Safety Overview of Semiconductor Process Gases, Part 2

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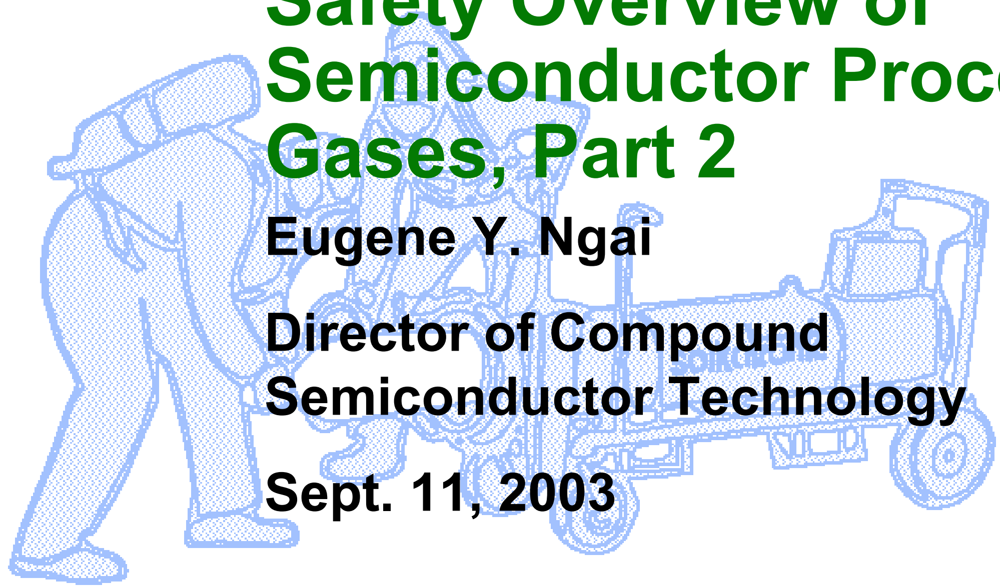
Sept. 11, 2003

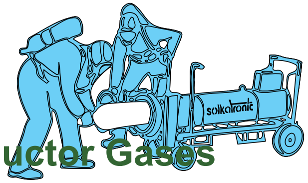


Highly Toxic Gases
DOT Poison Gas Hazard Zone A

- Arsine
- Cyanogen
- Cyanogen Chloride
- Fluorine
- Hydrogen Cyanide (Not a Compressed Gas but under 173.195 is treated as such)
- Hydrogen Selenide
- Nitric Oxide
- Nitrogen Dioxide
- Phosgene
- Phosphine

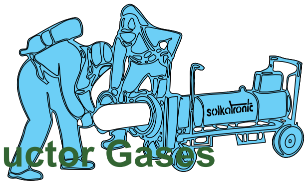
Other Hazards include: Flammability, Corrosivity

DOT special requirements under 49CFR173.40 for packaging



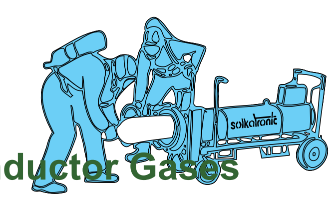
Arsine
Chemical & Physical Properties

- **Arsine is a liquefied gas which is highly toxic and flammable**
- **Arsenic Hydride, AsH_3**
- **CAS# 7784-42-1**
- **UN# 2188**
- **Molecular Weight 77.95**
- **Liquefied Gas with Vapor Pressure of 205 psig @ 70^{0}F (21^{0}C)**
- **Gas Density of 0.2025 lb/ft^{3} (3.24 gm/l) @ 68^{0}F (20^{0}C)**
- **Liquid Density of 83.55 lb/ft^{3} (1.335 kg/l) @ 70^{0}F (21^{0}C)**
- **Specific Gravity of Gas @ 70^{0}F (air = 1) 2.69**
- **Highly Toxic Gas with PEL of 50 ppb, LC_{50} of 20 ppm, IDLH of 3 ppm**
- **Boiling Point, 1 atm. -80.5^{0} F (-62.5^{0}C)**
- **Freezing Point, 1 atm. -178.4^{0} F (-116.9^{0}C)**
- **Critical Temperature 211.8^{0}F (99.9^{0}C)**

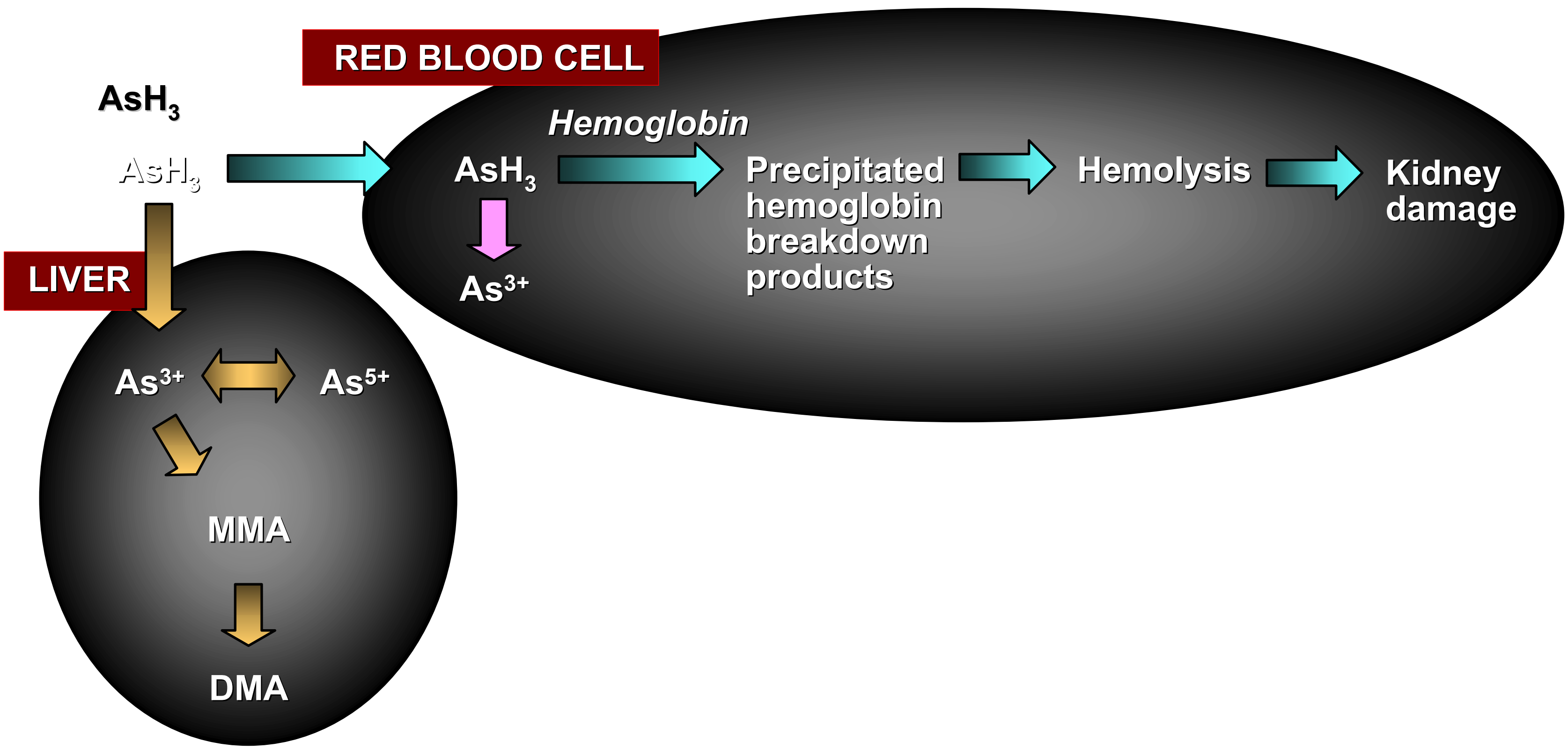


Arsine Poisoning

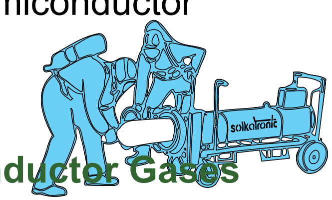
- Major effect is on Red Blood Cells causing hemolysis, hemoglobinura or free plasma hemoglobin
- Effects can occur from 20 min. to 36 hours after exposure as a function of concentration and time
- Most significant noticeable affect is red urine due to breakdown of Red Blood Cells which can lead to renal failure. Kidney function can return after a few months with proper treatment
- Is not absorbed through the skin
- Only effective treatment is whole blood transfusion
- US Health Dept Medical Treatment Protocol



