EUROPEAN INDUSTRIAL GASES ASSOCIATION (EIGA)

COMMENTS ON PFAS ANNEX XV RESTRICTION PROPOSAL

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

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1 Introduction

EIGA – is a safety and technically oriented organisation representing the vast majority of European and also non-European companies producing and distributing industrial, medical and food gases. The member companies closely co-operate in technical and safety matters to achieve the highest level of safety and environmental care in the handling of gases. EIGA is in frequent touch with Standardisation and Regulatory Organisations and Authorities as well as trade and industrial organisations. EIGA's membership comprises European companies that produce or distribute industrial and/or medical gases.

For information about our sector, please refer to https://www.eiga.eu/the-industry/statistics/

For information about application of gases, please refer to https://www.eiga.eu/applications/

We recognize the ambition to restrict PFAS to protect human health and the environment for future generations.

In parallel, the PFAS restriction as defined today will significantly impact all aspects of gas industry (e.g. industrial/medical gas production, storage and both cylinder and bulk supply). This includes supply of gases to a range of critical industries including but not limited to:

- liquid and gaseous oxygen for hospital and healthcare facilities, such as was needed for Covid primary treatment;
- oxygen for industrial purposes like steel production
- pure gases and gas mixtures for food industry
- green hydrogen (cryogenic and gaseous) to enable delivery for the EU's decarbonization targets;
- cryogenic and gaseous nitrogen for safety critical inerting processes;
- cryogenic helium for hospital MRI scanners;
- electronic gas (mixtures) towards the Semiconductor Industry;
- refrigerants.

This document describes 5 main uses that will be impacted by the PFAS restriction proposal. For each use our industry depends on the upstream supply chain of equipment for investigation on alternatives.

We understand that research and validation and potential implementation of alternatives will imply massive investment and time.

There are applications where alternatives seem to be not possible within derogation time or not at all. The lack of alternatives can lead to a future risk to not be able to produce and supply gases under the same safe conditions as today.

2 Lubricants (Annex E.2.14.)

2.1 Use of Lubricants containing PFAS in Gas Industry

PFPE based lubricants are widely used in gas equipment for great resistance in oxidizing atmospheres and high pressure. Introduction of these lubricants significantly reduced occurrence of oxygen ignitions (fire) and improved safety of our employees, customers and patients. These lubricants are also used in less severe conditions for their excellent mechanical properties.

The lubricants are used on:

- moving elements in cylinder valves
- moving elements (e.g., spindles, regulators) in equipment used in our applications
- moving elements in machines (e.g. pumps, compressors, vacuum pumps)

Also, other PFAS based substances are used for their good lubricating properties and resistance to harsh environment including oxygen. PTFE seals used in our applications are also considered as lubricant for their self-lubricating and low friction properties which doesn't require additional high performing lubrication containing PFAS.

Typical examples are product lubricated bearings. Fluoropolymer materials like PTFE or mixtures of fluoropolymers with other materials such as metals, ceramics and other polymers are used as product lubricated bearings, as they offer excellent chemical resistance and low friction, which helps to reduce wear and extend the life of the product.

2.2 Key Functionalities

As lubricants are used in very thin layers, they are extremely vulnerable to ignition in the oxygen environment and a wide range of temperatures. To withstand such conditions, lubricants must be extremely resistant to properly support functionality of the equipment. Today only lubricants based on PFPE oil can safely serve in these conditions.

Source of data below: ASTM M36, 2nd edition

	AIT (°C)*	HoC (cal/g)*	OI (%O_2)*
Hydrocarbon oils	150 - 260	8000 - 12000	17 - 25
Silicone oils	200 - 300	6000 - 6500	21 - 23
Dry lubes (graphite, MoS2)	>400	2400 - 3400	ND
Fluorinated oils (PFPE, CTFE)	>450	800 - 1000	>100

*Approximate ranges for comparison

AIT Auto-ignition temperature - temperature at which a material will spontaneously ignite under specified conditions

HoC Heat of Combustion - Energy released during combustion

OI Oxygen Index - minimum concentration of oxygen by volume percentage in a mixture of oxygen and nitrogen introduced at (23 ± 2) °C that will just support combustion of a material under specified test conditions

We use these lubricants also in less severe environments where their excellent mechanical properties guarantee reliable service during whole lifetime and reduce the maintenance need.

2.3 Emissions

Cylinder valves and regulators

Lubricants are applied at the beginning of the life inside the equipment and stay there for the whole life. In cylinder valves, it is a minimum of 10 years. During life, there are no PFAS emissions. End of life is under the control of gas companies or other companies who own the equipment so waste can be managed.

Total use of PFAS lubricants in this equipment in Europe is in the range of 2.5 tonnes per year. This is based on data from new cylinder valves purchases and estimation of quantities of equipment that we buy in lower volumes (e.g. regulators).

(Vacuum) Pumps, compressors

Lubricants are applied at the beginning of the life inside the equipment. Oil is changed based on the maintenance plan. For all equipment used in our industry in Europe, we estimate a change of 40 tonnes per year of PFAS based oil. This waste is under the control of gas companies and can be managed.

There is no clear evidence but based on available data lubricants can be destroyed by heat when metal melting during recycling as it is impossible to remove them from metallic components at the end of life. A study made by Karlsruhe Institute of Technology[1] confirms that 850°C is sufficient to break down the PFAS and brass melting temperature is 900°C. Other metals used together with PFPE lubricants (e.g. stainless steel, Monel) have even higher melting temperatures.

NOTE The study by Karlsruhe Institute of Technology is provided as separate attachment.

