Silane Safety

Spurred by the growth in the solar cell and specialty glass coating industries, silane's use is rapidly increasing worldwide.

Newer facilities using this gas need to be fully aware of the key issues associated with its safe use and handling.

Many newer users of silane (silicon tetrahydride) today do not have the knowledge and experience of older users such as those in the Integrated Circuit (IC), Thin Film Transistor-Liquid Crystal Display (TFT-LCD) industries. As a result, a number of major incidents involving silane have occurred at these facilities. Let's take a hard look at some of the key safety factors involved.

Demand, volume, and applications

Silane is the most widely used electronic specialty gas. For 2010 its estimated use is from 6,000 to 10,000 metric tons depending on the information source. All agree, however, that by 2015, its demand is expected to double – driven primarily by the solar cell industry.

Thin-film solar cell manufacturers use large quantities of silane, while the more traditional crystalline silicon solar cell manufacturers use smaller quantities supplied in cylinders. Both can use silane with lower purity levels.

Silane was first synthesized in the 1880's, but was not used commercially until the mid 1960's when the first Integrated Circuit manufacturers began their operations. Today, it is still used by the IC and TFT-LCD industry although in higher purity levels (99.9999+%) than in the past.

In addition, some of the larger fabrication IC or TFT-LCD facilities now use silane in such large quantities that an ISO module containing as much as six metric tons is used as the supply source along with an adjacent standby ISO Module.

A bit of history

In the 1970's and 1980's, most gas suppliers manufactured silane in small batch reactors. Now the gas suppliers distribute silane from large manufacturers. The two major manufacturers are Renewable Energy Corp. (REC Silicon), located at Silver Bow, MT, and Moses Lake, WA, along with Monsanto Electronic Materials Corp. (MEMC), Pasadena, TX.

Their combined U.S. capacity is larger than all of the other manufacturers in Korea, Japan, and Germany. New silane manufacturers such as Dow Corning Inc. will come on-stream in 2011.

Erratic pyrotechnics

While silane is technically a high-pressure pyrophoric gas, it does not always immediately ignite when released. The reason for this is still not fully understood despite 40 years of research.

This behavior has been the cause of significant incidents. In fact, silane has caused more fatalities in use than all of the highly toxic specialty gases (arsine, phosphine, diborane, hydrogen selenide) put together.

Since 1976 there have been 11 documented fatalities involving silane and a wide variety of injuries ranging from a ruptured ear drum to severe burns. Even the combustion by-products of silane have caused fatalities and injuries.

During the early days there was little information available on the safe handling of silane – or its behavior when released. Fires and explosions routinely occurred during use, handling, storage, transportation, and manufacturing.

When silane is released into air it can:

- Immediately ignite
- Not ignite at all
- Ignite after a delay

The first condition is the most common and the most desirable. It creates a yellow flame like that of a fire in a backyard barbeque. Under high pressures this can become a jet flame like a torch. When it doesn't ignite at once, it can form a **metastable mixture** with air which can **bulk auto-ignite**. This condition more closely resembles an explosion causing a damaging deflagration or detonation. Any confinement of the released unignited gas increases the chances of this happening.

My personal experience with silane cylinders

When I first started in the specialty gas industry at Precision Gas Products Inc., in 1972, I was more scared of silane than arsine or phosphine. Here's why.

In those days they used brass-diaphragm valves with nylon seats for silane. This, coupled with poor valve-purging, or valve-closing procedures by customers, created a condition in which a large percentage of the cylinders leaked. Sometimes this leakage caused what they called a "popper." A "popper" occurred when the silane was released with a bang as the cylinder valve's vapor-tight outlet cap was loosened with a wrench. The sound resembled a shotgun blast. In a few cases these "poppers" were severe enough to rupture eardrums. Stories of operators running out of the room in panic were common. After such an experience it is not uncommon for operators to break out in a sweat and cringe each time they must loosen a silane cylinder's vapor-tight outlet cap.

The first generation of spring-loaded metal diaphragm valves were also difficult to close tightly under pressure. When the valve is connected to a system and open, silane gas pressure is exerted against the metal diaphragm. This causes considerable resistance to closure if the pressure is high. Often this resistance leads the operator to think the valve was closed tight enough. In fact, double closing of the valve is recommended for these valves to achieve a truly tight closure. Improper purging of the system can also lead to formation of silicon dioxide particles which can coat the valve seat and also prevent a true tight closure.