Theoretical Mechanism for Arsine Metabolism and Toxicity in Humans



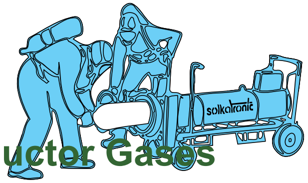
"Evaluation of the ACGIH TLV for Arsine and Current Research Needs", Report for Semiconductor Industry Association by Exponent, Oakland, CA., July 2000



Arsine Acute Exposures

- Exposure of 250 ppm (797 mg/m^3) can be lethal after a few minutes, 25- 50 ppm for 30 minutes
- Dangerous threshold of 6.25 ppm (20 mg/m^3) for 30 minutes and 15.5 ppm (50 mg/m^3) for 30 minutes
- No effect reported for 3.1 ppm (10 mg/m^3) for a few hours

Effects of Exposure to Toxic Gases, Matheson Gas Products, 1988



Arsine Exposure Estimate

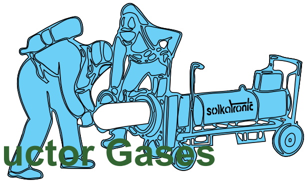
- An individual exposed to a PEL of 50 ppb for 8 hours will receive a dose of 1.28 mg. Estimated by 0.05 ppm x 3.2 mg/m^3 x 8 m^3 (normal breathing)
- Typically an individual breaths as follows:

Resting	7.4 liters/min
Light Work	29 liters/min
Heavy Work	60 liters/min

- Assuming a safe dose of 1 mg and individual would have to be exposed as follows:

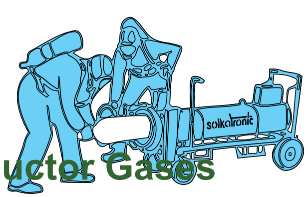
30 sec	21.6 ppm
1 min	10.8 ppm
5 min	2.4 ppm

"Report for Trinity Consultants", Dr. E.T.Wei, Prof of Toxicology, University of California, July 21, 1984



Arsine Fatalities From Arsine Use

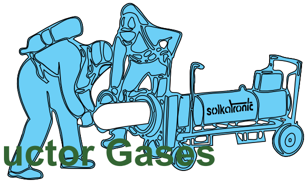
- MIT Lincoln Labs Technician on June 14, 1982, suicide
- M/A-Com Technician on June 11, 1984, deliberate exposure



Pyrophoric Gases

- Diborane
- Disilane
- Metal Alkyls e.g. Dimethyl Zinc
- Methyl Silane
- Phosphine
- Silane

Other Hazards include Toxicity

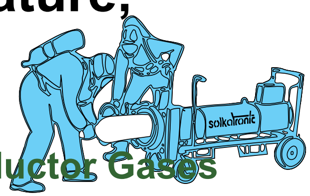


Pyrophoric Gas Characteristics

- Pyrophoric gases are flammable gases which have autoignition temperatures that are below 130^0F (54.4^0C).
- Pyrophoric gases require oxidizers to burn.
- Of all the Pyrophoric Gases, Silane is the most unpredictable. When released into air, Silane will react in one of the following manner:

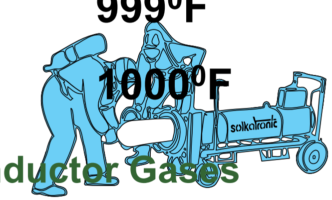
  Delayed Ignition (Explosion)
  No Ignition
  Immediate Ignition

Of these the latter is only safe condition. Temperature, humidity, flow rate, will influence the ignition.



Autoignition Temperature Of Common Gases

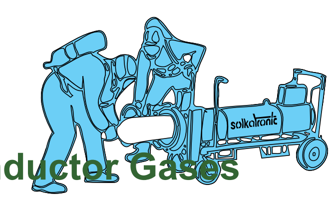
- **Silane** $<-148^{0}$F
- **Disilane** $<-100^{0}$F
- **Nickel Carbonyl** 68^{0}F
- **Phosphine** $<32^{0}$F
- **Diborane** $44\ ^{0}$F
- **Dichlorosilane** $111- 133^{0}$F
- **Diethyl Ether** 320^{0}F
- **Trichlorosilane** 360^{0}F
- **Hydrogen Sulfide** 500^{0}F
- **Butane** 550^{0}F
- **Acetylene** 581^{0}F
- **Diethyl Amine** 594^{0}F
- **Butylene** 725^{0}F
- **Hydrogen** 752^{0}F
- **1,3 Butadiene** 788^{0}F
- **Ethylene Oxide** 804^{0}F
- **Propane** 842^{0}F
- **Ethylene** 842^{0}F
- **Propylene** 851^{0}F
- **Vinyl Chloride** 882^{0}F
- **Ethane** 882^{0}F
- **Ammonia** 928^{0}F
- **Methane** 999^{0}F
- **Hydrogen Cyanide** 1000^{0}F



AIR PRODUCTS

Silane
Chemical & Physical Properties

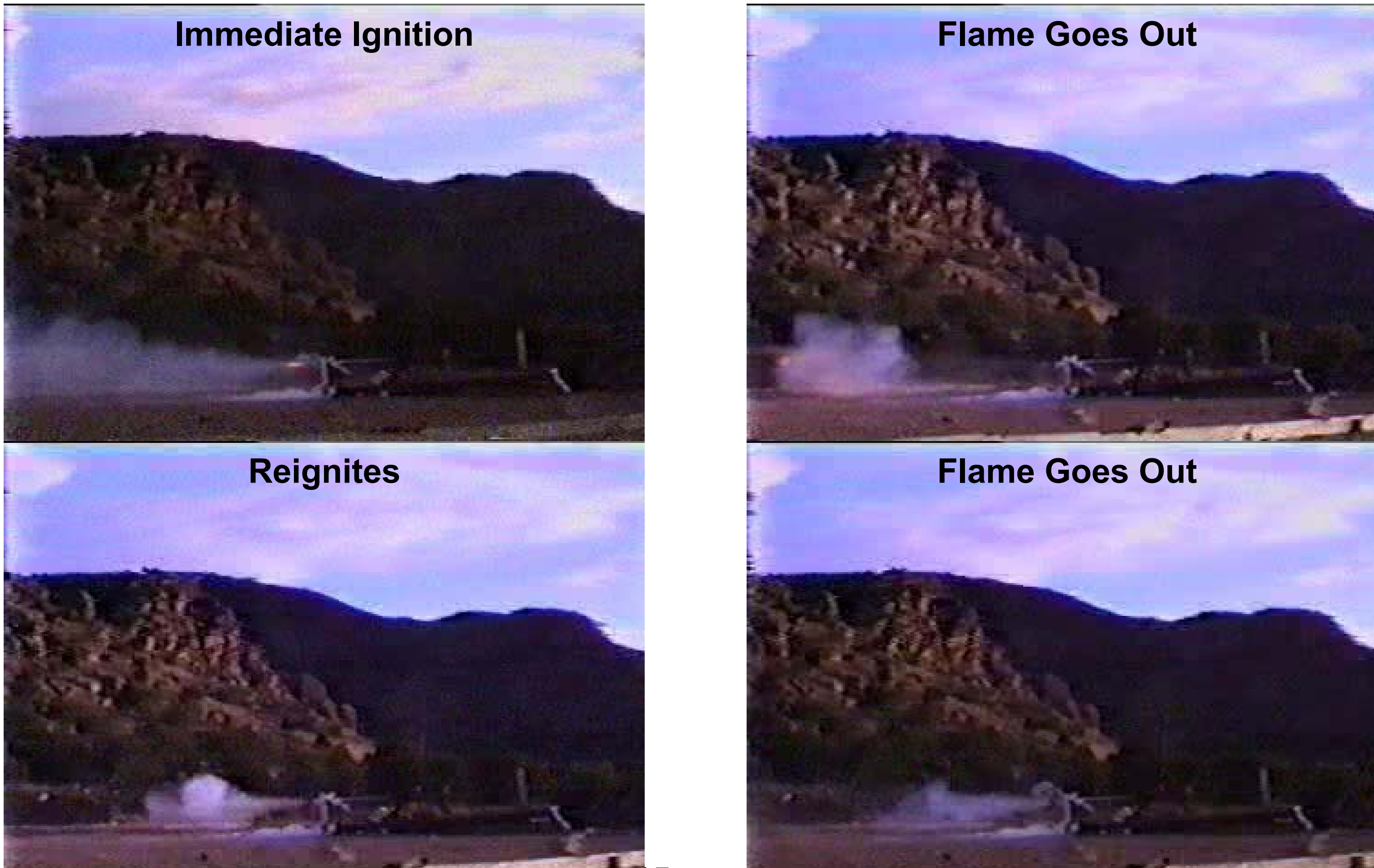
- Silane is a compressed gas which is pyrophoric (in Japan, Taiwan and Korea it is also classified as a Toxic Gas)
- Silicon Tetrahydride, SiH_4
- CAS# 7803-62-5
- UN# 2203
- Molecular Weight 32.11
- Compressed Gas which is filled by weight due to high compressibility
- Gas Density of 0.083 lb/ft^3, 1.33 gm/l @ 70^{0}F (21^{0}C)
- Liquid Density of lb/ft^3, (gm/l) NA at @ 70^{0}F (21^{0}C)
- PEL of 5 ppm, LC_{50} & IDLH are not reported due to pyrophoricity
- Boiling Point, 1 atm. -169.6^0 F (-112^{0}C)
- Freezing Point, 1 atm. -299^0 F (-184^{0}C)
- Critical Temperature 25.8^0 F (-3.4^{0}C)