2.4 Alternatives

According to different manufacturers and suppliers of lubricants, there are no available alternatives which can offer similar safety performance in our applications. Even though derogation for 12 years is proposed we have no indication from our suppliers that within this time period an adequate alternative can be developed. Once the alternative is developed it must be properly tested by independent laboratories to confirm safe performance before it can be used in any equipment. Limited laboratory resources within Europe may increase the time needed for introduction of alternatives.

2.5 Concluding Remarks

Based on above and taking in consideration our very high safety standards which cannot be compromised, we strongly insist that the use of PFAS lubricants shall be excluded from the restriction as proposed. We are not in a position to estimate sufficient time needed to develop alternatives. We request that a specific category with longer derogation time for lubricants is defined.

For more information on compatibility of materials and incidents with oxygen see EIGA O2-learning[2].

[1] Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas
Krasimir Aleksandrov[a], Hans-Joachim Gehrmann[a], Manuela Hauser[a], Hartmut Mätzing[a], Daniel Pigeon[b], *, Dieter Stapf[a], Manuela Wexler[a]
[a] Karlsruhe Institute of Technology, Karlsruhe, 76021, Germany
[b] W.L. Gore & Associates, Inc., Elkton, MD, 21901, USA

[2] https://www.eiga.eu/elearning-courses/oxygen/

3 PTFE-Tape (Construction products - Annex E.2.13.)

3.1 Use of PTFE thread sealing tape in Gas Industry

Our industry uses PTFE thread sealing tape in various applications.

1. Connection between gas cylinder valve and cylinder
2. Equipment for cryogenic and low temperature service (as low as -270°C)
3. Equipment for storage and transportation of gases
4. Equipment for gas distribution network

The Bulk Gas Industry mentioned in the restriction proposal includes examples of gases below (pure or mixtures in gaseous or liquid state):

- Industrial gases, e.g., air gases as nitrogen, oxygen and argon or other gases as hydrogen, helium, carbon dioxide
- Medical gases, e.g., oxygen, nitrous oxide, medical air, carbon dioxide, helium
- Food gases, e.g., nitrogen, oxygen, carbon dioxide, ethylene, argon, rare gases
- Specialty gases, e.g., rare gases, calibration gases, toxic gases, corrosive gases
- Electronic gases and liquids, e.g., gases for use in processes of semiconductor industry

These products are supplied in cylinders, cylinder bundles, cryogenic dewars, drums, bulk cryogenic tankers, bulk gas trailers, tanks, vessels, pipelines

Leak tight connections on these packages are essential as leaks can cause harm to people and environment (toxic, asphyxiating, corrosive, explosive, flammable, oxidizing)

3.2 Key Functionalities

PTFE as material for thread sealing tape is used because of some key functionalities.

From a practical point of view, one of the key functions is the ease of use of PTFE tapes in thread sealing. As already mentioned in Annex E (E.2.13.2.2.) of the proposal "*PTFE tapes have high tensile strength and by using PTFE tape the sealings becomes durable, water- and heat resistant.*" The high stability of PTFE thread sealing tape as lubricant permits the appropriate torque to be applied on conical thread connections to guarantee the pressure tightness over a wide pressure and temperature range during the life cycle of the equipment. Over the years of application, the gas industry has accumulated a long-term experience using PTFE tape or PTFE cones. Standards and procedures have been developed for the correct application achieving very reliable and reproducible sealings for the various applications. Thus, the level of safety in the gas industry has been significantly increased using PTFE thread sealing tape.

Another key functionality of PTFE is the high auto-ignition temperature (AIT) and low heat of combustion. These parameters are not only but especially very important for the use in oxidizing gases. The AIT of most materials is significantly reduced in oxygen-rich or oxidizing environments. Under high pressure (e.g., 200-300 bar) the risk of an ignition is much higher than under usual atmospheric conditions since it can easily be triggered by the contact of an ignitable material to a high flow of an oxidizing gas. In case of an oxygen fire, temperatures reach a level at which even steel equipment burns. Due to its considerably high AIT, PTFE reduces the risk of an oxygen ignition and consequently a violent fire in the facilities of the gas supplier but also in the customers' equipment as for example in hospitals.

In addition, PTFE offers a very high chemical resistance against all molecules in the gas industry. Besides oxidizing components, especially corrosive components must be mentioned in this case. PTFE sealing tape can thus be used as a universal component.

Due to their properties, components made from PFAS (PTFE, PCTFE, PFDF, FKM) are required by law for some applications, e.g. corrosive gases. The legal framework is given by e.g. ADR (Agreement of

International Carriage of Dangerous Goods by Road) through the mandatory application of ISO 11114-2 *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials.* The affected gases are e.g. chlorine, dichlorosilane or dimethylsilane.

3.3 Emissions

PTFE tape is used on all cylinders, cryogenic tanks, trailers and other packages with conical thread connections. For the different packages and dependent on the application of the gas products inside, there are different rules and legislations on how often a package must be checked.

For example, the check of the internal surface and the pressure test of a gas cylinder must be done every five to fifteen years, depending on the gas service and other parameters. To perform the so-called retesting, it might be necessary to remove the cylinder valve from the empty gas cylinder. In most cases, the retesting is the only time the cylinder valve and the PTFE sealing tape are removed from the cylinder. After the pressure test, the cylinder is equipped with a new cylinder valve and a new PTFE sealing tape. During the years of use, there is no generation of PTFE waste.

