Gollob Silane Incident

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Gollob Silane Incident, March 17, 1988

The tragic silane cylinder explosion at Gollob Analytical Services in Berkeley Heights, NJ killed 3 individuals, severely injured one and caused significant property damage. It had a profound impact worldwide on the compressed gas and the Semiconductor industries.

This summary is based on the numerous news articles, reports and other information from gas industry veterans.

Sequence of Events

1. Incident cylinder was filled with silane at Ethyl Corp, Baton Rouge, LA and shipped with other silane cylinders from the batch to Liquid Carbonic Corp, San Carlos, CA
2. Liquid Carbonic Corp selected several silane cylinders from the batch and shipped them to Gould American Microsystem, Pocatello, IH for use in their Semiconductor Fab.
3. Gould American Microsystem had process problems with the silane from the cylinder and complained to the Matheson Salesperson who happened to make a sales call.
4. The Matheson Salesperson offered to analyze the cylinder, so Gould American Microsystem shipped the cylinder to the Matheson Newark, CA facility.
5. The Matheson R&D Chemist attempted to analyze the cylinder by venting the gas into the Gas Chromatograph (GC) sampling system through a glass flowmeter. He noted that as the pressure dropped to 0 psig there was a flame in the glass flowmeter tube. The Chemist had previously analyzed many silane cylinders and had never had a flame in the flowmeter, he concluded that the silane was contaminated. After 6 attempts he was not able to get a sample into the GC for analysis. The Plant Manager reported this to the Liquid Carbonic San Carlos, CA Plant Manager.
6. The cylinder was picked up by a truck from the Liquid Carbonic San Carlos, CA facility. They attempted to analyze it but were not successful.
7. At that time the only Laboratory that could analyze high pressure pyrophoric or toxic gases was Gollob Analytical Services in Berkeley Heights, NJ. The cylinder was shipped there on a common carrier.

