Chlorine Trifluoride

Aug 2021

Background

ClF_3 was first developed in the 1930s and is one of the halogen fluoride compounds

ClF_3 is considered one of the most reactive chemicals known

Fig 1: ClF_3 Gas and New Leather Gloves

Chlorine Trifluoride (ClF_3) is a low pressure liquefied gas that is toxic, corrosive and a strong oxidizer. The vapor is colorless while the liquid is a pale yellow/brown.

In semiconductor facilities the primary use is as a reactor cleaner. It is efficient and does not require an external power source. An emerging application is for Disilane reactor vacuum pump foreline cleaning.

Physical Properties

CAS# 7790-91-2

UN# 1749

Molecular Weight 92.45

Liquefied Gas with Vapor Pressure of 6.8 psig (0.148 mPa) @ 70°F (21°C)

Gas Density of 0.2443 lb/ft^3 (3.19 gm/l) @ 70°F (21°C)

Liquid Density 136.7 lb/ft^3 (1.785 kg/l) @ 77°F (25°C

Toxic Gas with TLV of 0.1 ppm, LC_{50} 299 ppm, IDLH 20 ppm

Shipping Labels Toxic Gas (Zone B), Oxidizer and Corrosive

Boiling Point, 1 atm. 53.2°F (11.75°C)

Freezing Point, 1 atm. -105.4°F (-76.3°C)

Critical Temperature 367°F (186°C)

