



 - SILICONES EUROPE

 American Chemistry Council

 SEHSC  
Silicones Environmental,  
Health, and Safety Center

 SIAT  
Silicones Industry Association of Japan

# GLOBAL SAFE HANDLING OF CHLOROSILANES

Developed by the Operating Safety Committees of the  
Silicones Environmental, Health and Safety Center,  
CES-Silicones Europe, in partnership with the  
Silicones Industry Association of Japan

October 2017

## TABLE OF CONTENTS

|   |    |
|---|----|
| <b>CHAPTER 1 - INTRODUCTION</b>   | 3  |
| <b>CHAPTER 2 - CHLOROSILANE NOMENCLATURE</b>  | 5  |
| <b>CHAPTER 3 - HEALTH FACTORS</b>   | 6  |
| <b>3.1 GENERAL</b>  | 6  |
| <b>3.2 ACUTE TOXICITY</b>   | 6  |
| <b>3.3 CHRONIC TOXICITY</b>   | 8  |
| <b>CHAPTER 4 - PERSONAL PROTECTIVE EQUIPMENT</b>  | 9  |
| <b>4.1 GENERAL</b>  | 9  |
| <b>4.2 PROTECTIVE EQUIPMENT</b>   | 9  |
| <b>CHAPTER 5 - TRAINING AND JOB SAFETY</b>  | 12 |
| <b>CHAPTER 6 - FIRE HAZARDS AND FIRE PROTECTION</b>   | 13 |
| <b>6.1 FIRE HAZARDS</b>   | 13 |
| <b>6.2 FIRE PREVENTION</b>  | 13 |
| <b>6.3 EXTINGUISHING AGENTS</b>   | 14 |
| <b>6.4 MANUAL FIRE FIGHTING</b>   | 15 |
| <b>6.5 FIXED FIRE PROTECTION</b>  | 16 |
| <b>6.6 PLUME AND VAPOR CLOUD MITIGATION</b>   | 17 |
| <b>CHAPTER 7 - SPILL CONTAINMENT AND ENVIRONMENTAL IMPACT</b>                                 | 19 |
| <b>CHAPTER 8 - INSTABILITY AND REACTIVITY HAZARDS</b>   | 20 |
| <b>8.1 INSTABILITY HAZARDS</b>  | 20 |
| <b>8.2 REACTIVITY HAZARDS</b>   | 20 |
| <b>CHAPTER 9 - MINIMUM ENGINEERING CONTROL OF HAZARDS</b>                                     | 22 |
| <b>9.1 BUILDING DESIGN</b>  | 22 |
| <b>9.2 EQUIPMENT DESIGN</b>   | 22 |
| <b>9.3 VENTILATION</b>  | 25 |
| <b>9.4 ELECTRICAL EQUIPMENT</b>   | 25 |
| <b>9.5 STATIC ELECTRICITY</b>   | 25 |
| <b>CHAPTER 10 - SHIPPING, LABELLING AND MARKING</b>   | 27 |
| <b>CHAPTER 11 - HANDLING OF BULK CONTAINERS, DRUMS, PRESSURE DRUMS AND PRESSURE CYLINDERS</b> | 28 |
| <b>CHAPTER 12 - WASTE DISPOSAL</b>  | 33 |
| <b>CHAPTER 13 - EQUIPMENT CLEANING AND REPAIRS</b>  | 34 |

# GLOBAL SAFE HANDLING OF CHLOROSILANES

## CHAPTER 1. INTRODUCTION

The Silicones Environmental, Health and Safety Center (SEHSC) and CES-Silicones Europe are not-for-profit trade associations comprised of North American and European silicone chemical producers and importers. SEHSC and CES promote the safe use of silicones through product stewardship and environmental, health, and safety research. SEHSC's Operating Safety Committee (OSC) and CES' Operating and Safety Task Force, in partnership with the Silicones Industry Association of Japan (SIAJ), prepared this Global Safe Handling of Chlorosilanes 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 eight chlorosilanes i.e.: dimethyldichlorosilane, methyltrichlorosilane, trimethylchlorosilane, methyldichlorosilane, vinyltrichlorosilane, phenyltrichlorosilane, trichlorosilane and silicon tetrachloride. All of these clear liquids readily react with water to form corrosive and toxic hydrogen chloride gas and hydrochloric acid. All - except silicon tetrachloride and phenyltrichlorosilane - are flammable liquids.

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 full text of this guide should be consulted for information on the hazards of chlorosilanes and considerations for their safe handling and use. The information provided should not be considered as a directive or as an industry standard that readers must adopt or follow. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense. In addition, Safety Data Sheets (SDS) should be obtained from the manufacturer. The SDS may provide more specific detailed information. Start first aid immediately in all cases of contact with chlorosilanes (First aid - See Chapter III). All users are expected to comply with applicable federal, state, and local laws and regulations and should consult with legal counsel regarding such matters.

While SEHSC, CES and SIAJ may update this guide from time-to-time as significant new information becomes available regarding the handling of chlorosilane products, SEHSC, CES, SIAJ, 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, CES and SIAJ do not assume any liability for reliance on the information in this Guide.<sup>1</sup> New information may be developed subsequent to publication of this Guide that renders information contained herein incomplete or inaccurate and it cannot be assumed that all

---

<sup>1</sup> The information herein is offered WITHOUT WARRANTY, EXPRESS OR IMPLIED, AS TO MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, AND/OR ANY OTHER MATTER. Neither SEHSC, CES, SIAJ, nor any member company assumes any liability or responsibility for any use, or the results of such use, of the information presented in this guide. All persons involved in handling chlorosilanes products have an independent obligation to assure that their actions are in conformity all applicable laws and regulations, as well as company-specific policies and procedures.

necessary warnings and precautionary measures are contained in this document or that other additional measures may not be required or desirable due to particular or exceptional conditions or circumstances, or because of applicable federal, state, or local laws. Readers are encouraged to submit suggestions for improvement to SEHSC<sup>2</sup>.

Goggles, face shields, protective clothing and rubber gloves should be worn if, and as directed by the manufacturer. Liquid chlorosilanes and their vapours are corrosive to the skin, eyes, nose, throat and respiratory tract. All should be treated as strong acids.

