SAFE HANDLING OF SiH PRODUCTS

CONTENTS

CHAPTER I **INTRODUCTION**

The Centre Européen des Silicones (CES) is the European association which within the framework of the European Chemical Industry Council (CEFIC) represents the European producers of silicones and their starting materials. Member companies are Degussa, Dow Corning Europe, GE Bayer Silicones, GE Specialty Materials (Suisse), Rhodia Silicones, Shin-Etsu Silicones Europe and Wacker Silicones. This brochure has been produced by the CES Operating Safety Committee.

The purpose of this brochure is to provide all persons who will use, handle, or otherwise be exposed to silicon-hydrogen products with information about their safe handling and use. By definition, silicon-hydrogen products (or "SiH products" in short) are silicon products containing Si-H bonds. These products will liberate hydrogen in some circumstances, presenting a major risk of explosion or fire that is proportional to the rate and/or volume of hydrogen released. The silicon-hydrogen products concerned are:

- **Chlorosilanes** containing Si-H bonds such as Me_2HSiCl, $MeHSiCl_2$,$HSiCl_3$ and others which will also readily react with water to form corrosive and toxic hydrogen chloride gas and hydrochloric acid (See the «Safe Handling of Chlorosilanes » brochure from CES)
- **SiH silicone fluids** such as $Me_3Si\text{-}O\text{-}(Me2Si\text{-}O)_n\text{-}(MeHSi\text{-}O)_m\text{-}SiMe_3$ and others, generally with a very high SiH content.
- **SiH emulsions**
- and to a certain extend **Compounded elastomers** generally RTV2, HTV and LSR based on SiH-SiVinyl curing system
- **Functionalised silicone fluids** for their unreacted residual SiH

Careful attention to equipment and facility design, to operating and emergency procedures, and to storage and transport aspects is essential to eliminate risks.

The full text of this publication should be consulted for information on the hazards of SiH products and suggestions for their safe handling and use. In addition, Material Safety Data Sheets (MSDS) should be obtained from the manufacturer. The MSDS may provide more specific detailed information.

The information and advice in this brochure is given in good faith, but it is for the user to satisfy himself of the suitability of the recommended protective equipment, and of other safety information, for his own particular situation.

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CHAPTER II **NATURE OF HAZARD**

2.1 THE GASSING TRIANGLE

SiH Silicone products are quite stable and not generally considered as hazardous materials, but, under specific conditions, they can generate high volumes of hydrogen gas. Because of its specific physical properties (wide explosive limits, low flammability, ignition energy, etc.) the hydrogen generated by gassing can pose a hazard due to pressure build-up, fire or explosion.
In order to achieve the gassing phenomenon, three conditions are simultaneously required. These conditions are called “the gassing triangle”.

2.1.1 SiH source

All chemicals containing a silicon-hydrogen bond can generate hydrogen. As mentioned in Chapter IV, pure polymers or compounded products can be concerned.

2.1.2 Active hydrogen source

All chemicals with an “active hydrogen” can contribute to the gassing phenomenon. The most common is water and can be found in products as an impurity or as an ingredient (emulsion). But other chemicals such as alcohols, amines, acids or alkaline materials used for some processes have the same behaviour and can be a source of “active hydrogen”.

