

ATMOSPHERIC PRODUCTS AND SERVICES (APS)

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SafetyAlert-26 Silane

Warning: Improper storage, handling, or use of silane or its mixtures can result in serious injury and/or property damage. Handle this product in accordance with the Material Safety Data Sheet (MSDS) for silane.

General

Silane is a colorless, pyrophoric compressed gas. It has been reported to have a repulsive odor, but this is attributable to contaminants as the high-purity grades available today are odorless. Being pyrophoric, most leaks will immediately ignite on contact with air. However, under certain conditions such as high humidity or rapid release, it may not immediately ignite and may form pockets of gas which may cause a delayed vapor cloud explosion.

Manufacture

Silane is manufactured commercially by two methods. The hydrolysis of magnesium silicide yields a mixture of silicon hydrides requiring separation through distillation. The other commonly used method is the reduction of chlorosilanes.

Uses

Silane is widely used in the semiconductor manufacturing process. It is used in silicon epitaxy to deposit single crystal layers. Silane is also used in the production of polycrystalline silicon. In the chemical vapor deposition process, known as CVD, silane is used in conjunction with other gases to grow nitride films and amorphous silicon films used in the production of solar cells.

Safety Considerations

Health: The major hazards of silane stem from its ability to spontaneously ignite on contact with air and its toxicological properties. Contact with silane can cause irritation of the eyes. Inhalation may result in headache, nausea, and irritation of the mucous membranes and respiratory tract. Although silane has been reported to have an offensive odor, this is attributable to contamination and should not be taken as a warning signal for the presence of dangerous concentrations of the gas.

The combustion of silane forms silicon oxides that can cause irritation to the respiratory tract. Since silane is spontaneously flammable in air, its toxicological properties are difficult to determine. If low concentrations (less than one molar percent) of silane are inhaled, the silane may react with basic solutions in the body, forming silicates and hydrogen. With further hydrolysis in the body tissues, silicic acid could be formed.

Studies have been conducted on the carcinogenicity of amorphous silica, as generated in silane fires. The International Agency for Research on Cancer stated, "There is inadequate evidence in humans for the carcinogenicity of amorphous silica." (IARC, 1987, V42, p.93)

Flammability: Silane is a pyrophoric compressed gas. This means it is self-igniting in air because it has an autoignition temperature below ambient temperatures. Leaks of silane may cause a fire or possibly form explosive mixtures in air. Some very small leaks will not give a visible flame but may be detected by the presence of oxide buildup at the leak point. Sometimes leaks of this size will selfplug due to an oxide buildup (brown or white dust). The chief product of combustion is silicon dioxide SiO2 (sand). During unusual circumstances, silane may not completely oxidize and form darker colored dust or solids that can be pyrophoric or shocksensitive. Large fires may produce heavy clouds of silicon dioxide. These clouds can be knocked down with a water fog, but care must be taken not to extinguish any silane fires. Silane fires must only be extinguished by stopping the flow of silane to the fire. If a silane fire is extinguished before the flow of silane is stopped, the silane may accumulate, resulting in an explosion. The lower flammable limit is 1.37 volume percent. Silane mixtures in the 3 to 4 percent range can exhibit pyrophoric behavior. Ambient air temperature and humidity also have an effect on the pyrophoric limits. APS recommends all silane mixtures of 1.37 percent and higher be treated as if they were flammable/pyrophoric.



Containers

Silane and silane mixes are compressed gases shipped in containers at pressures up to 10.342 kPa (1500 psig) and 14,499 kPa (2100 psig) respectively. These containers are designed and manufactured according to the applicable codes for the region in which they will be transported. These codes are established by organizations that include the Department of Transportation in the United States and the ADR in the European Union. The codes cite the specific specifications required for the pressures and temperatures involved. These specifications include the material of construction, method of manufacture, testing, products permitted for filling and other details.

Cylinders

A typical cylinder is a hollow tube with a closed base that permits the cylinder to stand upright. The opposite end is tapered to a small opening that is threaded to accommodate the installation of a valve. A threaded neck ring is attached to the threaded end to allow a protective cylinder valve cap to be installed. Carbon steel and aluminum are the primary materials of construction for silane cylinders. When volume demands are too much for one or two cylinders, packs of cylinders are sometimes used. These packs are also called banks and commonly come in 6- and 12cylinder configurations. These cylinders are manifolded together in a portable frame.