The gas industry companies usually use a circular model for the gas cylinders. The filled gas cylinders are transported to the customer. When the gas inside a cylinder is consumed the cylinder is transported back to the gas industry companies and refilled. Maintenance or retesting of cylinders is only done by the gas industry companies. For all other gas packages very similar circular models are applied. This means that no PTFE waste is generated by the customers and disposal is solely the responsibility of the gas industry companies. Our industry can set up processes for PTFE tape collection and send for controlled waste management to eliminate emissions.

The number of high-pressure cylinders in Europe is estimated to about 50 millions pieces excluding low pressure cylinders for e.g. LPG. An average retest period of 10 years leads to approximately 5 million retested cylinders per year. This maintenance activity generates 15 tonnes per year of PTFE tape waste.

For threaded connection between other equipment (e.g. gauge to pipe…) in Europe, PTFE tape waste could be in the range of 5 tonnes per year

3.4 Alternatives

Before 40 years ago, thread sealing was done based on metallic cones. Materials were lead, silver, tin and/or aluminum. Apart from obvious reasons as the harmful properties of lead, there were especially safety reasons which led to the change from metal cones to PTFE tape. In principle, metallic sealing would be a possible alternative also today using tin, copper, nickel, zinc or others in a wide range of alloys. The experience of the gas industry shows that the reliability and the reproducibility of metallic cones for thread sealing are not comparable to use of PTFE tape and represents a massive safety issue. The use of metallic cones much more often requires the retightening of the threads when applying a new valve to the package. Furthermore, when using metallic cones, it is also necessary to apply a PFAS based lubricant/paste to them to achieve proper metal-to-metal contact to reach tightness. This lubricant/paste has the same compatibility and safety issues of PTFE tape. Nowadays, a sealing with metal foils (tin, copper, nickel, zinc, stainless steel, brass, or a mix) could be an alternative. But there is no data available on whether the sealing would be sufficient. Different gases will need a different metal foil for chemical compatibility. This could lead to mistakes and unsafe packages.

As described before the gas industry has developed a lot of procedures for the use of PTFE sealing tape. Therefore, the nearest solution would be an exchange of PTFE with other materials, e.g., PEEK. Unfortunately, the compatibility of PEEK with some gas molecules is limited. PEEK is for example not compatible with nitric oxide, nitrous oxide and nitrogen dioxide as well as halogen gases and halogenated gases. Research would have to be initiated in this area to fully determine chemical compatibilities.

In the restriction proposal permanent liquid or paste thread sealants (mentioned in Annex E (E.2.13.2.7 and E.2.13.2.11.)) are considered as alternatives. The gas industry has only limited experience in this area. However, the chemical resistance against oxidizing or corrosive components is of immense importance. Currently there is no knowledge available on this topic. No suitable alternatives have been identified so far either by the gas industry itself or by a survey of the gas industry to the suppliers of gas packages or related equipment.

In summary, finding an alternative for PTFE thread sealing tape is a complex and demanding task for the gas industry. Alternatives must comply to both, mechanical and chemical properties. In addition, safety issues must be considered. PTFE thread sealing tape was used as a universal component, compatible to nearly all gas molecules. Using different materials significantly increases the risk of confusion and may inevitably lead to a higher number of accidents.

Due to the life cycle of PTFE in cylinder packages up to 15 years, the alternative will have to be validated for this time frame, on top of the time to design it. It should be noted that this research must be conducted for all different molecules in the gas industry.

3.5 Concluding Remarks

The proposal for the PFAS restriction considers the use of PTFE thread sealing tape mainly in the area "construction products". For most of the construction work products, the key properties are high tensile strength, durability, water- and heat resistance [Annex E (E.2.13.2.2.)].

However, in the gas industry those properties are only one part of the key functionalities. The chemical resistance and the auto-ignition temperature are added to the key functionalities. These functionalities contribute significantly to the safe use of high-pressure gases but also cryogenic products by companies in the gas industry and their customers.

In ANNEX XV RESTRICTION REPORT in chapter 2.4.3.3. environmental impacts of restriction options, the restriction mentions in the part of "*lubricants*" a specific derogation for "*lubricants where the use takes place under harsh conditions or use is for safe functioning and safety of equipment*". Such a categorization is missing in the use for PTFE thread sealing tape. In the gas industry the impact on safety of equipment and safe functioning is similar as for the use of lubricants.

Regarding possible alternatives, different materials are listed. Unfortunately, no material has yet been identified which facilitates the same level of safety in the application of thread sealing as PTFE tape. The safety of employees, customers and patients is the number one priority for the gas industry. The development and validation of substitute materials requires careful research especially when considering long-term stability of the materials in contact with demanding gas molecules.

Comparable to the derogation proposal for "*lubricants where the use takes place under harsh conditions or use is for safe functioning and safety of equipment*", the gas industry proposes a similar derogation for PTFE thread sealing tape because the use takes place under harsh conditions or use is for safe functioning and safety of equipment. Unless the chemical industry can develop a suitable alternative for our applications, we request a maximum derogation time.

Taking everything into consideration the best approach would be responsible waste management at end of life cycle.

4 PFAS lined hoses

4.1 Use of flexible hoses with PFAS for filling gas in cylinders

PFAS lined flexible hoses for filling gases into cylinders are made by wrapping a PTFE hose with a stainless steel braid. The mechanical strength introduced by the external braid guarantees the resistance of the hose to high pressures (up to 400 bar), pressures that PTFE alone would not resist. The internal PTFE piping, on the other hand, provides flexibility and durability even if subjected to repeated daily bending for a period of years.

4.2 Key functionalities

The flexible hoses are used during manual operations. The customer or our operator is in close contact with the flexible hose and handles it regularly. Leaks or other accidents potentially have catastrophic consequences. The highest level of safety must be guaranteed.