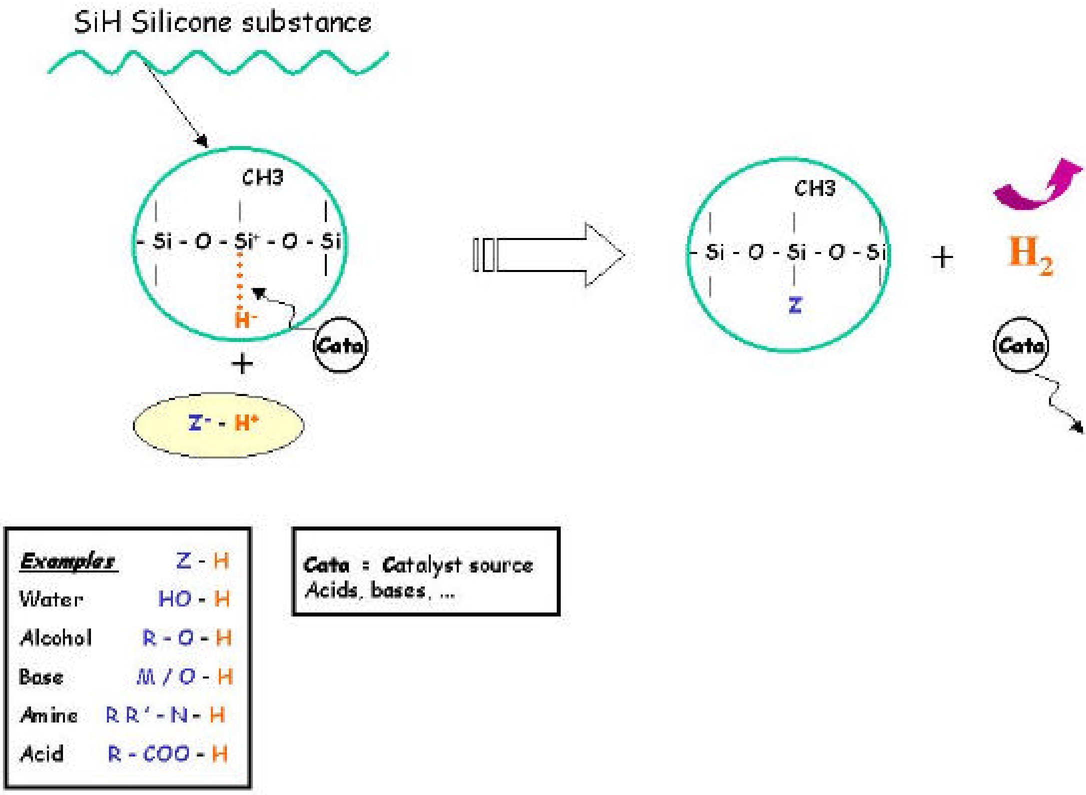
2.1.3 Catalyst source

Acids, bases, amines, alkaline or acid salts, metal soaps, products of corrosion and contaminants have a catalytic action on the gassing phenomenon.

The rate of gassing is related to the temperature, acidity and basicity (pH), activity of each component, concentration of the components, their solubility in the system and its viscosity. For example, amines are more active catalysts than alkoxides, which in turn are more active than hydroxides (see figure).

It is also important to mention that this phenomenon occurs sometimes with an induction time. Studies showed that, varying within the system studied, the reaction can “wait” for some random time and then occur with a quick evolution. This can explain that the gassing of hydrogen is not always easily predicted.

Nevertheless, if any of the above three conditions is missing, the “triangle” is broken and therefore no gassing occurs. However some products may be both the active hydrogen source and the catalyst (see above)



2.2 SPECIFIC DANGEROUS REACTIONS OF SiH PRODUCTS

It should be pointed out that even in the absence of an active hydrogen source, SiH products themselves may pose additional hazards. Polymerisation, de-polymerisation and equilibration processes can lead to side reactions producing dangerous volatile and highly flammable gases other than hydrogen.

In the presence of acid or basic catalysts (Lewis acids or bases, clays etc.) and - even in the absence of humidity – restructuring of the siloxane chain has been observed in association with the formation of highly flammable, gaseous by-products like for example Me_3SiH, Me_2SiH_2, $MeSiH_3$, depending on the nature of substituents (Me = Methyl, CH_3) present on the siloxane backbone.

In extreme cases (H-Siloxane) where tri-functional $HSiO_{1.5}$ units are present, the formation of SiH_4 has been reported. SiH_4 is a highly volatile (b.p. –112 °C) and self-ignitable gas on air.

Incompatibility: account should be taken of very severe reactions with peroxides and oxidizers leading to temperature increase and fire.

2.3 ASSOCIATED HAZARDS

As mentioned previously, build-up, fire or explosion can be generated by hydrogen gassing.

Stored in an inappropriate closed container, products can release enough hydrogen to develop a substantial pressure. The sudden release of overpressure can propel any loose part of the container as a dangerous projectile potentially causing serious injuries to people around. That's why venting devices are needed for storage as mentioned in Chapter VI "Control of Hazards" and closed glass bottles are not recommended for samples storage.

The release of hydrogen is also hazardous as hydrogen has exploding properties even at low concentrations (explosive limits for hydrogen in air are generally mentioned in literature between 4% and 74%). Exposed to an electric spark, heat or open flame, a hydrogen/air mixture burns with a very hot flame and can be source of bigger fires. All the necessary precautions for the safe handling of flammable gases should, therefore, be observed as mentioned in MSDS.

