



Nitrogen trifluoride

July 2022

Nitrogen trifluoride (NF_3) is a colorless, odorless, nonflammable, oxidizing compressed gas. Nitrogen trifluoride is the most common reactor cleaning gases used in the TFT-LCD industry because of its advantages, such as high etching rates, high selectivity, carbon-free etching, and minimal residual contamination. It is first decomposed in a remote plasma chamber into a reactive fluorine before fed to the reaction chamber where it is used to react solid deposits on the reactor walls to form gaseous byproducts such as silicon tetrafluoride.

Nitrogen trifluoride is not toxic, it has an LC_{50} of 6,700 ppm (1 hr. rat). It is not hazardous by skin contact and is a relatively minor irritant to the eyes and mucous membranes. Exposure of rats to a 100 ppm concentration for 7 hrs per day, 5 days per week over a 19 week period caused minor pathological changes to the liver and kidney. No other effects were noted. The ACGIH established the current TLV-TWA of 10 ppm based on 1/10 of this value. Some countries classify nitrogen trifluoride as a toxic gas because it has a TLV-TWA <200 ppm.

Under ambient temperatures and pressures, nitrogen trifluoride is inert. However, it can become extremely reactive under certain conditions. It is a strong oxidizer that is violently explosive at elevated pressures with flammable gases such as hydrogen or silane. Purification of nitrogen trifluoride using a solid absorbent media such as molecular sieve is to be avoided. Fires and explosions have occurred.

Nitrogen trifluoride is reported to be a significant greenhouse warming gas with a Greenhouse Warming Potential (GWP) >10,000 as compared to carbon dioxide. Properly design remote plasma cleaning system will react 100% of the nitrogen trifluoride, so it has a GWP comparable to fluorine under these conditions.

There have been reported incidents of nitrogen trifluoride reacting with flammable oils used in vacuum pumps. Systems for nitrogen trifluoride must be designed similar to the requirements for fluorine. Adiabatic compression and heating can initiate the decomposition reaction of nitrogen trifluoride into reactive fluorine. Incidents have occurred with improperly designed or cleaned systems during routine activities such as pressurizing the system. Internationally the maximum fill limits for nitrogen trifluoride cylinders is 0.5 kg/liter. At 21°C the cylinder pressure will be 10.78 MPa. Quickly opening the cylinder valve into a system with a small dead volume will cause adiabatic compression and heating to 307°C. In the presence of a reactive nonmetal component or a contaminant, this can initiate the decomposition reaction. Given sufficient energy and pressure, the reaction can cause the metal system to also become involved. The fill pressure is limited to 1450 psig to reduce the adiabatic compression heat from triggering the decomposition.

Adiabatic compression temperature of NF_3 Fill @ 0.462 kg/l and 0.500 kg/l



0.462 kg/l

Cylinder Temp °F	Pressure psig	Compression Temp °F
70	1450	574
90	1609	629
110	1764	683

0.500 kg/l

Cylinder Temp °F	Pressure psig	Compression Temp °F
70	1549	584
90	1716	640
110	1883	694

Figure 1 shows a burnt valve in a nitrogen trifluoride line caused by adiabatic compression.

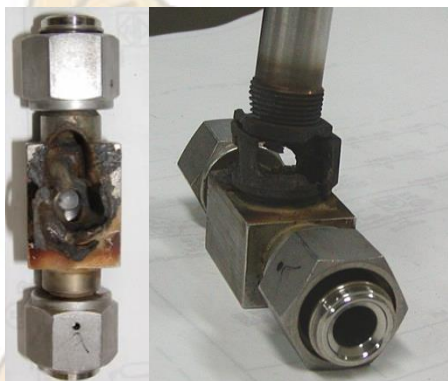


Fig. 1: A burnt valve in a nitrogen trifluoride line caused by adiabatic compression

CGA G-14, Code of Practice for Nitrogen Trifluoride (EIGA Doc. 92/03)

As NF_3 is an oxidizer, consideration must be given to the following issues when designing systems to handle NF_3 :

- materials of construction and compatibility of lubricants and sealing compounds
- minimisation of the effects of adiabatic compression
- gas velocities
- initial cleanliness and passivation
- valve types
- filter materials
- operating procedures
- maintenance procedures
- separation of NF_3 from flammable gases (see also 6.9)
- heat dissipation

– compression

Considerable testing has been done. Wendell Hull and Associates, “Industry Research Steering Group Testing On Materials Compatibility with Nitrogen Trifluoride”. WHA 01HT001, March 18, 2003