Silane is also available in large skid-mounted cylinders, referred to as "Y" cylinders. These containers are mounted horizontally and are tapered and threaded at both ends. A valve assembly is installed on one end and a pressure relief device usually installed in the opposite end.

Tube Trailers and ISO Modules

If large amounts of product are required, silane can be provided in tube trailers or ISO modules. The most common configurations for these units are in four- or eight-tube bundles of 22-inch (56-centimeter) diameter by either (20-ft) or (40-ft) long tubes. These units carry as much as 6 metric tons of silane. Tube trailers have the tubes mounted horizontally on a truck chassis while the ISO module mounts the tubes horizontally inside an ISO shipping frame.

For more information on the safe handling of cylinders, see APS SafetyAlert-10, "Handling, Storage, and Use of Compressed Gas Cylinders."

Valves and Connections

Valves

Containers used in silane service are equipped with diaphragm valves. Diaphragm valves come in two basic configurations, spring-loaded and tied diaphragm. APS uses the spring-loaded diaphragm valve on its lecture bottles and lower grades of silane while the tied diaphragm valve is used on the higher grades of silane. The tied diaphragm valve is provided in a manual operation design and pneumatically operated design for remote operation. For information on the construction and operation of these valves, refer to APS SafetyAlert-23, "Cylinder Valves." Some regulatory agencies or local codes may require these cylinder valves be equipped with restrictive flow orifices (RFOs). The RFO is a small plug that screws into the valve outlet. It has a hole in the middle that can range in size from 0.006 to 0.16 inches (0.15 to 4 millimeters) in diameter. The purpose of the RFO is to restrict the amount of flow that can come from the cylinder in the event of a system failure. There are recommended sizes for silane, but customers can specify their requirements. Users should be aware of any local code requirements regarding silane cylinder RFO sizes.

The area should be monitored with the use of UV/IR monitors to detect fires. Outdoor systems using a large amount of potential leak sources (fittings and connections) should employ metal hydride monitors to detect leaks. Both monitors should be interlocked (failsafe) to shut off the flow of silane upon detection. Monitoring systems should be equipped with a source of backup or emergency power. A remote emergency shutdown device should be present to shut off silane at the source. Sprinkler systems or fire protection water should be used only to cool cylinders, not to extinguish the fire. The preferred piping for gas lines is seamless 316 or 316L stainless steel and should be of welded construction, rated for 1.5 times the maximum operating pressure and leak tested with outboard helium detection to at least 1.5 times the normal delivery pressure up to the maximum rating. The ideal system would be all welded; however, due to the necessity of maintenance and replacement of portions of the system, properly installed mechanical fittings can be used. The number of mechanical fittings should be kept to a minimum and should not be used where they would be subject to rotational or vibrational forces. These fittings should be leak-checked regularly and after any operations are conducted on the fittings. The distribution piping between the silane supply and point of use should be double-wall piping with monitoring of the annular space. Eliminate all possible interconnecting piping between silane systems and oxidizers. Packed valves should not be used on systems containing silane. Only packless diaphragm or bellows type valves should be used. An excess-flow valve or excess-flow switch should be installed on all dispensing systems to shut off flow in the case of a downstream line rupture. This shutoff valve should be located as close to the source as possible. The recommended regulators are diaphragm regulators with stainless steel diaphragms. All regulators should be equipped with a bonnet vent that is capable of withstanding a diaphragm rupture and should be piped to route the escaping gas to a suitable, safe location. Steel cylinders are preferred over aluminum cylinders due to steel's better heat resistance if a fire occurs. Aluminum cylinders may be used if flame

impingement protection is considered between adjacent silane cylinders. Stainless steel cylinder valves should be used with a DISS connection preferred, but other standard connections may be used. The cylinder valve should have a restricted flow orifice (RFO) installed in the cylinder valve with a maximum orifice size of (.010 inch) in diameter. Installation of the restrictive flow orifice shall be indicated on the cylinder.

Pneumatic cylinder valves or cylinder valve operators are highly recommended for remote operation with line-of-sight capability. The pneumatic valves or valve operators should be of fail-closed design.