The chemical resistance of PTFE is required for compatibility with flammable, oxidising, corrosive and especially toxic components in our gases. A high auto-ignition temperature (AIT) is especially required to resist the high temperatures created by high flow in oxygen environment. In case of ignition in oxygen environment the low heat of combustion of PTFE reduces the consequences of the incident.

PTFE lined hoses show long term reliability, reaching 50000 cycles (as defined by ISO 16964).

4.3 Emissions

PTFE lined hoses do not produce PFAS waste during use. The only source of waste is at the end of life when the hose must be replaced. End of life is under the control of gas companies or other companies who own the equipment so waste management can be controlled.

Our industry on average replaces hoses every 5 years, generating approximately 2 tonnes per year of PTFE waste in Europe.

4.4 Alternatives

Our industry relies on safe equipment with high performance. The known alternatives do not provide the same safety and handling performance.

Existing alternatives are hoses where the internal liner is made of corrugated metal or a different polymer. Another alternative is a coiled metal pipe (called pig tail).

The corrugated metal liner hoses are an alternative but bring with them other safety issues. They require more detailed evaluation for each application to eliminate risks connected to the design/configuration. For example, for acetylene the complex surface friction could generate heat that can lead to an ignition. For oxygen there is an extra risk that small particles impact the surface, generating heat and leading to ignition and extra measures need to be implemented for safe use. In case of carbon dioxide, hydrogen and helium turbulence creates high frequency noises, increasing the risk of failure and reducing the lifetime of the hose.

These hoses have shorter lifetime (10000 cycles instead of 50000) due to lower flexibility than PTFE lined ones, which can increase risk of failure/rupture.

Hoses with liners made of different polymers offer similar functionality like PTFE lined hoses when used with its compatible gas. External appearance of polymer lined hoses is identical, and it is impossible to identify the material of the liner if not marked by the hose manufacturer. Use of different hoses made of different materials in a filling site increases the risk of incompatible hose installation. The risk is also high for customer applications due to limited knowledge of material compatibility at customer site. When an incompatible hose is installed, it can leak, rupture or burn.

Coiled metal pipes (pig tails) are used in specialty gas applications but not commonly in industrial application. There are restrictions in handling, because the tubes must be permanently bent to the cylinder connections, which is for the operator more difficult compared to a hose. Permanent tension on the connecting valve could lead to leaks. It also requests significantly more space compared to hoses which means complete redesign of filling systems to accommodate these pipes. In addition, structural changes occur that lead to hardening of the tubes. They therefore have to be stress-relieved about once a year because at some point they can no longer be handled by the operators. PTFE lined hoses eliminate all these restrictions.

4.5 Concluding Remarks

Alternatives with the same advantages as PTFE lined hoses are not existing today. It will take time to do the research and update industrial standards.

If our industry would need to revert to the listed existing alternatives, they are technically a step back in terms of safety, operator ergonomics and material consumption. The change will require several years due to the high number of installations. Replacing a PTFE lined hose with an existing alternative is also requiring a redesign of the surrounding filling system. Systems to control material compatibility of different hoses must be introduced to minimize/prevent risk of incident due to material mix.

Regarding possible alternatives, different materials are listed. Unfortunately, no material has yet been identified which facilitates the same level of safety for employees and customers, which is the number one priority for the gas industry.

Unless the chemical industry can develop a suitable alternative for our applications, we request a maximum derogation time.

Taking everything into consideration the best approach would be responsible waste management at end of life cycle.

5 Cryogenic applications in the (Industrial Bulk) Gas Industry[3]

5.1 Use of PFAS in the cryogenic part of the Gas Industry

The current restriction proposal does not consider cryogenic phase of gas production in any aspect. Most common production and supply processes for industrial bulk gases work at cryogenic temperatures.

Examples of boiling point for most common gases:

- Oxygen -183°C
- Nitrogen -195.8°C
- Helium -268.9°C
- Argon -185.7°C
- Hydrogen -252.9°C
- Carbon Dioxide -78.5°C
- Nitrous Oxide -88.5°C

The gases are used in various applications in cryogenic phase:

- Oxygen
  - Critical medical treatment therapy (e.g., covid)
  - Combustion application for glass, steel, non-ferrous metal production
  - Aerospace/Space
  - Semiconductor
  - Food packing and preservation
- Nitrogen
  - Biomedical cryogenic storage
  - Inerting for hazardous chemical/material storage
  - Food packing and preservation
  - Semiconductors
  - A wide range of manufacturing processes requiring inert atmospheres
- Helium
  - MRI magnets in hospitals
- Argon
  - Welding and metal fabrication
  - Atmosphere control for inerting many high temperature annealing processes (e.g., glass and metal production)
  - Temperature shielding in windows to reduce energy consumption in buildings
- Hydrogen
  - Cryogenic hydrogen will be critical in delivering the EU's decarbonisation strategy as part of the hydrogen economy. Cryogenic hydrogen will be needed for storage and distribution of large volumes of hydrogen
  - Electronics, glass, aerospace industry
  - Refineries (e.g., desulphurisation)
  - Chemical feed stock (e.g., Haber-Bosch process for ammonia production)
- Carbon dioxide (see recent years CO_2 shortages)
  - Food and beverage production
  - Dry ice for transportation of critical goods (e.g., medicines)
- Nitrous Oxide

[3] The restriction proposal refers to our industry as Industrial Bulk Gas Industry

- Critical healthcare medicine for pain relief. Primary pain relief during labour and one of the few pain relief medicines that can be widely administered by paramedics/first responders