Sometimes, for viscous products, hydrogen gassing can bring out foaming and overflowing of containers due to build-up. Appropriate storage conditions are recommended to help spill management (see Chapter IX "Spill management").

Reaction of SiH containing products may also form – besides hydrogen gas - solid/resinous products capable to block pipes, exhausts or safely values which may lead to a rise of pressure in the manufacturing system.

C H A P T E R III **SPECIFIC HAZARDOUS CAUSES**

As stated earlier, the three conditions which make up the gassing triangle are necessary and sufficient to cause the gassing phenomenon. As SiH is always present by definition of the product family, conditions for presence of active hydrogen compounds and catalysts have to be checked.
There are many ways in which these conditions can arise as mentioned in the following examples.

3.1 INADEQUATE EQUIPMENT CLEANOUT

Generally, equipment cleanout includes both solvent and water flushing followed by drying. When inadequate cleanouts occur, trace amounts of catalyst and active hydrogen compounds (water for example) may be left behind completing the gassing triangle for the following batch. Caustic cleaning will cause the same phenomena.

3.2 INCOMPLETE PROCESS SEPARATION

If an active hydrogen compound (water, alcohol, amine, etc) is used during the manufacturing process of the SiH fluid or compound, and incompletely separated after, the active hydrogen left behind could later complete the gassing triangle if a catalyst is also present.

3.3 POOR CONTAINER LINERS OR UNPROTECTED STORAGE CONDITIONS

Poor container liners or unprotected storage conditions can cause moisture (water is an active hydrogen source) contamination due to cracking of liners or bad water tightness of venting devices.

3.4 RUSTING OR POLLUTION OF CONTAINERS

Rusting in containers occurs due to damage such as denting, rupturing, or cracking of container liners, thereby allowing 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.
Also, accidental introduction of rust or of other contaminants during container filling operations can have the same consequences.

3.5 PRODUCT BREAKDOWN

In some cases, hydrogen evolution may be caused by the chemical breakdown of a product due to aleing. Most products have recommended shelf lives which should be safely observed.

C H A P T E R IV **POTENTIAL GASSING PRODUCTS**

4.1 EMULSIONS

Emulsions are the most sensitive potential gassers because they usually contain a fairly high SiH level and have an unlimited supply of active hydrogen in the form of water. So they are therefore very sensitive to catalyst pollution.

4.2 COMPOUNDED ELASTOMERS

Some RTV, HTV and LSR silicone products contain more SiH compounds. Moisture from fillers, polymerization catalyst residues from polymers and contamination during repackaging may cause reaction and gassing. If viscosity is high, foaming and overflowing could happen.

4.3 SiH SILICONE FLUIDS

Hydrogen siloxane fluids can have a very high SiH content. Used and processed under "clean" conditions, they are quite insensitive to gassing. With no active hydrogen content and catalyst, they are stable products, but it remains imperative that water, acids and bases be excluded.

4.4 FUNCTIONALISED SILICONE FLUIDS

Functionalised silicone fluids can generate gassing problems due to unreacted residual SiH. Depending on process conditions, some active hydrogen products can remain. Specific analysis for catalyst contamination should be done.

4.5 CRITERIA

Consult MSDS of the SiH product for information on the degree of SiH hazard posed by this product.

CHAPTER V PERSONAL PROTECTIVE EQUIPMENT

For the determination of what personal protective equipment (PPE) for a specific SiH product is needed you should first consult the supplier's MSDS.
In general, gloves made of nitrile (NPR), butyl rubber, neoprene, or PVC coated are considered to be adequate.
For eye protection the use of safety glasses is recommended. Eye baths and safety showers at the working place should be available.
Regarding ventilation, the level of respiratory protection must be adapted to the local situation.

CHAPTER VI **CONTROL OF HAZARDS**

6.1 REACTOR OPERATIONS

6.1.1 Inerting

Before starting a new batch involving the use of SiH containing materials, the reaction system must be inerted with nitrogen to ensure that the oxygen content is reduced below a level at which ignition can occur. 3% oxygen is generally regarded as the maximum safe limit. Inerting can be done, for example, by repeated pressurisation and depressurisation, or by pulling a vacuum on the system and then breaking it with nitrogen, or by purging with nitrogen. The procedure selected should be initially validated by analytical testing to check that it will reduce the oxygen content to the required level.