For additional information, please contact at the following address:

**Silicones Environmental Health and Safety Center**

Attn: Tracy Guerrero, Director  
700 2<sup>nd</sup> Street, NE  
Washington, D.C. 20002  
Tel: (202) 249-6196  
E-mail: [tracy\\_guerrero@americanchemistry.com](mailto:tracy_guerrero@americanchemistry.com)

**CES Silicones Europe**

Attn: Dr Pierre Germain  
Avenue E. van Nieuwenhuysse 4, box 2  
B - 1160 Brussels  
Tel: (Int. + 32 2) 676 7377 Fax: (Int. + 32 2) 676 7392  
E-mail: [pge@cefic.be](mailto:pge@cefic.be)

---

<sup>2</sup> Submissions should be made to Tracy Guerrero at [tracy\\_guerrero@americanchemistry.com](mailto:tracy_guerrero@americanchemistry.com).

## CHAPTER 2. CHLOROSILANE NOMENCLATURE

This publication is applicable to the following commercially available chlorosilanes:

| Chemical Names                   | Other Names   | Formulas  | CA Reg. No. | UN-No. |
|----------------------------------|---|---|-------------|--------|
| Dimethyldichlorosilane           | Dichlorodimethylsilane,   | $(\text{CH}_3)_2\text{SiCl}_2$                          | 75-78-5     | 1162   |
| Dimethylchlorosilane             | Chlorodimethylsilane,<br>Chlorohydrogenomethylsilane,<br>Chloro(hydrogen)methylsilane       | $(\text{CH}_3)_2\text{HSiCl}$                           | 1066-35-9   | 2924   |
| Methyltrichlorosilane            | Trichloromethylsilane   | $\text{CH}_3\text{SiCl}_3$                              | 75-79-6     | 1250   |
| Trimethylchlorosilane            | Chlorotrimethylsilane   | $(\text{CH}_3)_3\text{SiCl}$                            | 75-77-4     | 1298   |
| Methyldichlorosilane             | Dichloromethylsilane,<br>Dichlorohydrogenomethylsilane,<br>Dichloro(hydrogen) methylsilane, | $\text{CH}_3\text{HSiCl}_2$                             | 75-54-7     | 1242   |
| Ethyltrichlorosilane             | Trichloroethylsilane  | $\text{C}_2\text{H}_5\text{SiCl}_3$                     | 115-21-9    | 1196   |
| Propyltrichlorosilane            | Trichloropropylsilane   | $\text{C}_3\text{H}_7\text{SiCl}_3$                     | 141-57-1    | 1816   |
| Chloropropyltrichlorosilane      | Trichlorochloropropylsilane   | $\text{C}_3\text{H}_6\text{ClSiCl}_3$                   | 2550-06-3   | 2987   |
| Chloropropylmethyldichlorosilane | Dichlorochloropropylmethylsilane  | $\text{C}_3\text{H}_6\text{ClCH}_3\text{SiCl}_2$        | 7787-93-1   | 2987   |
| Vinyltrichlorosilane             | Trichloroethylsilane  | $\text{CH}_2\text{CHSiCl}_3$                            | 75-94-5     | 1305   |
| Vinylmethyldichlorosilane        | Dichloroethylmethylsilane   | $\text{CH}_2\text{CHCH}_3\text{SiCl}_2$                 | 124-70-9    | -      |
| Phenyltrichlorosilane            | Trichlorophenylsilane   | $\text{C}_6\text{H}_5\text{SiCl}_3$                     | 98-13-5     | 1804   |
| Dipenyldichlorosilane            | Dichlorodiphenylsilane  | $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$                 | 80-10-4     | 1769   |
| Phenylethyldichlorosilane        | Dichlorophenylethylsilane   | $\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{SiCl}_2$ | 1125-27-5   | 2435   |
| Trichlorosilane                  | Silicon chloroform  | $\text{HSiCl}_3$  | 10025-78-2  | 1295   |
| Silicon tetrachloride            | Silicon chloride, Tetrachlorosilane   | $\text{SiCl}_4$   | 10026-04-7  | 1818   |

Many more than the above sixteen chlorosilanes are known and some are used in commerce. Their properties vary; and, even though all chlorosilanes are classifiable as members of a single group of compounds, they may or may not react similarly in similar environments. Hydrochlorosilanes are chlorosilanes that contain at least one SiH bond. Hydrochlorosilanes can liberate hydrogen as well as hydrogen chloride which makes their handling and emergency response more complicated.

For detailed properties refer to the applicable Safety Data Sheets (SDS).

## **CHAPTER 3. HEALTH FACTORS**

### ***3.1 GENERAL***

The primary potential acute health hazards are severe corrosive burns of the skin, eyes or respiratory tract. Ingestion (swallowing) of liquid chlorosilanes may cause severe internal injury or death.

All chlorosilanes react with moisture in the air or water to produce toxic and corrosive hydrogen chloride that can cause acute injury to any body tissue contacted.

Chronic health effects are not expected other than resulting from severe acute injury. Medical advice should be obtained immediately after exposure to chlorosilanes.

#### ***First Aid and Medical Treatment***

- First aid should be started immediately after contact with any form of chlorosilanes.
- It is important to remove the injured person from the contaminated area as soon as possible.
- For those providing assistance, avoid exposure to yourself or others. Use adequate respiratory protection and/or other personal protection.
- Treatment is supportive and symptomatic: no specific antidotes.
- The primary goal of medical management is effective and immediate relief of symptoms.

### ***3.2 ACUTE TOXICITY***

Chlorosilanes will cause corrosive injury to any body tissue that they contact. For treatment of any exposures, the primary resource will be manufacturers SDS and medical professionals.

#### **EYES**

Direct contact of chlorosilane liquid with the eyes causes severe corrosive damage that may result in total loss of sight.

Vapour exposure to the eyes may result in significant irritation and/or severe chemical burns that may result in total loss of sight.

#### ***First Aid and Medical Treatment***

- Follow guidance provided by manufacturer SDS regarding appropriate medical responses.
- Irrigate eyes immediately with large amounts of water for a minimum of 15 minutes.
- Medical assistance should be contacted immediately. If the medical assistance is not immediately available, the eye irrigation should be continued for an additional 15 minutes.

- If it is necessary to transport the patient to a hospital or medical assistance, irrigation of the eyes should be continued during transport.

## **SKIN**

Skin contact with either chlorosilane vapour or liquid can cause burns varying in severity from first to third degree, depending on concentration and length of exposure.

