Materials Handling Guide:
Hydrogen-Bonded Silicon Compounds

SEHSC®

Developed by the Operating Safety Committee
of the Silicones Environmental, Health and Safety Council of North America
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Introduction

1.1 Introduction

The Silicones Environmental, Health and Safety Council of North America (SEHSC) is a not-for-profit trade association comprised of North American silicone chemical producers and importers. SEHSC promotes the safe use of silicones through product stewardship and environmental, health, and safety research. SEHSC's Operating Safety Committee (OSC) prepared this Materials Handling Guide for Hydrogen-Bonded Silicon Compounds (SiH) as a service to industry. The purpose of this Guide is to provide the industrial user with supplemental information on various practices developed over time, which are designed to promote the safe handling of SiH products. Because it addresses this product category generally, this Guide is not a substitute for either a manufacturer's product-specific directions or in-depth training on chemical safety and handling. The Guide cannot replace education or experience and should be used in conjunction with professional judgment. The practices described in this Guide may not be applicable or appropriate for all SiH products or in all circumstances. Specific questions regarding the handling of a particular product should be directed to your material supplier and/or a competent professional.

SEHSC will strive to update this Guide as significant new information becomes available regarding the handling of SiH products. Readers are encouraged to submit suggestions for improvement to SEHSC. Importantly, however, neither SEHSC nor any member company assumes any responsibility to amend, revise, or otherwise update this Guide to reflect information that may become available after its publication. While offered in good faith and believed to be correct, SEHSC does not assume any liability for reliance on the information in this Guide.[1]

1.2 SiH Materials

Hydrogen-Bonded Silicon Compounds (SiH) are reactive under certain conditions and care is required when handling these materials. These hydrogen functional silicon compounds include some silanes, siloxanes and silicones, such as the methyl hydrogen polysiloxanes, and come in many forms, such as emulsions, fluids, elastomers and resins. SiH-containing products can be

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stored, handled, and used safely, however, there are significant potential hazards that should be considered:

- SiH products (*e.g.*, SiH emulsions, fluids, elastomers, and resins) may evolve hydrogen on contact or when mixed with strong acids or bases; amines; primary or secondary alcohols and water in the presence of acids, bases or catalytic metals; some catalytic and reactive metals; or metal salt forming compounds. When contacting these materials, SiH compounds can rapidly evolve hydrogen gas and form **<u>flammable and explosive</u>** mixtures in air.
- Many SiH emulsions will evolve hydrogen continuously under normal conditions of storage and use, without any additional catalytic or reactive agents.
- SiH products used in platinum-catalyzed addition-curing systems, such as SiH elastomers, can also release **<u>flammable and explosive</u>** hydrogen gas if these products are combined with each other or with incompatible materials.

In light of these potential hazards, careful review of the information provided on the Material Safety Data Sheets (MSDS) provided by your supplier(s) of these products is critical.

1.3 Organization

The Guide is divided into chapters that describe various practices designed to enhance the safe handling and use of SiH containing materials. The techniques and practices described in this Guide are to be utilized by personnel who have been trained in basic chemical safe handling practices and are to be used as an enhancement to programs already in place at user sites. This Guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this Guide may be applicable in all circumstances.

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Nature of Hazard

This chapter provides further details on the potential hazards associated with SiH products. In particular, this chapter describes the conditions under which the SiH products may evolve hydrogen gas, as well as other potential hazards. A comprehensive discussion of hazards associated with SiH products is beyond the scope of this document. For more information, contact your SiH product supplier and refer to your supplier's MSDS.

2.1 The Gassing Triangle

SiH products, such as methyl hydrogen polysiloxanes and hydrogen functional silanes, are stable, but under certain conditions they can generate significant volumes of hydrogen gas. Because of hydrogen's physical properties (*i.e.*, wide explosive limits, low ignition energy, *etc.*), any hydrogen evolved from SiH products can pose a hazard due to pressure build-up, fire, and/or explosion.

Three conditions, referred to as the "gassing triangle," are simultaneously required for the above-referenced gassing phenomenon to occur. These conditions are the presence of SiH, a proton donor (or available hydrogen source), and a catalyst.

2.1.1 SiH Source

All chemicals containing a silicon-hydrogen bond can generate hydrogen.

2.1.2 Active Hydrogen Source

All chemicals with active hydrogen can contribute to the gassing phenomenon. The most common is water, which can be found in products as an impurity or as an ingredient (emulsion). But other classes of chemicals such as alcohols, amines, acids, or bases have the same behavior and can be a source of active hydrogen.

2.1.3 Catalyst Source

Acids, bases, amines, salts, oxidizers, peroxides, metal soaps, products of corrosion, and other similar contaminants, as well as active catalysts of platinum, rhodium, palladium, iron, and others, have a catalytic action promoting the gassing phenomenon.

The rate of gassing is related to the temperature, pH, concentration, solubility, and viscosity of each component (see Fig. 1).

The gassing phenomenon might occur with *an induction period.* The evolution of hydrogen may occur rapidly or over an extended period of time. As many factors can influence the rate of hydrogen evolution, this is not readily predictable.

If any of the above three conditions is missing, the "triangle" is broken and no gassing will occur.

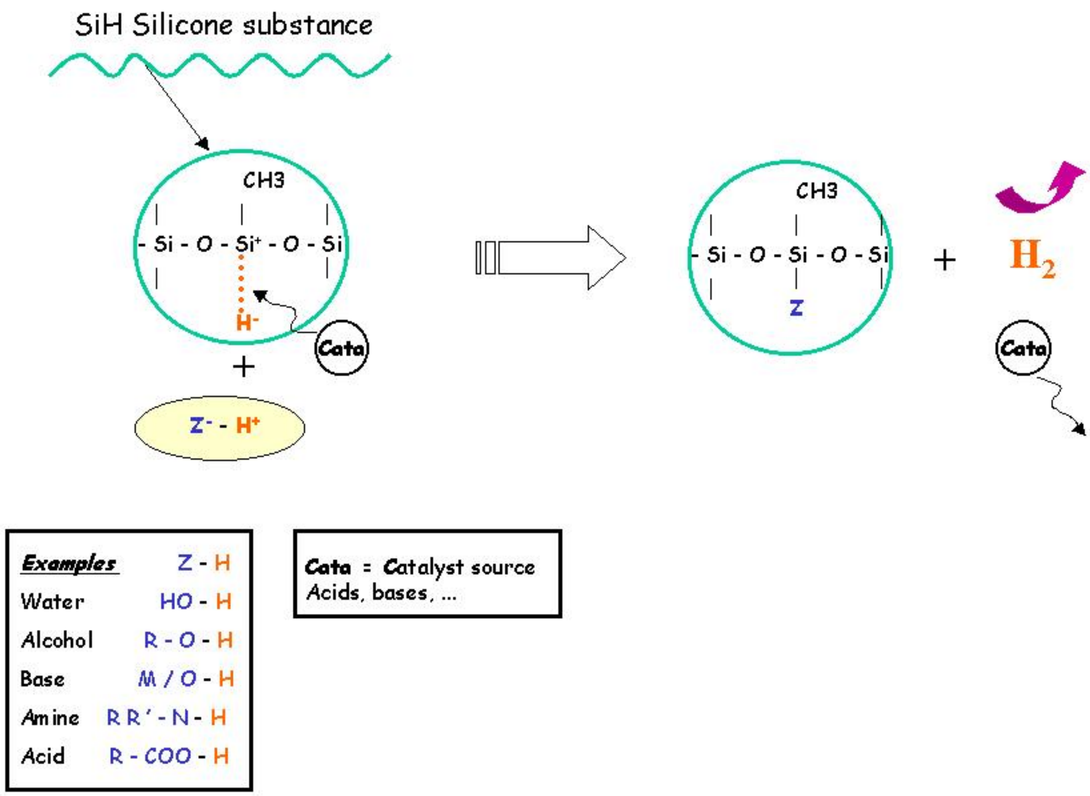


FIG. 1—Gassing Phenomenon of SiH Products.