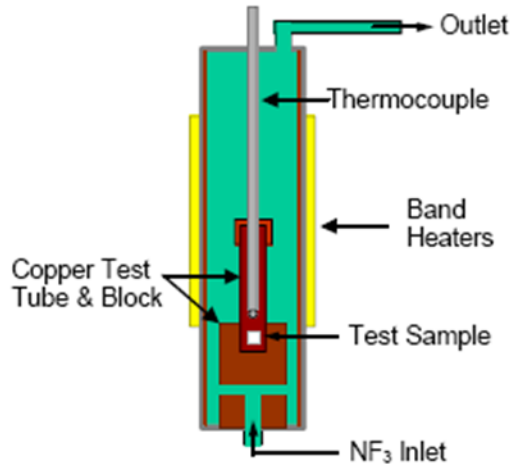


Figure 3: Drawing of the AIT reaction chamber

Table 5: Material Ranking Based on NF ₃ AIT Data			
Ranking	Material	NF ₃ AIT (°C)	O ₂ AIT (°C)
1	Virgin Teflon	> 475	479
1	Glass-Filled Teflon	> 475	479
1	Bronze-Filled Teflon	> 475	
1	Perfluoroalkyl (PFA)	> 475	
1	Krytox 240 AC	> 475	>427
1	Halocarbon	> 475	>427
1	Fomblin	> 475	>427
2	Kalrez	~448	355
3	Neoflon (crystalline)	437	426
4	Neoflon (amorphous)	436	426
5	Tefzel (ETFE)	413	243
6	Poly-vinylidene-fluoride (PVDF)	392	294
7	Halar (ECTFE)	333	171
8	Filled Viton A	272	266 - 322
9	Unfilled Viton A	240	266 - 322



Table 6: Material Ranking Based on Temperature Rise After Ignition

Ranking	Material	Temperature Rise (°C)	Standard Deviation (°C)
1	Tefzel (ETFE)	239	28
2	Neoflon (amorphous)	242	15
3	Neoflon (crystalline)	276	45
4	Halar (ECTFE)	319	124
5	Poly-vinylidene-fluoride (PVDF)	367	160
6	Unfilled Viton A	388	83
7	Filled Viton A	441	80

Incidents

The most serious have occurred in manufacturing. The following are known incidents and their root cause. There are likely to be others

1. Gas Manufacturer, US, 1984, Purifier Explodes
Mole Sieve trap as it was being moved exploded, 316ss Hoke Cylinder blew into 2 large pieces plus other smaller ones, it had been immersed in a Methylene Chloride and Dry Ice bath. Purged at end of process with Nitrogen while cold, Both ends open, Placed on cylinder cart and bumped over door jam and detonated
2. Gas Manufacturer, US, July 30, 2000, NF_3 Reboiler Explosion
This was because a LIN delivery was made at the plant and the reboiler temperature went low due to subcooled LIN. The colder temperature condensed F_2 into the sump, which was the origin of the reaction, Loss of LIN caused F_2 to liquefy in column. This reacted with the stainless steel packing. This then started the decomposition of the NF_3 . The sudden gas pressure could not vent fast enough and reboiler blew up at 8,000 psig
3. Gas Manufacturer, Korea, Feb 23, 2003
Flammable liquid coolant reacted explosively with the fluorine generated,
4. Gas Manufacturer. Japan, Nov. 4 2004, Tube trailer tire fire, Japan
It is probable that the differential pressure between the tubes caused high density, high volume NF_3 to flow through the tube valve. The flow friction caused the temperature of the tube valve to rise.

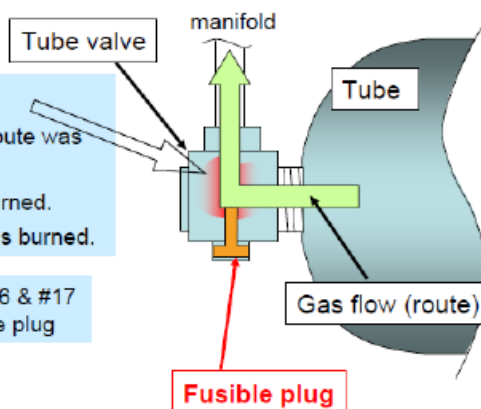
All tube valves were opened when there is pressure difference between tubes

High density NF₃ flew through #16 and #17 valves with high flow

Flow friction caused higher temp.

- Stainless steel on the surface of flow route was reacted with NF₃
- PCTFE around diaphragm seat was burned.
- PCTFE packing around fusible plug was burned.

Burst #16 & #17 fusible plug



[Refer to MCI report on web site]

Heat from the fire causes an adjacent tube trailer tire to ignite. The tire fire causes tube on the trailer to explode from overpressure.

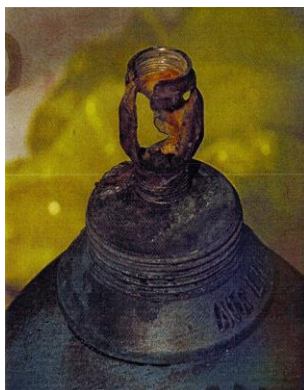
Feel the Heat

- Gas Supplier, US, Oct 18, 2007, Purifier Explodes
As a new 13X mole sieve trap was being commissioned the line into the trap ruptured and burned when NF₃ was introduced. Burned through in 2 places on outlet (1 cm hole). Had just been baked and evacuated.
- Gas Manufacturer, Korea, April 5, 2012
Plant exploded and one person were dead and four people were injured.
- Aug 3, 2016 Korea
The recently built factory experienced an explosion in an NF₃ transfer line, as a result of a leak – actual cause of the leak is yet unknown. As a result of the explosion, seven people were injured, one of them seriously.

Use

Users have experienced smaller incidents many caused by improperly designed or cleaned systems.

Flow friction



Flow friction or adiabatic compression will trigger the decomposition and the resulting fluorine will react with the metal burning a hole

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Flow friction when a Cylinder That was not filled in the bundle was opened

Feel the Heat

Lessons Learned

1. Absorbents can catalyze the decomposition reaction of NF_3 into reactive fluorine
2. Flow friction is the more common cause of the reaction
3. Adiabatic compression heat is another

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