### ***First Aid and Medical Treatment***

- In cases of skin contact, clothing contamination or both, immediately remove all contaminated clothing and shoes, go directly under the shower.
- Wash skin area with large quantities of water; continue washing for at least 15 minutes.
- No salves or ointments should be applied to chemical burns unless ordered by a medical assistant. Consult medical assistance or the manufacturer SDS for treatment of all chemical burns.
- Bag and clean clothing with appropriate precautions.

## **INHALATION**

Inhalation of chlorosilane vapours or hydrochloric acid vapours or mist may cause irritation of and/or damage to the respiratory tract.

Inhalation of chlorosilanes primarily affects the upper respiratory tract, causing inflammation, edema and corrosive burns of the oral, nasal and pharyngeal mucosa and the upper airways.

### ***First Aid and Medical Treatment***

- Remove any person overcome by chlorosilane vapours or hydrochloric acid fumes at once from the contaminated atmosphere.
- If the victim is not breathing, initiate artificial respiration immediately; oxygen should be administered when warranted.
- An injured person should be kept comfortably warm, but not hot.
- Never attempt to give anything by mouth to an unconscious person.
- Evaluate and treat any persons who have had inhalation exposures to chlorosilanes vapours or hydrochloric acid vapors or mist by emergency response personnel and/or a medical assistant.

## **GASTROINTESTINAL TRACT**

Ingestion of liquid chlorosilane could cause severe corrosive burns of the mouth, esophagus and stomach, potentially resulting in perforations of internal organs with subsequent chemical pleuritis, mediastinitis and peritonitis.

### ***First Aid and Medical Treatment***

- Evaluate and treat any person ingesting liquid chlorosilanes by emergency response personnel and/or a medical assistant.

- Do not induce vomiting. Keep the injured person comfortable and warm. Never give anything by mouth to an unconscious person.

### ***3.3 CHRONIC TOXICITY***

Repeated contact with dilute solutions of chlorosilanes or hydrochloric acid mists may cause irritant dermatitis. Repeated inhalation of the mist may cause an inflammation of the upper and lower respiratory tract.

#### ***First Aid and Medical Treatment***

- Evaluate and treat any persons who have had repeated inhalation exposures to the mist by emergency response personnel and/or a medical assistant.

## **CHAPTER 4. PERSONAL PROTECTIVE EQUIPMENT**

### ***4.1 GENERAL***

Personal protective equipment is not an adequate substitute for proper management of working conditions, adequate ventilation, training, and responsible conduct on the part of employees working with chlorosilanes.

During an emergency response and in certain operations involving chlorosilanes, a complete set of protective equipment is essential.

Training in the correct use of personal protective equipment is essential.

When taking samples, opening equipment or performing similar operations where chlorosilane vapour or liquid may be present, adequate personal protective equipment and clothing should be utilized.

### ***4.2 PROTECTIVE EQUIPMENT***

#### **EYE AND FACE PROTECTION**

##### ***Safety glasses***

Consider using safety glasses with unperforated side shields where continuous eye protection is desirable, as in laboratories. Eye glasses are not sufficient where complete eye protection is needed; such as when handling bulk quantities, where there is danger of splashing or if the material may be under pressure.

##### ***Chemical splash goggles***

Consider using chemical splash goggles when there is danger of chlorosilanes coming in contact with the eyes. Goggles should be properly fitted.

##### ***Face shields***

Consider using plastic shields with chemical splash goggles or a full-face respirator where face protection is desired.

##### ***Contact lenses***

Consider prohibiting wearing contact lenses where there is risk of exposure to chlorosilanes because they may trap material between the lens and eye.

#### **RESPIRATORY PROTECTION**

Severe exposure to hydrochloric acid vapour may occur during chlorosilane equipment cleaning and repairs, or in cases of failure of piping or equipment.

Employees who might be subject to such exposures should be provided with proper respiratory protective equipment and trained in its use and care.

### ***Self-contained breathing apparatus***

Self-contained breathing apparatus, which permits the wearer to carry a supply of breathing air in a cylinder, allows considerable mobility. However, the length of time the apparatus provides protection varies according to the amount of air available in the cylinder AND the respiratory rate of the user. In all cases the apparatus should be equipped with a face piece that maintains positive pressure at all time. This prevents flow of contaminated atmosphere into the face piece.

### ***Air-line full face masks***

Positive pressure (continuous flow or pressure demand) airline masks, supplied with clean compressed certified breathing air, are suitable for non-emergency use, such as routine maintenance tasks.

### ***Cartridge/Disposable respirators***

Cartridge respirators may provide lung protection when working with chlorosilanes if the proper cartridge for absorbing hydrochloric acid type vapour is used. They are not suitable for lack of oxygen conditions. They should be used for relatively short exposure periods and are considered adequate only for low concentrations or for emergency egress.

Cartridge respirators should not be used for emergency ingress or in areas of unknown vapour concentrations or oxygen content. The wearer should be warned to leave the contaminated area immediately on detecting any odours through the respirator. The odour may indicate that the mask is not functioning properly, that the vapour concentration is too high, or that the mask is not properly fitted.

## **BODY AND FOOT PROTECTION**

### ***Body Protection***

Protective clothing offers protection for a limited time only.

Materials for protective clothing (including gloves) were tested on behalf of the Silicones Environmental Health and Safety Council (SEHSC). The results of this study were published in the American Industrial Hygiene Association Journal, February 1997, pages 110 –115 (AIHA Journal (58) 110 –115 (1997)). Consult publications such as the AIHA Journal to identify protective clothing suitable for their application where the manufacturer has not already done so.

### ***Hand Protection***

To protect hands and arms, consider wearing long-sleeved gloves (preferable) or gauntlets that cover the forearms and are arranged under the coat sleeves and properly sealed to protect hands and arms. This will provide only limited protection.

### ***Foot Protection***

Consider wearing rubber boots or rubber-coated high-top safety-toe shoes with shoe tops tucked under the trousers or coveralls to provide limited protection to the feet and lower legs.

### ***Head Protection***

"Hard" hats should be worn whenever there is a possible hazard to the head; their use is also recommended in processing loading or unloading operations.