Measures should be taken to prevent oxygen entering the equipment. During the batch sequence the reaction system should be blanketed with nitrogen to ensure that the inert atmosphere is maintained and that hazardous levels of hydrogen are not reached.

6.1.2 Raw material verification

Robust procedures must be put in place to avoid the inadvertent addition of the wrong raw materials to the reactor. As explained in Section 2 some materials if added in error may lead to a dangerous uncontrolled reaction.

Raw material verification can be done at two stages in a batch sequence.

Firstly the materials should 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.

Once the materials have been charged into the reactor a second stage of validation can usually 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 it is within prescribed limits.

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.

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 activies are being carried out. If hot work (e.g. welding) is to be carried out then a rigorous risk assessment is recommended to ensure that all hazards have been identified and appropriate precautions taken.

When restarting equipment after clean out it is essential to ensure that all vessels and associated piping systems are 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 lead to the consideration of, but not be limited to, 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 nitrogen. Grounding and bonding must be provided for tanks and ancillary transfer equipment, and when filling drums and IBCs (see Section 7.5). Free-fall or splash filling of vessels and containers should be avoided by the use of, for example, dip pipes.

High levels of static electricity can be generated when filtering SiH materials. Care should be taken to ensure that effective 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 up.

C H A P T E R VII **MINIMUM ENGINEERING CONTROL OF HAZARDS**

7.1 BUILDING DESIGN

SiH containing products are best processed – whenever possible – in separate plant units.

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

Buildings should be provided with a well working exhaust ventilation. Special precautions should be taken against possible accumulation of hydrogen at œiling level by properly designed ventilation channels.

Depending on the fire hazard potential of the processed SiH products and other raw materials (solvents) perhaps used in the specific reaction routes or for cleaning procedures, adequate fire protection should be incorporated in the building. Fire walls of sufficient quality could be necessary according to national regulations if larger volumes of hazardous (flammable) SiH products and perhaps flammable solvents are processed inside buildings. All structures containing flammable SiH products should be of non-combustible materials. Exterior walls of enclosed buildings may warrant explosion relief panels.

The building's structure should have a permanent reliable electrical bonding and earthing system that meets appropriate codes.

Eyewashes and safety showers should be located in appropriate locations.

Personnel evacuation routes or means of exits should be planned and practised.

7.2 EQUIPMENT DESIGN

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

7.2.1 General

The total equipment, such as lines, pumps, valves, vessels, etc., must be thoroughly dried with no trace of water remaining 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 (nitrogen) and each joint painted with soap solution and checked for bubbles.

Whenever necessary, totally enclosed systems should be used. Atmospheric openings or vents will allow moisture to enter the system causing the generation of hydrogen under unfavourable conditions (see “gassing triangle” chapter 2.1).

Use only dry inert gas (nitrogen), when any of the following must be done: pressurising vessels, priming pumps, blanketing tanks, and filling or withdrawing of tank contents.

7.2.2 Materials of construction

Dependant on process conditions (pressure, temperature, corrosiveness etc) the following materials can be chosen:

- carbon steel or better stainless steel to exclude rust which may cause catalytic side effects on SiH products (decomposition, rearrangement, hydrogen formation)
- enamel
- lined materials (care should be taken to control static electricity)
- Monel, Hasteloy, Inconel.

7.2.3 Vessels

Storage vessels should be designed and fabricated in accordance with local regulations.

Storage tanks, the associated design pressure must meet the requirements based on local regulations with respect to the properties of the stored SiH product

Generally vessels should have emergency vents. They should satisfy the requirements stated in the local regulations.

Vessels should be equipped with pressure-relief valves to relieve excess internal pressure due to outside (fire) or inside pressurising causes (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 preventive maintenance schedule programme should be established to inspect pressure relief systems especially when clogging is a possible danger for malfunction.

A further improvement on safety is the conduction of hazardous decomposition or reaction products (gas / liquid mixture) across the safety relief valve to a distant located reception release tank thereby decreasing the danger of fire or explosion inside the plant building.

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 recommended. See previous materials of construction comment.

Welded and flanged piping connections are preferred in order to maintain a leak-tight system.

The class of flange is to be based on the pressure- temperature rating of the process.

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

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

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

7.2.5 Pumps

Pump selection should be based on the one that provides the best features against leakage to the atmosphere. In general, canned pumps, magnetically driven pumps are the best choice.

