

Safetygram

Chlorine Trifluoride

Chlorine trifluoride (ClF₃) is a toxic, corrosive, strongly oxidizing liquefied compressed gas packaged in cylinders under its own vapor pressure of 1.55 bar(a) at 21°C (22 psia at 70°F). ClF₃ will ignite incompatible chemicals on contact without the presence of an ignition source. It rapidly hydrolyzes to hydrofluoric acid (HF) and other toxic and/or corrosive compounds.

ClF₃ is a useful chemical in operations requiring a high-energy fluorinating agent or an incendiary material, especially since it can be handled at low pressure at room temperature. However, those same factors that make it useful as a reactive material also contribute to ClF₃'s hazards.

Lessons from History

In 1930, ClF₃ was successfully produced as a potent oxidizing alternative to overcome the storage and handling challenges associated with cryogenic fluorine (F₂). Due to the liquid's hypergolic (self-igniting) nature with fuels and as a general incendiary material, military uses were common.

ClF₃ was first tested in the U.S. in 1948 in a rocket motor using hydrazine as the fuel. This testing yielded favorable results. However, all rocket materials of construction (including metals and seals) that could contact ClF₃ had to be scrupulously selected, cleaned, and passivated to prevent the components from burning during exposure. ClF₃ was recognized as an extremely hazardous propellant due to its reactivity, toxicity, and hazardous reaction products.

In the 1980s, the semiconductor industry began using ClF₃ in the cleaning process for certain chemical vapor deposition (CVD) tool chambers. In situ cleaning of the tool was desirable because the solid residues on the chamber interior were removed from the walls without dismantling the tool or risking personnel exposure to the hazardous residues or cleaning agents. It also yielded quicker turnaround time for the tool to resume wafer processing. The high reactivity of ClF₃ allowed the cleaning to be accomplished at relatively low temperatures, without requiring plasma or other energy to dissociate it for use.

Because the use of ClF₃ in semiconductor applications increased, Air Products tested the reactivity of ClF₃ with materials of construction, personal protective equipment and contaminants commonly found in systems and equipment. This safetygram provides recommendations for safe handling and use that reflect the results of the testing.

Table 1 shows the physical and chemical properties of ClF₃.

Safety Considerations

Health

ClF₃ is toxic and reacts with moisture to form a variety of other toxic and corrosive materials, including hydrofluoric acid (HF). Hydrolysis can occur with the moisture in the air or, in the case of human contact, with the moisture in the human body. Direct skin contact with ClF₃ vapor or liquid can result in a thermal burn in addition to the chemical burns produced with exposure.

Since HF is a major hydrolysis product, the health hazards associated with HF can be considered as primary health hazards for ClF₃. Depending on the degree of exposure, contact may result in immediate or delayed and progressive irritation. Medical treatment for HF exposures is very specialized. Not only can this strong acid cause local chemical burns, but the fluoride ion can also be quickly absorbed through the skin, attacking underlying tissues, and can be absorbed into the bloodstream. Systemic effects, including heart failure and death, are possible from serious overexposure. If inhaled in high concentrations, HF can cause obstruction of the airway and acute pulmonary edema.

Air Products' Safetygram, *Medical Treatment Protocol for Hydrofluoric Acid Burns*, provides detailed information on the health effects and



treatment for HF. All users of ClF₃ should use this medical treatment safetygram to educate their employees, emergency responders and local medical providers so they may know in advance what is required to address exposures to HF and other corrosive fluorides.

Table 2 gives toxicity and exposure limits for ClF₃.

Reactivity

ClF₃ ignites on contact with many materials. It is extremely reactive with most inorganic and organic materials. These reactions can be very violent or explosive. All materials that come into contact with ClF₃ must be evaluated for compatibility and cleaned and maintained for oxidizing gas service. Like other oxidizers, an increase of pressure or temperature increases the risk of ignition in the system.

Violent reactions including explosions may occur when ClF₃ comes in contact with water.