## CHAPTER 5. TRAINING AND JOB SAFETY

Safe handling and use of chlorosilanes 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 chlorosilanes, the supervisor should be familiar with the contents of the SDS and the hazardous characteristics of chlorosilanes and the precautions explained in the SDS. Many chlorosilanes will trigger OSHA, PSM, or EPA RMP regulations. Before handling, supervisors need to determine if you will meet those requirements, which may include provisions for risk analysis, process control, and training.

The supervisor should consider consulting with industrial hygiene and safety specialists before finalising a safety review of operations involving chlorosilanes.

After becoming familiar with the hazardous characteristics of chlorosilanes, the supervisor should review each procedure step-by-step. During the review, 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 chlorosilanes 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 eye wash stations, safety showers, fire extinguishers, alarms, etc.

Train employees on proper medical response procedures, as described in Chapter 1.

Hazards should be avoided or satisfactorily controlled. Additionally, safety precautions should be part of the operating procedures.

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

To the extent practicable, 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.

Consider undertaking the safety review regularly, for example annually for chlorosilanes processing operations and before there is a change in the process. Complete standard operating procedures with safety information may be helpful to supervisors when training new workers.

## **CHAPTER 6. FIRE HAZARDS AND FIRE PROTECTION**

### ***6.1 FIRE HAZARDS***

Except for silicon tetrachloride, all of the chlorosilanes covered in this document may cause fire hazards. Silicon tetrachloride will not be addressed in this section.

Chlorosilane vapours are heavier than air, and, except for trimethylchlorosilane, the liquids themselves are heavier than water.

All of the chlorosilanes react vigorously with water, producing hydrogen chloride and, in the case of trichlorosilane and methyldichlorosilane, flammable hydrogen gas and hazardous residues. Trimethylchlorosilane will react with water to also produce hexamethyldisiloxane, which is a flammable liquid itself.

The chlorosilanes are non-conductors and, therefore, can accumulate static electrical charges when processed, handled or dispensed.

### **BURNING CHARACTERISTICS**

Except for trichlorosilane, the chlorosilanes burn in a manner similar to burning hydrocarbons, producing large amounts of grey or black smoke. However, the quantity of heat produced by burning chlorosilanes is typically lower than that of most flammable hydrocarbons. Generally speaking, the hydrocarbon-like character of chlorosilanes increases with the number of methyl groups present.

Burning trichlorosilane is unique in character, producing copious quantities of dense white smoke and very small amounts of radiation heat. After extinguishing of trichlorosilane fires there is always a high risk of re-ignition due to the formation of hydrogen. In addition, trichlorosilane ignites with a rapid flashover at the liquid surface and generates very little or no noticeable flames.

Burning chlorosilanes evolve hydrogen chloride, oxides of silicon, oxides of carbon (except for trichlorosilane), and various other combustion by-products (such as chlorine in the case of trichlorosilane).

Many of the chlorosilanes have a flash point below room temperature. Additional information on the fire hazards of the chlorosilanes (e.g., flash points and flammable limits) can be found in the appropriate SDS.

### ***6.2 FIRE PREVENTION***

As with all flammable liquids, fire prevention is extremely important when using or storing chlorosilanes. This includes the provision of measures to minimise the potential for ignition and the design of equipment and facilities to prevent the release of chlorosilanes.

No special fire prevention measures other than those typically recommended for flammable liquids are necessary when storing or using chlorosilanes. Some of these measures include, but are not limited to the following:

- Provision of mechanical exhaust ventilation to remove flammable vapours
- Provision of adequate drainage and collection facilities to isolate any spilled liquids
- Provision of classified electrical equipment (see national legal requirements)
- Purging and inerting of equipment and containers with a dry inert such as nitrogen
- Grounding and bonding to control static electricity
- Control of cutting, welding and other "hot work"
- Control of smoking and other potential ignition sources

### **6.3 EXTINGUISHING AGENTS**

Due to its reactivity with chlorosilanes, **water should NOT** be used as an extinguishing agent for chlorosilane fires. Water can be used to protect exposures and personnel and on the vapour cloud to disperse and dilute the HCl vapour. (Care should be taken, however, to prevent any over-spray or runoff from contacting the chlorosilane in the spill containment.)

**Dry Chemical** fire extinguishers have proven effective to extinguish small chlorosilane fires, except those involving hydro-chlorosilanes (those substances with an  $R_x-Si-H_y$  structure, where R=non-hydrogen substituent, H = hydrogen and  $x*y = 4$ .), where success has been marginal at best. Expect to use much larger quantities of dry chemical than would be required to extinguish a similar hydrocarbon fire. Dry chemical is not effective on large fires because an adequate amount of agent cannot be delivered quickly enough. Use of dry chemical on hydrogen-containing chlorosilanes will release hydrogen, which may ignite explosively.

**CO<sub>2</sub>** fire extinguishers can be used on small fires. CO<sub>2</sub> is not effective on large fires. Please note that the use of CO<sub>2</sub> in an enclosed area can create an asphyxiation hazard.

**Class B Medium Expansion Alcohol Resistant Aqueous Film Forming Foam (AR-AFFF<sup>3</sup>)** is the most effective agent overall for use on chlorosilane spills and fires. For hydrochlorosilanes containing Si-H (silicon-hydrogen) bonds, e.g., trichlorosilane and methylchlorosilane, medium expansion AR-AFFF is highly recommended for maximum effectiveness. Using AR-AFFF with a compressed air foam (CAF) system improves the stability of the foam, increases the distance the foam can be projected and uses the least amount of water.

Since foam solutions contain water, reaction with the chlorosilane will normally be observed when foam is applied. Be aware that application of foam will release

---

<sup>3</sup> Rolf Jensen & Associates. 2012. Fire Testing of Low Molecular Weight Silicones Fluids. Prepared for the Silicones Environmental, Health and Safety Council (SEHSC) to summarize the results of certain fire testing conducted by SEHSC and its member companies.

significant amounts of toxic and corrosive hydrogen chloride vapors. In addition, hydrogen vapors can be released from hydrochlorosilanes and may be trapped under the foam blanket. Repeated applications of foam may be required for fire extinguishment. As the foam reacts with the chlorosilane, depending on the chlorosilane, a film of silicone oil or gels typically form at the interface of the foam and chlorosilane. As this film forms the reaction between the water in the foam and the chlorosilane will stop. Extreme care should be taken not to disturb the foam blanket during and after foam application. If the interface is disturbed the reaction between the water in the foam and the chlorosilane will begin again. (See Section 6.4 for more information on manual fire fighting.)