7.2.6 Instrumentation

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

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

Stainless steel diaphragm pressure switches or coated ones, pressure and differential pressure transmitters are recommended in all cases where a risk of pressure drop or rise has to be controlled.

Level indication with a high-level alarm is recommended 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 a high hazard potential is given.

Storage tanks should have independent level control equipment to prevent overfilling. Process-actuated high-level switches are recommended for alarming high-level condition and interlocking to process shutdown.

Flanged connections are recommended to minimise possible leak paths.

7.3 VENTILATION

Enclosed processing buildings should be ventilated at a rate that formation of explosive atmosphere is excluded. If mechanical ventilation is used, the electrical equipment should meet legal requirements. Special provisions have to be made for a prevention of hydrogen accumulation inside buildings.

7.4 ELECTRICAL EQUIPMENT

All electrical equipment must conform to national legal requirements.

Vapour-tight and corrosion-resistant electrical equipment is recommended.

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 vapour. 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 dip tube is installed, vessels, tanks should be filled from the bottom.

To eliminate static charges and avoid spark discharges, a continuous path from the point of generation to ground must be provided. This is best accomplished by electrically interconnecting (bonding) all vessels, piping and related flanges, and grounding all equipment.

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 made.

C H A P T E R VIII **FIRE AND EXPLOSION PROTECTION**

8.1 FIRE HAZARDS

The SiH containing materials cause a particular hazard for fire and explosion, as these have the potential to develop hydrogen.
Hydrogen is lighter than air, has a very low Lower Explosion Limit of 4 vol. % in air (the Higher Explosive Limit is 74 vol. %). The hydrogen/air mixture burns with a very hot, non-luminous flame that is extremely difficult to see during the daylight. Particular SiH products, with a relatively high flashpoint, but sensitive to gassing, can create unexpected fire and explosion hazards, for example SiH containing emulsions.

Additional information on the fire hazards of the particular SiH containing material you're dealing with can be found in the appropriate MSDS.

8.2 FIRE PREVENTION

Depending on the flashpoint listed on the corresponding MSDS document, the typically recommended fire prevention measures are necessary, such as:

- Provision of classified electrical equipment
- Purging and inerting of equipment and containers with dry nitrogen. (When purging and inerting are carried out, it is of high importance that levels of O_2 present are low. The maximum O_2 concentrations required for H_2 is approx. 3 vol. %, which is half that for typical hydrocarbons.)
- Control of static electricity (loading and unloading of materials by use of dip pipes or by bottom filling is also recommended to reduce the risk of static electricity, grounding and bounding is important where possible etc.)
- 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. These are mostly provided with vented bungs, and should be stored and used in a well ventilated area. It's important for potential H_2 liberating materials, that high level ventilation is present, and that potential pockets of H_2 are avoided (due for example to roof structure).

In case the MSDS documents lists a relatively high flashpoint, but warns for a potential Hydrogen release (for example for the SiH containing emulsions), extra care should be taken for:

- 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

As a non-control of these points can result in an explosion, due to the uncontrolled hydrogen release.

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 or carbon dioxide. However extinguishment, particularly for well-developed fires, is best done with AFFF alcohol compatible foam. Water streams on their own should be avoided as they can agitate and disperse the burning liquid and increase the severity of a fire. Care should be taken when using caustic dry powder or water based materials as hydrogen can be liberated and, once the fire is put out, accumulate in poorly ventilated or confined areas and result in flash fire or explosion if ignited. Foam blankets may also trap hydrogen or flammable vapours, with the possibility of subsurface explosions.

Dry chemical extinguishers should not be used because they are typically very alkaline or acidic. If used on SiH materials, they will cause hydrogen evolution. The same rationale applied for the cationic or the anionic surfactants.

The products of combustion of SiH polysiloxane materials are silicon dioxide (silica), carbon dioxide, water vapour and various partially burned compounds of silicon and carbon. The products of combustion should be avoided and self-contained breathing apparatus worn when fighting fires to avoid inhalation of particulate silica.

C H A P T E R IX **SPILL MANAGEMENT**

When taking care of spills, personnel must wear safety goggles and rubber hand-gloves (see Chapter V for details).

In case of small and large spills prevent further runoff if possible. In particular try to prevent spills from entering drains or sewers where they could create an explosion risk.