Fire Potential

While ClF₃ is nonflammable, it is a strong oxidizer that can essentially decrease the autoignition temperature of potential fuels including materials of construction, e.g., metals. Particles and other contaminants in ClF₃ systems can burn with sufficient heat to propagate the ignition to system components.

As previously mentioned, Air Products tested the reactivity of ClF₃ with a variety of materials that may come in contact with the product within systems or due to a release. These materials were exposed to both vapor and liquid phases of ClF₃. The testing showed the presence of contamination compromised many materials that did not react with ClF₃ when clean. Figure 1 shows the results of vapor ClF₃ exposure to clean and used polyethylene. The testing results stress the need for maintaining cleanliness in ClF₃ systems.

Cylinders

ClF₃ is shipped as a liquefied compressed gas in cylinders. Carbon steel is the normal material of construction for ClF₃ cylinders filled by Air Products. Air Products specially selects cylinders for their internal finish, internally processes them to remove any residual scale and cleans them for oxidizing gas service.

ClF₃ cylinders are not fitted with pressure relief devices.

Valves

Cylinders in ClF₃ service are equipped with different valves depending on the application. Commercial grade cylinders are valved with an aluminum silicon bronze wrench-operated valve

Table 1

Physical and Chemical Properties

Molecular Weight	92.45 g/mol
Boiling Point (1 atm)	11.7°C (53°F)
Melting Point	-76.3°C (-105°F)
Gas Density (21°C)	3.9 kg/m ³ (0.24 lb/ft ³)
Specific Volume (21°C)	0.26 m ³ /kg (4.1 ft ³ /lb)
Specific Gravity (air = 1)	3.2
Vapor Pressure (21°C)	1.55 bar(a) (22 psia)
Critical Temperature	174°C (345°F)
Critical Pressure	57.8 bar(a) (838 psia)
Appearance	Gas/colorless
Odor	Bleach-like. Acidic.

Odor varies with hydrolysis products; low concentrations are described as bleach-like while higher concentrations are described as acidic or suffocating.

Table 2

Toxicity and Exposure Limits for Chlorine Trifluoride

LC ₍₅₀₎	299 ppm for 1 hour (rat)
OSHA PEL	0.1 ppm Ceiling
EU ELV	2.5 mg/m ³
ACGIH TLV	0.1 ppm Ceiling
NIOSH IDLH	20 ppm

Table 3

Valve Connections

USA	CGA 670	728 Ultra High Integrity (DISS)
UK	BS 6	
Germany	DIN 8	
Japan	JIS A (22 R)	

while cylinders used in high purity applications are equipped with a pneumatic stainless steel diaphragm valve. Cutaway drawings and valve details for the wrench-operated valve are available in the Safetygram, *Cylinder Valves*. Figure 2 shows a cutaway drawing of the pneumatic diaphragm valves.

Valve Outlet Connections

Valve outlet connections for ClF₃ vary by country. Table 3 lists some of the standard connections used in various countries. For more information on cylinder valve connections, refer to the Safetygram, *Cylinder Valve Outlet Connections*.

Cylinder Storage and Handling

Cylinders of ClF₃ and other compressed gases must be stored properly, handled correctly, and used with the correct equipment to reduce the risk of incidents and injuries. The Safetygram, *Storage, Handling and Use of Compressed Gas Cylinders*, describes good practices. The Compressed Gas Association's (CGA's) publication P-1, *Safe Handling of Compressed Gases in Cylinders*, also provides safe handling guidance.

Figure 1

Vapor ClF_3 Exposure to Polyethylene Tubing, Clean and Used



reaction of the adjoining materials and generate enough heat to even react with adjacent metals. Elastomers should not be used where they will be exposed to liquid ClF_3 since even fluorinated elastomers may deteriorate rapidly and possibly ignite, especially at elevated temperatures.

Most non-fluorinated elastomers show little or no resistance to ClF_3 and should be avoided. Others like neoprene, rubber, polyethylene and PVC have shown resistance during short exposures but are very susceptible to any contamination—the reaction of ClF_3 with the contaminant can rapidly propagate to the elastomer.