In these cases leakage across the valve seat (a cross-port leak) could be 1×10^{-5} to 10^{-6} cc/sec, an amount which is not readily detectable unless an electronic gas leak detector is used. Over a period of three months while in storage and transportation to a customer, this situation can produce a leak of up to 78 cc of silane with the gas trapped behind the cylinder valve vapor-tight outlet cap. Since the average dead volume between the vapor-tight outlet cap and the valve seat is 1 cc, the valve can be pressurized to 1,100 psig. This means a considerable amount of pressured silane is suddenly released when the vapor-tight outlet cap is eventually loosened ***(See Figure 1)*** producing three potential conditions:

- Immediately ignite **(a flamer)**
- Not ignite at all
- Ignite after a delay **(a popper)**

Figure 1. *A silane flamer.*

The good news, however, is that with recent improvements to valve designs, maintenance, and procedures, the frequency of a silane release from a vapor-tight outlet cap has been significantly reduced. One gas supplier I know reduced a relatively large percentage down to 1 in 10,000.

Explosion hazards

Other problems also occurred. Larry Britton in his 1989 article, "Combustion Hazards of Silane and its Chlorides," described a severe explosion in 1977. A piggyback trailer containing 20 cylinders of silane and 28 drums of antifreeze exploded as the train was moving at 70 mph. Investigation of this incident and another like it indicated that a diaphragm valve's hand-wheel can vibrate open during transportation and handling causing a leak. ***(Figure 2)***.

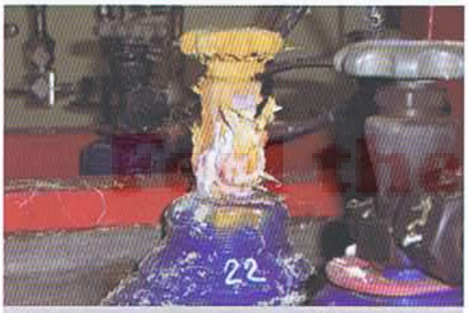


Figure 2. Silane leaker: a hazard during transportation.

This discovery led the gas industry to adopt a best practice of wiring valve hand-wheels shut to prevent movement. The Department of Transportation (DOT) also mandated the use of a **vapor-tight outlet cap** for silane rather than the dust caps that were in use to provide a secondary seal.

Restrictive Flow Orifice

Due to these types of incidents a lot of research was done to improve silane safety. Matheson Gas Products, Superior Valve, and IBM collaborated on the first cylinder valve Restrictive Flow Orifice (RFO) in 1984 This was originally a 0.006" dia. RFO which was increased to 0.010" diameter for silane. ***(Figure 3)***.

Figure 3. Valve outlet with a 0.005" Restrictive Flow Orifice (RFO).

Based on release testing conducted by Hazards Research Inc. in the 1980's the industry adopted as the silane standard a 0.010" dia. RFO with a minimum exhaust velocity of 200 ft./min. when the first *Hazardous Materials Fire Code, Article 80* was adopted in 1988. This standard was later revised based on the research studies by Dr. Franco Tamanini, FM Global Inc. for SEMATECH. The gas cabinet exhaust ventilation now must be at least 250 times the flow rate from the RFO. The Compressed Gas Association standard *ANSI/ CGA G13 – 2006, "Storage and Handling of Silane and Silane Mixtures". 2nd edition* requires 300 times.

Figures 4 and 5: *A silane release from a cylinder valve without (left) and one with a 0.010" RFO (right).*

As shown ***(Figures 4 and 5)***, a 0.010" dia. RFO can dramatically reduce the silane flow rate from an open cylinder valve. The flow rate ranges from 333 cfm (9,430 lpm) to 2.5 cfm (70.8 lpm). The resulting jet flame is 3 m versus 0.5 m.

Gas cabinet explosions

Testing by Hazards Research, FM Global and others have further demonstrated silane's explosive energy when released and ignited after a delay in confinement. IBM funded studies at Hazards Research Inc in 1982 made the industry aware of the violence of a gas cabinet explosion.