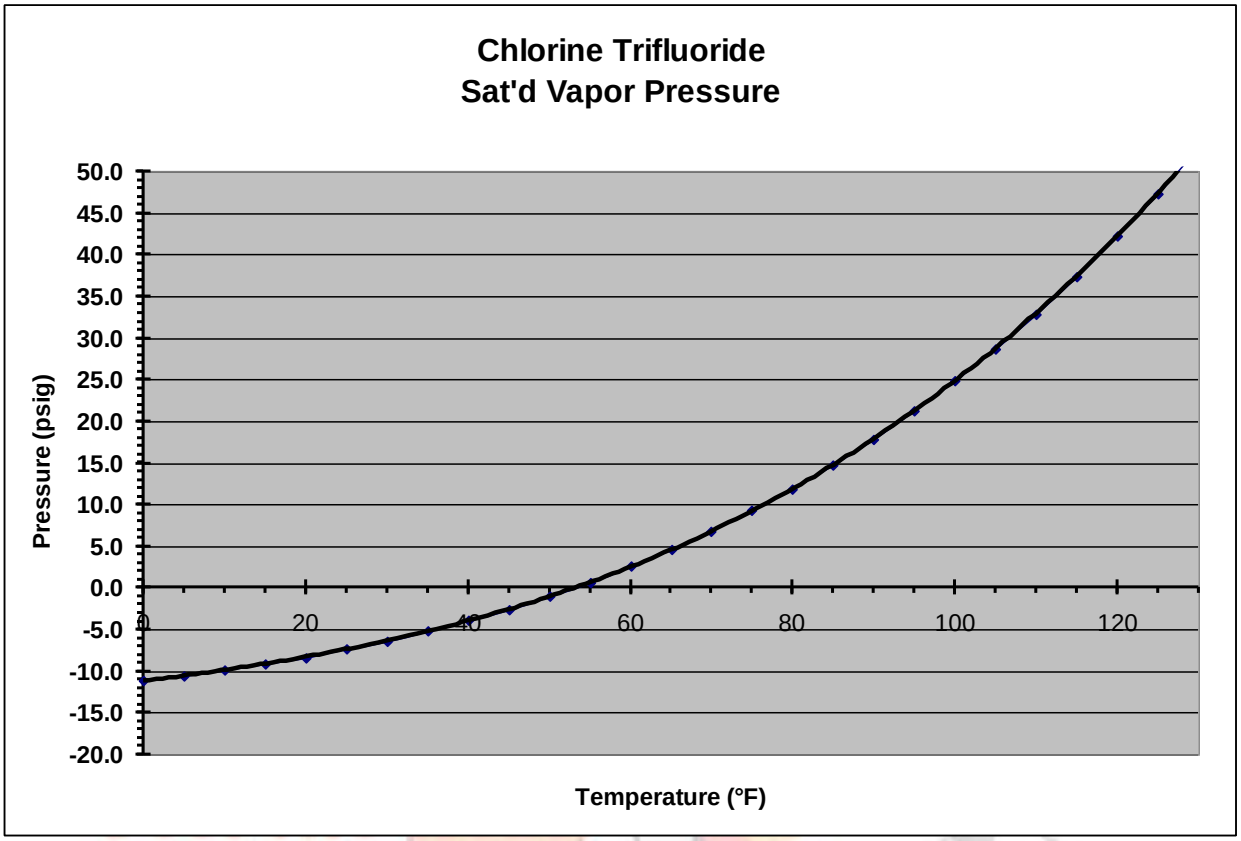


Fig. 2: ClF_3 Vapor Pressure Curve

Health

Chlorine trifluoride is a potent, rapidly-acting mucous membrane irritant. Contact with the skin and eyes produces burns and inhalation causes pulmonary irritation and edema.

When released into air the hydrolysis byproducts are:

- Hydrogen Fluoride
- Hydrogen Chloride
- Chlorine Monofluoride
- Oxygen Difluoride
- Chlorine Oxyfluorides
- Chlorine Dioxide

Some of these compounds may be shock sensitive and more toxic than ClF_3

All exposures must be treated as HF

Package

Typically 16 liter high pressure (minimum working pressure of 2015 psig) seamless chrome-moly steel cylinder, cleaned and passivated. Ceoduex tied diaphragm valve, stainless steel, no pressure relief device. Optional pneumatic cylinder valve from Neriki. Outlet Connection is high integrity DISS 728 with replaceable nickel gasket. 20 kg (44 lbs) fill.

Shipped in vertical position to prevent liquid sloshing against valve seat

Reactivity

Hypergolic Oxidizer Hypergolic means self igniting or igniting on contact with a fuel
The liquid can react violently with water or ice
In some cases, the hydrolysis heat from a water reaction can be enough to ignite the material.
Explosive reactions with most organic materials
Highly reactive with most inorganic materials
Compatible with completely fluorinated materials under most conditions (vapor phase)

Reactivity Testing (2002), Key Findings[1]

Various materials were exposed to vapor and liquid ClF_3 to determine behaviour du to exposure.
In low humidity, the ClF_3 vapors were colorless and there was no fuming
High drop height creates greater energy and a more vigorous reaction
Surface Cleanliness is critical. Even on surfaces that did not react with the liquid immediately, contact with other contaminants and their reaction generated enough heat to ignite the material
Liquid ClF_3 even at temperatures of 85 F does not vaporize easily
Oil and Water are most common contaminants both react vigorously
Most dangerous condition was where the ClF3 was able to saturate a flammable material forming an explosive material. With the Tyvek, this reaction was triggered by the hydrolysis heat of a drop or water
The PPE had to be tested with large pieces, small pieces ignited due to exposure of the underside to the ClF_3
None of the metals reacted, except for fine pieces of Carbon and Stainless Steel

Stainless	Copper
Carbon Steel	Epoxy Painted Carbon Steel
Brass	Aluminum

Material	Vapor	Liquid
Nitrile Glove	No reaction	Ignited a fraction of a second after liquid hit it and burned vigorously after the first drop charred it
Nitrile Glove with Oil Film	Ignition as soon as the vapor hit it	Not Tested
Smooth Leather Glove	Burning at point of impingement and shriveling.	Instant flash and shriveling
Smooth Leather Glove, Used	Not Tested	The flame was more intense and the glove shriveled
Rough Leather Gloves, New	Orange flame which went out when flow stopped. Burned a hole	With new rough leather, the liquid flashed on the surface and the second drop charred it
Rough Leather Gloves, Oil Film	Intense flame at oil spots and charring of area	Not Tested
Acid Suit	First test had Intense flame and burn through. Second test had no reaction	There was a explosion upon contact that left charred surface where the liquid contacted, material still pliable

The reaction with water is energetic if vapor touches the surface of a container of water or a liquid droplet is introduced. Spraying water at a vapor stream of ClF3 quickly vaporized the droplets but was not violent, a liquid droplet onto a thin puddle of water instantly vaporized the water but was not violent. Vapor stream hitting a piece of ice steadily melted a hole I the ice.
Reaction with oils is violent. Vapor reaction with raw chicken skin is intense. Liquid is explosive.