2.2 Specific Dangerous Reactions of SiH Products

Even in the absence of an active hydrogen source, SiH products can pose hazards. Polymerization, de-polymerization, and equilibration processes can lead to side reactions producing flammable gasses or vapors other than hydrogen.

In the presence of acid or basic catalysts (*e.g.*, Lewis acids or bases, clays, *etc.*) -even in the absence of humidity- redistribution of the siloxane chain has been observed associated with the formation of highly flammable by-products such as Me_3SiH, Me_2SiH_2, and $MeSiH_3$, depending on the nature of the siloxane backbone.

In extreme conditions where tri-functional $HSiO_{1.5}$ units are present, the formation of silane gas (SiH_4) is possible. SiH_4 is a highly volatile (b.p. -112 °C) and pyrophoric (self-ignitable gas) in air.

2.3 Associated Hazards

Hydrogen gassing can result in pressure build-up, fire, and/or explosions.

When stored in a closed container, SiH products can potentially generate enough hydrogen to exceed the pressure rating of the storage container. Over pressurization can cause container bulging or container failure resulting in flammable hydrogen release with inherent fire and/or explosion hazard. Container failure also can result in projectile hazards. Pressure relief valves or venting devices may help mitigate the hazard during storage (see Chapter 6-Control of Hazards). Closed glass bottles are not recommended for sample storage.

In viscous products, hydrogen gassing can cause foaming and overflowing of containers. SiH product containers in storage should be checked periodically to ensure that the containers are not showing evidence of gassing (bulging or venting).

3

Specific Reactions Leading to Hazardous Conditions

This Chapter describes several example scenarios associated with the handling of SiH products that can potentially give rise to the gassing phenomenon described in Chapter 2. As previously indicated, all three conditions that comprise the gassing triangle must be present for the gassing phenomenon to occur. The following examples are for illustration purposes only and should not be construed as being representative of all possible scenarios.

3.1 Inadequate Equipment Clean-out

Equipment clean-out generally includes both solvent and water flushing followed by drying. When inadequate clean-out occurs, trace amounts of catalyst and active hydrogen compounds (*e.g.,* water) may be left behind completing the gassing triangle for the following batch. Cleaning with caustic solutions should be performed with extreme care. Basic materials are catalysts in the gassing reaction. If the clean-out involves an alcoholic caustic solution, the potential problem is compounded because of the higher solubility of alcohols in silicones as compared to aqueous solutions. Clean-out procedures must include steps to insure all basic materials are removed from the system prior to introduction of SiH materials. A recommended practice is to include a pre-manufacturing step that checks the system for contamination before the start of the manufacturing operations.

Some manufacturing equipment may have low spots that will trap liquids. Clean-out with appropriate solvents followed by vacuum drying should be considered for such equipment.

3.2 Incomplete Process Separation

If an active hydrogen compound (*e.g.*, water, alcohol, amine, *etc.*) is used during the manufacturing process of the SiH fluid or compound, and not completely removed after processing, the residual active hydrogen could complete the gassing triangle if a catalyst is also present.

3.3 Container Liners and Unprotected Storage Conditions

Poor container liners or unprotected storage conditions can cause moisture contamination (*e.g.,* cracked liners, drum leakage, gasket failure, or failure of venting devices).

Liners can be cracked because of improper processing by the drum manufacturer or if the drums have been dented during handling before or after filling. Inspection of drums prior to filling is recommended.

Use of closed head drums should be considered to minimize potential leakage. If an open head drum is used, a bolt ring closure type should be considered.

Drums left outside during a rain can hold standing water on the drumheads for long periods of time. Use of drum covers should be considered. Venting bungs have gaskets that can harden and loose effectiveness with time. If using venting bungs, use should not extend beyond the period recommended by the manufacturer or beyond the warranty period. Regular inspection of vent bungs is recommended.

3.4 Rusting or Contamination of Containers

Rusting in containers occurs due to damage such as denting, rupturing, or cracking of container liners, which allows moisture to enter the container and to cause chemical corrosion. The by-products of the corrosion process often have a catalytic action on the gassing phenomenon. Inspection of drums prior to filling is recommended. Accidental introduction of rust or of other contaminants during container filling operations can yield similar consequences.

3.5 Product Breakdown

In some cases, hydrogen evolution may be caused by the chemical breakdown of a compound over time. Attention should be given to a product’s recommended shelf life, which should be followed.

4

Examples of SiH Products

4.1 Emulsions

SiH emulsions typically emit hydrogen continuously at a slow rate because they contain an unlimited supply of active hydrogen in the form of water. Typical components of an emulsion would include a SiH fluid, water, emulsifiers, and buffering agents. The rate of hydrogen emission is dependent on such factors as:

- pH-pH levels over 8 or under 3 greatly increase the rate of hydrogen release
- Temperature-long-term exposure to temperatures over 30^{o}C increases the rate of hydrogen release
- Degree of hydrogen substitution on the SiH material-the more SiH bonds present the more hydrogen that is available for release
- Degree of branching in the SiH polymer-branched SiH polymers react more readily than linear polymers
- Quantity of SiH material in the emulsion -- the higher the percentage of SiH polymer in an emulsion the more potential there is for gassing to occur

Emulsions are very sensitive to contact with catalysts and catalytic metal compounds. Inadvertent mixing with catalytic preparations or active metals (*e.g.*, flaked or powdered aluminum pigments) can promote the rapid release of hydrogen.

4.2 Compounded Elastomers

Some room-temperature vulcanizable (RTV) silicone products and liquid rubber compounds contain SiH fluids. These materials generally contain silicone polymers, SiH fluids, inorganic fillers, pigments and modifying agents. Typically these are viscous fluids or paste-like materials, unless they have been dispersed in organic solvents.

These materials are generally less reactive than emulsions or fluids. Due to their physical nature and lack of solubility in water, the SiH groups are less accessible to contact with incompatible chemicals. Unless the incompatible chemicals are actively mixed into the product the only SiH available for reaction would be that on the exposed surface area of the product.

Moisture from fillers, free radical polymerization initiators and catalyst residues from other polymer components and container contamination during repackaging may cause reaction and gassing. If viscosity is high, foaming and overflowing can occur.

4.3 SiH Silicone Fluids

Hydrogen containing silane, siloxane, and silicone fluids can have a very high SiH content. When used and processed appropriately, they are unlikely to present a gassing hazard. When no active hydrogen content or catalyst is present, they are stable products.

4.4 Functional Silicone Fluids

Functional silicone fluids, in which another reactive group has replaced the hydrogen on the SiH polymer chain, can still generate hydrogen-gassing hazards due to the presence of unreacted residual SiH groups. Depending on process conditions, some active hydrogen products can remain. Specific analysis for SiH content should be done in order to properly evaluate the potential for hazardous reactions.