For the user, the most common problem occurs when the gastight outlet cap is removed

Silane Tube Trailer Release Studies Conducted by CGA at Socorro, NM, 1996

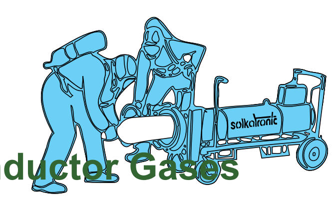
Silane Cylinder Release from 1/8” Tube Conducted by CGA at Socorro, NM, 1996



Silane Incidents

A number of major incidents have occurred with Silane use. The following caused fatalities

- Release and detonation of gas cabinet
  - IBM, Zurich
  - Hitachi
- Contamination of cylinder with Nitrous Oxide
  - Osaka University
  - Gollub Labs
- Solid Byproducts of Reaction exposed to air



OSAKA UNIVERSITY INCIDENT
Oct. 2, 1991

BASED ON JUNE, 1992 MITI REPORT

Eugene Y. Ngai

INCIDENT

- Location

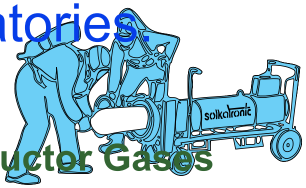
  Plasma CVD Laboratory on the 5th floor of Department of Basic Technology at Osaka University, Osaka, Japan

- Event

  On the afternoon of Oct. 2, 1991 at 4 PM as a graduate student opened the cylinder valve of a 10 liter silane cylinder it exploded killing him and another graduate student. Another 5 students were seriously injured.

- Aftermath

  The explosion also sheared a natural gas line and shattered solvent cabinets which ignited, destroying two Laboratories.

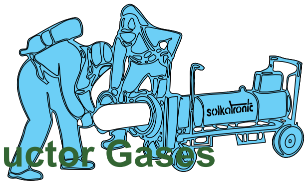


BACKGROUND

- 10 liter cylinder of pure Silane from which only 13 grams was used. Was filled almost 4 years prior.
- 4 cylinders for reactor were stored in same Gas Cabinet and used the same purge Nitrogen

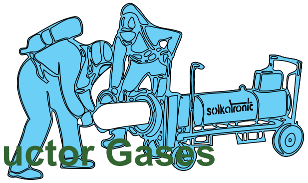
  10% Silane/Hydrogen
  100% Nitrous Oxide
  100% Sulfur Hexafluoride
  100% Silane

- System installed and used since 1987

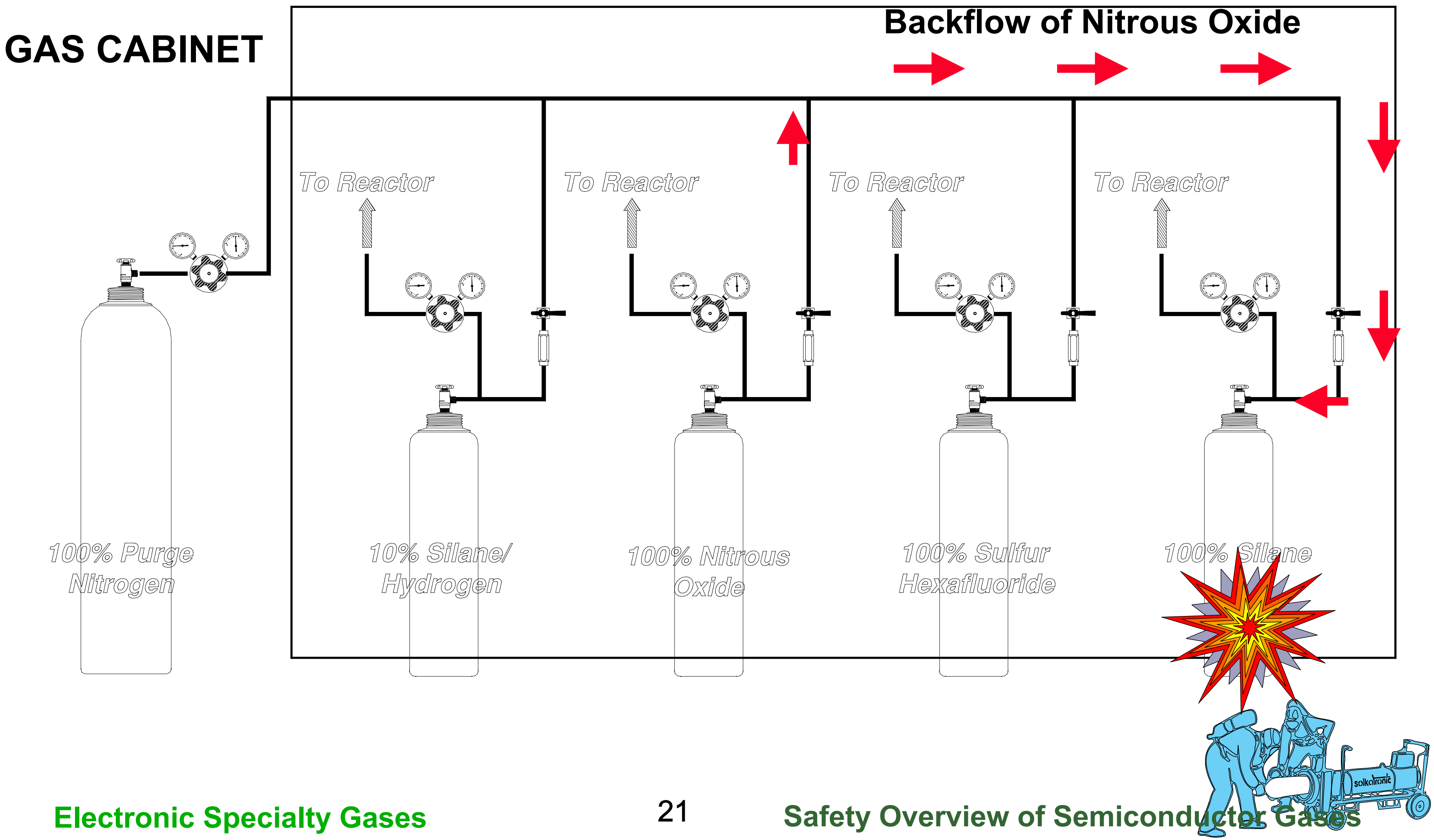


CAUSES

- Common Nitrogen purge system allowed the interchange of incompatible gases
- Degradation of check valve elastomer seat in Nitrous Oxide service
- Opening of purge valves for Silane and Nitrous Oxide cylinders at the same time
- Vapor pressure of Nitrous Oxide is 745 psig @ 70^0F which is higher than the Silane cylinder pressure of 600 psig



SYSTEM FLOW SCHEMATIC



HITACHI INCIDENT
SILANE EXPLOSION, Dec. 13, 1990

A VALID **REASON FOR THE RECENT INCIDENT** AT THE MUSASHI PLANT OF HITACHI, IS A MAJOR LEAKAGE OF MONOSILANE

On 13. December of last year, an explosion occured at the Musashi Plant of Hitachi (Kodaira City, Tokyo, Mr. Sadao Yoneyama, Factory Superintendant). According to the investigation held afterwards, the most plausible explanation at this time would seem to be that monosilane, which had reached a very high degree of density, exploded at the operations section which is located alongside of the cylinder cabinet.

This theory is based on the on-the-spot inspection carried out shortly after the explosion by a high pressure gas expert. A new fact is that, "Compared to the damage done to the cylinder cabinet and the gas control board themselves, the damage done to the operations section was far greater." "Powders of such items as silica found to have accumulated nearby seem to back up the theory of the explosion being caused by a leak of monosilane." These statements seem to make the cause of the explosion rather clear.