Sealants and Lubricants

PTFE tape is the most common sealant used on threaded connections in ClF_3 service. Lubricants of any kind should be avoided if possible. Where needed, a perfluorinated type should be used. Hydrocarbon-based lubricants must never be used in ClF_3 service, and even perfluorinated lubricants must never be exposed to liquid ClF_3 .

System Preparation (Cleaning and Passivation)

Due to the potential for ignition, systems used for ClF_3 must be carefully cleaned to remove readily oxidized impurities and scrupulously maintained to prevent contamination. Passivation is the final preparation process that must be performed on ClF_3 systems. It is accomplished by introducing ClF_3 to the system at low pressure then gradually increasing the pressure. Passivation allows a controlled reaction with any remaining contaminants left behind by imperfect cleaning and allows the formation of a thin metal fluoride surface that is resistant to further reaction with ClF_3 .

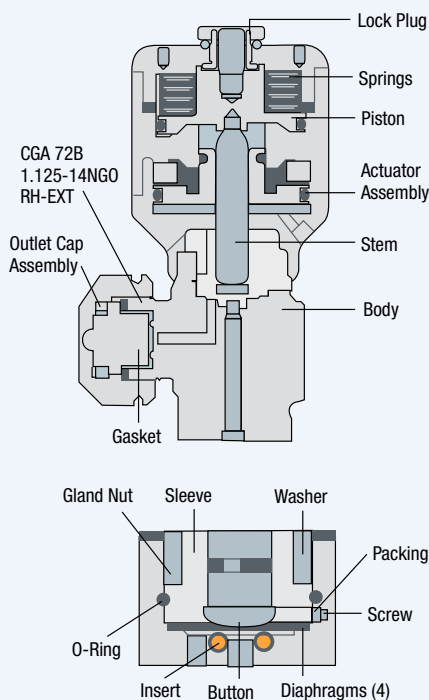
The recommended cleaning and passivation procedure for ClF_3 systems is summarized below. A means of introducing inert gas must be provided so the system can be purged without disconnecting any lines.

1. The entire system must be adequately cleaned for oxygen service per a recognized standard (CGA G-4.1, *Cleaning Equipment for Oxygen Service*, or equivalent).
2. After cleaning, the system must be purged with pure nitrogen (never air from an oil-lubricated compressor) to remove cleaning agents and moisture. Cleaning agents can become fuels in the presence of ClF_3 .

Heating of system components during purging should be considered to ensure removal of low-volatility cleaning agents.

Figure 2

Pneumatic Diaphragm Valve



any significant distance and to prevent condensation in the piping.

Use ClF_3 only in well-ventilated areas designated for its use. Where the material is stored and used, the toxicity, reactivity and corrosivity of ClF_3 may require ambient air monitoring for leakage.

System design should minimize the use of mechanical connections to limit potential leakage and the use of elastomers to limit potential reactivity and contamination. Similarly, system valves incorporating metal seats should be used if possible to reduce the chance of ignition of elastomeric seats. Where elastomers are required, the component design should incorporate as little elastomer as possible and should shield the elastomer as much as possible with metal.

National or local regulations may require additional safeguards for storage or use.

Materials of Construction

Metals

Carbon steel, copper and stainless steel are acceptable at ambient temperatures. If the potential for elevated temperatures exist, Monel and nickel are the metals of choice. These metals are compatible with ClF_3 , provided the metal is cleaned for oxidizer service and passivated prior to use (see System Preparation section).

Brass can be dezincified by ClF_3 and should not be used.