The cylinder valve and pigtail valve operators should be of failclosed design. Plastic pneumatic tubing should be used to actuate the silane valve operators. The intent is for the plastic to melt during a fire condition and cause the silane valves to automatically fail closed. The cylinder valve and pigtail cylinder connection should always be visually inspected for signs of leakage or defects prior to connection to the system. Valves should be opened slowly with specific recommended opening procedures to be followed, dependent upon the type of cylinder valve used. For information regarding the opening and closing of the various types of cylinder valves, consult APS SafetyAlert-23, "Cylinder Valves."

The number of silane cylinders in use should be kept to the minimum necessary for operations. On multiple cylinder silane supply systems, the cylinders should be separated from each other by a noncombustible partition extending beyond the footprint of the cylinder. This partition should extend from above the tope of the cylinders and piping to 18 inches below the cylinder valve. Design and installation of noncombustible partitions must not impede natural or forced ventilation across the silane cylinder valve and panel

components. The partitions must not impede the UV/IR flame detectors from properly viewing the silane cylinder valve connection, pigtail, and panel components.

All gas lines, valves, and functional components should be labeled to indicate their use in silane service. The line labels should indicate direction of gas flow and type of gas.

Leak testing with inert gas should be completed on the system after each cylinder change. The preferred method is a high-pressure outboard helium leak test using helium or a helium mix from a dedicated gas source. A high-pressure retention test using an inert gas may be considered if the leak sensitivity is appropriate (at least 10⁻³ sccs leak detection capability). Hand-held electronic detectors may be used to detect the presence of a silane leak at the cylinder connection or any point where the connection's integrity is in question.

Dedicated inert gas sources (cylinders) must be used for puraina and leak-check operations. Each purge gas cylinder system should be equipped with an appropriate regulator, relief device, back-flow protection, and a low-pressure alarm. Where possible, the purge gas cylinder pressure should be maintained at a level higher than the silane cylinder pressure. Redundant backflow check valves should be used to prevent contamination of the purge gas cylinder with silane; an additional isolation valve should also be present as redundant protection. House nitrogen systems should not be used as purge or leak-check gas sources.

Do not return potentially contaminated purge gas cylinders without explicit instructions from your cylinder gas supplier. If backflow of silane into the nitrogen system is suspected, the system should be treated as if silane were present.

Dedicated vacuum sources (pumps or venturis) for silane and silane mixture manifold evacuation should be used rather than "house" vacuum systems.

The silane and silane mixture vent system should be independent of other gas vent systems. Backflow prevention should be present, along with a constant inert flow through the system. This flow should be monitored and interlocked to prevent venting if the vent system is not in operation. Valves that isolate the continuous inert flow purge of the vent lines should be minimized or administratively controlled to be kept open. The silane vent system should either terminate at an effluent treatment system or discharge to open air in a safe area. For silane mixtures, the effluent treatment necessary will vary dependent upon the other gas present in the mixture and on the silane concentration. The vent discharge should be in compliance with all national and local regulations.

Silane has a critical temperature of -3.4°C (25.9°F) and a critical pressure of 47.8 atm (702.5 psia), and the gas will start to liquefy at these conditions. Engineering analysis and appropriate controls are required in systems where liquid silane could cause operational problems or liquid-full conditions. In addition, systems where multiple cylinders or tubes are being used simultaneously may be susceptible to a phenomenon called product migration. This occurs where the vapor from a warmer vessel condenses in a cooler vessel. See APS SafetyAlert-38, "Product Migration of Liquefied Compressed Gases in Manifolded Systems."

Interior Dispensing Systems: In some cases, open air exterior dispensing stations may not be possible due to site or environmental considerations or if other constituents of silane mixtures are toxic. Previously mentioned controls for exterior systems apply to interior systems in addition to the recommended controls in this section.