4.5 Water Reactive SiH Materials

Water reactive silicon compounds such as chlorosilane compounds, which include SiH functional groups, can evolve hydrogen on contact with water in the absence of other catalytic components due to the formation of hydrochloric acid. Since these compounds generate their own acid, which can serve as a catalyst for hydrogen formation, hydrogen release will occur when they come in contact with water.

For example,

$$CH_3\text{-}\underset{CH_3}{\overset{H}{Si}}\text{-}Cl + xH2O \rightarrow CH_3\text{-}\underset{CH_3}{\overset{H}{Si}}\text{-}OH + HCl + xH2O \rightarrow CH_3\text{-}\underset{CH_3}{\overset{OH}{Si}}\text{-}OH + HCl + H_2 + xH2O$$

Typical chlorosilane compounds with active SiH would have the general formula: $Cl_xR_ySiH_z$ where x = 1-3, y = 0-2 and z = 1-3, and R represents other substituent groups (if present) such as methyl, ethyl, etc.

These materials form cross-linked gels when reacted with water, and small pockets of trapped flammable by-products might form within or under the gelled material. These trapped flammables can reignite when they are exposed and emergency responders should be prepared for the potential reignition during cleanup.

Note: Responding to chlorosilane emergencies is covered in the *ASTM Manual on Chlorosilane Emergency Response Guidelines*, MNL33.

4.6 Information Sources

Consult the label, MSDS, and technical specifications or bulletins of the SiH product for information on the degree of SiH hazard posed and any special storage, handling, use, or disposal instructions.

5

Personal Protective Equipment

This chapter presents general information on appropriate personal protective equipment (PPE). To determine the type and level of PPE needed for a specific SiH containing product, consult the supplier's MSDS. PPE should be chosen that is appropriate for the specific job function being performed.

5.1 Skin protection

In general, any liquid-tight glove made of nitrile (NPR), butyl rubber, neoprene, or PVC coated material is ordinarily considered to provide adequate protection for SiH fluids and aqueous emulsions of SiH fluids.

If the SiH material is dispersed in an organic solvent, a glove should be selected that is resistant to the solvent in question.

5.2 Eye Protection

The use of safety glasses with side shields or goggles is recommended for eye protection.

If the SiH material is part of a mixture of chemicals, then the level of protection may need to be increased based on the potential eye hazards associated with the other components of the mixture.

Eye wash stations and safety showers in the workplace should be available.

5.3 Respiratory Protection and Ventilation

The level of respiratory protection and ventilation must be adapted to the specific application.

In general, hydrogen gas itself does not require any respiratory protection. However, the presence of other volatile vapors or gases should be considered when evaluating the level of respiratory protection required. If there are other hazardous chemicals present in the composition of the SiH material, which have respiratory hazards, then the level of respiratory protection should be determined based on those chemicals.

The primary concern for ventilation is to control the concentration of the flammable and/or toxic gases generated by preventing their accumulation in enclosed areas.

6

Control of Hazards

This chapter and subsequent chapters describe certain hazard mitigation and management practices that have proven helpful in handling SiH products. These chapters are not intended to present an exclusive or exhaustive list of such practices. Furthermore, companies may need to vary their approach with respect to a particular practice and/or implement one or more alternate measures depending on the specific circumstances of their situation.

6.1 Process Reactor Operations

6.1.1 Inerting

Before starting a new batch involving the use of SiH containing materials, the reaction system should be inerted with nitrogen or other inert gas to ensure that the oxygen content is reduced below a level at which ignition can occur. Three percent oxygen is generally regarded as the maximum safe limit. Inerting can be done by repeated pressurization and depressurization, pulling a vacuum on the system and then breaking it with an inert gas, or by purging and padding with inert gas based on a volumetric requirement to displace the oxygen in the reactor. Analytical testing to check that it will reduce the oxygen content to the required level should initially validate the procedure selected.

Measures should be taken to prevent oxygen from entering the equipment. During the batch sequence, the reaction system should be blanketed with nitrogen to ensure that a safe, non-explosive atmosphere is maintained in the vessel.

6.1.2 Raw Material Verification

Robust procedures should be put in place to avoid the inadvertent addition of the wrong raw materials to the reactor. As explained in Chapter 2-Nature of the Hazard, the inadvertent mixing of certain can lead to dangerous reactions. Raw material verification can be done at two stages in a batch sequence.

First, the materials can be checked before they are charged into the process to ensure that they are the correct ones for that particular batch. There are many ways in which this can be done. For example, some companies use a bar coding system to enter the identity of the materials into a computer control system that will only allow the batch sequence to proceed if the correct materials have been made available. Others have a system whereby materials have to be crosschecked by another operator.

After the materials have been charged into the reactor, a second stage of validation can be undertaken before the reaction is started. For example, before adding the catalyst, the SiH content of a sample taken from the reactor can be checked to ensure that it is within prescribed limits.

In order to minimize the potential for cross-contamination during material addition, either charge the SiH fluids first and then add the other raw materials to flush the system piping, or reserve a portion of a reactant to flush the system piping after charging the SiH fluid. The catalyst should not be charged directly before or after SiH charge as a dangerous reaction could occur.

6.2 Equipment for Reacting and Storing SiH Materials

6.2.1 Equipment Cleaning and Repairs

When cleaning out equipment that has contained SiH materials it is possible for hydrogen to be formed by contact with the cleaning agent. Caution should be exercised when using cleaning materials such as surfactants and detergents that are alkaline in nature (see section 3.1). Where possible, nonionic or neutral cleaning solutions or high flash hydrocarbon solvents should be used to avoid hydrogen-releasing reactions.

Any hydrogen formed during clean out or maintenance may collect in confined spaces inside or around the equipment creating an explosive atmosphere. Good ventilation is therefore required in areas where these activities are being carried out. If hot work (*e.g.*, welding) is to be performed, then a rigorous risk assessment will help ensure that all hazards have been identified and appropriate precautions taken.

Prior to restarting equipment after clean out, all vessels and associated piping systems should be verifiably clean and dry. In particular, trace acids and bases must be removed prior to charging reactors, and filling storage tanks, and packaging containers.

6.2.2 Safety Equipment

Hazard studies and risk assessment should be undertaken to determine the appropriate level of safety protection required for a specific SiH reaction system. Such studies would normally involve, but would not necessarily be limited to, consideration of the need for the following measures:

- Temperature and pressure indication with high temperature and pressure alarms
- Level indication with high-level alarm interlocking the feed system to prevent overfilling
- Agitator running/stopped (or speed) indication with stopped alarm
- Emergency water supply to back up the normal cooling water supply
- Catalyst deactivation system
- Emergency shut down system that isolates the feeds and any heating source, and applies full reactor cooling in the event of high pressure, high temperature or agitator failure
- Mechanical pressure relief system

6.2.3 Storage and Filtration Equipment

All storage tanks for SiH products should be “blanketed” or “padded” with inert gas such as nitrogen. Grounding and bonding should be provided for tanks and ancillary transfer equipment, and when filling drums and Intermediate Bulk Container (IBCs) (see section 7.5). Free-fall or splash filling of vessels and containers should be avoided by the use of grounded dip pipes, bottom filling methods, *etc*.

Silicone fluids generally have low electrical conductivity; therefore, high levels of static may be generated when filtering SiH materials. Care should be taken to ensure that effective bonding and grounding is in place, and that lines are purged with nitrogen prior to and after filtration, particularly if the equipment is to be subsequently opened.