Elastomers

As previously mentioned, the use of elastomers should be limited and metal components are preferred. If an all metal component cannot be used, only fluorinated elastomers such as polytetrafluoroethylene (PTFE) should be used in ClF_3 systems. Cleanliness of these materials is critical as reactions with any contamination may initiate

System Design and Preparation

ClF_3 is a challenging material to properly manage from a code compliance standpoint. Some locations require special planning when storage of ClF_3 exceeds specific threshold quantities. Before purchasing ClF_3 , contact the local authorities to determine the requirements for the storage and use of this material. Local authorities also may require the source containers be positioned remotely from the consumer's main facility or occupants. However, the low vapor pressure of ClF_3 at ambient temperature provides challenges to distribute the vapor

3. The system should be leak tested to meet quality and safety requirements, typically at pressures equal to or above the anticipated operating pressure.
4. The system should be evacuated.
5. Passivation is accomplished by a careful introduction of ClF_3 in small incremental steps [~ 0.1 - 0.3 bar (~ 2 - 5 psi) per step] with hold times from 5 to 30 minutes. After each incremental pressure increase, the ClF_3 supply must be isolated immediately by closing the cylinder valve. This is critical to limit the amount of ClF_3 available if a reaction takes place anywhere in the system. Monitor the system for pressure change and detectable heating of any system components. Pressure changes or temperature increases may indicate undesirable reactions with contaminants or system components.

If system heating or pressure changes are noted, vent and purge the system before restarting the ClF_3 introduction process.
6. If no pressure change or heating is noted, continue the stepwise passivation until the maximum operating pressure is achieved.
7. Allow ClF_3 to remain in the system for at least several hours. After the system has been passivated, vent and purge the ClF_3 . If system use must be delayed, maintain it under a slight positive nitrogen pressure.

Operations and Maintenance

ClF_3 is used as a vapor to limit its reactivity with system components and other materials. Unless special precautions are taken, ClF_3 should only be removed from cylinders as a vapor.

At typical use temperatures, ClF_3 vapor pressure is low, which can result in unacceptably low system pressure and flow rates, especially from cylinders with little remaining inventory.

Care must be taken to prevent condensation by keeping the ClF_3 system pressures well below the ClF_3 vapor pressure (see Figure 3) at the temperature of the coolest component in the process, commonly with an absolute pressure regulator. Preventing condensation also allows optimal flow control.

If the supply cylinder is heated to permit higher flows, it is even more critical to protect against condensation in cooler downstream components by employing uniform heating throughout the system.

As with any hazardous gas cylinder, operators should confirm the cylinder valve is firmly closed before loosening the valve outlet seal to connect a cylinder to the system. The outlet seal should be loosened slowly to limit the release rate of any ClF_3 that may have leaked into the valve outlet. The same procedure should be used to disconnect the cylinder from the use system, and the pigtail must be vented and purged thoroughly before loosening the connection.

When connecting new ClF_3 cylinders, care is needed to prevent contamination of the valve outlet connection, especially if a gasketed connection is used. New gaskets must be thoroughly degreased and dried prior to installation unless specially cleaned and packaged gaskets are used directly from the manufacturer. New cleanroom gloves or equally clean alternatives should be used to install replacement gaskets. Similar precautions must be taken when changing other system components to avoid introduction of easily ignited contaminants.

When ClF_3 supply cylinders are initially opened, the operator should always be prepared to quickly reclose the valve should any evidence of reaction, overheating, or leaks develop. If any uncertainty exists about the cleanliness of system components, the cylinder valve should only be opened to introduce a minimal amount of ClF_3 vapor and then immediately closed. This will limit the amount of ClF_3 available to sustain ignition if a problem develops.

Prior to any maintenance, including supply cylinder changes, special care must be taken to ensure that no ClF_3 remains in the equipment. Thorough purging with inert gas should always be done after the ClF_3 cylinder valve is firmly closed. If there is any suspicion of condensed ClF_3 in the system, the process system should be heated and ideally evacuated to confirm that no ClF_3 remains before the system is opened.

ClF_3 systems must be kept dry to minimize corrosion and contamination from acids that will form on contact of ClF_3 with moisture. When not in use, equipment should be depressurized and purged with dry inert gas. For extended out-of-service periods, equipment should be kept sealed under positive pressure with dry inert gas.