In one memorable video the gas cabinet with no exhaust ventilation disappeared in one video frame. A second test with a two-cylinder gas cabinet exhausting at 500 cfm violently blew apart a few seconds after the silane flow was turned off.

There have been six fatalities from gas cabinet explosions where silane was released unignited into the cabinet. The two most recent occurred in Taiwan in 2005, the second in India in 2007. Both were at solar cell companies. Other major incidents also occurred in solar cell companies in China and the U.S. in 2009 that could have also led to the loss of life.

The most devastating explosion that I have reviewed was the one reported to me while I was in India in 2007. In this case the following four serious safety errors were made:

1. The operator was never trained on silane safety.
2. The operator was working alone.
3. The gas cabinet was installed improperly.
4. The operator was never trained on how to operate the gas cabinet.

The operator suspected something was wrong and wrote in his notebook that he intended to contact the gas supplier to discuss the problem. As he was attempting to operate the gas cabinet, a release of unignited silane occurred within the cabinet. Something ignited the metastable mixture of silane and air. The explosion was so violent that the gas cabinet window decapitated him. The cabinet door propelled his body across the room damaging a brick wall.

Testing for safe release method

Since the 2005 incident in Taiwan, I have been collaborating with Professor Jason Chen, Kaohsiung First University on numerous silane tests. In hundreds of releases, we were able to easily release silane without immediate ignition. In almost all cases they did ignite once the flow was stopped.

In one test we replicated the Hazards Research test with a single cylinder gas cabinet bolted to a concrete pad. Exhaust ventilation was provided to the cabinet with a nitrogen powered ***venturi eductor*** mounted at the top of the cabinet. The eductor created an exhaust ventilation flow using nitrogen pressure. Silane was supplied to the cabinet through a ¼" diameter stainless steel tube that terminated at the height of a typical cylinder and angled upward to simulate a sheared pigtail.

Silane at a pressure of 480 psig was fed into the cabinet at a flow estimated at 74 cfm (2,100 slpm), unignited *(Note: Cylinders at maximum fill can be at a pressure of 1,600 psig)*. The silane mixed with the cabinet 141 cfm (4 m^3/ min) exhaust air which entered from a louver at the bottom of the cabinet and exited from the cabinet at the venturi eductor. The silane and air mixed, forming a metastable mixture which flowed under a steady-state condition. The silane flow was continued for more than 10 seconds then abruptly shutoff. An explosion ruptured the cabinet three seconds later. It ripped the gas cabinet door off its hinges and threw it 50 ft away. The window and louver separated from the door and the bolts securing the cabinet to the ground were sheared off ***(Figures 6-9)***.

More details on this test and others can be found in the article, Chen, J. R., Huang, P. P.,

Figures 6-9: A gas cabinet silane explosion triggered during testing.

Ngai, E.Y., et al, "Field Tests of Release, Ignition and Explosion from Silane Cylinder Valve and Gas Cabinet," Process Safety Progress, Vol. 26, No. 14, Dec. 2007.

Tips for safe handling of silane:

As a result of my experience and research I can suggest the following key tips for the safe handling of silane:

1. Follow the guidelines outlined in *CGA G13*.
2. Use and store silane in a well ventilated area separated from other incompatible gases.
3. Monitor area for silane fire using an approved UVIR detector.
4. Monitor for gas leaks using silane specific gas detector.
5. Install an RFO on the cylinder outlet valve.
6. Place the pneumatic shutoff valve as close to the source as possible. The best practice is to use a pneumatic cylinder valve.
7. Use welded connections whenever possible. Where removable connections are used they should be a metal-gasket type like a VCR in a well-ventilated area.
8. Leak test the system at the silane cylinder pressure or higher.
9. Purge and evacuate the system prior to opening the cylinder valve or removing the silane cylinder.
10. When opening the system always anticipate a leak.
11. Wear appropriate PPE.
12. Participate in a silane safety training program.
13. Develop an emergency plan so that. procedures and equipment are in place in the event of an incident.