7

Engineering Control of Hazards

7.1 Building Design

Dedicated process units are preferred for SiH products however, if this is not possible, process units should not have any direct connections to other storage or processing units where catalytic contaminants are present.

Storage vessels should be located outside, remote from buildings and other facilities and process piping.

Buildings should be provided with an exhaust ventilation system. Special precautions should be taken against potential accumulation of flammable gasses and vapors within the building confines by properly designed ventilation systems. Hydrogen, being lighter than air, will tend to accumulate at ceiling level.

Depending on the fire hazard potential of the processed SiH products and other raw materials (*e.g.*, carrier or cleaning solvents), adequate fire protection for the specific hazards should be incorporated into the design and construction of the building housing SiH process units. Firewalls of adequate rating may be necessary in accordance with National Fire Protection Association (NFPA) and local codes. All structures containing flammable SiH products should be constructed of non-combustible materials. Exterior walls of enclosed buildings may require explosion relief panels.

The building's structure should have a permanent electrical bonding and grounding system that complies with appropriate codes.

Eyewashes and safety showers should be located appropriately.

Adequate exits and emergency plans for evacuation routes or means of exits should be utilized for units producing or using SiH products.

7.2 Equipment Design

The design of piping and equipment where SiH products are involved is strongly dependant on the specific reaction process in question. The following subsections provide only general information about neutral SiH products.

7.2.1 General

The total equipment (*e.g.*, lines, pumps, valves, vessels) should be designed so that it can be thoroughly drained and dried before introducing any SiH product, unless SiH emulsions and dispersions are produced.

Prior to operation, the system should be tested for leaks at or above operating pressure with dry inert gas (*e.g.*, nitrogen). After major maintenance activities each joint should be "soap-tested" and checked for leaks.

Whenever necessary, totally enclosed systems should be used. Atmospheric openings or vents may allow moisture to enter the system potentially causing or contributing to the generation of hydrogen (see section 2.1).

Dry inert gas (nitrogen) should be used for pressurizing vessels, priming pumps, blanketing tanks, and filling or withdrawing tank contents.

7.2.2 Materials of Construction

Depending on process conditions (*e.g.*, pressure, temperature, corrosiveness), the following materials may be used:

- Carbon steel
- Better grades of stainless steel to exclude rust which may cause catalytic side effects on SiH products (e.g., decomposition, rearrangement, hydrogen formation)
- Enamel
- Lined materials (care should be taken to control static electricity)
- Monel, Hastelloy, Inconel

7.2.3 Vessels

Storage vessels should be designed and fabricated in accordance with applicable codes and standards.

For storage tanks, the associated design pressure must meet the requirements of applicable codes, standards, and regulations with respect to the properties of the stored SiH product.

Generally, vessels should have emergency vents that meet applicable code requirements.

Vessels should be equipped with pressure-relief valves to relieve excess internal pressure due to external fire impingement or inside overpressurization (decomposition, hydrogen formation). A non–fragmenting-type rupture disk should be used ahead of the relief valve. "Rain hats" should be used over the ends of the vent pipe outlets.

A remote impoundment tank to receive viscous gassing SiH materials, located downstream of the reactor and outside of the process area, can help decrease the danger of fire or explosion inside the process structure.

A preventive maintenance schedule program should be established to inspect pressure relief systems especially when clogging is a possible danger for malfunction.

Vessel and storage tank supports should be made of reinforced concrete or structural steel protected by fire-protective coatings.

7.2.4 Piping

Stainless steel, enamel, or lined piping is preferred (see section 7.2.2).

Welded and flanged piping connections will help maintain a leak-tight system. The class of flange should be based on the pressure-temperature rating of the process.

Prior to use, all piping should be checked by pressurizing with inert gas (nitrogen) for tightness. All piping should be checked for leakage.

Valves can be stainless steel, lined steel, Teflon® coated steel, or enamel valves.

Within production facilities having a high potential of fire or explosion hazard, remotely controlled valves are preferred for bottom connections on vessels and storage tanks. A quick shut-off in case of fire or other emergency can minimize domino effects.

7.2.5 Pumps

Pumps with features that prevent leakage to the atmosphere are preferred. In general, magnetically driven pumps (canned pumps) are preferred, although inert gas-driven diaphragm pumps can also be used depending on the properties of the material being pumped. Care should be taken to assure that blocked flow conditions cannot be achieved, as the introduction of heat may cause these materials to decompose.

7.2.6 Instrumentation

Equipment should be chosen according to the demand for a safe process control.

Modulating leak-tight control valves are preferred. Remote control of all-important valves should be installed in plant sections with high hazard potential.

Stainless steel, diaphragm or coated metal pressure switches, and/or pressure transmitters are preferred in all cases where a risk of pressure drop or rise must be controlled.

Level indication with a high-level alarm is preferred on all vessels and storage tanks. Feed and bottom discharge valves on storage tanks and vessels should be remotely controlled as well as pumping equipment and integrated in emergency shut-down switches where there is a high hazard potential.

Independent level control equipment on storage tanks will help prevent overfilling. Process-actuated high-level switches can be used for alarming high-level condition and interlocking to process shutdown.

Flanged connections on instrument lines will help minimize possible leak paths.

7.3 Ventilation

Enclosed processing buildings should be ventilated at a rate to prevent the formation of explosive atmospheres. If mechanical ventilation is used, the electrical equipment must meet applicable code requirements. Special provisions should be made for prevention of hydrogen accumulation inside buildings. Since hydrogen is lighter than air, it can accumulate at ceiling level.

7.4 Electrical Equipment

All electrical equipment must conform to applicable code requirements. Vapor-tight and corrosion-resistant electrical equipment is preferred.

7.5 Static Electricity

Pure SiH fluids show a very low electrical conductivity in general. Thus, SiH fluids are extremely prone to accumulation of static electricity.

Static electricity discharges can ignite flammable SiH product vapor. It is therefore essential to inert the whole system in which flammable SiH products or mixtures are present. Dry inert gas (nitrogen) should be used for transfer operations.

Static electricity may be generated when SiH products flow through or are discharged from a pipe or fall freely through space. Splash filling is particularly hazardous and should be avoided. Unless a grounded dip tube is installed, vessels and tanks should be bottom filled. Fill lines should be conductively bonded to provide a path to ground externally.

Ground wiring should be designed to provide reasonable protection against physical wear. Periodic checks of continuity to ground should be conducted.

8

Fire and Explosion Protection

8.1 Fire Hazards

SiH containing materials pose a unique fire and explosion hazard, because they have the potential to evolve hydrogen, or rearrange to form flammable methylsilanes.

Hydrogen is lighter than air, has a broad explosion range (Lower Explosive Limit of 4 vol % and the Upper Explosive Limit is 74 vol %). The hydrogen/air mixture can be ignited with very low energy ignitions sources (*e.g.*, static sparks), and burns with a hot, non-luminous flame that is difficult to see. SiH materials with relatively high flashpoints that are releasing hydrogen gas (*e.g.*, SiH emulsions) can create unexpected fire and explosion hazards.

The mechanisms of Methylsilane formation are reviewed in Chapter 2-Nature of the Hazard. Methylsilanes are flammable gases that will ignite in low oxygen-containing atmospheres, with low energy ignition sources (*e.g.*, static sparks).

Some SiH siloxanes may pose a fire hazard through spontaneous combustion if in contact with absorbent material, such as open cell insulation. This is a phenomenon exhibited by certain other polysiloxanes and many organic materials. Care should be taken to prevent leaks and spills from contacting such materials. Closed cell insulation can also be installed in areas of anticipated liquid leaks or spillage.