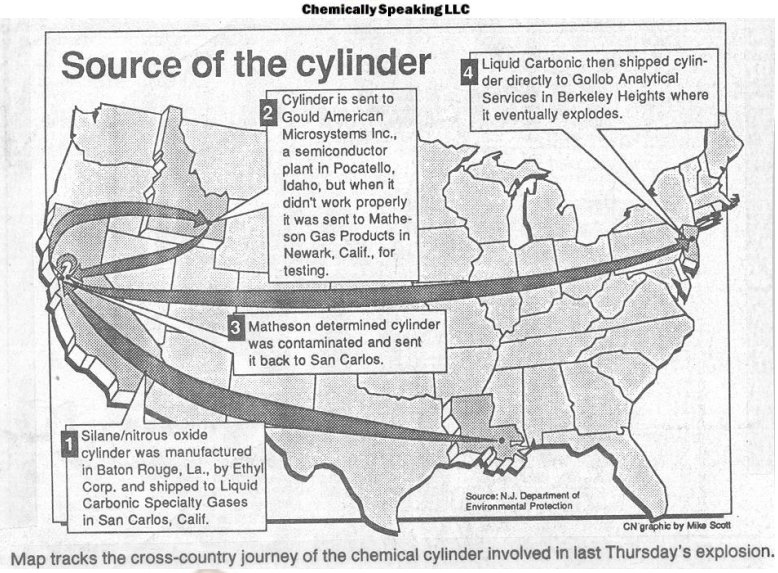

Fig. 1: Silane Cylinder Travel

8. On March 16, 1988, the Gollob analytical team determined that there was a high concentration of nitrous oxide in the silane cylinder, an explosive gas mixture. Liquid Carbonic in Chicago (Headquarters) was immediately contacted by phone. They then notified the Liquid Carbonic Plant Manager in Harrison, NJ.
9. Other companies were consulted that day on what to do. Matheson and Hazards Research Corp advised Gollob and Liquid Carbonic to sandbag the cylinder and to use a remote valve opener to open the cylinder valve to vent it They however decided not to wait for sandbags because it would delay the disposal for 3-4 hours.
10. Two Gollob Employees, Lou Molinini (Retired) and Senior Mass Spec Operator (James Cavellas) remained at the site that evening. Lou Molinini had come in to help out while Fred Gollob was on vacation. They both had sold the company and recently retired.
11. Dennis Feeney, LC Harrison Plant Manager arrived at the Gollob site after midnight. James Deimer LC Plant Engineer who earlier travelled to Matheson East Rutherford, NJ to get equipment arrived shortly after. Since the remote valve opener had to be shipped by plane from Newark, CA and would not arrive until the next day, he left with only a purge manifold, a coil of tubing and a flash arrestor.
    Jack Faught, Matheson Plant Manager gave him specific instructions on what to do with the cylinder which included sandbagging it above the cylinder height.
12. They moved the cylinder to an outside pad adjacent to the gas room. To dispose of the gas mixture, they connected the purge manifold to the cylinder, a nitrogen purge cylinder, ran a 20' length of 1/8" tubing away from the cylinder and were to attach the flash arrestor to the end where it would vent into the air.
13. James Deimer (LC) was on the phone with Frenk Olejko, VP Operations, LC Chicago who told him to Frank told them not to attempt to blow down the cylinder until after they got the remote valve opener. When the call ended he stepped to the door way outside and noted that the flash arrestor was no longer attached. He was told it was no longer needed. He then saw a flame at the end of the tubing and then suddenly the explosion occurred. Three firefighters found him

tangled up with hoses from a helium bundle in a dumpster. He lost part of a leg and 4 fingers. The explosion occurred at 1:51 AM


Figs. 2 and 3: Damage to Building and Room

The explosion blew apart the one story building causing considerable damage. Numerous cylinders were thrown around and there was a fire in the building. Dennis Feeney, Lou Molinini and James Cavellas who were outside venting the cylinder died instantly. It appeared that they were trying to escape as the bodies were found 15-60' from each other.

A phosphine mixture cylinder was leaking and on fire for almost a week. Since it was next to an arsine cylinder there was concern that it would cause it to leak as well. The officials extended the evacuation zone to ½ mile. Approx 1500 people including a nursing home (120 residents) were evacuated from Thursday to Sunday as the DEP and private contractors worked to stabilize and remove the leaking or damaged cylinders. There was concernt hat the phosphine cylinder would leak for a few more weeks so the waste disposal company placed the phosphine cylinder onto a metal plate and surrounded it with sandbags. They then put a shaped charge on it and blew it up. A number of arsine cylinders were leaking. Seven cylinders were placed in cylinder overpacks and removed.

Fig. 4: Cylinder Overpacks

Silane Cylinders filled by Ethyl Corp

Immediately after this incident, cylinders filled in the same batch at Ethyl were identified and quarantined at facilities throughout the US. As the only survivor was in intensive care, the details of

what might have happened was lacking. Many believed that it was the movement of the cylinder that triggered the explosion. As a result, sandbags were used to shield the surroundings in the event of another explosion.

Gould American Microsystems, Pocatello, IH

Two cylinders were quarantined at Gould American Microsystems. Over 2800 sandbags filled and placed against the wall of the gas room.

A nearby nursing home was evacuated, 91 residents. The silane cylinder was vented in 40 minutes and was determined to have not been contaminated.

Silicon Valley, San Mateo and Santa Clara Counties

At the Liquid Carbonic San Carlos, CA facility there were over 400 cylinders of silane, 55 cylinders were identified as being from the same batch. 1,000 sandbags were used to protect the surroundings while other cylinders and chemicals were removed from the facility. The 55 cylinders were then transported to the nearby Redwood City salt flats on San Francisco Bay. Over 100 area residents were evacuated during the removal of the cylinders and 2 miles of Highway 101 was shutdown.

Over a 2-day period, they were blown up using a ¼ stick of dynamite on the sidewall of each cylinder. For safety the cylinders were immersed in a 10' long 5' deep trench of water to minimize shrapnel from flying out of the area. To save time 2-3 were blown up at the same time. None were contaminated with nitrous oxide as evidenced by the intact cylinder with just a hole in it.