5.2 Key functionalities

PFAS materials are used in cryogenic applications mostly as sealing materials and are critical for the safety of the process. Typical PFAS materials used are PTFE, PCTFE, CTFE, FEP, FKM, FFKM, PFPE lubricants. Main properties of these materials which make them superior in cryogenic applications are:

- Reliable functionality in low temperatures
- Universal compatibility with different gases
- Low friction

Failure of the sealing elements means leakage which creates a safety risk to operators and public. Liquified gases contain around 800 times the volume of the gaseous phase. Loss of containment can lead to:

- Anoxia
- Cold burns
- Fire promotion and explosions for oxidising gases
- Rapid fires and explosions from oxygen incompatibility
- Explosions, fireballs and jet fires from hydrogen releases

5.3 Emissions

Equipment used in cryogenic phase is not producing PFAS waste during the use. PFAS materials are part of internal equipment used for gas manufacturing and supply. The only source of waste is during maintenance or at the end of life when equipment must be decommissioned. End of life is under the control of gas companies or other companies who own the equipment so waste management can be controlled.

Examples of cryogenic equipment include air separation unit compressors, cryogenic pumps, valves in liquid service, cryogenic storage tanks, cryogenic transfill hoses, bulk road tankers and tanker hoses.

All this equipment is installed and typically runs for decades without maintenance. Back-up equipment parts are replaced even less frequent. PFAS seals used on regular connections (e.g., hose connections) are replaced more frequently when worn.

The amount of generated PFAS waste is included in the total calculations together with the non-cryogenic equipment in the related document.

5.4 Alternatives

Historically, other materials with inferior properties were used, of which some are prohibited (e.g., asbestos). Some have been replaced by PFAS materials.

Alternatives for PFAS seals with the same level of safety in cryogenic equipment are not known to our equipment suppliers. To identify suitable alternatives, long term research and testing will be required because information about low temperature behaviour is missing for most of the materials.

Industrial standards (ISO 11114 series, ISO 21010) which define material compatibility with different gases refer only to PFAS materials for cryogenic applications. These standards are created on long term (decades) experience and will need adequate time to develop knowledge about potential alternatives.

5.5 Concluding Remarks

Due to specific application running under harsh conditions (low temperatures down to -270°C) where equipment is designed and used for decades, it is essential to have access to spare parts for maintenance of running plants and downstream supply chain. There are no known suitable alternatives to replace PFAS in cryogenic applications. A long timeframe will be needed to identify/develop alternatives, prepare/test new solutions, plan and execute exchange of the current equipment.

If the search for alternatives fails and PFAS materials are not available, delivery of gases into critical infrastructure like oxygen for hospitals or hydrogen as source of clean energy will be at high risk.

Ideally PFAS in cryogenic installations should get an unlimited derogation. In the case of maximum derogation, before the derogation expires, a re-evaluation of the progress in the research process for alternatives should be included in the restriction.

6 Non-cryogenic applications in the (Industrial Bulk) Gas Industry[4]

6.1 Use of PFAS gaskets, sealing and o-rings in non-cryogenic application

Our industry uses gaskets, seals and o-rings in valves, regulators (e.g. gaskets, packing or seat material, gland nut) and other parts of the gas production and supply equipment. PFAS materials ensure the leak tightness and functionality of the complete equipment.

This applies to all products of the gas industry (pure or mixtures in gaseous or liquid state):

- Industrial bulk gases, e.g., air gases as nitrogen, oxygen and argon or other gases as hydrogen, helium, carbon dioxide
- Medical gases, e.g., oxygen, nitrous oxide, medical air, carbon dioxide, helium
- Food gases, e.g., nitrogen, oxygen, carbon dioxide, ethylene, argon, rare gases
- Specialty gases, e.g., rare gases, calibration gases, toxic gases, corrosive gases
- Electronic gases and liquids, e.g., gases for use in processes of semiconductor industry

Leak tight equipment is essential as leaks can cause harm to people and environment (toxic, asphyxiating, corrosive, explosive, flammable, oxidizing).

6.2 Key functionalities

Gaskets, seals and o-rings made from PFAS materials are used due to the following key functionalities:

- reliable functionality in a wide temperatures range
- very high chemical resistance against all molecules
- low friction
- high auto-ignition temperature (AIT) in oxidizing environment
- low heat of combustion

6.3 Emission

PFAS contained in gas production and supply equipment do not lead to waste during the use since PFAS materials are only used in internal components. Waste can only be generated during maintenance or at the end of life when equipment is decommissioned. Both cases are under the control of gas companies or other companies who own the equipment so waste management can be controlled.

Our industry on average replaces valves every 5 or 10 years. Regulators usually remain in use for longer periods. Other equipment (cryogenic and non-cryogenic) is not exchanged on predicted periods.

For Europe, we estimate a generation of 30 tonnes per year of PFAS waste from seals and gaskets, including cryogenic applications.

6.4 Alternatives

For the equipment of gas production and supply our industry follows the legal framework as given by e.g., ADR (Agreement of International Carriage of Dangerous Goods by Road) through the mandatory application of ISO 11114-2 *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials).*

The possibility for alternatives is thus severely limited depending on the applied gas molecule.

For the application of polymer materials in contact with gases there are two different lists which must be considered. ISO 11114-2 and the “BAM-List”, which is the BAM database for resistance assessment of polymeric materials (as of 2013). (BAM: scientific and technical Federal institute in Germany).

Both lists consider 134 products of the gas industry and show the compatibility with PCTFE, PVDF, PI, PA, PP, POM, PEEK and PPS as sealing material.

[4] The restriction proposal refers to our industry as Industrial Bulk Gas Industry

A compilation of the 2 lists is attached in Annex 1.