Additional information on the fire hazards of the particular SiH containing material being utilized can be found in the supplier's MSDS.

8.2 Fire Prevention

Depending on the flashpoint listed on the supplier's MSDS, generally recommended fire prevention measures include:

- Use of classified electrical equipment, where appropriate
- Purging and inerting of equipment and containers with dry nitrogen. When purging and inerting are carried out, it is critical that levels of oxygen (O_2) be kept low. The minimum O_2 concentrations required for hydrogen combustion are approx. 5 vol % (which is less than half that of typical hydrocarbons), and an adequate safety factor should be applied to this value
- Control of static electricity including loading and unloading of materials by using dip pipes or by bottom filling and by using bonding and grounding equipment
- Control of cutting, welding and other "hot" work
- Control of smoking and other potential ignition sources

Adequate ventilation should be provided where hydrogen gas generating materials are stored or handled. Since most SiH materials are provided with vented bungs that slowly release hydrogen, these materials should be stored and used in a well-ventilated area. It's important to ventilate the upper areas of buildings or storage facilities using or storing potential hydrogen-liberating materials, to avoid the generation of pockets of hydrogen.

In cases where the MSDS lists a relatively high flashpoint, but warns for a potential hydrogen release (*e.g.*, SiH containing emulsions), extra care, similar to those used with flammable liquids, should be taken, including:

- Control of static electricity
- Control of cutting, welding and other hot work
- Control of smoking and other potential ignition sources
- Good ventilation of the container when stored and opened up

8.3 Extinguishing Agents

Fires involving SiH polysiloxane materials can be difficult to extinguish. Control can be accomplished with most extinguishing agents such as water fog, foam, dry chemical agents (though certain of types of dry chemical agents can increase the release of hydrogen), or carbon dioxide. AFFF alcohol compatible foam has been shown to be an effective method for extinguishing well-developed fires. As with all burning liquids, straight water streams should be avoided as they can agitate and disperse the burning liquid and increase the intensity of a fire.

Appropriate caution should be exercised with the handling and collection of SiH materials after a fire, since caustic dry powder or water based extinguishing materials may provide sufficient contamination to generate hydrogen and other flammable by-products. Hydrogen may accumulate in poorly ventilated or confined areas and result in flash fire or explosion, if ignited. Foam blankets may also trap hydrogen or flammable vapors, with the possibility of explosions or ignitions under the foam layer.

The products of combustion of SiH polysiloxane materials are silicon dioxide (silica), carbon dioxide, carbon monoxide, water vapor and various partially burned compounds of silicon, and carbon. Exposures to these products should be avoided by use of appropriate personal protective equipment and ventilation.

9

Spill Management

When responding to spills, personnel should follow established industrial safety procedures and wear proper personal protective equipment as detailed in Chapter 5-Personal Protective Equipment. Personnel must be adequately trained and adhere to all local, state, and federal spill management and reporting regulations.

The area in which a spill occurs should be isolated and the spilled material contained to prevent runoff. It is important to prevent spills from entering drains or sewers, where they could create an explosion hazard, and from entering environmentally sensitive areas.

Neutral, non-combustible absorbent materials (*e.g.*, sand, clay absorbent, calcined diatomaceous earth) should be used to collect spilled SiH containing materials. Used absorbent should be properly packaged, labeled, and disposed of in accordance with local, state, and federal regulations.

For leaking containers, contain and control the leak. If necessary, transfer the liquid into another vessel or portable container. To avoid the possibility of electrostatic discharge, take appropriate precautions (*e.g.*, inerting, bonding, and grounding) for possible hydrogen-containing environments.

Recovered product may be contaminated thereby increasing the risk of chemical reactions that generate hydrogen and other flammable by-products. Contaminated material should be kept separate from uncontaminated product in an appropriate container, label correctly, and if necessary, consult with the supplier on disposal (see Chapter 2-Nature of the Hazard).

Contaminated roadways, storage areas, and walking surfaces should be cleaned to remove slippery residues. Medium pressure water and non-ionic emulsifying agents should be used.

10

Waste Management

SiH containing waste can be generated during the following operations:

- Sampling of raw materials to check quality
- Sampling reactors to determine SiH content (conversion control)
- Draining of reactors, pipework, or hoses
- Generation of process wastes such as:
    - Distillates (volatiles)
    - Filter cake
    - Reactor waste, reinstates
    - Off-grade or scrap material

SiH containing waste must be managed in accordance with local, state, and federal waste management regulations. Because many chemicals (*e.g.*, amines, alcohols, aqueous acids, and alkali) react with SiH materials, **SiH waste should be segregated from non-SiH waste.** These segregation measures should include:

- Keeping pure SiH product waste separate from contaminated or catalyzed SiH waste
- Separating waste collected from different production units or sources to avoid unintentional mixing
- Not mixing SiH containing filter cake with solid wastes from other processes
- Informing waste disposal contractors of the nature of SiH containing wastes and advising them to incinerate or otherwise process the material separately
- Not using SiH containers to hold other wastes

When storing SiH wastes, care should be taken to ensure that the containers are:

- Suitable for the purpose
- Correctly labelled (preferably with the warning "SiH containing waste-may liberate hydrogen")
- Fitted with vented bungs
- Properly cleaned and decontaminated
- Not stored in areas where they will be exposed to moisture, high temperatures. or direct sunlight (solar heating)

Contact your supplier immediately in the event of a bulging container (see section 13.5).

Care should be taken when adding waste material to a container that cannot be grounded (plastic or lined metal) and which has already been partially filled with SiH waste and left standing for a period. Hydrogen may have been released and accumulated in the container's headspace (the unused internal portion of the container) forming an explosive mixture. This can be ignited by the insertion of an earthed metal object, such as a filling lance (filler tube), due to the spark discharge of static electricity that has built up on the container.

Before inserting the lance, it is good practice to let the container stand for several minutes after removing the filling cap. This will allow the hydrogen, which is a very light gas, to escape and dilute the headspace to a safe concentration. An additional precaution is to purge the container with nitrogen prior to adding more material.

11

Training and Job Safety

Safe handling of SiH products depends in large part on knowledgeable supervision and effective employee education including proper training in industrial safety practices and use of safety equipment. Training must comport with local, state, and federal regulatory requirements.

Before undertaking any training of the employees who are engaged in handling or processing SiH products, the supervisor should be thoroughly familiar with the contents of the MSDS. In addition to being well acquainted with the hazardous characteristics of SiH products and the precautions explained in the MSDS, the supervisor should seek further supplementary information and assistance.

If possible, the supervisor should consult with industrial hygiene and safety specialists before finalizing a safety review of operations involving SiH products.

After becoming thoroughly familiar with the hazardous characteristics of SiH products, the supervisor should review each procedure step-by-step, preferably with the workers directly involved in the use and handling of SiH products. During this review, all potential hazards should be identified and appropriate precautionary measures determined. The review should be concerned not only with the hazards of contact with or exposure to SiH products, but also with the hazards that may be involved in handling containers, in operating equipment, waste disposal and any other hazards associated with the work. The need for personal protective equipment should be determined, including its proper use as well as its limitations. All significant hazards, together with the precautions to be followed, should be addressed in the standard operating procedures.

Emergency procedures should be established, including the location and operation of safety showers, fire extinguishers, alarms, *etc.*

For critical steps in the process, (*e.g.*, where overcharge or undercharge may cause uncontrollable reactions) consideration should be given to making these supervisory checkpoints.