Gas Cabinet Supply Safety Considerations

One method to effectively manage ClF_3 hazards is through the use of properly designed gas cabinets that are specially engineered to house ClF_3 cylinders and distribution control piping and components. When ClF_3 is used in gas cabinets, consideration should be given to the following system design elements:

- Automatic sprinkler protection is not recommended for ClF_3 gas cabinets due to the potential for violent reaction with leaking ClF_3 (supported in 1997 by a major industrial insurance company's specific recommendations regarding ClF_3 gas cabinets for the semiconductor industry).
- Pneumatically operated cylinder valves should be considered to allow automatic and immediate supply shutdown should there be a downstream incident.
- A gas detector should be located in the cabinet interlocked to provide an automatic shutdown and alarm indication if a release is detected.
- Heat or smoke detectors should be located in the gas cabinet to monitor and cause an automatic shutdown and alarm on an internal or external fire condition.
- The delivery tubing should be coaxial (double contained) with a monitoring alarm for loss of primary containment.

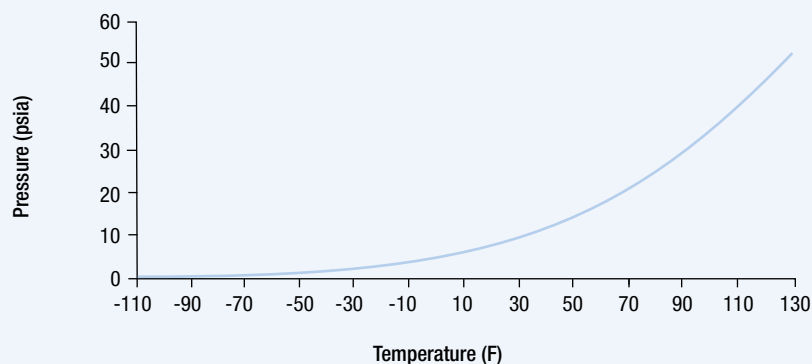
Disposal

Return unused product remaining in the supply cylinder to the supplier for proper disposal. Disposal of liquid ClF_3 is extremely hazardous and is not recommended.

In process applications, gaseous ClF_3 can be disposed of in dry or wet (liquid) scrubbers. Dry scrubbers work well under normal operating conditions for small quantities of ClF_3 but are not recommended for large or emergency releases unless specifically designed to withstand the heat generated in the event of a large release. Wet scrubbers typically use caustic solutions such as potassium or sodium hydroxide. Wet scrubbers handle the heat of reaction better than dry scrubbers and can readily neutralize ClF_3 . It may be beneficial to add an inert gas flow as a diluent when ClF_3 vapor is being introduced to a scrubber to control the heat of reaction.

Figure 3

Vapor Pressure of Chlorine Trifluoride



Shipment of Chlorine Trifluoride

Compliance with applicable Dangerous Goods regulations is required for all shipments by motor freight, rail and water. Air transport of ClF₃ is forbidden. International shipments by water must comply with International Maritime Organization (IMO) regulations.

Dangerous Goods regulations specify the identification and labeling requirements shown in Table 4.

To maximize safety by reducing the likelihood of a liquid leak, all ClF₃ cylinders should be secured in an upright position during transport, storage and use. For small cylinders, special shipping pallets should be used to keep cylinders upright. Never load additional freight on top of the cylinders.

Figure 4

Vapor ClF₃ Exposure to Nitrile Glove, Clean and Oil-Contaminated



Personal Protective Equipment

When handling cylinders, safety glasses with side shields, safety shoes, and sturdy work gloves should be worn.

For other operations, polycarbonate face shield over safety glasses, a PVC splash suit, smooth leather inner gloves and thick (17 mil or thicker) nitrile outer gloves are recommended.

Because personal protective equipment (PPE) may react with ClF₃ in the presence of dirt or water, all chemical protection equipment must be clean and dry.

Natural fiber clothing should be worn under external PPE because of the possibility of an exothermic reaction with ClF₃. This minimizes the risk of any melted material binding to the skin.

Hearing protection should be considered due to the possibility of loud reactions. Figure 4 demonstrates the importance of clean PPE. Upon exposure to ClF₃ vapor, the new glove exhibits no reaction. The same glove, when contaminated with a small amount of oil, instantly bursts into flame.