The following information can be obtained from this compilation:

1. The two gasket materials affected by a complete PFAS ban (PCFTE, PVDF) are compatible with all 134 substances.
2. 23 of the 134 substances on the list are not compatible with any other sealing material that could be used as a valve seat seal. The main criterion for this is ball indentation hardness, with PCTFE representing the lowest possible value - even being almost too soft. A question mark in the list was interpreted as non-compatibility, since the behavior of the seal material with the respective substance is not known. These substances are marked with a solid red bar.
3. 82 of the 111 substances that could be replaced by other gasket materials can be covered by the gasket material polyamide (PA), according to two sources listed above. These are marked orange in the list.
4. A further 20 substances of the remaining 29 substances, which are not compatible with PA, can be sealed by the sealing material PEEK. These substances are marked in blue in the list.
5. 7 of the remaining 9 substances, which can be covered neither by PA nor by PEEK, have proved to be compatible with the sealing material polypropylene (PP). Marking in the list: green
6. Polyimide (PI or Vespel) can be used for the remaining two substances. Marking in the list: yellow
7. The two other gasket materials listed (PPS and POM) also show some compatibilities. However, the respective substance can always be covered by one of the other 4 sealing materials (PA, PEEK, PP, PI).

A) Gases for which alternatives are mentioned in the documents
Although alternatives are listed in ISO 11114-2, they are not commonly in use because PFAS materials provide guaranteed performance. Before they could be introduced further testing needs to be executed to confirm compatibility with intended application.

B) Gases for which alternatives are not known
In order to replace PFAS the identification of alternatives will be a long term process (research, testing). Afterwards, the authorities/notified bodies would have to accept and approve the substitution materials. This requires a high amount of effort and data. In terms of timescale, a complete replacement of PFAS in the gas production and supply equipment as used today will not be achievable within a period of 12 years.

6.5 Concluding Remarks

Gaskets, seals and o-rings used in valves, pressure regulators or other gas supply and production equipment are important. They often contain PFAS. They are compatible with the gases used, guarantee functionality and leak-tightness of the equipment. Their application is on the inside of the equipment. To avoid risk of using incompatible materials and to provide safe gas supply, the same PFAS gaskets, seals and o-rings are used even if an alternative exists.

Depending on the gas molecule, the research for alternatives will require time and effort, not only for our industry but also for the responsible authorities/notified bodies. New materials have to be found, classified, tested and approved. Regulations and ISO/CEN standards have to be changed.

Ideally, PFAS applied as sealing material in gas production and gas supply equipment should get an unlimited derogation. In the case of maximum derogation, a re-evaluation of progress in the research process for alternatives before the derogation expires should be included in the restriction.

7 Closing statement

Our industry understands the need to reduce the impact of PFAS materials on human health and environment. At the same time we are very concerned about the impact of the restriction on the safety performance of our industry and about the impact on our employees, customers and patients. The proposed restriction will affect the possibility to supply critical and strategic gases including medical oxygen, specialty gases and hydrogen for decarbonisation.

Annex 1 Compatibility of materials with different gases

(red)	Only PFAS are compatible
(yellow)	PI compatible
(orange)	PA compatible
(green)	PP compatible
(blue)	PEEK compatible

Gas	PCTFE	PVDF	PI	PA	PP	POM	PEEK	PPS	
Ball Indentation Hardness	63 MPa	95 Mpa	170 MPa	100 MPa	62 MPa	145 MPa	190 MPa	190 MPa	Information Source
1,1- Difluorethylen (R1132a)	+	+	?	+	-	+	+	+	ISO 11114-2
1,1,1- Trifluorethan (R143a)	+	+	?	+	-	-	-	+	ISO 11114-2
1,1,2-Trichlortrifluorethan (R113)	S+	+	?	W+	+	S+	+	+	ISO 11114-2
1,2 Dichlorethan	+/-	+	+	-	-	-	+	-	ISO 11114-2
1,2-Butadien	+	+	+	+	+	+	+	+	ISO 11114-2
1,2-dibromtetrafluorethan (R114B2)	S+	+	?	+	-	-	-	-	ISO 11114-2
1,2-dichlorethylen (R1130)	-	+	?	-	-	-	?	-	ISO 11114-2
1,2-Propadien	+	+	+	W+	+	+	+	+	ISO 11114-2
1,3-Butadien	+	+	+	+	+	+	+	+	ISO 11114-2
1-chlor-1,2,2,2-tetrafluoretan (R124)	+	+	?	+	-	-	-	-	ISO 11114-2
Alkane	+	+	+	+	+	+	+	+	ISO 11114-2
Ammoniak	+	-	-	+	+	+	+	+	ISO 11114-2
Antimonpentafluorid	?	+	?	?	+	?	+	+	BAM compatibility list
Argon	+	+	+	+	+	+	+	+	ISO 11114-2
Arsin	+	+	+	+	+	+	+	+	ISO 11114-2
Arsin (max. 7% in H_2, N_2 oder VE)	+	+	+	+	+	+	+	+	ISO 11114-2
Bortrichlorid	+	+	?	-	+	-	+	+	ISO 11114-2
Bortrifluorid	+	+	?	-	+	-	+	+	ISO 11114-2
Bromaceton	?	+	?	?	-	?	?	?	BAM compatibility list
Bromchlormethan (Halon 1011)	?	+	?	+	-	-	?	?	BAM compatibility list
Bromtrifluorid	+	+	?	-	+	-	+	+	ISO 11114-2
Bromwasserstoff	+	+	?	-	+	-	-	-	ISO 11114-2