Silane used indoors should be located in ventilated gas cabinets or exhausted enclosures or in separate, ventilated gas rooms. Incompatible materials (e.g., oxidizers) must not be located within the same enclosure. The interior dispensing system should be located in a blast-resistant containment room or cutoff room designed for handling hazardous materials, with at least one outside wall, and should be separated from occupied areas of the building. Local building codes should be consulted regarding building requirements for the indoor storage and handling of silane. The velocity of forced ventilation across all unwelded fittings should be adequate to prevent the accumulation of silane in the case of a leak. (Some fire codes require a minimum mechanical ventilation rate of 200 fpm across the cylinder neck and all unwelded fittings.) The gas cabinet or enclosure should be designed to prevent gas pocketing. The enclosure or room ventilation should be monitored with an automatic gas system alarm or shut down in the event of ventilation failure.

Metal hydride gas monitors should be located in the cabinet exhaust discharge or room exhaust system and set to shut down silane flows upon detection of no more than 5 ppm. UV/IR detectors should also be used to detect fire and should hut down the system upon detection. In addition, temperature detectors may be used to detect a fire in the cabinet or room.

Dedicated inert gas cylinders located in the same gas cabinet or exhausted enclosure should be used for purging operations. Ideally, each purge gas cylinder and the cylinder it supports should share an enclosure. However, if adequate backflow protection is provided for the purge gas source, the cylinders may be located external to the silane enclosure. Each purge gas cylinder system should be equipped with an appropriate regulator, relief device, backflow protection, and a low-pressure alarm. Where possible, the purge gas cylinder pressure should be maintained at a level higher than the silane cylinder pressure. Redundant backflow check valves should be used to prevent contamination of the purge gas cylinder with silane; an additional isolation valve should also be present as redundant protection. The house

nitrogen system must not be used for a purge source.

Additional detailed information on silane systems is available in the Compressed Gas Association Pamphlet P-32, "Safe Storage and Handling of Silane and Silane Mixtures."

Procedures/Operation: All operators must be trained in system operation and the hazards of silane, and only authorized personnel should have access to the system. The gas controller used on silane dispensing systems should be outfitted with a delay between starting the system and the initiation of the flow of gas into the piping to allow the operator to move away from the system being energized. Critical detection devices (such as metal hydride gas and UV/IR flame sensors) should be periodically calibrated and proof-tested to verify that they are operating properly. See the training section of this publication.

Cylinder change operations, or any operation that requires opening the system or where potential exposure to silane exists, should only be conducted by two-member teams wearing appropriate personal protective equipment (PPE). See the section on Personal Protective Equipment for recommended PPE.

Maintenance on any part of the system should be conducted as if the system were pressurized. Appropriate PPE should be worn. The system should be visually inspected daily with attention paid to any mechanical fittings, valve bonnets, pressure gauge inlets, etc., looking for brownish/whitish dusting, which is indicative of a slight leak. Safe work permit procedures, including lockout and tagout procedures, should be followed with a minimum of a double block valve and bleed system between an operating system and the work area.

Silane may ignite spontaneously on contact with air. Leaks may cause a fire or form explosive mixtures with air. If a leak occurs, immediately evacuate all personnel from the danger area. Use proper personal protective equipment, including selfcontained breathing apparatus, to shut off the silane supply if there is a fire and if it can be done without risk. Use great caution if there is a serious leak that is not burning, as silane may be accumulating and the potential may exist for an explosion. If the flow of gas cannot be shut off, allow the fire to burn out. Cool any adjacent containers with water spray from the maximum possible safe distance, being careful not to extinguish the fire. Pressure relief devices on cylinders can be activated by the flame impinging on the cylinder. Contact supplier for information on disposition of cylinders involved in fire.

Combustion products can be controlled with a water spray or fog. Ventilate the area of the leak prior to the return of personnel. In some cases, leaks of silane will not ignite immediately. A delayed ignition vapor cloud explosion can take place with devastating force. For more information see APS SafetyAlert-11, "Emergency Action for Handling Leaking Compressed Gas Cylinders."

Personal Protective Equipment (PPE)

For any operation that requires the removal of cylinder valve outlet seals, changing out silane supply cylinders, or exposure to operating silane systems, the recommended minimum PPE that should be used is:

- Polycarbonate face shield and safety glasses
- Leather gloves or equivalent flameresistant hand protection
- Nomex[®] or equivalent fire-resistant full body protection with fireresistant hood or equivalent head protection (e.g., hard hat, full face shield, fire-resistant neck flap)
- Safety shoes Hearing protection is recommended.