2 silane cylinders from AMD Santa Clara containing 5 kg each and 2 containing 2 kg each from Teledyne Mountainview were removed and blown up by Santa Clara County bomb squad. None were contaminated with nitrous oxide as evidenced by the intact cylinder with just a hole in it.

Observations:

Connecting a silane cylinder to a nitrous oxide cylinder is impossible without an adapter. Silane has a CGA 350 connection which is a left-handed thread bullet while nitrous oxide has a CGA 326 right-handed thread gasket connection.

Contamination of the silane cylinder with nitrous oxide was likely to fill the silane cylinder up to the vapor pressure of nitrous oxide (745 psig @ 70°F). For it to be 70% would mean the pressure of the silane had to have dropped to 225 psig at some point. There are other reports that the concentrations were reverse silane 70% and nitrous oxide 30%, both are well in the explosive range.

Adiabatic compression heat is generated in the piping system every time the cylinder valve was opened, did not ignite the mixture. This cylinder had been opened at least once at Gould American Microsystem, 6 times at Matheson, at least once at Liquid Carbonic and at least 2 times at Gollob.

Once ignited, the mixture flame speed was fast enough to backflash against the gas flow rate out into the cylinder even at the valve seat which likely had the gas mixture flowing at sonic velocity (343 m/sec). The flame noted in the flowmeter did not backflash into the cylinder since the procedure is to pressurize the sampling system, shut the valve and vent the pressure. The shut valve isolated the cylinder preventing the flame from travelling back into it.

Lessons Learned

1. Normal cylinder handling and transportation will not exert enough energy to ignite an explosive gas mixture. The cylinder had been handled and transported numerous times for over 3,000 miles.
2. Silane is a very pyrophoric gas almost always igniting when released, researchers however have mixed it with oxygen without it igniting immediately.
    a. Emeleus and Stewart demonstrated that silane and oxygen in a 1 : 2.3 mol ratio at a total pressure of 0.6 bar do not react appreciably even when kept at 70°C for many days.
    b. In 1970 Germantown Laboratories, Philadelphia, PA conducted a series of safety tests for a gas supplier on silane. In one test (The study of the stability and inflammability characteristics of some potentially dangerous gases and gas mixtures). In one test silane was mixed with oxygen.
    A 3.85% SiH_4/76.85% Ar/19.30% O_2 mixture was made in a cylinder at 1800 psig, 65-72°F Mixture kept for 30 minutes. Then a 25 lb weight dropped onto it with no effect. When it was vented, it ignited backflashed into the cylinder causing the entire mixture to react rupturing it.
    A 2.04% SiH_4/87.76% Ar/10.20% O_2 mixture was made in a cylinder at 1800 psig, 65-72°F Mixture kept for 30 minutes. Then a 25 lb weight dropped onto it with no effect. When it was vented, it ignited and backflashed into cylinder causing the entire mixture to react the cylinder bulged 0.5 mm. Copper tubing was heat tinted (damaged) from the high reaction temperature.

    Physical impact does not provide sufficient energy to ignite the explosive mixture. Like the Gollob cylinder, ignition of the mixture occurred when it was vented.
3. A common practice in the 1980's was to use a common purge gas system for all of the gases. This typically was house nitrogen at 100 psig. Protection from backflow of gases into the purge gas system is with the use of check valves which can fail and the user is not aware of it. As a result, many companies will not allow it to be used as a primary safeguard in a system. As a result of this and other incidents the Fire Code and CGA Standards require a dedicated high pressure purge cylinder for silane.
4. Adiabatic compression heat of nitrous oxide has reacted the soft seats in check valves and pressure relief devices in several incidents. This was the root cause of the nitrous oxide backflow through the purge gas system into the silane cylinder at Osaka University. This mixture exploded in 1991 killing the two graduate students.

The cause of the nitrous oxide contamination has never been found. This incident caused many companies and Fire official to examine silane and other systems more closely. Many safety standards specific to silane were issued from the Compressed Gas Association, Semiconductor Safety Association and Factory Mutual.

Eugene Ngai