Based on all of the above, a line of reasoning is gathering strength which seems to be able to refute the theories in the papers blaming the incident on "an explosion of a vacuum pump" or "Monosilane and nitrogen trifluoride mixed in the piping and reacted, causing the explosion"

On an official level, the Kodaira Police Station confiscated the cylinder cabinet and the vacuum pump, and conducted a thorough investigation as to the cause of the explosion. Up to now, however, they have not released the results of their investigation.

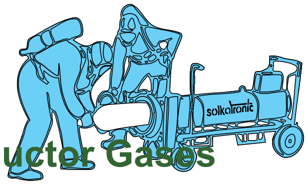
Also, the KHK, or High Pressure Gas Safety Institute in Japan, in January of this year, based on the intentions of MITI, formed a Comittee for Adopting Safety Measures for Specialty Gases, appointing Prof. Keiho Namba, an honorary professor of Tokyo University as chairman. This comittee, along with the piping diagram submitted by Hitachi, is conducting an investigation at the sight of the explosion and will submit a preliminary report to MITI by the end **of March**.

Silane Explosion At Hitachi Fab Sets Off Regulatory Furor In Japan

An explosion Dec. 13 in Hitachi's Musashi chip fab, across the bay from Tokyo, has rocked the Japanese electronic chemicals industry and could create severe regulatory aftershocks.

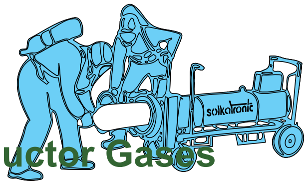
One worker died, one was heavily injured and two were lightly injured when monosilane gas leaked from a gas cabinet and exploded on contact with air, according to reports in Japanese newspapers the following day. The explosion reportedly occurred just after the ringing of an alarm bell signaled the leak.

The precise cause of the explosion is still under investigation, according to Hitachi officials, but it has alarmed local governments across Japan. "It's still too early to say whether this event will be enough to trigger the institution of new regulatory measures, but this remains a strong possibility," said Robert Stevenson, an electronic chemicals industry analyst at Kline & Co.'s Tokyo office.



Silane Incidents

- Technician forgot washer in connection- Dec. 21, 1997, Shizuoka Prefecture
- During routine maintenance to a gas panel it was removed. Technician did not cap the vent line. Technician was purging Silane gas cabinet and a few minutes later the Silane exploded. Technician was hit on back of head with cabinet door



Hazards of Silane Combustion and Reaction Byproducts

- **Burning in open Air is ineffective in oxidizing Silane to Silicon Dioxide. A dull Orange flame and Brown solids will indicate formation of**

  $$SiO_XH_Y$$

  Which is flammable

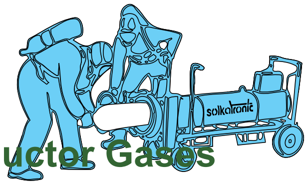
- **Exhaust from Silicon Nitride CVD can create unstable solids which are air reactive**

  $$SiO_XN_YH_Z$$

  Which has been involved in a number of incidents

  1997 - Worker Fatality - Japan

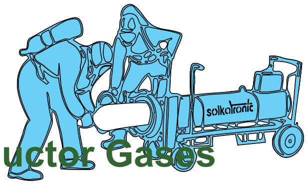
  1998 - UMC Fire $ 1 Billion Loss



Flammable Gases

- Acetylene
- Carbon Monoxide
- Ethylene
- Hydrogen
- Hydrogen Sulfide
- Propane
- Methane
- MAPP Gas (Methyl Acetylene and Propadiene)

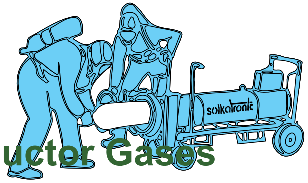
COMMON HAZARDS: Flammability, Toxicity



For additional information see References in Chapter 10

Flammable Gases

- **Wide Flammability Range**
  - Acetylene
  - Diborane
  - Dichlorosilane
  - Hydrogen
  - Phosphine
  - Silane
- **Low Ignition Energy**
  - Acetylene
  - Hydrogen



Flammable Gases Definition

- **DOT**

  Is Flammable in concentrations of <13% in air or has a flammability range wider than 12% regardless of lower flammability concentration.

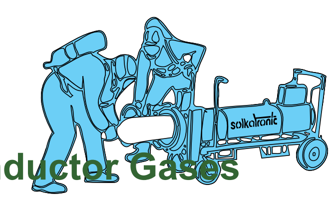
  Will not identify some gases which are flammable under certain conditions e.g..

  Ammonia (16-25%)

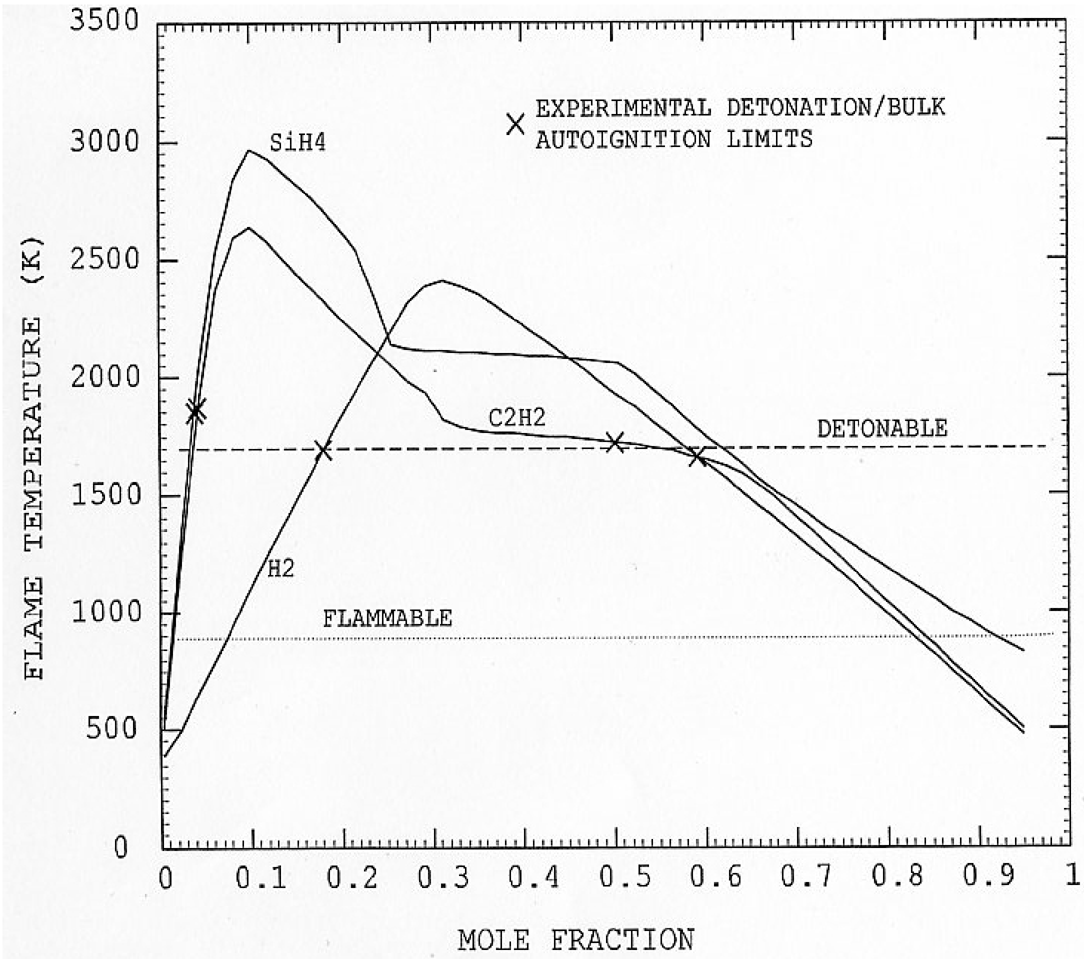
  HCFC's e.g. 134b

- **Internationally (ISO 10156)**

  Same, however a second definition which covers gases that are flammable in any concentration in air for storage



Flammable versus Explosive



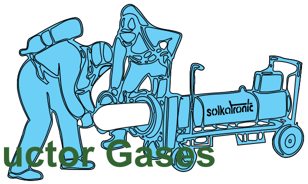
AIR PRODUCTS

Electronics Division

Ignition Energy Of Gases In Millijoules @1 Atm,25^0F Stochiometric Conc.