Gas	PCTFE	PVDF	PI	PA	PP	POM	PEEK	PPS	
Ball Indentation Hardness	63 MPa	95 Mpa	170 MPa	100 MPa	62 MPa	145 MPa	190 MPa	190 MPa	Information Source
But-1-en	+	+	+	+	+	+	+	+	ISO 11114-2
But-1-in	+	+	+	+	+	+	+	+	BAM compatibility list
Butan	+	+	+	+	+	+	+	+	ISO 11114-2
Carbonylfluorid	+	-	-	-	-	-	-	-	ISO 11114-2
Carbonylsulfid (COS)	+	+	-	+	-	-	-	-	ISO 11114-2
Chlor	+	+	-	-	-	-	-	-	ISO 11114-2
Chlorcyan	+	+	?	?	?	+	+	+	ISO 11114-2
Chlorcyan	+	+	?	?	?	+	+	+	ISO 11114-2
Chlorethan (R160)	+	+	?	+	-	-	-	-	ISO 11114-2
Chlorkohlenoxid (Phosgen)	+	-	-	-	-	+	+	+	BAM compatibility list
Chlorpentafluorid	+	-	-	-	-	-	-	-	ISO 11114-2
Chlortrifluorid	+	-	-	-	-	-	-	-	ISO 11114-2
Chlorwasserstoff	+	+	+	+	+	-	-	-	ISO 11114-2
cis-But-2-en	+	+	?	+	+	+	+	+	BAM compatibility list
Cyan / Cyanwasserstoff	+	+	?	-	+	-	-	-	ISO 11114-2
Cyanwasserstoff	+	+	?	-	+	-	-	-	BAM compatibility list
Cyclopropan	+	+	+	+	+	+	+	+	ISO 11114-2
Diboran	+	+	+	+	+	+	+	+	ISO 11114-2
Diboran (max. 10% in H_2, N_2 oder VE)	+	+	+	+	+	+	+	+	ISO 11114-2
Dibromdifluormethan (R12 B2)	S+	+	?	+	-	-	-	-	ISO 11114-2
Dichlorsilan	+	+	?	-	-	-	-	-	ISO 11114-2
Dicyan	+	+	?	?	+	?	?	?	ISO 11114-2
Difluorchlorbrommethan (R12B1)	+	+	+	+	+	-	-	-	ISO 11114-2
Difluordichlormethan (R12)	+	+	+	+	-	+	-	-	ISO 11114-2
Difluorethan (R152a)	+	+	+	+	-	-	-	-	ISO 11114-2
Difluormonochlormethan (R22)	+	+	+	+	P+	+	S+	S+	ISO 11114-2
Dimethylamin	+	-	+	+	+	+	+	-	ISO 11114-2
Dimethylether	+	+	?	-	-	+	+	+	ISO 11114-2
Erdgas	+	+	?	+	-	+	?	?	BAM compatibility list
Ethan	+	+	+	+	+	+	+	+	ISO 11114-2
Ethylamin	+	+	+	+	+	+	+	+	ISO 11114-2

Gas	PCTFE	PVDF	PI	PA	PP	POM	PEEK	PPS	
Ball Indentation Hardness	63 MPa	95 Mpa	170 MPa	100 MPa	62 MPa	145 MPa	190 MPa	190 MPa	**Information Source**
Ethyldichlorarsin	?	+	?	?	-	?	?	?	BAM compatibility list
Ethylen	+	+	+	+	+	+	+	+	ISO 11114-2
Ethylenoxid	+	+	+	-	-	-	-	-	ISO 11114-2
Ethylenoxid +CO_2 (Ethylenoxid > 9%)	+	+	?	?	?	?	?	?	BAM compatibility list
Ethylfluorid (R161)	S+	+	+	+	P+	+	+	+	ISO 11114-2
Fluorwasserstoff (HF)	+	+	?	-	+	-	-	-	ISO 11114-2
German (Monogerman - GeH4)	+	+	+	+	+	+	+	+	BAM compatibility list
Helium	+	+	+	+	+	+	+	+	ISO 11114-2
Hexafluoraceton	+	+	-	?	-	-	-	-	ISO 11114-2
Hexafluorethan (R116)	S,W+	+	+	+	-	-	-	-	ISO 11114-2
Hexafluorpropylen (R1216)	+	+	+	+	-	-	-	-	ISO 11114-2
Hexan	+	+	+	+	-	+	+	+	BAM compatibility list
Isobutan	+	+	+	+	+	+	+	+	ISO 11114-2
Isobutylen	+	+	+	+	+	+	+	+	BAM compatibility list
Kohlendioxid	+	+	+	+	+	-	+	+	ISO 11114-2
Kohlenmonoxid	+	+	+	+	+	+	+	+	ISO 11114-2
Krypton	+	+	+	+	+	+	+	+	ISO 11114-2
Lachgas	+	+	-	+	-	-	-	-	ISO 11114-2
Methan	+	+	+	+	+	+	+	+	ISO 11114-2
Methlysilan	+	+	?	?	?	+	+	+	ISO 11114-2
Methylamin	+	-	+	+	+	+	+	-	ISO 11114-2
Methylbromid (R40B1)	+	+	+	+	-	+	+	-	ISO 11114-2
Methylchlorid (R40)	+	+	+	+	-	-	+	-	ISO 11114-2
Methylenfluorid / Difluormethan (R32)	-	+	+	+	-	-	-	-	ISO 11114-2
Methylfluorid / Fluormethan (R41)	S+	+	+	+	-	+	+	+	ISO 11114-2
Methyljodid	?	+	?	?	-	?	?	?	BAM compatibility list
Methylmercaptan	+	+	?	+	?	+	+	+	ISO 11114-2
Monofluordichlormethan (R21)	+	+	+	+	P+	-	-	-	ISO 11114-2
Monosilan (max. 20% in H_2, N_2 oder VE)	+	+	+	?	?	+	+	+	ISO 11114-2
Neon	+	+	+	+	+	+	+	+	ISO 11114-2
Nickelcarbonyl	?	+	?	+	+	?	?	?	BAM compatibility list