Employees should understand the chemistry and chemical reactions of the process as well as sources of potential cross-contamination in the dedicated or shared equipment.

The safety review described above should be conducted regularly (*e.g.*, annually) for all chemical processing operations and in advance of initiating a change in a process. The supervisor should periodically check to make certain employees are following prescribed instructions and precautions. Written standard operating procedures with safety information are also helpful when training new workers.

The following subjects should be addressed in the safety training lessons for the employees:

- Potential hydrogen generation from SiH products
- Hazards resulting from pressure build-up, fire or explosion

- Hazard potential and properties of hydrogen (highly flammable gas, lower explosion limit (LEL), upper explosion limit (UEL)) and hydrogen/air mixtures (very hot, non-luminous flame, extremely explosive)
- Handling of bulging (over-pressurized) drums or containers (consulting specialists, fire brigade) (see also section 13.5).
- Cleaning procedures for vessels, tanks, drums, and IBCs, *etc*.
- Separation of waste with SiH products from all other waste to avoid consecutive reactions (hydrogen generation) see also Chapter 10-Waste Management
- PPE Selection
- Spill Management

12

Shipping, Labelling, and Marking

For shipping, labeling, and marking requirements, reference should be made to the Material Safety Data Sheet (MSDS) or the shipping documents received from the supplier, as well as to applicable codes and regulations. Shipments must be prepared in accordance with U.S. Department of Transportation (DOT), Canadian Transport Dangerous Goods (TDG) and any carrier-specific requirements. Personnel involved in preparing shipments must be appropriately trained.

For shipment of SiH products, careful attention should be given to the possibility of hydrogen release and accumulation inside of shipping vehicle or compartment.

Air shipments should specifically comply with the International Air Transport Association (IATA) packaging requirements, which forbid the use of vented containers.

A stability test or a quarantine procedure (refer to your supplier) should be considered on a case-by-case basis.

Chapter 2.12 (substances which, in contact with water, emit flammable gases) of the GHS (*Globally Harmonized System of Classification and Labeling of Chemicals*) provides guidance on classification and labeling that may apply to SiH products.

Appendix A provides an example test method, which if used in conjunction with the MSDS and other resources, may aid personnel in identifying and classifying SiH materials for shipment and disposal.

13

Handling of Containers (Tankers, Drums, *etc.*)

13.1 General Considerations

All safety and other precautions documented in other sections of this manual should be observed when loading or unloading SiH products. It is particularly important that personal protective equipment be used. Normal procedures for handling corrosive and flammable materials may also apply. The following general considerations are relevant:

- Drums, IBCs, and trailers used for SiH type materials should be verified to meet all applicable Department of Transportation (DOT)/Transport of Dangerous Goods (TDG) regulations
- All containers and equipment that can be exposed to SiH type materials should be checked for compatibility in accordance with guidance from your suppliers MSDS sheet
- Containers should be inspected for leaks both before and after filling operations
- Protective equipment as specified by your supplier's MSDS should be used for all operations involving SiH type materials
- Only employees who have been trained on the hazards of SiH type materials should be assigned to loading, unloading, and handling of these materials
- Prior to unloading or use of SiH materials it is advisable to verify that the correct material is being used by verifying package labeling, COA, *etc.*
- An operator or control equipment should continuously monitor all operations. The supplier's guidelines for safe handling and transfer should be followed
- An emergency shower and eyewash station should be provided at the loading or unloading area (see Chapter 5-Persona Protective Equipment)
- The fill level in the container should consider the heat expansion of the liquid so that the container doesn't overflow
- Hose-fitting or pipe connections should be closed with a cap or a blind flange while not in use
- The storage area for containers that contain SiH products should protect the containers from heat or mechanical damage. Store the containers in accordance with the local code requirements for SiH products
- If a drum, rail tank car, road tanker, demountable tank, or IBC is involved in an accident or develops a leak; the local emergency services should be notified. Contact the manufacturer of the SiH product immediately using emergency response information on the MSDS or label (see also Chapter 9-Spill Management). All local, state, and federal spill reporting and response requirements must be satisfied.

13.2 Emptying Containers

When emptying containers that contain SiH products the following general guidelines should be employed:

- Containers should be located in a well-ventilated area or in an area where local exhaust is available for use
- Containers should be connected to a grounding device
- Containers should be purged or pressured with an inert gas (such as nitrogen)
- Trailers should be emptied via the rear unloading connection

13.3 Filling Containers

When filling containers with SiH type materials the following general guidelines should be employed:

- Containers should be filled in well-ventilated areas or those areas provided with local exhaust systems
- Containers should be inspected to assure they are clean and dry. If the container has been recently cleaned it should be verified that a strong acid, base or detergent was not the last cleaning agent
- Containers should be connected to a grounding device
- Containers should be purged with an inert gas (such as nitrogen) prior to filling
- Drums and IBCs should be filled utilizing a drumming nozzle that extends to near the bottom of the container to avoid splash filling
- Trailers should be filled via the rear loading connection to avoid splash filling
- Filled containers such as drums or IBCs should be equipped with a self-venting bung

13.4 Handling Empty SiH Product Containers

The following general guidelines should be employed for safe handling of empty SiH containers:

- Drums and IBCs should be rinsed with water until residual SiH materials are removed Never clean directly with caustic or acid solutions, as residual SiH materials will react to release hydrogen
- Empty SiH containing containers should not be reused unless they have been thoroughly cleaned and dried. Empty SiH containers should only be reused to hold SiH materials
- Trailers should be emptied as thoroughly as possible then rinsed with water prior to cleaning by standard commercial means

13.5 Bulging, Leaking, or Defective Containers

If a container is found to be bulging or leaking refer to the following general guidelines:

- Bulging containers should be treated as though hydrogen under pressure is present. Only trained HAZMAT specialists should handle these containers. Non-sparking tools and appropriate personal protection equipment (PPE) should be used. Work should be conducted in an open well-ventilated area free from sources of ignition. The container's pressure should be released gradually. The material supplier should be contacted for further instructions

- Leaking containers should be handled in accordance with guidelines established in Chapter 9-Spill Management
- Contact the supplier immediately upon receipt of defective containers

Appendix Glossary of Terms

absorbent—a material having capacity or tendency to absorb another substance [adj.] having power or capacity or tendency to absorb or soak up (liquids); “as absorbent as a sponge.”

active hydrogen—a hydrogen atom that is available to participate in disassociation and condensation reactions (i.e., where the hydrogen is not strongly bound to another atom covalently sharing electrons). For example, hydrogen atoms bonded to carbon atoms in methyl groups are non-reactive while hydrogen atoms bonded to more electronegative elements (i.e., more ionic compounds) such as oxygen in water or strong acids are more readily available for reaction.

adsorbent—a material having capacity or tendency to adsorb another substance having capacity or tendency to adsorb or cause to accumulate on a surface.