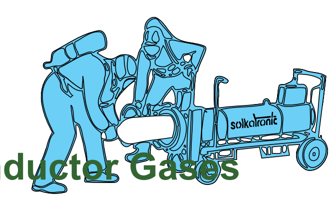
	AIR	OXYGEN
Acetylene	0.017-0.018	0.0002
1,3 Butadiene	0.13	
Butane	0.25	
Cyclopropane	0.17	
Ethane	0.24	0.002
Ethylene	0.07-0.08	0.001
Ethylene Oxide	0.06	
Hydrogen	0.017-0.018	
Hydrogen Sulfide	0.068	
Methane	0.28	0.003
Methyl Acetylene	0.11	
Propane	0.25	
Propylene	0.28	
Vinyl Acetylene	0.082	

NOTE: A spark generated from a person shuffling across a rug is 200 mj



Hydrogen
Chemical & Physical Properties

- Hydrogen is a compressed gas which is flammable
- Pure element, H_2
- CAS# 1333-74-0
- UN# 1049 for gas and 1966 for liquid
- Molecular Weight 2.02
- Compressed gas filled in cylinders to pressures >2000 psig
- Gas Density of 0.005 lb/ft^3 (0.083 gm/l) @ 70^{0}F (21^{0}C)
- Liquid Density of 4.43 lb/ft^3 (71 g/l) @ boiling point
- Specific Gravity of Gas @ 70^{0}F (air = 1) 0.07
- Flammable Range in air @ 1 atm 4% – 76%
- Boiling Point, 1 atm. -423^0 F (-253^{0}C)
- Freezing Point, 1 atm. -435^0 F (-259^{0}C)
- Critical Temperature -400^{0}F (-240^{0}C)



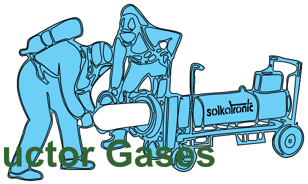
Acetylene Plant Fire

Oxidizer Gases

- Chlorine
- Chlorine Trifluoride
- Fluorine
- Nitrogen Dioxide
- Nitrous Oxide
- Nitric Oxide
- Oxygen

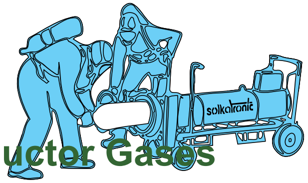
Some are also highly toxic and/or corrosive

For additional information on Oxygen see References in Chapter 10

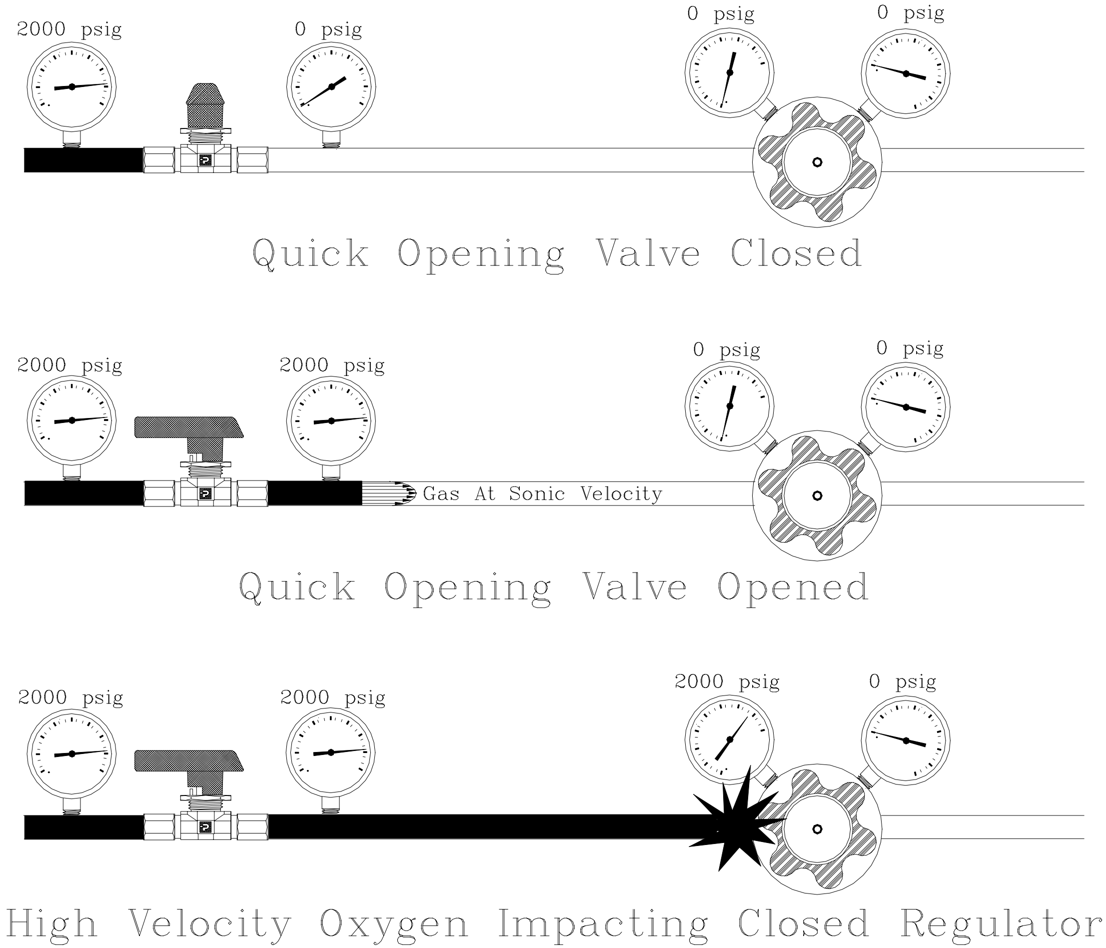


Oxidizer Gas Characteristics

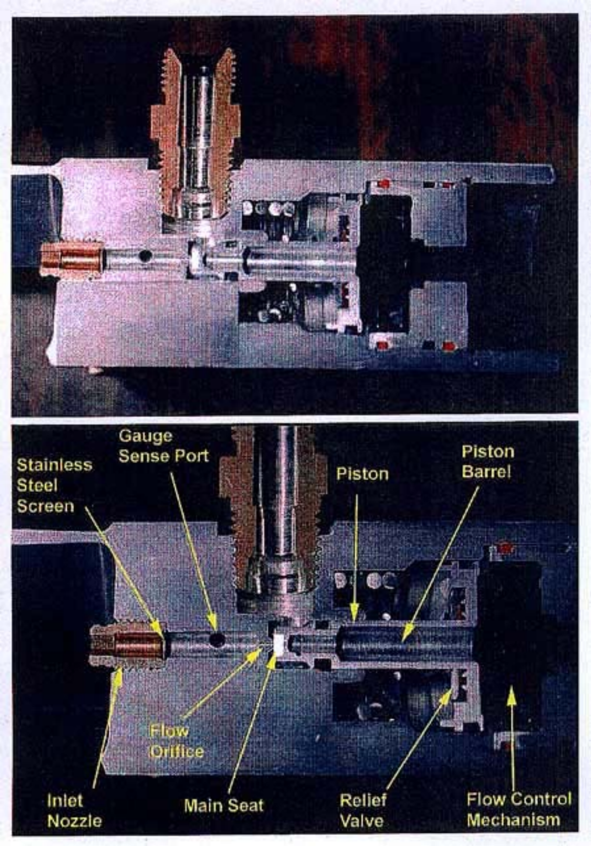
- Oxidizer gases will promote and accelerate combustion
- Is reactive with all fuels
- Some Oxidizer Gases require some energy to cause it to react
  - Nitrogen Trifluoride
  - Nitrous Oxide



Oxygen Adiabatic Compression & Explosion From Quick Opening Valve



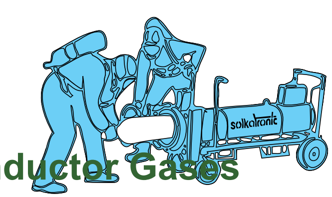
Oxygen Regulator Fire, During Pressure Check, June 12, 1998



How not to handle Liquid Oxygen

Nitrous Oxide
Chemical & Physical Properties

- Nitrous Oxide is a liquefied gas which is an Oxidizer
- Nitrous Oxide, N_2O
- CAS# 10024-97-2
- UN# 1070
- Molecular Weight 44.01
- Liquefied Gas with Vapor Pressure of 739 psig @ 70^0F (21^0C)
- Gas Density of 0.115 lb/ft^3 (1.947 gm/l) @ 70^0F (21^0C)
- Liquid Density of 48.25 lb/ft^3 (773 gm/l) @ 70^0F (21^0C)
- Nonflammable Gas with TLV of 50 ppm, LC_{50} none established, IDLH none established
- DOT Nonflammable Gas
- Boiling Point, 1 atm. -127.4^0 F (-88.5^0C)
- Freezing Point, 1 atm. -131.5^0 F (-90.8^0C)
- Critical Temperature 97.6^0 F (36.4^0C)