For emergency response situations:

- Full-body Nomex[®] with hood
- SCBA
- Leather gloves or equivalent flameresistant hand protection Hearing protection is recommended.

Note: Some emergency situations may require fire entry or proximity suits.

First Aid

If silane is inhaled, remove the victim to fresh air. If breathing has stopped, give artificial respiration. If breathing is difficult or weak, give oxygen. Call a physician. Provide a silane MSDS to the physician.

Exposure to a high concentration of silane may result in delayed pulmonary edema. Therefore, individuals should be observed for delayed respiratory impairment and treated appropriately if pulmonary edema occurs. In the event of skin or eye contact, the affected areas should be washed with tap water for 15 minutes. If irritation persists, a physician should be consulted.

Skin burns from ignited silane should be treated like any thermal burn.

Transportation Information

Shipping Name: Silane Hazard Class: 2.1 Shipping Label: Flammable Gas Identification Number: UN2203 Description: Silane, 2.1, UN2203

Important: When returning any cylinder, ensure that the cylinder valve is properly closed, the outlet seal is in place and properly tightened, and the valve protecttion cap is correctly installed.

Training

All personnel involved with the handling of silane should be trained in the following areas:

Product Knowledge: A thorough knowledge of silane and its hazards is required. These would include physical properties, toxicology, and the other characteristics of silane.

Connections

Valve connections for silane may vary from country to country. Table 4 gives some of the connection designations used by the various countries. For more information on cylinder valve connections, refer to APS SafetyAlert-31, "Cylinder Valve Outlet Connections."

Pressure Relief Devices

Pressure relief devices are not required on cylinders with internal volumes of <50 liters when filled to a density of less than or equal to 0.274 grams per cubic centimeter and 85 atm @ 21.1°C (1250 psig @ 70°F) or less. Larger containers, such as "Y" cylinders, tube trailers, and ISO module tubes, use a combination frangible disk with a fuse metal backing. The disk is rated for the test pressure of the container, and the fuse metal has a nominal melting temperature of 165°F. Both the temperature and pressure requirements must be met for the device to function. (In Europe, relief devices are not commonly used for silane cylinders and tubes.) For more information on pressure relief devices, see APS SafetyAlert-15, "Cylinder Pressure-Relief Devices."

Cylinder Storage and Handling

Always store and handle cylinders containing silane and other compressed gas cylinders in accordance with ISO 11625, "Gas Cylinders-SFe Handling." For more information, refer to APS SafetyAlert-10, "Handling, Storage, and Use of Compressed Gas Cylinders."

International or local regulations may require additional safeguards for storage or use. Personnel must know and understand the properties, proper uses, and safety precautions for the specific product before using the product or associated equipment.

Storage

Cylinders should be secured in an upright position and stored in a wellventilated area protected from the weather. The storage area should be secure with limited access. The flammability of silane requires area monitoring for leakage where silane is stored and used. Storage area temperatures should not exceed 125°F (52°C) and should be free from combustible materials and free from ignition sources. Storage should be away from heavily traveled areas and emergency exits. Avoid areas where salt or other corrosive materials are present. Valve protection caps and valve outlet seals must remain on cylinders that are not connected. When returning a cylinder to storage, the valve outlet seal must be installed leaktight. Separate full and empty cylinders. Avoid excess inventory and storage time. Visually inspect stored cylinders on a routine basis, at least weekly, for any indication of leakage or other problems. Use a first-in, first-out inventory system and keep up-to-date inventory records. The use of "FULL," "IN USE," and "EMPTY" tags is highly recommended. Some locales require special planning when storage of silane exceeds a specific amount. Before purchasing silane, contact the local authorities to determine the requirements for the storage of this material. Silane is typically stored in areas specifically designed for silane. Storage areas must be posted with the proper signage.

Handling and Use

Use only in well-ventilated areas designated for silane. Use a suitable handcart designed for cylinder movement. Do not drag, roll, or slide cylinders. Never attempt to lift a cylinder by its cap. Secure cylinders at all times during storage, transport and use. Use a pressure-reducing regulator or separate control valve to discharge gas from the cylinder. Never apply flame or local heat to any part of a cylinder. Do not allow any part of the cylinder to exceed 125°F (52°C). High temperature may cause damage to the cylinder. If user experiences any difficulty operating the cylinder valve, discontinue use and contact the supplier. Use an adjustable strap wrench to remove overly tight cylinder caps. To prevent accidental opening of the cylinder valve, never insert anything into the cap holes to assist in cap removal.