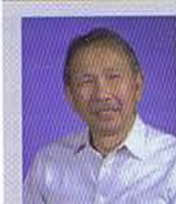
The proper procedure to remove a vapor-tight outlet cap

In addition to the tips listed above, it is important to be aware that the most likely point for a leak in preparing a silane cylinder for use is when the cylinder valve vapor-tight outlet cap is removed. With that in mind, to avoid operators becoming surprised or injured, they must be properly trained and fully clothed with the proper Personal Protection Equipment (PPE). The following minimum guidelines should be followed:

1. Operators should wear all appropriate PPE including fire gloves, Nomex suit or Firefighter turnout, faceshield, earplugs, and safety glasses.
2. Operators should have a "buddy" equipped with the same PPE visually observing the operation and ready to assist if necessary.
3. Physically secure the cylinder away from other hazards as required by *CGA P1*.
4. Stand to the side of the cylinder valve outlet, then remove the plastic bag and the hold-down wire.
5. Confirm that the valve is closed tightly.
6. Position the cylinder to pull down with a wrench (a box wrench is preferred) when loosening the vapor-tight outlet cap.
7. Be aware that flames can come out of the leak-check hole in a Diameter Index Safety System (DISS) vapor-tight outlet cap.
8. Pull down slowly on the vapor-tight outlet cap and anticipate the possibility of a leak. Be ready to push up on the cap to reseal the system if a leak does occur.
9. Again, if silane is behind a vapor-tight outlet cap, one of the following will occur:
   - Immediately ignite (a "flamer")
   - Not ignite at all
   - Ignite after a delay (a "popper")
10. Once the cap has been removed, visually check the valve outlet surface for damage or debris. Never look directly into the outlet. Instead, use a dental mirror for visual inspection ***(Figure 10).*** SGR

Figure 10. Dental Mirror Inspection of Valve Outlet.

Eugene Ngai

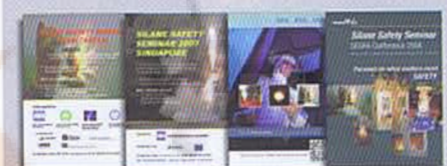


Eugene Ngai has over 35 years of experience in all areas of Specialty Gases. He retired from Air Products in 2009. As President of Chemically Speaking LLC he provides safety and emergency response consulting and training to many gas suppliers, manufacturers and users. He remains active in CGA, SEMI and NFPA. More information can be found at **www.chemicallyspeakingllc.com.**

Safety Training

Proper training in safe procedures is vital. From 1984 through the 1995, a series of silane technical and safety seminars were conducted in the United States and Europe. These created awareness of potential problems and helped to dramatically reduce the number of incidents and/or their severity by establishing industry safe practices, regulations, and training throughout the industry.

In 2005 immediately after the fatal accident in Taiwan, I became increasingly concerned with the silane safety knowledge of the new users in the solar cell industry. I began a campaign to bring silane experts together to provide a series of safety seminars throughout the world. Working with the Asia Industrial Gas Association and the Taiwan High Pressure Industry Gas Association we were able to fast track a full day seminar in May 2006, just six months after the accident. This was hosted by the Industrial Technology Research Institute, Taiwan, (ITRI) and funded by the Taiwan EPA. Other presentations and seminars were offered from 2007-2009 throughout Asia, U.S. and Europe **(Figures 11 through 13)**.



Figures 11-13. *Silane seminar brochures.*

As a responsible Product Steward, Air Products funded my activities for the seminars and the testing with Prof Chen, as well as providing other Air Products speakers. In addition they fully or partially funded seminars in Korea and Portland, OR.

In fact all the major gas suppliers and industry have also been supportive of these seminars.

In addition to the seminars, hundreds of people have now been trained on silane safety through the "Feel the Heat" program. After a classroom training program on silane safety, students properly dressed in PPE get to experience the heat from a silane flamer or the shock wave from a popper. They each remove the cylinder valve vapor-tight outlet cap, with high-pressure silane trapped behind it. During this training the students also have the opportunity to observe the value of preparation.

They are awarded the patch which is an embroidery of a picture of my hand demonstrating a flamer from a class in 1993 **(Figures 14 and 15)**. Next up, REC Silicon will also sponsor a seminar at Intersolar, Munich in June.

Figures 14 and 15. *"Popper Training" and Student Award Patch.*