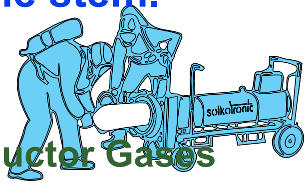
Corrosive Gases – Acid

- Boron Trifluoride
- Boron Trichloride
- Chlorine
- Hydrogen Bromide
- Hydrogen Chloride
- Hydrogen Fluoride (Not a compressed gas)

HAZARDS: Material Corrosion, Tissue Destruction, Irritation, Toxicity

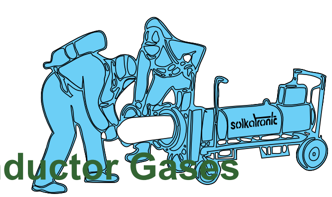
Corrosive Gas, Acid

The acidic gases are noncorrosive in their anhydrous forms but upon contact with water or moist air become strongly corrosive. Operations performed at elevated temperatures also increase the severity of corrosive reactions. Cylinders can be seriously weakened by corrosive reactions over a long period of time with some reactions forming gaseous products that may increase cylinder pressures to unsafe levels. For example, cylinders contaminated with water containing Hydrogen Chloride or Hydrogen Bromide can form Hydrogen while corroding away the cylinder wall. Cylinder failures have been known to occur due to this action. Cylinder valves and regulators can malfunction because of corrosion. For example, solid corrosion products can build up in a regulator and produce creep, a gradual increase in the delivery pressure when flow is terminated. Uncorrected creep can cause hazardous pressures on the delivery side of the regulator under prolonged no-flow conditions. Similarly, cylinder valves exposed to moist air for long lengths of time will have a build up of corrosive products in the stem.



Hydrogen Chloride Chemical & Physical Properties

- Hydrogen Chloride is a liquefied gas which fumes white
- HCl, Halogen Acid
- CAS# 7647-01-0
- UN# 1050
- Molecular Weight 36.46
- Liquefied Gas with Vapor Pressure of 613 psig @ 70^{0}F (21^{0}C)
- Gas Density of 0.095 lb/ft^3, (1.522 gm/l) @ 70^{0}F (21^{0}C)
- Liquid Density of 52.7 lb/ft^{3,} (842 gm/l) @ 70^{0}F (21^{0}C)
- Poison Gas with TLV of 2 ppm, LC_{50} 3120 ppm, IDLH 50 ppm
- DOT Poison Gas and Corrosive
- Boiling Point, 1 atm. -121^0 F (-85^{0}C)
- Freezing Point, 1 atm. -173.6^0 F (-114.2^{0}C)
- Critical Temperature 124.5^0 F (51.4^{0}C)

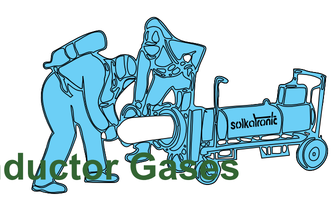


Tied Diaphragm Corrosion
Hydrogen Chloride, Leaked for 18 Months

Hydrofluoric Acid Exposure

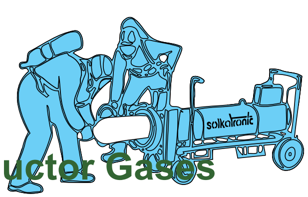
- < 50% conc. Can be painless with symptoms delayed 2-24 hrs.
- > 50% immediate pain
- 25 in^2 exposure of skin is critical if left untreated
- As a weak acid it will move undissociated into deep tissue where it will react with calcium or magnesium cations forming insoluble salts which increases cell membrane permeability to potassium causing intense pain.
- Immediate flushing with water for 20 minutes (AP is 5 minutes) followed by topical application of 2.5% Calcium Gluconate gel. (note not FDA approved)
- Wet soaks of Zephiran (benzalkonium chloride), Hyamine (benzethonium chloride) and Magnesium Sulfate have also been used
- If severe pain continues for 45 minutes after topical treatment, injections of 5% Calcium Gluconate solution have been used.

Dr. Mark Upfal & Dr. Constance Doyle, *" Medical Management of Hydrofluoric Acid Exposure",* Journal of Occupational Medicine, Vol. 32, No. 8, Aug. 1990, pp 726-731



Air Products Guidance On HF Exposures

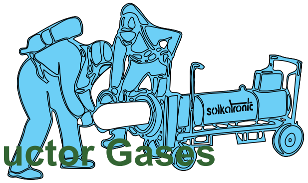
- Planning for Hydrofluoric Acid (HF) Medical Emergencies, GEG EHS SOP
- APCI Safetygram 29, Treatment Protocol for Hydrofluoric Acid Burns, 9/99
- Hydrogen Fluoride Product Safety Training-GEG Product Safety Group



Bad Gloves

Fluoride Gases

- Some Fluoride Gases can react with the moisture (Hydrolysis) in the air to form HF. These include:
  - Arsenic Pentafluoride
  - Chlorine Trifluoride
  - Fluorine
  - Germanium Tetrafluoride
  - Silicon Tetrafluoride
  - Tungsten Hexafluoride

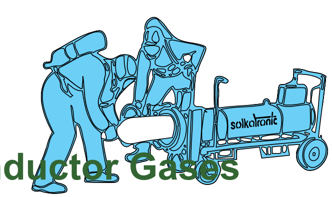


Corrosive Gases – Base

- **AMMONIA**
- **MONO, DI and TRI METHYLAMINES**
- **MONOETHYLAMINE**

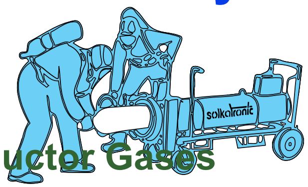
HAZARDS;

Material Corrosion, Tissue Destruction, Irritation, Toxicity



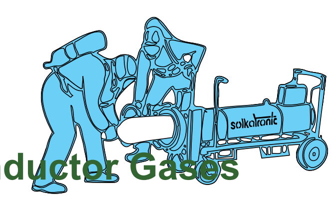
Corrosive Gas, Base

Ammonia and the Amines, such as Methyl and Ethylamine, will react with moisture or water to form basic materials which are corrosive to certain metals, particularly copper and copper alloys. These materials are extremely irritating to human tissue, and low concentrations will create severe eye irritation. Spills of liquid on the skin will cause immediate burns. These materials are also flammable, particularly the amines, which are shipped as flammable gases. In handling these gases, not only should they be treated as regular flammable gases, but protective equipment should be worn to protect against eye and skin injury if spillage should occur. Face shields, and rubber or plastic coated full aprons, and gloves are recommended when handling these materials, particularly when handling them in the liquid phase.

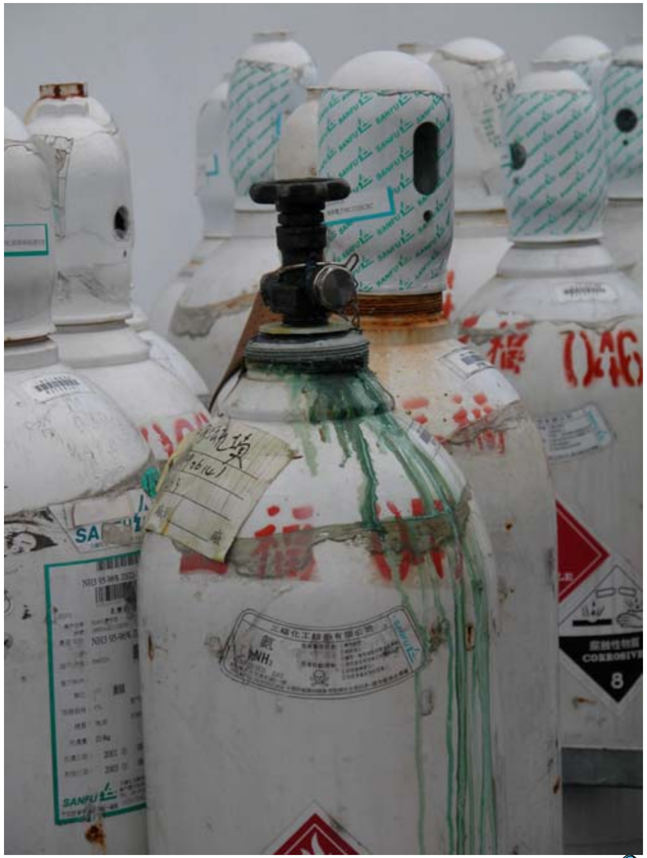


Ammonia, Chemical & Physical Properties

- Ammonia is a liquefied gas which is flammable at concentrations higher than the DOT definition and highly corrosive. Outside the US it is classified as a Toxic Gas
- Anhydrous Ammonia, NH_3
- CAS# 7664-41-7
- UN# 1005
- Molecular Weight 17.03
- Liquefied Gas with Vapor Pressure of 114.4 psig @ 70^0F (21^0C)
- Gas Density of 0.045 lb/ft^3 (0.724 gm/l) @ 70^0F (21^0C)
- Liquid Density of 38.0 lb/ft^3 (609 gm/l) @ 70^0F (21^0C)
- Corrosive Gas with PEL of 50 ppm, LC_{50} of >7300 ppm, IDLH of 300 ppm
- DOT Nonflammable Gas with LFL of 16% and UFL of 25%
- Boiling Point, 1 atm. -28.1^0 F (-33.4^0C)
- Freezing Point, 1 atm. -107.9^0 F (-77.7^0C)
- Critical Temperature 271.4^0F (133^0C)