Fig. 3: ClF_3 Vapor and Raw Chicken

Systems

Special design and cleaning to prepare system for ClF_3 service

1. Be designed with compatible materials
2. Be cleaned for oxygen service
3. Be F_2 passivated

Incidents

In the 1950's General Chemical Company, Shreveport, LA cooled a carbon steel ton cylinder with dry ice to make it easier to fill the first shipment. As they were lifting it to placed it onto a dolly, it split open. 2,000 lbs (900 kg) of ClF_3 burned through 12" (30 cm) of the concrete floor and 36" (90 cm) of gravel. Severe corrosion of area. Civil Defense evacuated local residents due to the fumes. The operator that was handling the ton cylinder ran to get away. Had a heart attack 500' away and died.[2]

Does liquid ClF_3 react violently with concrete**?** The testing in 2004 with cinder block and concrete with liquid dripping onto it was unreactive. The reaction may have been due to contaminants on the surface or due to the drop height which would increase the reactivity.

Liquefaction

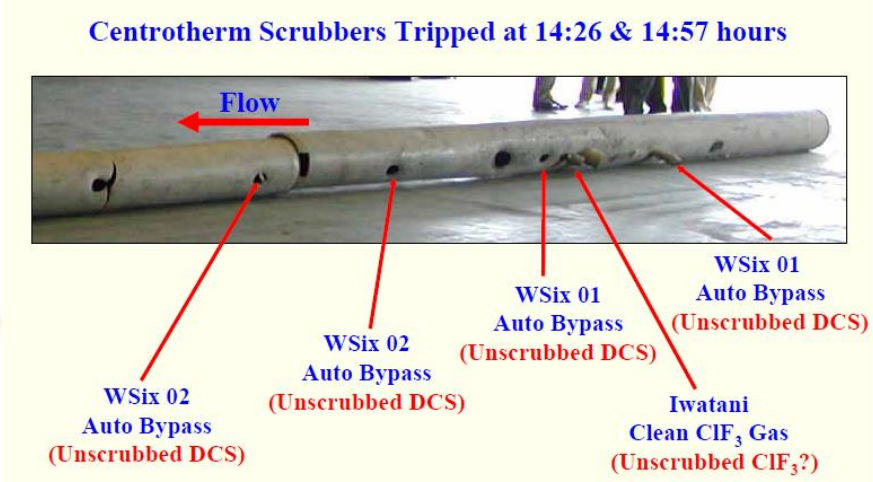
Most incidents were due to ClF_3 liquefying in the system, once this happens it is a real challenge to vaporize. Since 2003 there have been at least 12 incidents worldwide where ClF_3 has liquefied in the system. Many users heat the cylinder to boost the delivery pressure. This creates a need for the temperature to be hotter downstream of the cylinder. Any slight temperature drop, even 1o will cause it to liquefy. Incidents caused by heater taps=es failing, deadlegs not heated properly, operating

procedure to pressure pule purge N_2., Connection leaks, Checkvalve failure and backflow into a DCS system.
In one case the heat trace shorted on the line, The short and the liquid ClF_3 burned right through the tubing and released into Fab.

User, Taiwan, 1997
Valves in a gas panel were mounted in reverse and the ClF_3 ignited the Kel F valve seats. Kel F and PTFE can with stand ClF_3 statically not in direct flowing conditions.

User, Taiwan, 1997
Venting of 0.3% DCS and 0.3% ClF_3 reacted in vent duct, Fire burned down the facility

$$SiH_2Cl_2 + ClF_3 \rightarrow 2HCl + ¼\ SiCl_4 + ¾\ SiF_4 \quad -1081\ kJ/mole$$



User, Japan, 2003
ClF_3 Duct Explosion. Reactor used for WF_6 and SiH_2Cl_2. Switchover valve after pump exhaust for scrubbers leaked and there was an explosion even at very low concentrations, <0.5%.