AFFF—aqueous film forming foam.

amine—a compound derived from ammonia by replacing hydrogen atoms by univalent hydrocarbon radicals.

blanketed—inerting a container with an inactive gas such as nitrogen

bonding—the electrical connection of two containers to equalize static electricity charges

branched SIH polymers—any silanic hydrogen containing material, where the active hydrogen is not attached to the ends of the molecule, but are attached to pendant groups within the silicon backbone throughout the molecule. These materials are typically depicted by the nominal structure MDxD’yM where the D’ unit represents the hydrogen containing species.

caustic—any strongly corrosive chemical substance, especially one that attacks organic matter. A caustic alkali is a metal hydroxide, especially that of an alkali metal; caustic soda is sodium hydroxide, and caustic potash is potassium hydroxide

dip pipes (tubes)—dip and inlet pipes are designed to introduce fluids at the bottom of the vessel to minimize static electricity generation

drumming nozzle—a filling tube or pipe designed to fill at the bottom of the vessel to minimize static electricity generation

gassing triangle—three conditions are simultaneously required to produce hydrogen in SiH containing silicones. These conditions are called “the gassing triangle” and include the presence of SiH, the presence of a proton donor or active hydrogen, and a catalyst.

elastomer—any of various elastic materials that resemble rubber (resumes its original shape when a deforming force is removed)

electrical conductivity—a measure of how well a material accommodates the transport of electric charge.

emulsion—*in chemistry,* a colloid in which both phases are liquids, *e.g.*, an oil-in-water emulsion.

emulsifying agents—a substance that can be used to produce an emulsion out of two liquids that normally cannot be mixed together (such as oil and water).

explosive (flammable) limits—the range of concentrations over which a flammable vapor mixed with proper ratios of air will ignite or explode if a source of ignitions is provided.

functional silicone fluids—silicone fluids that contain other chemical groups in place of the methyl groups found in ordinary polydimethysiloxane. For example, in SiH fluids some of the methyl groups are replaced by hydrogen. Other common constituent groups include hydroxyl groups, methoxy groups, amino groups, etc.

Globally Harmonized System Of Classification And Labeling Of Chemicals (GHS)—a system that is designed to promote common, consistent criteria for classifying chemicals and developing compatible labeling and safety data sheets. The United Nations Economic and Social Council Subcommittee adopted the GHS and recommended that it be disseminated throughout the world. This system is intended to enhance public health and environmental protection, as well as to reduce barriers to trade.

grounding—the fastening of electrical equipment to the earth.

head space—a term used to describe the “air space” above/around the product in a package.

hydrogen functional silanes—silanes are non-polymeric silicon compounds of the form SiR_4 where R can be a variety of different chemical groups. In a hydrogen functional silane there can be from one to four hydrogen groups and the empirical formula would have the form SiH_xR_{4-x}.

IATA—International Air Transport Association.

inerting—the partial or complete substitution of the air or flammable atmosphere by an inert gas as a method of explosion prevention.

intermediate bulk container (IBC)—a rigid or flexible portable packaging, other than a cylinder or portable tank, which is designed for mechanical handling. Standards for IBCs manufactured in the United States are set forth in 49 CFR Part 178, subparts N.

Lewis acids or bases—the Lewis theory defines an acid as a compound that can accept a pair of electrons and a base as a compound that can donate a pair of electrons. Boron trifluoride, BF_3, can be considered a Lewis acid and ethyl alcohol can be considered a Lewis base.

magnetically driven pump—a seal-less pump that utilizes a magnetically coupled drive mechanism.

methyl silane—silanes are non-polymeric silicon compounds of the form SiR_4 where R can be a variety of different chemical groups. In a methyl silane, there can be from one to four methyl groups and the empirical formula of the silane would have the form $Si(CH_3)_xR_{4-x}$.

padded—the process of inerting the headspace of a vessel with an inactive gas such as nitrogen.

PTFE—Polytetrafluoroethylene (Trade name: Teflon®).

pyrophoric—a material that ignites spontaneously on contact with air.

RTV silicone—room-temperature vulcanizing silicone. A silicone that usually comes as a flowable liquid is used in sealants, mould making, encapsulation and potting.

SiH—a material or product containing hydrogenosilane groups.

Si–H—the hydrogen–silicium bond or the hydrogenosilane group.

SiH polysiloxane—a silicone polymer where some of the silicon atoms in the polymer chain have hydrogen directly attached to the silicon.

For example:

$$\begin{array}{lccccccl} & CH_3 & & H & & CH_3 & \\ & | & & | & & | & \\ -[-O-- & Si & --O-- & Si & --O-- & Si & -]_n- \end{array}$$

| | |
CH_3 CH_3 CH_3

siloxane—any of a large class of compounds that have alternate silicon and oxygen atoms.
vent bung—a pressure-relieving device used on drums.

APPENDIX A

SiH CONTAINING MATERIAL

HYDROGEN RELEASE RISK EVALUATION TEST[2]

1.0 Purpose

1.0.1 This test is designed to enable the user to evaluate the potential for hydrogen gas release from SiH materials when in contact with caustic (pH ≥ 12.5) solutions.

2.0 Scope and Application

2.0.1 This procedure measures both the amount and rate of hydrogen release.

2.0.2 This procedure can be used on any solid or liquid SiH material except for water reactive SiH compounds, such as chlorosilanes (*e.g.* monochlorosilane, dichlorosilane, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, tetrachlorodisilane, *etc*.).

3.0 Classification Scheme Summary

3.0.1 If a sample of a SiH material generates more than 1 ml/g of H_2 per hour (1 ml per g per Hour is equivalent to 1 L per Kg per Hour) when in contact with a basic challenge solution, it should be considered a candidate for further risk assessment.

4.0 Apparatus and Equipment

4.0.1 100 ml round bottomed flask (two neck)

4.0.2 Stirring apparatus set to produce approximately 30 rpm. This can be a rotating magnet and stirring bar combination or a motor driven propeller stirrer.

4.0.3 Addition funnel

4.0.4 Collection vessel for measuring the volume of gas release typically a U tube (1 mm gas delivery tube, see diagram item H) or inverted graduated cylinder (up to 250 ml) arrangement where the volume of gas released can be measured by water displacement

[2] This test method has not been adopted by any regulatory agency; but is designed as an aid to assist the user in characterizing material, AND should be used in conjunction with MSDS, supplier information, experience, and professional judgment.

OR

A flow meter set up to measure (and record) the rate of gas release and the total volume released during the duration of the test.

4.0.5 A clock or other time measuring device.
4.0.6 Flexible tubing
4.0.7 Glass connectors and plugs appropriate to the flask configuration, stirring apparatus, addition funnel and collection device
4.0.8 Graduated cylinder for measuring liquids
4.0.9 Scales for weighing samples
4.0.10 Safety shield

5.0 <u>Reagents</u>

5.0.1 0.1 – 0.5 g, 1 g and/or 10g samples of the SiH material to be tested
5.0.2 50 ml of 1.0 N Potassium hydroxide (KOH) in 80% Ethanol / 20% Water solution per test run
5.0.3 Deionized water used to fill the gas collection vessel

6.0 <u>Safety Precautions</u>

6.0.1 Wear appropriate gloves, such as disposable nitrile rubber when handling sample material and test solutions.
6.0.2 Wear safety glasses with side shields or chemical goggles when working with the basic test solution.
6.0.3 Avoid contact with KOH solutions.
6.0.4 Remember that the H_2 gas produced is highly flammable. Avoid sources of ignition.
6.0.5 Be alert for any signs of over-pressurization of the apparatus
6.0.6 Because a large volume of hydrogen can be released from a small amount of material (every 2 g of H_2 released as gas will displace 24.5 liters), in order to avoid rapid over-pressurization and failure of the test set-up, the size of the sample tested should start out small and proceed to larger sample sizes only if necessary for accurate measurement purposes.
6.0.7 Where feasible, a safety shield should be used during testing to limit the potential for personal injury if a failure of the test set-up should occur.