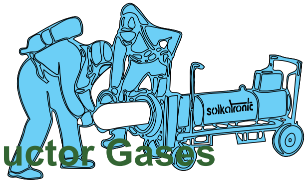
Ammonia Leaker



Inert Gases

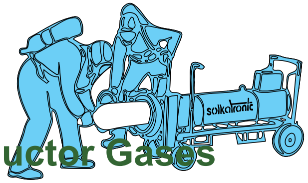
- Argon
- Nitrogen
- Helium
- Neon
- Krypton
- Sulfur Hexafluoride
- Carbon Tetrafluoride
- Xenon

HAZARD: Oxygen Deficiency



Nitrogen
Chemical & Physical Properties

- Nitrogen is a compressed gas which is inert
- Pure element, N_2
- CAS# 7727-37-9
- UN# 1066 for gas and 1977 for liquid
- Molecular Weight 28.01
- Compressed gas filled in cylinders to pressures >2000 psig
- Gas Density of 0.072 lb/ft^3 (1.153 gm/l) @ 70^{0}F (21^{0}C)
- Liquid Density of 50.47 lb/ft^3 (808 g/l) @ boiling point
- Specific Gravity of Gas @ 70^{0}F (air = 1) 0.967
- Boiling Point, 1 atm. -320^0 F (-196^{0}C)
- Freezing Point, 1 atm. -346^0 F (-210^{0}C)
- Critical Temperature -232^{0}F (-147^{0}C)

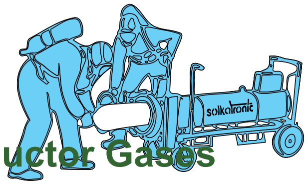


Oxygen Deficiency

The normal oxygen content of air is 20.9%. Depletion of oxygen content in air, either by combustion or displacement with inert gas, is a potential hazard to personnel throughout industry. A general indication of what can potentially occur relative to the percentage of oxygen available is given in the table below.

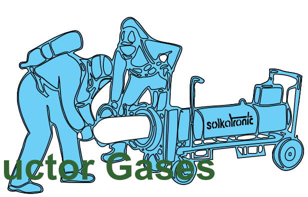
Note: These indications are for a healthy average person at rest. Factors such as individual health (e.g., smoker), degree of physical exertion, and high altitudes can affect these symptoms and the oxygen levels at which they occur.

Oxygen Content (% by Volume)	Effects and Symptoms of Acute Exposure (at Atmospheric Pressure)
15-19%	Decreased ability to perform tasks. May impair coordination and may induce early symptoms in persons with heart, lung, or circulatory problems.
12-15%	Breathing increases, especially in exertion. Pulse up. Impaired coordination, perception and judgment.
10-12%	Breathing further increases in rate and depth, poor coordination and judgment, lips slightly blue.



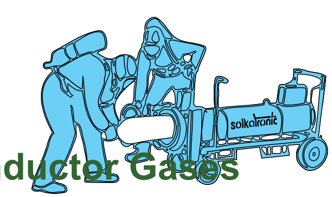
Gases With Multiple Hazards

- Many gases have multiple hazards
- Chlorine Trifluoride is one of the gases with the most hazards
  - Toxicity
  - Corrosivity
  - Oxidizer
  - Reactivity
- Very little energy is required to cause it to react with most materials
- Hypergolic with flammable liquids and solids.



Chlorine Trifluoride ER & Safety Information

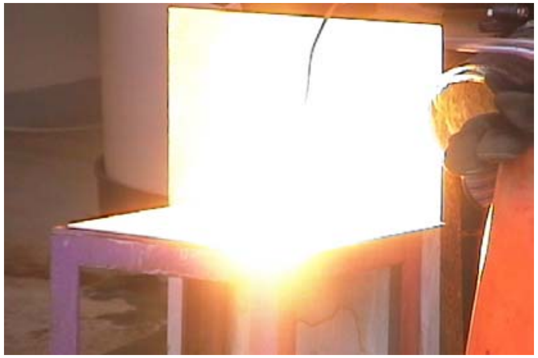
- Vapor Pressure 6.8 PSIG (46.85 kPa)
- Gas Density 0.244 lb/ft^3 (3.908 kg/m^3)
- Specific Gravity (air=1) 3.19
- Boiling Point 53.2^{o}F (11.75^{o}C)
- Freezing Point –105.4^{o}F (-76.3^{o}C)
- Dissociation starts at 250^{0}C with 50% at 450^{0}C



Chlorine Trifluoride Exposure Testing

Liquid Onto Asphalt

Liquid Onto Raw Chicken

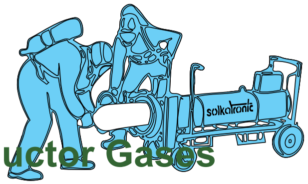


Liquid Onto Oil Film

Vapor Onto Raw Chicken

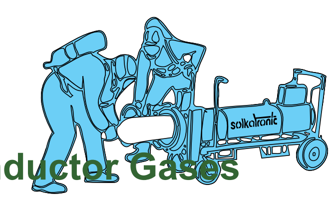
Self Reacting Gases

- **Gases which can react with themselves given sufficient energy.**
- **Ignition outside of the cylinder can flashback into the cylinder**
- **The heat given off by the decomposition or polymerization accelerates the reaction**



Self Reacting Gases/Liquids

- **Acetylene**
  - is absorbed into acetone and in a solid matrix
- **Ethylene Oxide**
  - Stabilized by mixing with Carbon Dioxide or Freon. 60 lb cylinders will not explode because the heat is adsorbed. Will create a lot of polymer
- **Germane**
  - Fill limit based on complete reaction
- **Hydrogen Cyanide**
  - Stabilized with 0.06% Sulfuric or Hydrochloric acid
- **Tetrafluoroethylene**
  - Stabilized with D-Limonene. Without it, it can explode at 2.7 atm (39 psia)
- **Nitric oxide**
  - Pressure is limited to 480 psig
- **Nitrous Oxide**
  - Reaction can only propagate in gas phase
- **Tetrafluorohydrazine**



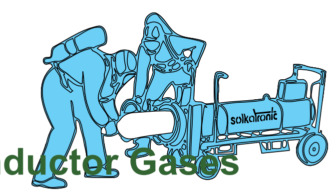
Linde AG, Nitrous Oxide Explosion 2001
Dry Pump Caused Overtemperature

Matheson Germane Explosion

- Incident on Nov. 26, 1984 at Nippon Sanso Kawasaki facility in Japan
- Two workers injured in explosion
- MITI investigation
- 44 liter cylinder filled with 10 kg which is 5% full of liquid
- Germane has negative heat of formation
- Will heat byproducts of decomposition (Germanium & Hydrogen) to 1719^{0}F

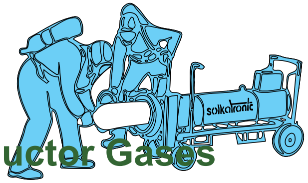
$$GeH_4 \Rightarrow Ge + 2H_2 + Heat$$

- Decomposition is deflagration in 100 milliseconds with a pressure of over 9000 psig
- Germane is now filled to 25% of original