If a drum or a container is leaking put the leaking side on top. Then cover the spill with an absorbent. Use material that is neither acid nor alkaline (e. g. sand, universal absorber such as mineral perlite or high absorption capacity or calcined diatomaceous earth). The used absorbent should then be properly packed, labelled and disposed of.

If a tank is leaking, close valves where possible, and/or cover the leaked fluid with dry material.

Whenever there is the possibility to pump out remaining liquid from the leaking tank, transfer it into a tote bin to get rid of the main amount. Note the possibility of an electrostatic discharge. Absorb the rest with an absorbent.

Recovered product is very likely to be contaminated – keep separate from normal product in an appropriate container, label correctly and, if necessary, consult with the supplier on disposal.

Finally any contaminated roadways, storage areas, etc., should be cleaned to remove slippery residues with medium pressure water and for instance a hydrocarbon-based self-emulsifying solvent.

CHAPTER X **WASTE MANAGEMENT**

There are several ways in which SiH containing waste can be generated:

- Sampling raw-materials for quality checks
- Sampling a reactor for SiH content (conversion control)
- Draining a reactor, pipework or hoses
- Distillate (volatiles) containing SiH materials
- Filter cake containing SiH materials

Because many chemicals react with SiH materials (e. g. amines, alcohols, aqueous acids and alkali), **it is recommended that all SiH waste be segregated from other waste.** This includes:

- Keeping pure SiH product waste separate from contaminated SiH waste.
- Collecting waste from different production units or sources separately 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 the material separately.

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 if previously used for SiH waste storage.
- Not stored in areas where they will be exposed to moisture, high temperatures or direct sunlight (solar heating).

Contact your supplier in the event of a bulging container.

Care should be taken when adding waste material to a non-groundable (plastic, or lined metal) container that has already been partially filled with SiH waste and left standing for a period. Hydrogen may have been released and accumulated in the ullage space (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, 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 disperse to a safe concentration. An additional precaution is to purge the container with nitrogen prior to adding more material.

C H A P T E R XI **TRAINING AND JOB SAFETY**

Safety in handling SiH products depends to a great extent upon effective employee education, proper training in safe practices and the use of safety equipment and knowledgeable supervision.

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 finalising 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 the review, all danger points should be identified and the precautionary measures determined. The review should be concerned not only with the dangers of contact with or exposure to SiH products but also with the dangers that may be involved in handling containers, in operating equipment, 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. Procedures for all foreseeable emergencies should be established, including the location and operation of safety showers, fire extinguishers, alarms, etc.

All significant hazards that cannot be avoided or satisfactorily controlled should be explained together with the precautions to be followed in the standard operating procedures. Preferably, these safety precautions should be an integral part of the operating procedures.

If there are extremely critical steps in the process where, for example, overcharge or undercharge may cause uncontrollable reactions, consideration should be given to making these supervisory checkpoints. It then becomes the supervisor's responsibility to verify that the employee has followed the proper procedure before undertaking the critical step.

The employee should understand the chemistry and chemical reactions of the process as well as any potential cross-contamination in the existing equipment or common shared equipment.

The safety review described above should be made at least annually for all chemical processing operations and always before there is a change in the process. It is the supervisor's responsibility to periodically check his or her employees to make certain they are following instructions and precautions as directed. Complete standard operating procedures with safety information are also helpful to supervisors when training new workers.

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

- possible hydrogen generation of SiH products
- hazards due to pressure build-up, fire or explosion
- hazard potential and properties of hydrogen (highly flammable gas, lower explosion limit of 4 vol. %) and hydrogen/air mixtures (very hot, non-luminous flame, extremely explosive)

- handling of bulging (over-pressurised) drums or containers (consulting specialists, fire brigade).
- cleaning procedures of vessels, tanks, drums, IBCs etc.
- separation of waste with SiH products from all other waste to avoid consecutive reactions (hydrogen generation)

C H A P T E R XII **SHIPPING, LABELLING AND MARKING**

For shipping, labelling and marking requirements, reference should be made to the Material Safety Data Sheet (MSDS) of the suppliers.

If air shipment of SiH products is considered, careful attention must be given to the possibility of hydrogen release, taking into account the specific product and its container.

Air shipments should specifically comply with the IATA “Dangerous Goods Regulations” on “limitations” (forbidden dangerous goods) and on the packaging (venting of packages is not permitted).

A stability test or a quarantine procedure can be considered case by case (refer to your supplier).

