



Unstable/Reactive Gases

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This summary is not an all-inclusive list of unstable/reactive gases that could cause a catastrophic cylinder failure. Gases become dangerous when they undergo an exothermic self-sustaining decomposition reaction that transitions to a detonation in the cylinder. The second problem is when the reaction byproducts exceed the working pressure of the cylinder.

The UN GHS (Global Harmonization System) that was adopted in Dec 2006 has an unstable classification for liquids and solids. There is not one for gases. The proposed test by BAM is intended to cover this deficiency. This was originally proposed by BAM in 2006.

When this was first proposed there was significant concern by the CGA member companies that it would classify Nitrous Oxide as unstable. A CGA EWP was formed to try to defeat the proposal in Dec 2006. CGA spoke and DOT spoke against this in the July and Dec 2006 UNTDG meetings. This was not successful, the other UN delegates voted to allow the effort to continue. CGA then proposed alternate test methods such as Accelerating Rate Calorimeter (ARC) which is based on thermal activation rather than hot wire/ignitor at meetings in Berlin and Geneva. This is the test method used to determine reactivity under NFPA 704. This was unsuccessful when the task force (Praxair, Air Products and Airgas) did not perform the agreed upon ARC testing. The data was to be used for comparison to the BAM method to determine which was the better test method.

On July 2008 the task was then able to limit the unstable classification to cover only flammable gases, excluding Nitrous Oxide as well as other “unstable” gases like Nitrogen Trifluoride or Nitric Oxide. This would now cover gases such as Acetylene, Diborane, Germane, Ethylene Oxide, etc.

Determining what gases exhibit this behavior is not an easy task. Prediction based on high positive heats of formation is not accurate. High decomposition energy is also not a predictor.

For some gases that are known to decompose exothermically, the filling of these cylinders take this into account to ensure the cylinder will not be ruptured under normal environmental (temperature, pressure) conditions. Shelf life is not an issue.

The key gases are:

- 1. Acetylene**



At pressures above 15 psig the decomposition can accelerate to detonation. Cylinder solid acts as flash arrestor to quench a reaction. Damage to the solid can cause a reaction. Liquid acetylene is shock sensitive.

Testing of mixtures up to 10% and pressure of 3,500 psig did not decompose

2. Germane

Fill density has been reduced so that the adiabatic decomposition will not pressurize the cylinder beyond its service pressure. The fill density was reduced by GeH₄ suppliers since the incident in 1984. Two recent incidents confirmed the safety of the practice.

Mixing with H₂, He, N₂ or Ar stopped the decomposition

3. Nitric Oxide

Decomposition reaction requires a high energy and pressure input. The fill density was reduced to 500 psig to insure the cylinder can withstand the sudden decomposition and not rupture the cylinder. This has been the practice by gas suppliers since the 1968 fatal accident.

4. Nitrous Oxide

If there is any liquid (Nitrous Oxide) in the cylinder, the decomposition reaction will be quenched. If the system only contained vapor a self-sustaining decomposition can occur. Also requires large diameter and long tube length for the decomposition reaction to accelerate to a detonation. Violent tanker explosions involving 8' diameter 40' long tankers in Holland (2001) and Florida (2016). The Space Ship Two (Rutan) rocket explosion in 2007 was believed to have been due to N₂O.

5. Tetrafluorohydrazine

Fill pressure is limited to 100 psig to minimize adiabatic compression heat

6. Tetrafluoroethylene

Can be stored at dry ice temperatures for long periods of time. Will polymerize slowly at room temperature except when gas is extremely pure or is inhibited.

Uninhibited can violently polymerize even under Subatmospheric pressures. The presence of small quantities of oxygen can cause the spontaneous polymerization.

Nitrogen trifluoride can undergo a decomposition reaction that is self-sustaining if there is a fire heating the cylinder. The fill pressure of 1450 psig has been selected to reduce the potential for sudden adiabatic compression heat from triggering the decomposition reaction when the cylinder valve is opened.

To control this, some gases have stabilizers that can become ineffective over time. These typically have a shelf life.

1. Bromotrifluoroethylene - 1% tributylamine stabilizer (also pyrophoric)



2. 1,2 Butadiene
3. 1,3 Butadiene- Stabilized with trace amounts of hydroquinone, catechol, tertiary alcohol or tertiary butyl-catechol
4. Cyanogen -
5. Cyanogen Chloride -
6. Chlorotrifluoroethylene – 1% tributylamine stabilizer
7. 1, 1 Difluoroethylene – no inhibitor
8. Ethylene oxide – typically mixed with a halocarbon gas or carbon dioxide
9. Hydrogen cyanide – 0.06% Sulfuric or phosphoric only good for 30 days
10. Tetrafluoroethylene – 1% terpene stabilizer (D-Limonene) Without it can explode at 2.7 atm (39 psia). DuPont patent as a 30% mixture in CO₂ cannot deflagrate
11. Trifluoroethylene – terpene stabilizer (D-Limonene)
12. Tetrafluorohydrazine – reduced fill pressure, 100 psig
13. Vinylacetylene - stabilized in a 50 wt% mixture with xylene
14. Vinyl bromide – 0.1% phenol or 0.2% B Terpene (Limonene) stabilizer
15. Vinyl chloride – 0.1% phenol or 0.2% B Terpene (Limonene) stabilizer
16. Vinyl Fluoride - 0.1% phenol or 0.2% B Terpene (Limonene) stabilizer
17. Methyl Vinyl Ether -

NF₃ in stainless steel can form N₂F₄ in long term storage

Richter, M., Shantz, J., Davis, J., “Disposing of explosive laboratory chemicals”, Chemical Health and Safety, ACS, March/April 1995

Diborane is one of the few gases that will slowly decompose at room temperature of 70°F to the high Boranes and H₂. The decomposition rate increases with temperature. The DOT regulations require the cylinder fill limits to consider this decomposition and resulting cylinder pressure. Pure diborane can only be shipped in cylinders chilled to dry ice temperatures in order to have a high fill density, these are shipped under special permits and must arrive within a certain time limit. Pure diborane is normally not sold to users, only mixtures.

Under high temperatures/pressures the following gases can also polymerize

Ethylene – ethylene monomer

Propylene – propylene monomer

Active sites such as rust (Fe₂O₃) on the cylinder walls can catalyze a slow decomposition reaction with some gases. These are not self-sustaining but can continue until the cylinder is compromised such as, Hydrogen fluoride and hydrogen bromide can react over time with rust to form H₂ as a byproduct. This reaction is slow but steady. In normal use this is not a problem as the excess pressure is vented when the valve is opened and the gas is used. After extended



storage of 20+ years these cylinders have suddenly ruptured due to the excessive H₂ pressure (<3,000 psig).

Unstable metal hydride

1. Stannane (most energetic)
2. Stibine
3. Hydrogen Telluride
4. Germane
5. Digermane

Medard, L. A., "Accidental Explosions, Vol 2: Types of Explosives", John Wiley and Sons, 1989, Pg 760-3



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