Gas	PCTFE	PVDF	PI	PA	PP	POM	PEEK	PPS	
Ball Indentation Hardness	63 MPa	95 Mpa	170 MPa	100 MPa	62 MPa	145 MPa	190 MPa	190 MPa	Information Source
Octafluorcyclobutan (RC318)	+	+	+	+	-	+	+	+	ISO 11114-2
Octafluorpropan (R218)	S+	+	+	+	-	-	-	-	ISO 11114-2
Oktan	+	+	+	+	+	+	+	+	ISO 11114-2
Pentafluorchlorethan (R115)	+	+	+	+	-	-	-	-	ISO 11114-2
Pentafluorethan (R125)	+	+	+	+	+	+	+	+	ISO 11114-2
Pentan	+	+	+	+	+	+	+	+	ISO 11114-2
Perchlorylfluorid	+	?	?	-	-	-	-	-	ISO 11114-2
Phenylcarbylaminchlorid	?	+	?	?	?	?	?	?	BAM compatibility list
Phosphin	+	+	?	-	?	+	+	+	BAM compatibility list
Phosphorpentafluorid	+	+	?	?	?	+	+	+	ISO 11114-2
Prop-1-in	+	+	+	-	+	+	+	+	BAM compatibility list
Propan	+	+	+	+	+	+	+	+	ISO 11114-2
Propylen	+	+	+	+	+	+	+	+	BAM compatibility list
R134a (1,1,1,2 Tetrafluorethan)	+	+	?	+	-	?	?	+	BAM compatibility list
R404a (44% R125 +52% R143a +4% R134a)	+	+	?	?	?	?	?	?	BAM compatibility list
R500 (74% R12 + 26% R152a)	+	+	?	?	+	?	?	?	BAM compatibility list
R502	+	+	?	+	?	?	?	?	BAM compatibility list
Sauerstoff	+	+	+	+	+	+	+	+	ISO 11114-2
Schwefeldioxid	+	+	+	-	+	-	+	?	ISO 11114-2
Schwefelhexafluorid	+	+	+	+	+	+	+	+	ISO 11114-2
Schwefeltetrafluorid	+	+	+	+	+	+	+	+	ISO 11114-2
Schwefelwasserstoff	+	+	+	+	+	-	+	+	ISO 11114-2
Schwerer Wasserstoff (Deuterium)	+	+	+	+	P+	+	+	+	ISO 11114-2
Selenwasserstoff	+	+	+	+	+	+	+	+	ISO 11114-2
Silan	+	+	+	?	?	+	+	+	ISO 11114-2
Siliziumtetrafluorid (SiF4)	+	+	?	-	+	-	-	-	ISO 11114-2
Stibin	+	+	+	+	+	+	+	+	ISO 11114-2
Stickstoff	+	+	+	+	+	+	+	+	ISO 11114-2
Stickstoff mit max. 5% Ethylen	+	+	+	+	+	+	+	+	ISO 11114-2
Stickstoffdioxid	+	+	-	-	-	-	-	-	ISO 11114-2
Stickstoffmonoxid	+	+	-	-	-	-	-	-	ISO 11114-2

Gas	PCTFE	PVDF	PI	PA	PP	POM	PEEK	PPS	
Ball Indentation Hardness	63 MPa	95 Mpa	170 MPa	100 MPa	62 MPa	145 MPa	190 MPa	190 MPa	Information Source
Stickstofftetroxid	+	+	-	-	-	-	-	-	ISO 11114-2
Stickstofftrifluorid	+	+	-	-	-	-	-	-	ISO 11114-2
Sulfurylfluorid	+	-	?	-	-	-	-	-	ISO 11114-2
Tetrafluordichlorethan (R114)	+	+	+	+	-	-	-	+	ISO 11114-2
Tetrafluoretylen (R114)	+	+	?	+	-	+	+	+	ISO 11114-2
Tetrafluormethan (R14)	+	+	+	+	+	-	-	-	ISO 11114-2
Trichlorfluormethan (R11)	+	+	+	-	-	?	?	+	BAM compatibility list
Triethylboran	?	+	?	?	-	?	?	?	BAM compatibility list
Trifluorbrommethan (R13B1)	+	+	+	+	+	+	-	-	ISO 11114-2
Trifluorchlorethylen (R1113)	+	+	?	+	-	-	-	-	ISO 11114-2
Trifluorchlormethan (R13)	+	+	+	+	-	-	-	-	ISO 11114-2
Trifluormethan (R23)	+	+	?	+	+	+	+	+	ISO 11114-2
Trimethylamin	+	-	?	-	+	+	+	-	ISO 11114-2
Vinylchlorid (R140)	+	+	?	?	-	-	-	-	ISO 11114-2
Vinylfluorid (R141)	+	+	?	?	-	-	-	-	ISO 11114-2
Vinylmethylether	+	+	?	-	-	-	-	-	ISO 11114-2
Wasserstoff	+	+	+	+	+	+	+	+	ISO 11114-2
Wolframhexafluorid	+	+	+	?	+	+	+	+	ISO 11114-2
Xenon	+	+	+	+	+	+	+	+	ISO 11114-2