Gas User, US, 2004
Operator removing vaportight cap from D1 cylinder, wrench hit the valve handle and loosened it Leather gloves sparked, Able to close valve

Gas Supplier, US, 2005
Operator ignored the cylinder labels and CGA outlet connection and assumed he was drilling into a chlorine cylinder. As soon as the drill bit penetrated the cylinder it exploded into flames severely injuring the operator.

Ship Port, Korea, 2007
Residue ClF_3 cylinders being returned to supplier in Japan. A port in Ulsan there was a report of white cloud from 2 cargo containers (ClF_3 and DCS)

Found 4 ClF_3 cylinder valve handwheel and vaportight outlet cap loose.

Fig

Gas Cabinet Leaks, Users,

Most leaks react and damage all no metal components that they touch. No catastrophic failures

Emergency Response Notes

If the ClF_3 release is large enough it will etch glass such as the gas cabinet window, making it difficult to see the gas panel.

While ClF_3 is violently water reactive, the vapors are colorless and will not provide visual indication of a leak. Such as fuming

ClF_3 is a hypergolic compound which readily ignites organic compounds. A large release in the gas cabinet can ignite the tags, pneumatic tubing, etc.

Liquid ClF_3 is considerably more reactive than vapor.

Never move cylinder in a horizontal position. This would allow liquid ClF_3 to slosh in the cylinder against the valve seat, potentially causing ignition.

All systems used for ClF_3 must be Oxygen cleaned and F_2 passivated

Small ClF_3 leaks may form a liquid corrosive acid which may collect at the leak point and drip down.

Venting the vapor into scrubber will quickly drop the vapor pressure to 0 psig, slowing the leak.

Cooling the cylinder with ice will slow or stop the leak. It will cause a partial vacuum, sucking air into the cylinder.

A ClF_3 cylinder leaking as a gas while contained in an exhausted gas cabinet is under control and does not present an immediate danger to the surroundings. The team can take the time to determine a safe mitigation plan. The leak will not get worse within a short period of time (week). Once the combustible materials such as tags, polypropylene tubing have reacted, any fire will stop. The metal gas panel and cabinet walls will not react under these conditions.

During the winter you can receive a cold cylinder at 32°F (0°C) which will be at a partial vacuum (0.7 atm)

ClF_3 leaks will cause adjacent surfaces to be contaminated with Hydrochloric and Hydrofluoric acids

Materials that initially resist ClF_3 reaction can begin to react due to the heat from a water/ClF_3 reaction.

Use a Non Passivated ERCV, Taiwan, 2004

In Jan 2004 a Fab ER Team starting up a new 300 mm Fab used a new 5502 ERCV to contain a ClF_3 cylinder that they didn't realize had the valve wide open on the cylinder. Use of a ERCV for strong oxidizers like ClF_3 is prohibited by the procedures since the ERCV cannot be cleaned and passivated. As the flange was being closed the ClF_3 immediately started to react with the O Rings and Seal. The ER Team panicked and pushed it out into the parking lot where the leaking ClF_3 liquid proceeded to burn a hole through the carbon steel. The reaction was so hot that it charred the epoxy paint.

ERCV With ClF_3 Liquid Reacting With Carbon Steel

References:

1. Croll, D.W., Martrich, R. l., Ngai, E.Y., VanOmmeren, J., "Chlorine Trifluoride Exposure and Reactivity Study", Center for Chemical Process Safety Symposium, International Conference and Workshop on Managing Chemical Reactivity Hazards in High Energy Release Events 2003
2. Clark, J. D., "Ignition! An Informed History of Liquid Rocket Propellants", Rutgers University Press, Jan 1971, pg 67
3. Ohtani, H, Sang, G. L. & Aramaki, M. "Experimental Study on flammability limit of Chlorine Trifluoride/Dichlorosilane/Nitrogen Mixture", J. Loss Prev. Process Ind. 1992, Vol 5, No. 3, p192-195