Ensure that the cylinder valve is properly closed, the valve outlet seal has been reinstalled leak-tight, and the valve protection cap is installed before returning to storage, moving, or shipping the cylinder.

Disposal

Return unused product to the supplier. Disposal by incineration followed by filtration is the most commonly used method for product disposal. Disposal of this product must be done in an environmentally acceptable manner in compliance with all applicable national and local codes.

System Design

Exterior Dispensing Systems:

The preferred design of a silane distribution system is an automated, exterior cylinder manifold or dispensing open rack system with remote line-of-sight operation. Manual systems need to be evaluated for safe operation, and automatic remote operation should be considered for silane systems. The purpose for remote operation is to ensure that personnel are not potentially exposed to silane leaks during the initiation of flow and to allow for remote shut-down if a system problem develops. Line-ofsight capability may also be achieved through the use of video monitors. The dispensing system should be located in an isolated area away from buildings, streets, and property lines in accordance with local building and fire codes. Firewalls should be used on two sides of the installation. They should be arranged to allow ventilation around the installation

and will afford additional protection. If firewalls are used, it is important to note that most fire codes define exterior storage as requiring 75% of the perimeter to be open. A noncombustible roof or canopy should be in place over the dispensing manifold; however, measures should be taken to prevent confinement of the silane if there is a release. The storage and dispensing area should be secured to limit access by using a chain link fence or similar barrier. The secured area should meet all life safety code egress requirements.

Table 2 Toxicity
OSHA: PEL-TWA none established
ACGIH: TLV-TWA 5 ppm
NIOSH: IDLH not established
LC (50): 9600 ppm (4 hour rat)
extrapolates to 1.92% (1 hour rat) pyrophoricity prevents actual testing at this concentration

Table 3 Flammability	
In Air	
Lower Flammability Limit	1.37%
Upper Flammability Limit	96.0%
Autoignition Temperature	-50°C (-58°F)
In Nitrogen Trifluoride	
Lower Flammability Limit	0.66%
Upper Flammability Limit	95.3%

Note: Silane may burn outside these limits in the presence of added diluents.

Unknown

Autoignition Temperature

USA

510 (<500 psig)

350 (500 psig and greater)

632 Ultra High Integrity (DISS) This connection has been adopted by ISO

UK

DIN 1

Germany

DIN 1

France

NF E

Japan

JIS 22-0L

Emergency Response Telephone Numbers <u>USA</u>

CHEMTRAC

1-800-424-9300 (Toll Free in the U.S., Canada, and U.S. Virgin Islands) 703-527-3887 for calls originating elsewhere (Collect calls are accepted)

CHEM-TEL, INC.

1-800-255-3924 (Toll Free in the U.S., Canada, and U.S. Virgin Islands) 813-248-0585 for calls originating elsewhere (Collect calls are accepted)

INFOTRAC

1-800-535-5053 (Toll Free in the U.S., Canada, and U.S. Virgin Islands) 352-323-3500 for calls originating elsewhere (Collect calls are accepted)

3E COMPANY

1-800-451-8346 (Toll Free in the U.S., Canada, and U.S. Virgin Islands) 760-602-8703 for calls originating elsewhere (Collect calls are accepted)

NATIONAL RESPONSE CENTER (NRC)

Call NRC (24 Hours) 1-800-424-8802 (Toll Free in the U.S., Canada, and U.S. Virgin Islands) 202-267-2675 in the District of Columbia

MILITARY SHIPMENTS

703-697-0218 Explosives/Ammunition Incidents (Collect calls accepted) 1-800-851-8061 All other dangerous goods incidents

NATIONWIDE POISON CONTROL CENTER (United States Only) 1-800-222-1222 (Toll Free in the U.S.)

CANADA

CANUTEC 613-996-6666 (Collect calls are accepted) *666 Cellular (In Canada only)

Visit Web Site: www.apsusa.biz for further information or

Call 410-833-7170

or

Ask your local sales representative