#### **6.4 MANUAL FIRE FIGHTING**

Prevent extinguishing agents from entering a container or vessel that contains chlorosilane. The resulting release of hydrogen chloride vapours may over-pressurise the container or vessel, resulting in a sudden rupture of the container or vessel.

##### ***IMPORTANT:***

Much of the experience fighting chlorosilane fires has been obtained either in a controlled test environment or on a relatively small scale. Experience with fighting chlorosilane fires on a large scale has been extremely limited. Actual fire conditions could present unique and challenging fire-fighting situations, and fire extinguishing in some cases could be extremely difficult. Therefore, the specific situation must be thoroughly analysed before attempting to fight a chlorosilane fire, and extreme caution must be exercised during fire fighting operations. In some cases, the best alternative may be to protect personnel and important facilities and to allow the fire to burn itself out. If this is the path chosen, minimize the downwind impact of the hydrogen chloride vapour cloud. Please see Section 6.6.

As in the case of all fires, the safety of personnel is of primary importance. Therefore, all persons in the immediate vicinity and downwind of a chlorosilane fire should consider evacuating to a safe area.

Personnel fighting chlorosilane fires should be properly trained and provided with proper personal protective equipment in accordance with all applicable government requirements.

Even though water **SHOULD NOT** be used to fight chlorosilane fires it can still be used, however, to protect personnel and exposures from radiant heat. Water can also be used to disperse and dilute combustion effluents. (NOTE: The resulting water runoff will normally be acidic, thus, provisions should be made for the collection and neutralisation of this water. It is also imperative that this water runoff does not come into contact with the chlorosilane spill.)

As indicated in Section 6.3, medium expansion AR-AFFF has proven to be the most effective extinguishing agent on chlorosilane fires<sup>4</sup>. When using medium expansion AR-AFFF, the following guidelines should be followed.

- Apply foam as gently as possible. **DO NOT 'PLUNGE' OR AIM FOAM STREAMS DIRECTLY INTO A CHLOROSILANE.** This will result in severe reactions between the chlorosilane and the water contained in the foam solution.
- Wherever possible, aim foam streams in front of the chlorosilane or bounce off fixed objects (such as tanks or dike walls) to allow the foam to flow gently onto the liquid surface. Occasionally, however, it may be necessary to "lob" foam in order to deliver foam to the centre of a fire.
- Except in the case of very small fires, and where possible, use at least two nozzles to enhance distribution of the foam over the surface of the chlorosilane.
- Establish a relatively thick blanket of foam (e.g., 12 to 18 inches/30 - 50 cm minimum) over the entire liquid surface. Once this has been done, temporarily suspend foam application to allow extinguishing to take place. Reapply foam when the intensity of the fire and/or the evolution of smoke/vapours appear to stabilise or even increase. Repeat this process as often as necessary until extinguishing is effected or until other emergency measures can be initiated.
- It is theorised that the fire is extinguished through the gradual hydrolysis of the chlorosilane by the water draining from the foam. This hydrolysis reaction forms a layer of siloxanes (fluid or gel) on the surface of the chlorosilane, which inhibits vapour production and excludes oxygen, thereby extinguishing the fire.
- Exercise extreme caution when applying foam and when approaching the fire area. The hydrolysis layer formed in the extinguishing process can trap flammable vapours, and, if this layer is disturbed (e.g. by impinging foam-streams), subsurface ignitions and rapid flashovers may occur.

## **6.5 FIXED FIRE PROTECTION**

Application of only water to a chlorosilane fire is generally ineffective. If water alone is used, then the fire will become more pronounced and the fire will continue until all of the fuel is consumed. A foam system is critical for mitigation of chlorosilane spills and fires. The foam system requires matching the foam concentrate with the foam educator (line proportioning system), the foam nozzle, the pressure drop across the educator, and the pressure at the foam nozzle to make a foam of the right expansion with slow water drainage and the correct dilution of the foam concentrate. Use only a foam system compatible with the foam. Because all chlorosilanes are water reactive, medium expansion or CAF generated foam is preferred because it uses the least amount of water to extinguish the fire.

---

<sup>4</sup> Rolf Jensen & Associates. 2012. Fire Testing of Low Molecular Weight Silicones Fluids. Prepared for the Silicones Environmental, Health and Safety Council (SEHSC) to summarize the results of certain fire testing conducted by SEHSC and its member companies.

An adequate number of hydrants and, where appropriate, monitor nozzles should be provided wherever chlorosilanes are stored, handled or processed. Please reference Section 6.6 on Plume and Vapor Cloud Mitigation.

Of critical importance is the provision of adequate spill control facilities to safely drain away burning chlorosilanes and prevent other important areas and property from being exposed to the fire. This may include such features as diking, curbs, sloped surfaces, drainage trenches and remote impounding areas. Spill control facilities should be designed to comply with government regulations.

Additional fire protection features that may be warranted include (but are not limited to) those items listed below.

- Water supplies of sufficient capacity and duration
- Fire proofing of structural steel and steel supporting vessels and equipment
- Explosion-relief panels and explosion-resistant construction
- Fire walls with doors and dampers
- Vapour detection systems
- Fire detection and alarm systems

All fire protection should be designed and installed in accordance with all government requirements and other recognised standards in your country/region.

## ***6.6 PLUME AND VAPOR CLOUD MITIGATION***

In the event of a chlorosilane spill or fire consider mitigating the downwind effects of a plume of hydrogen chloride and chlorosilane by scrubbing as much of the vapor from the air as possible. By scrubbing some of the hydrogen chloride and chlorosilane out of the air, downwind exposure can be minimized.

Three key concerns should be considered. The responders may be in the cloud because of shifting wind conditions. If so, then complete personal protective equipment will be needed to avoid acid burns. Second, the water in contact with the hydrogen chloride and chlorosilane will form hydrochloric acid. This dilute acid may cause damage to whatever it comes in contact with. An effort should be made to collect, analyze, and if necessary, neutralize this acid. Third, the water runoff from scrubbing the plume needs to be prevented from entering the spill containment area holding the chlorosilane. Water entering the spill containment area may generate additional hazardous vapors and may make emergency response more difficult.