7.0 <u>Procedure</u>

7.0.1 Set up glassware and stirring apparatus.
7.0.2 Weigh 0.1 g of the SiH material to be tested, and transfer into the round-bottomed flask.
7.0.3 Measure 50 ml of basic challenge solution into the addition funnel.

7.0.4 Start the stirrer and add the contents of the addition funnel to the flask. Stir sample and test solution for 5 minutes.
7.0.5 Observe the reaction closely as it progresses, record the amount of gas evolved at 1-minute intervals for the first 5 minutes, then record the amount of gas evolved at 5-minute intervals for up to one hour.
7.0.6 If the amount of hydrogen released is too small to measure accurately, repeat the test using a 1 g sample.
7.0.7 If the amount of hydrogen released is still too small to measure accurately, repeat the test using a 10 g sample.
7.0.8 Based on the recorded amounts of gas evolved calculate the release rate(s).

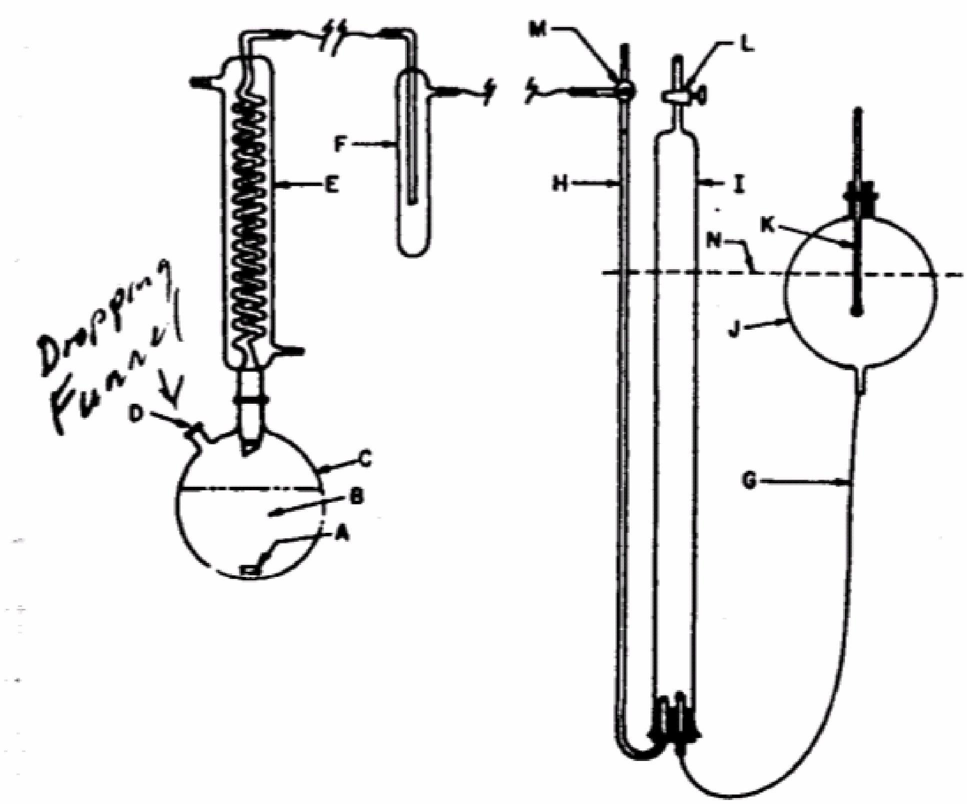
NOTE: If a 10-gram sample does not yield any measurable hydrogen, the material may be considered not to present any significant risk of hydrogen release. Further testing with larger sample sizes should not be necessary.

8.0 Interpretation of Results

8.0.1 If the volume of gas released exceeds the capacity of the collection vessel this indicates a high level of available SiH reactive sites. The potential for high volume H_2 gas releases during an upset condition such as inadvertent mixing with an incompatible material should be considered during product stewardship hazard evaluation and risk assessment.
8.0.2 If the rate of H_2 release from the sample is exceptionally rapid or violent this should also be considered during hazard evaluation and risk assessment, especially in the design of pressure relief systems and process safety.
8.0.3 If the release rate is too low to accurately measure at the largest sample size tested (10 g) then the SiH hazard potential should be considered very low and not significant for risk evaluation purposes.
8.0.4 If the release rate were less than 1 L per Kg per Hour the SiH hazard potential would be considered low.
8.0.5 If the release rate is equal to or over 1 L per Kg per Hour but less than 20 L per Kg per Hour the SiH hazard potential would be considered moderate.
8.0.6 If the release rate were equal to or over 20 L per Kg per Hour the SiH hazard potential would be considered high.
8.0.7 If the SiH release rate is rapid and is equal to or over 10 L per Kg per Minute [the corresponding DOT threshold for the “highest” level of water reactive materials is 10 L per KG per Minute See 49 CFR 173.125(d)] the SiH hazard potential would be considered extremely high.

9.0 Diagrams

Figure 1.



A. Magnetic stirring bar
B. Hydrolysis solution
C. 3-neck or 2-neck 100-mL round bottom flask
D. Dropping funnel
E. Spiral condenser
F. Cold trap (dry ice)
G. Flexible Polyvinyl tubing
H. Heavy wall glass tubing (1 mm inner diameter)
I. 250-mL graduated burette
J. Leveling bulb (separatory funnel)
K. Thermometer (Was not used)
L. Straight-bore stopcock

M. T-bore stopcock
N. Water level

Prior to use, the inside of the glass tubing (Item H) was silanized with a solution of 20% dichloromethyl silane in methylene chloride

After assembly of the apparatus, dry ice is added to the cold trap (Item F). A known amount of sample was added to the bottom of flask C and 50 mL of basic solution was added to the graduated dropping funnel (Item D). The apparatus is assembled as in Figure 1 with stopcocks L and M opened to vent. Water levels in units H, I, and J are confirmed as co-planar and an initial reading is taken from the graduations in burette I. Stopcock L is closed and the t-bore stopcock, M, turned to vent the system externally. Clamps are secured and the system is purged with nitrogen through the bypass in the dropping funnel. The t-bore stopcock is turned to flow internally and the dropping funnel capped. The magnetic stirrer is engaged and the dropping funnel (D) stopcock released to allow solvent to mix with the sample in flask C.

The leveling bulb (J) is lowered just below the bottom of the curve of inlet tube H. To take measurements, the leveling bulb is raised until water levels were co-planar in H, I, and J and the water level in burette I is recorded, once a minute, for the first five minutes and every five minutes thereafter for one hour or until the reaction is complete. The level of the water at graduations in burette I are recorded. Following completion of the test, the generated gas is released into the laboratory fume hood.

10.0 <u>References</u>

10.0.1 United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria 3rd revised edition, ST/SG/AC.10/11/Rev.3, 1999, Section 33.4 Test N.5: Test method for substances, which in contact with water emit flammable gasses.

10.0.2 Global Harmonized System for Classification and Hazard Communication Reference Document 2 Physical Hazards, Chapter 2.12 Substances Which, In Contact With Water, Emit Flammable Gasses

10.0.3 United States Environmental Protection Agency, SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Chapter 7, Characteristics Introduction and Regulatory Definitions, 7.3 Reactivity

10.0.3.1 Interim Guidance for Reactive Cyanide

10.0.3.2 Interim Guidance for Reactive Sulfide