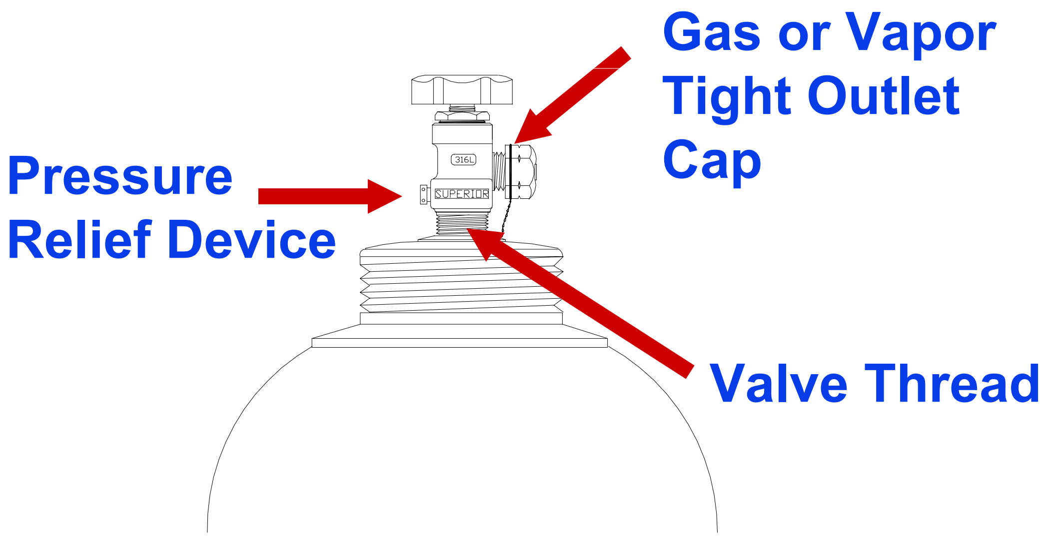


Basic Gas Safety Rules

- Limit Inventory and store in the approved location
- Do not mix incompatibles
- Review MSDS for Hazards
- Leakcheck cylinder and system before use
- Purge system with inert gas before and after use
- Wear appropriate PPE



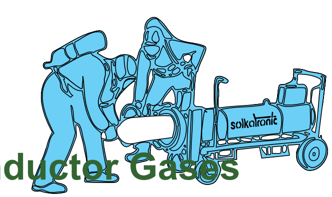
Potential Leak Points



Cylinder Safety Rules

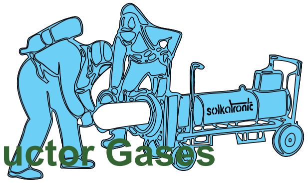
Cylinders and Containers present a physical hazard when handling

- Proper lifting techniques should be used in lifting
- Use approved handcart to move >6 ft
- Do not lift using cylinder cap
- Move with cylinder cap and vaportight cap/plug in place
- Cylinders shall not be marked “Empty” unless they have been purged with inert gas
- Do not reduce pressure to <10 psig
- Do not fill cylinder with another gas
- Heat cylinders only with approved devices and never above 125^{o}F
- Do not cool cylinders below -20^{o}F
- Do not allow cylinders to become part of an electric circuit



A Safety Alert By Willard Graham, Mine Safety & Health Administration, Dept. of Labor

On January 2, 2003 three employees were attempting to plug a tire on a Ford F-250 pickup. Earlier in the day they had inflated the left rear tire with a can of "fix-a-flat" and topped it off with oxygen from the cutting torch tanks mounted on the truck. They had plugged the front tire of the truck and noticed the rear tire was leaking again. An employee had reamed the hole in the rear tire and as he reached for the plug tool, another employee knelt down and removed the reamer from the tire, at which point the tire exploded. All three employees were blown ~10 ft away from the truck, resulting in critical injuries to one employee and serious injuries to the other two. Currently, one of the employees with serious injuries has been released from the hospital and the most critically injured employee remains in the trauma center and is expected to recover after several surgeries and lengthy recovery.



Air Products
Product Information Sources

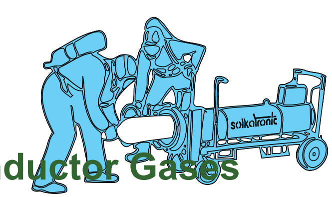
- **Air Products Product Safety Web Site**

  www.airproducts.com/productstewardship

- **Air Products Technical Information Center at:**

  800-752-1597

- **Air Products MSDS's**
- **Air Products Safetygrams**
- **Air Products Gases and Equipment Fact Book**



Air Products Safety Literature

AIR PRODUCTS

MATERIAL SAFETY DATA SHEET

SECTION 1. PRODUCT IDENTIFICATION

PRODUCT NAME:	**Nitrogen, refrigerated liquid**
CHEMICAL NAME:	Nitrogen FORMULA: N_2
SYNONYMS:	Liquid Nitrogen, LIN, Cryogenic Liquid Nitrogen, Nitrogen
MANUFACTURER:	**Air Products and Chemicals** 7201 Hamilton Boulevard Allentown, PA 18195-1501
PRODUCT INFORMATION:	1-800-752-1597
MSDS NUMBER: 1041	REV REV

SECTION 2. COMPOSITION/INFORMATION ON

Material Safety Data Sheets
MSDS

AIR PRODUCTS

Safetygram-7

Liquid Nitrogen

General

Liquid nitrogen is inert, colorless, odorless, noncorrosive, nonflammable, and extremely cold. Nitrogen makes up the major portion of the atmosphere (78.03% by volume, 75.5% by weight). Nitrogen is inert and will not support combustion; however, it is not life supporting.

Nitrogen is inert except when heated to very high temperatures where it combines with some of the more active metals, such as lithium and magnesium, to form nitrides. It will also combine with oxygen to form oxides of

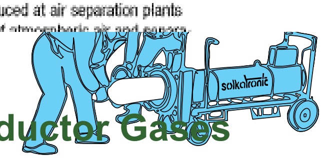
to keep heat away from the liquid that is contained in the inner vessel. Vaporizers convert the liquid nitrogen to its gaseous state. A pressure control manifold controls the pressure at which the gas is fed to the process. Processes that use nitrogen as a liquid do not require the vaporizers and pressure control manifold.

Physical and chemical properties are listed in Table 1.

Manufacture

Nitrogen is produced at air separation plants

Safetygram - 7
Liquid Nitrogen



Air Products Safetygrams

Safetygram-1: Gaseous Oxygen

Safetygram-2: Gaseous Nitrogen

Safetygram-3: Gaseous Argon

Safetygram-4: Gaseous Hydrogen

Safetygram-5: Gaseous Helium

Safetygram-6: Liquid Oxygen

Safetygram-7: Liquid Nitrogen

Safetygram-8: Liquid Argon

Safetygram-9: Liquid Hydrogen

Safetygram-10: Handling, Storage, and Use of Compressed Gas Cylinders

Safetygram-11: Emergency Action in Handling Leaking Compressed Gas Cylinders

Safetygram-12: Regulator Selection, Installation, and Operation

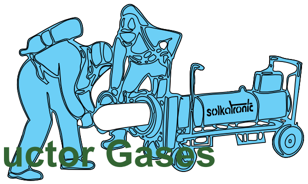
Safetygram-13: Acetylene

Safetygram-14: Don’t Turn a Cylinder Into a Rocket

Safetygram-15: Cylinder Pressure-Relief Devices

Safetygram-16: Safe Handling of Cryogenic Liquids

Safetygram-17: Dangers of Oxygen-Deficient Atmospheres



Air Products Safetygrams

Safetygram-18: Carbon Dioxide

Safetygram-19: Gaseous Carbon Monoxide

Safetygram-20: Nitrous Oxide

Safetygram-21: Safe Handling Procedures for Medical Oxygen Cylinders and the Use of Regulation Equipment

Safetygram-22: Liquid Helium

Safetygram-23: Cylinder Valves

Safetygram-24: Hydrogen Chloride

Safetygram-25: 20% Fluorine/Nitrogen Mixture

Safetygram-26: Silane

Safetygram-27: Cryogenic Liquid Containers

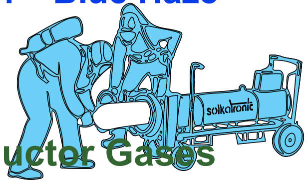
Safetygram-28: Nitrogen Trifluoride Safe Handling Practices

Safetygram-29: Treatment Protocol for Hydrofluoric Acid Burns

Safetygram-30: Handling Liquefied Compressed Gas

Safetygram-31: Cylinder Valve Outlet Connections

Safetygram-32: The Facts About Amine-Induced Visual Disturbances: Halovision – Blue Haze - Glaucopsia



Air Products Safetygrams

Safetygram-33: The Hazards of Oxygen and Oxygen Enriched Mixtures

Safetygram-34: The Toxic metal Hydrides

Safetygram-35: Air Products Policy on Oxygen Sales to Oxygen Bars

Safetygram-36: Recommendation to Air Products' Customers for the Transportation of Hazardous Chemicals

Safetygram-37: Chemical Security

Safetygram-38: Product Migration of Liquefied Gases in Manifolded Systems

Safetygram-39: Chlorine Trifluoride

Safetygram-40: Epoxy Systems Spray Coating Operations

Safetygram-41: APEC UHP Developer Safe Handling Practices

Safetygram-42: Fluorine