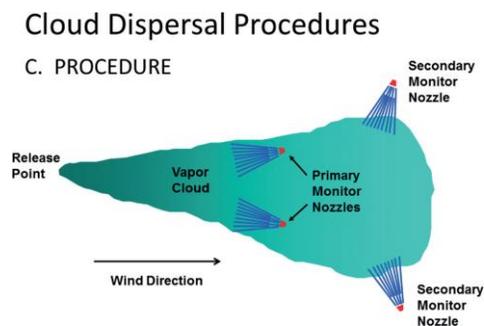
One possible procedure for downwind plume, whether visible or not: Set up a monitor nozzle(s) (or if not available, a 2-1/2 in. [6.4-cm] nozzle) downwind of the actual release. See Figure below, Primary and Secondary Nozzle Location, as an example of monitor nozzle locations. The nozzles should be set up so that the water from these nozzles does not come in contact with the spilled chlorosilane (or fire if one has occurred). A decision on how many nozzles to use will be based on the incident itself, the size of the plume, the wind, what is around the incident in the way of buildings, etc. Set the nozzles to spray as much as possible directly into the vapor cloud. The water

spray should be aimed into the wind and therefore into the vapor cloud. This will provide the best mixing and will put the maximum number of water particles in contact with the vapor cloud. Putting the water in perpendicular to the vapor cloud will have some effect, but it is not as effective as the recommended procedure.

When applying the water, three things are happening:

1. Hydrolysis of any airborne chlorosilane to hydrogen chloride.
2. Dispersion of hydrogen chloride with introduction of air.
3. Some scrubbing of hydrogen chloride from the air by the water.

The use of water spray from a monitor nozzle will make the cloud look more opaque but will make downwind concentrations of hydrogen chloride less than in an unmitigated condition.



## **CHAPTER 7. SPILL CONTAINMENT AND ENVIRONMENTAL IMPACT**

An accidental spill or release of chlorosilane results in a hydrogen chloride vapour fog, which should be minimised or controlled as quickly as possible.

Appropriate protective equipment is needed for individuals who must work in a chlorosilane vapour cloud.

### **SMALL SPILLS**

In the case of small spills (up to 5 litres), absorb the spill with dry inert absorbent material like dry sand, diatomaceous earth or the special absorbent PetroGuard®. The resulting material should then be properly packaged and disposed of.

(Note: this material will react with water and must carry an appropriate warning label!).

Clear the affected area thoroughly with copious amounts of water.

### **LARGE SPILLS**

For large spills provide diking or other appropriate containment, one possible procedure: Cover spill with medium expansion foam (alcohol resistant). Pump uncontaminated pure material into appropriate portable tanks, pressure cylinders or drums. Neutralise residual material with alkali base. Caution! Hydrogen gas may be evolved during hydrolysis and neutralisation with some chlorosilanes (UN1183, UN1242, UN1295, UN2988). By-product of hydrolysis is an insoluble liquid or a solid in which still reactive chlorosilanes might be trapped.

Hydrogen chloride vapours resulting from a large spill can be reduced by means of a water spray into the acid plume, being careful not to spray water directly into the spilled liquid chlorosilane pool. The resulting acidic waste water may require neutralisation prior to discharge to sewer systems.

In the event of accidental spillage of chlorosilanes to surface waters or to a municipal sewer system, promptly notify the appropriate pollution control agencies.

The impact of chlorosilane on the environment is mainly in the air compartment. The acidic fumes will burn plants and trees that come in contact with it. The impact on the terrestrial environment is limited and local. Contaminated soil should be treated as described above, neutralised and sent for disposal. Spills in the aquatic environment result in an increase in water acidity (because of the hydrochloric acid formation) which may harm aquatic life.

(For details on waste disposal see Chapter XII).

## **CHAPTER 8. INSTABILITY AND REACTIVITY HAZARDS**

### ***8.1 INSTABILITY HAZARDS***

Chlorosilanes are stable in the absence of air, moisture and catalytic agents.

Due to the low flash point and high vapour pressure of many chlorosilanes a flammable or explosive environment can be easily obtained in the presence of air. Many chlorosilanes have flash points lower than room temperature. It is very important to understand the physical properties and safe handling requirements on the SDS prior to handling a chlorosilane. Inerting, grounding and bonding of equipment are key in mitigating these hazards.

When chlorosilane is exposed to moisture in the air, the chlorosilane and water will react to form toxic and corrosive hydrogen chloride. Precautionary measures should be used to avoid contact between water or moisture when handling chlorosilanes. Reference the SDS for proper personal protective equipment and ventilation when handling chlorosilanes.

Hydrochlorosilanes, chlorosilanes containing at least one SiH bond, can generate hydrogen in addition to hydrogen chloride when exposed to moisture in the air. This will contribute to the flammability or explosive environment noted above.

### ***8.2 REACTIVITY HAZARDS***

#### **AIR**

Chlorosilanes, except for silicon tetrachloride, are flammable and can form explosive mixtures with air. Moisture in air causes hydrolysis; hydrogen chloride fumes will be generated.

#### **WATER**

Water reacts vigorously with chlorosilanes, forming large volumes of toxic and corrosive hydrogen chloride. Hydrochlorosilanes such as trichlorosilane and methyldichlorosilane when reacted with water can also produce hydrogen. The hydrogen formation rate will increase with the presence of acids, such as hydrogen chloride, and significantly increase with the presence of bases, such as sodium hydroxide. Chlorosilanes with 3 and 4 chlorides will form silicone gels when reacted with water. Chlorosilanes with 1 or 2 chlorides will form silicone oils that are generally lighter than water.

#### **ALCOHOLS AND ORGANIC ACIDS**

Primary alcohols and organic acids react with chlorosilanes almost as rapidly as water, forming hydrogen chloride; secondary and tertiary alcohols react less rapidly. As with water, due to the presence of OH, hydrochlorosilanes will also generate hydrogen.

## **AMMONIA AND AMINES**

Ammonia and the aliphatic amines react rapidly with chlorosilanes, generating heat and solids (ammonium and amine salts).

## **BASES**

Bases react violently with chlorosilanes, generating heat and potentially generating hydrogen with hydrogen-containing chlorosilanes.

