hydrocarbon and Silicone oils have a significantly lower AIT <300DegC, higher HoC 25,000 to 50,000J/g and lower OI 17-25%, making them completely unsuitable for use in all Oxygen service. Accidental use or contamination of these lubricants can lead to catastrophic fires in O2 service.

In order to reduce the risk of flammable particles accumulating in the valves the amount of lubricant applied is kept to a minimum. Across all new valves and pump requirements use of fluorinated oils in Linde is estimated in the range of hundreds of Kg per year

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Components in valves, pumps, compressors, and turbines
PTFE, PTFE/metal mixes, and FKM are used within valves, pumps, compressors and turbines as static seals, dynamic seals, valve seats and sliding or rolling components such as piston rings.

Valves, pumps, compressors and turbines are used to transfer cryogenic or high pressure gases both in the industrial gases industry and customer uses that can include, food products, medical products and industrial uses.

The materials are selected to ensure consistent properties across a wide temperature range (-269DegC to +50DegC), high pressure up to 450Barg, and different gas compatibility (eg O2, H2).

Key properties include some or all of the following:

- Low friction coefficient – mechanical and particulates friction are to be avoided in H2 and O2 systems as these can increase energy release or temperature and be ignition mechanisms that can lead to Oxygen fires or Hydrogen explosions. In some uses it can also reduce the need for additional lubricant.
- Low wear rate - increased wear leads to increased particles which may initiate ignitions.
- Low thermal expansion (across the operating range) many seals are sited within a machined groove to maintain a gas tight seal. If there is large thermal expansion across the operating temperature range (-269DegC to 50DegC) the seal may be compromised and leaks will occur.
- H2 Compatibility – Embrittlement of materials is faster in H2 service which can lead to early leakage.
- Low permeability – Required for containment of small gas molecules such as H2 and He.
- O2 compatibility – Any reduction in O2 compatibility (as described above) significantly increases the chance of Oxygen ignitions and intense fires.

Linde and our customers are estimated to have hundreds of thousands of PFAS components within valves, pumps, compressors and turbines.

In summary, Polymeric PFAS materials are renowned for outstanding insulation capabilities, reliable performance in emergency running and emergency lubrication scenarios, long-term durability, secure electrostatic discharge properties, acceptable dimensional stability, excellent machinability, and exceptional mechanical resilience in cryogenic conditions.

Currently, there are no known alternatives that meet all these special requirements at once. For example, PEEK is not a viable alternative to PTFE for piston rings in oxygen service because it has a far lower LOX impact energy (ignites more easily from particle impact), and therefore has inadequate Oxygen compatibility and could lead to potential fires.

Liners for hoses
Flexible hoses or connections are extensively used for frequent manual connection and disconnection to high pressure gaseous cylinders in the filling process or at the customer gas dispensing system. Different hose designs are employed in different service duties.

- Stainless steel, copper or Monel tubing pigtails (coiled flexible metallic tubing)
- Fluoropolymer-lined hoses with stainless steel or Kevlar braiding
- Corrugated Metal Hoses

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Polymeric PFAS lined hoses are used by preference for the following uses:

- Filling of high pressure Oxygen cylinders. The PTFE or PCTFE liner combine high Oxygen compatibility as described above, with mechanical properties such as flexibility and durability.
- Filling of most standard gas applications (Nitrogen, Argon, Nitrous, Mixtures) due to their flexibility and durability.
- Filling of Hydrogen/Helium due to low permeability and wide range of operating temperatures.

The alternative hose designs listed above have the following limitations making them unsuitable for all uses:

- Corrugated Metal hoses have lower life expectancy and are unapproved for use in O2 service due to concerns with maintaining cleanliness and compatibility at increased pressure.
- Metallic pigtails (monel or copper must be used in Oxygen service (increasing cost)), have limited flexibility compared to hoses, making them unsuitable for filing mixed cylinder sizes and existing filling stations may not have adequate space to install, requiring a full redesign.

It is estimated that Linde and our customers have tens of thousands of high-pressure cylinder filling hoses across the EU.

Emissions during use and end of life

During use, no waste emissions are expected from the above applications of Polymeric PFAS as they are specifically selected for their durability, and they are primarily used directly within the gas technical and chemical process area without contact with the atmosphere.

As a responsible Industry user, committed to sustainability and minimizing our own environmental resource intensity, we would welcome the opportunity to work with local partners and regulators to ensure continuous improvement and compliance in end-of-life waste management.

Detail for proposed derogation on use of fluorinated gases in existing refrigeration equipment

In addition to the missing sector and sub-uses described above, refrigeration units are critical components on air separation plants where atmospheric gases are made. Plants typically run 24 hours a day, 7 days a week, 52 weeks per year and are only programmed to shut down for maintenance and improvement work once every 5-10 years for 10-30 days at a time.

Many of these plants are still using fluorinated gases controlled by the F-GAS regulations. New refrigeration units can be designed to use Ammonia or Carbon Dioxide, however existing equipment will need to continue to use the fluorinated gas as designed until the equipment can be replaced.

The Annex XV report proposes a ban with a transition period of 18 months and a 12-year derogation for maintenance and refilling of existing HVACR equipment without drop-in alternative(s), because the alternative to permitting maintenance including topping up of systems would be to require system replacement. There is insufficient capacity in the market to carry out this work on a short or medium timescale. Drop-in alternatives are not available.

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Replacement of the refrigeration unit will require full shut down of the entire process plant and rework and redesign to accept the replacement.

It is estimated that to complete this work in 13.5 years from EiF will require multiple replacements a year. With the restrictions in capacity in the market to carry out this work (already identified in the Annex XV report) along with the expected spike in demand from multiple industry users, this may not be feasible.

Emissions of fluorinated gases during use will be kept to a minimum due to the control and management of these products by the F-Gas regulations. All product at end of life is recovered for reuse in other equipment.

References

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[2] ISO 11114-2:2021 Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials
[3] ISO/TR 15916:2015 Basic considerations for the safety of hydrogen systems
[4] COMMISSION REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R0010&qid=1691658799251)
[5] Good Manufacturing Practice, European Medicines Agency (https://www.ema.europa.eu/en/human-regulatory/research-development/compliance/good-manufacturing-practice)
[6] Doc_44/18_Hazards_of_Oxygen-Deficient_Atmospheres, European Industrial Gases Association AISBL (https://www.eiga.eu/uploads/documents/DOC044.pdf)
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