Table 4

Transportation Information

Shipping Name:	Chlorine Trifluoride
Hazard Class:	2.3
Shipping Labels:	Toxic Gas, Oxidizer, Corrosive
Identification Number:	UN 1749

When shipping via common carrier, all cylinders must be secured in an upright position and be located at the rear of the trailer. Never load additional freight on top of the cylinders. For small cylinders, special shipping pallets are mandatory.

First Aid

As described under the "Health" section of this safetygram, ClF₃ is toxic and reacts with moisture to form a variety of toxic and corrosive materials, including hydrofluoric acid (HF). Medical treatment for hydrofluoric acid exposures is very specialized. Air Products' Safetygram, *Medical Treatment Protocol for Hydrofluoric Acid Burns*, provides detailed information on the health effects and treatment for exposure to HF and other corrosive fluorides.

Emergency Response

For emergency response, self-contained breathing apparatus (SCBA), totally encapsulating chemical protective suit (TECP), smooth leather inner gloves and heavy (17 mil or thicker) nitrile outer gloves should be considered.

Only new gloves and new totally encapsulating suits should be used in emergencies to minimize the chance of reaction of ClF₃ with contaminants on PPE.

For leaks at the cylinder or through the valve, isolate the cylinder and contact the Air Products Emergency Response System.

For small vapor leaks, shut off gas flow by closing the cylinder valve using the appropriate PPE. Purge residual vapor in systems to a scrubber, using an inert gas. Repair the leak. Decontaminate all exterior surfaces that may be contaminated with ClF₃ and hydrolysis products. A dilute sodium bicarbonate (baking soda) solution is effective for

decontamination. Be sure to thoroughly inspect the area surrounding the leak for any signs of corrosion, which may require replacement of that part of the system. After repairs, the system must be passivated again.

In the case of a large vapor release or small liquid spill, immediately evacuate the area. If possible, without risk and while wearing appropriate PPE, close the cylinder valve to limit the supply of ClF₃. Allow released ClF₃ to vaporize and disperse.

Warning: Any attempt to neutralize or absorb a liquid spill may result in an explosion.

Product Security

When not in use, store gas cylinders in a safe, secure well-ventilated area.

Additional special security requirements apply to ClF₃. The US Department of Homeland Security (DHS) includes ClF₃ on their list of high-risk chemicals of interest. DHS requires facilities manufactur-

ing, storing or using high risk chemicals exceeding certain on-site threshold quantities to complete security vulnerability assessments, develop site security plans, and implement protective measures necessary to meet DHS-defined risk-based performance standards (6 CFR §27.230). Facilities outside of the U.S. where ClF₃ is stored or used should also employ these security practices to prevent misuse. Air Products' Safetygram, *Product Security*, provides additional information.

Additional Information

If further information about ClF₃ is desired, please contact the Air Products Technical Information Center. Material safety data sheets are available at www.airproducts.com/MSDS.

Emergency Response System

For assistance involving Air Products and Chemicals, Inc. products call:

- Tel 1-800-523-9374 (Continental U.S. and Canada)
- Tel +1 610 481 7711 (other locations)

24 hours a day, 7 days a week

Product Safety Information

- For MSDS, Safetygrams, and Product Safety Information www.airproducts.com/productsafety

For More Information

Corporate Headquarters

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Technical Information Center

Monday–Friday, 8:00 a.m.–5:00 p.m. ET

- Tel 1 -800-752-1597 (U.S.)
- Tel +1 610 481 8565 (other locations)
- Fax: 1-610-481-8690
- E-mail: gastech@airproducts.com

Information Sources

- American Chemistry Council (ACC) www.americanchemistry.com
- Asia Industrial Gases Association (AIGA) www.asiaiga.org
- Compressed Gas Association (CGA) www.cagnet.com
- European Industrial Gases Association (EIGA) www.eiga.org

tell me more
www.airproducts.com/productsafety