## **CHLORINE**

Chlorine will react violently with any hydrogen-containing chlorosilane. The catalysts that may cause decomposition and rearrangement include bases; Lewis acids, such as aluminium chloride and iron trichloride; and anhydrous bases, such as Grignard reagents, organoalkali compounds and metal hydrides. When it is necessary to mix hydrochlorosilanes with such reagents, allow for the formation of hydrogen and other flammable and pyrophoric gases such as silane, dichlorosilane and methylsilane

## **CHAPTER 9. MINIMUM ENGINEERING CONTROL OF HAZARDS**

### ***9.1 BUILDING DESIGN***

Consider building chlorosilanes process installations outdoors in open structures with good access for mobile fire fighting and spill equipment.

Consider locating storage vessels outside, remote from buildings and other facilities such as overhead utilities and process piping. All spills should be contained in a safe location and diverted away from municipal sewer systems and natural waterways.

Consider firewalls for the isolation of larger volumes of flammable chlorosilanes when outside storage is not possible.

When it is necessary to handle chlorosilanes within buildings, consider providing exhaust ventilation at floor level since the vapours are denser than air.

In case of flammable chlorosilanes incorporate appropriate fire protection in the building or open structure.

The structure containing flammable chlorosilanes should be of non-combustible materials. Exterior walls of enclosed buildings may warrant explosion relief panels.

Plan and practice personnel evacuation routes or means of exits.

The surfaces of equipment and building structures should be covered with a protective coating that will withstand accidental chlorosilane exposure.

Eyewashes and safety showers should be located in appropriate locations.

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

### ***9.2 EQUIPMENT DESIGN***

The design of piping and equipment for chlorosilanes is highly specialised because of the flammable and corrosive properties of these substances. These special concerns are briefly mentioned in this and following subsections.

The application of these concerns, and others, in the design of equipment, provision for adequate ventilation, and formulation of operating procedures can best be handled by appropriate engineers and safety and fire protection specialists.

### **GENERAL**

The total equipment, such as lines, pumps, valves, vessels, etc., must be thoroughly dried with no trace of water remaining before introducing any chlorosilane.

Prior to operation, the system should be tested for leaks at or above operating pressure using a procedure such as application of dry nitrogen and each joint painted with soap solution and checked for bubbles.

Totally enclosed systems should be used. Atmospheric openings or vents will allow moisture to enter the system causing the generation of hydrogen chloride, which will attack the equipment.

Use dry nitrogen (or other dry inerting agents including CO<sub>2</sub> and Argon), when any of the following must be done: pressurising vessels, priming pumps, blanketing tanks, and filling or withdrawing of tank contents.

Operational vents from nitrogen blanketing systems should be directed to a vent recovery system, or a vent scrubber or both.

## **MATERIALS OF CONSTRUCTION**

In the absence of water, carbon steel is satisfactory for piping and other equipment used to contain chlorosilanes.

Non-ferrous metals and alloys such as aluminium, bronze, copper, zinc or magnesium are more readily corroded and many, in case of fire, have low melting points.

Cast iron may be too brittle to contain chlorosilanes; consider using cast steel and forged steel.

Plastics are generally incompatible and reactive with chlorosilane service.

## **VESSELS**

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

Generally storage tanks should be completely vacuum resistant or should be equipped with automatic pressure controlled nitrogen supply and shut down systems which avoid dangerous underpressure. Design pressure is dependent on the properties of the chlorosilanes stored. Generally vessels should have emergency vents. They should satisfy the requirements stated in the local regulations. As an alternative to emergency vents, consider equipping the storage vessels with safety devices which will stop all pressure producing units immediately as soon as a predetermined pressure is reached.

Vessels being equipped with pressure-relief valves to relieve excess internal pressure due to fire or other pressurising causes should have for preference a non-fragmenting-type rupture disk ahead of the relief valve on chlorosilane storage vessels; otherwise, it must be avoided that the valve can be clogged with hydrolysis products from chlorosilane contact with moisture in air. Appropriate blow down systems have to be designed in order to recover chlorosilanes released by safety valves.

A preventive maintenance schedule programme should be established to inspect pressure relief systems.

Vessel supports should be made of appropriate materials which may include reinforced concrete or structural steel. Fire-protective coatings should be used if the stored chlorosilane is flammable.

## **PIPING**

Consider carbon steel piping.

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.

Only flange gaskets which are stable to chlorosilanes (such as non-asbestos compressed materials, Teflon, graphite) must be used to provide a leak-tight joint. Chlorosilane producers should be contacted for advice on appropriate materials.

Spiral-wound metallic gaskets or metal/graphite gaskets should be considered for fire resistance.

Prior to use, all piping has to be checked by pressurising with nitrogen for tightness. All piping should be checked regularly for leakage.

Valves of all sizes can be ductile iron, forged steel, or cast steel valves with stainless steel or steel trim.

Consider using remotely controlled valves for bottom connections on vessels for quick shut-off in case of fire exposure or other emergency cases.

The interconnection of road / rail tank cars or portable tanks to permanent piping can be made with swing arm rotary joints (best solution) or seamless, braided flexible metal hose. Consider using flanged or union connections. Do not use quick disconnect couplings, due to the fact that they may be inadvertently released.

## **PUMPS**

Pump selection should be based on the one that provides the best features against leakage to the atmosphere, such as canned pumps.

## **INSTRUMENTATION**

Best available equipment should always be used.

Modulating leak-tight control valves and remote control valves limit operator exposure in the event of an incident.

Consider stainless steel diaphragm pressure switches and differential pressure transmitters.

Use thermometers with a sleeve welded to the equipment to avoid breakage and inconsistent positioning

Level indication with a high-level alarm is recommended on all vessels. Feed and bottom discharge valves of chlorosilane storage tanks should be remotely controlled as well as pumping equipment and integrated in emergency shutdown switches.

Chlorosilane storage tanks must always 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.

### ***9.3 VENTILATION***

Enclosed processing buildings should be ventilated at a rate that threshold limit values for HCl are satisfied. If mechanical ventilation is used, the electrical equipment should meet legal requirements.

### ***9.4 ELECTRICAL EQUIPMENT***

All electrical equipment must conform to applicable legal requirements.

Area classifications should be established for all areas in which chlorosilanes are handled or stored. Consider vapour-tight and corrosion-resistant electrical equipment due to the corrosive nature of areas in which chlorosilanes are stored and handled.

### ***9.5 STATIC ELECTRICITY***

Static electricity discharges can ignite flammable chlorosilane vapour. Inerting the whole system in which chlorosilanes are transferred with dry nitrogen is therefore of utmost importance.