C H A P T E R XIII **HANDLING OF CONTAINERS (TANKERS, DRUMS, ETC.)**

13.1 GENERAL CONSIDERATIONS

All safety and other precautions documented in other sections of this manual must be observed when loading or unloading SiH products. It is particularly important that personal protective equipment is used. Normal procedures for handling corrosive and flammable materials also apply.

Use only containers, IBC's, tankers and drums as required by local or government regulations for SiH products handling. (see Chapter VI)

All shipping containers should be inspected for leaks before they are allowed to leave the plant. Some products might be heat sensitive. Ensure that the containers will not heat above the temperature mentioned on the label.

Only fully trained employees should sample, connect, load, unload or disconnect any SiH product shipping container. The training should be repeated on a yearly basis. (see Chapter XI)

An operator or monitoring equipment should continuously supervise all operations. The shipper's instructions for unloading should be followed.

Proper protective clothing and equipment should be worn during connecting, loading, unloading and disconnecting operations. An emergency shower and eyewash station should be provided at the loading or unloading area. (see Chapter V)

Specified technical safety equipment must be used. It should be well maintained to keep in functional order. Technical safety equipment should not be ignored or disengaged.

All devices (fittings, pumps, hoses, etc.) must be suited for use with SiH products. These devices have to keep clean, free of contamination and dry at all time while not in use. They should be regularly checked and damaged parts repaired.

At all times, valves, piping and the interior and exterior of protective valve housings should be kept clean and free of contaminants (gel or gel-like material).

To verify the content and avoid mixing of products, identification numbers on shipping containers should be compared with that on the shipping papers or on the invoice. The content should be sampled and analyzed before transfer.

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. Notify the manufacturer of the SiH product immediately. (see also chapter IX)

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 prevent the containers from extensive heat or mechanical damage. Store the containers regarding the local safety regulations for SiH products.

13.2 EMPTYING CONTAINERS

All equipment used for removing SiH products from containers should be electrically grounded.

The area should be well ventilated or equipped with a local exhaust system.

The container being emptied should be vented with nitrogen.

13.3 FILLING CONTAINERS

SiH products should only be filled into suitable containers. Drums and IBCs should be equipped with vented bungs. The level in the filled container should leave enough room for volume expansion due to temperature changes (see local and/or international regulations).

13.4 HANDLING EMPTY SiH PRODUCT CONTAINERS

Drain containers as thoroughly as possible. Rinse empty containers at least twice and leave them open to allow for complete drying. See section 6.2 for details.

Attention: residues in the container may react with caustic to produce hydrogen gas.

Empty SiH drums should not be reused unless properly cleaned.

13.5 BULGING, LEAKING OR DEFECTIVE CONTAINERS

Contact your supplier. See Chapter IX (Spill Management).

CHAPTER XIV **GLOSSARY OF TERMS**

AFFF	Aqueous Film-forming Foam
Cefic	Conseil Européen des Fédérations de l'Industrie Chimique, the European Chemical Industry Council
CES	Centre Européen des Silicones, the European Silicones Industry Association
Hastelloy	Hastelloy B is an International Nickel co. alloy having a nominal composition of nickel (Ni) 66.7%; iron (Fe) 5%; molybdenum (Mo) 28%; vanadium (V) 0.3%. Hastelloy C is an International Nickel co. alloy having a nominal composition of nickel (Ni) 59%; iron (Fe) 5%; molybdenum (Mo) 16%; tungsten (W) 4%; chromium (Cr) 16%.
HTV	High Temperature Vulcanising silicone
IATA	International Aviation Transportation Association (www.iata.org)
IBC	Intermediate Bulk Container
Inconel	A nickel-base alloy with chromium and iron
LSR	Liquid Silicone Rubber
Monel	An alloy of nickel and copper and other metals, such as iron and/or manganese and/or aluminum
MSDS	Material Safety Data Sheet, the internationally recognised term for Safety Data Sheet
NPR	Nitrile rubber/polyurethane
pH	A measure of alkalinity (14 > pH > 7) and of acidity (7 > pH > 0)
PPE	Personal Protective Equipment
RTV	Room Temperature Vulcanising silicone capable of converting from a liquid to a solid at room temperature
SiH	A material or product containing hydrogenosilane groups
Si-H	The hydrogen-silicium bond, or the hydrogenosilane group

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