Static electricity may be generated when any of these compounds flow through or are discharged from a pipe or fall freely through space. Splash filling is particularly hazardous and should be avoided.

To drain off static charges and avoid spark discharges, a continuous path from the point of generation to ground must be provided. This may be accomplished by electrically interconnecting (bonding) all vessels and piping (jumper cables fixed to piping flange screws in order to guarantee a good electrical contact over the flange gaskets) and grounding all vessels and piping.

Ground wiring should be of sufficient size to provide reasonable protection against physical wear. Periodic checks of continuity to ground should be made. If possible, use grounding stations that continually monitor the status and indicate the existence of an effective connection.

All fixed tanks and all road / rail tank cars or portable tanks should be effectively grounded and bonded.

**CAUTION:**

Drums, road / rail tank cars or portable tanks and reactors may be coated on the interior with a non- conductive coating. This will reduce the effectiveness of any external connection to ground. Therefore, in addition to bonding and grounding, drums, road / rail tank cars or portable tanks may be purged with dry nitrogen before filling with a flammable chlorosilane. Purging with dry nitrogen before filling with any kind of chlorosilane suppresses hydrolysis steps leading to contamination.

Fill lines should be conductively bonded to provide a path to ground externally.

Road / rail tank cars, portable tanks, pressure drums or pressure cylinders filled through top connections should have dip lines that extend to within 15 centimetres of the bottom of the container to prevent the free fall of liquid and to maintain a conductive path to the dip tube

## **CHAPTER 10. SHIPPING, LABELLING AND MARKING**

For shipping, labelling and marking requirements, refer to the GHS compliant Safety Data Sheets (SDS) or the shipping documents received from the supplier, as well as to applicable codes and regulations. Shipments must be prepared in accordance with applicable transportation regulations, as well as any carrier-specific requirements. Personnel involved in preparing shipments must be appropriately trained.

## **CHAPTER 11. HANDLING OF BULK CONTAINERS, DRUMS, PRESSURE DRUMS AND PRESSURE CYLINDERS**

### **GENERAL CONSIDERATIONS**

Refer to the safety and other precautions in other sections of this manual when unloading chlorosilanes. It is particularly important that appropriate personal protective equipment is used. Normal procedures for handling corrosive and flammable materials also apply.

Bulk containers include road / rail tank cars and portable tanks.

Use only bulk containers or other packaging units as required by local or government regulations for chlorosilane handling. No bulk container or other packaging units should be completely filled and the degree of filling is specified by product in the appropriate regulations.

Inspect shipping containers for leaks before they are allowed to enter or leave the plant.

Exclude moisture and air.

Only appropriately trained employees should sample, connect, unload or disconnect any chlorosilane shipping container.

Operations should be continuously attended and the shipper's instructions for unloading should be followed.

Proper protective clothing and equipment should be worn during connecting, unloading and disconnecting operations. An emergency shower and eyewash station should be provided that services the unloading area.

All devices (fittings, pumps, hoses, etc.) must be suited for use with chlorosilanes. These devices should be used only for chlorosilanes, kept free of moisture or other contaminants and properly protected against mechanical damage.

Keep valves, piping and the interior and exterior of protective valve housings clean and free of contaminants, gels or gel-like material caused by the reaction of chlorosilanes with water.

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

If a drum, pressure drum, pressure cylinder, road / rail tank car or portable tank is involved in an accident or develops a leak, the required emergency services must be notified and the public warned to stay away. Notify the manufacturer of the chlorosilane immediately.

## **DRUMS**

The following equipment should be available to service chlorosilane drum unloading stations: emergency eyewash and shower, dry-chemical fire extinguisher and cartridge respirators. Adequate ventilation must be provided at enclosed locations. Electrical grounding connections, provisions for spill containment and a source of dry, nitrogen gas are also necessary.

### ***Withdrawing Chlorosilanes***

The area should be well ventilated or equipped with local exhaust equipment. Before withdrawing chlorosilanes from drums, the drum must be electrically grounded and bonded to the receiving container.

Chlorosilanes can be withdrawn through a steel valve installed in the drum bung. Dry nitrogen (air or oxygen must not be used due to the flammability of chlorosilanes) should be introduced into the drum through the other bung to replace the volume of liquid. The nitrogen supply system should include a check valve, shut-off valve, pressure regulator and pressure relief valve. The system can be modified to withdraw chlorosilanes by gravity or to feed a pump. Application of pressure to a drum is not recommended.

### ***Handling Empty Chlorosilane Drums***

Empty drums should be isolated and thoroughly rinsed inside and out with water before disposal in accordance with local regulations. Water washing creates hydrogen chloride gas and a solution of dilute hydrochloric acid, therefore making sure drums are thoroughly drained of chlorosilanes before flushing to avoid dangerous pressure rise inside the drum. Flooding the drum with water while the bungs are removed will absorb acid fumes as well as the heat of the reaction (see Chapter 4 above for general PPE precautions recommended to follow before rinsing drums).

### ***Defective or Leaking Drums***

When handling leaking drums of chlorosilanes, personal protective equipment as necessary due to the situation should be worn. Clear the surroundings of non-essential personnel and material. If this is not possible, then move the leaking drum (if it can be done safely) to an outdoor area protecting the leaking drum from wet weather. If the material cannot be transferred into a new, purged drum then put the leaking drum in an oversized "salvage drum". Be sure to properly label the salvage drum. Contact the material manufacturer for information on how to handle the situation.

## **PRESSURE DRUM / PRESSURE CYLINDER**

One possible procedure is provided for illustrative purposes; other procedures may be more appropriate given a facility's particular circumstances and design.

### ***Connecting up and unloading***

Wearing proper safety clothing, inspect the pressure drum or pressure cylinder for any damage or leakage around the valve area. Attach an approved grounding cable to the

pressure drum or pressure cylinder. Close liquid and vapour valves; then carefully remove the threaded plugs. Be aware of potential valve leakage upon plug removal.

Clean and dry the unloading transfer line and vapour line connections; then make the respective connections to the pressure drum or pressure cylinder. Avoid using quick-type connections. Once the connections are complete, pressurise lines with nitrogen to check for leaks.

To start transfer, slowly open the pressure drum or pressure cylinder valves; check for leaks in the transfer line hook-up. Operate the pump or apply nitrogen pressure slowly until there is a normal flow of liquid into the storage tank.

When pumping, avoid a vacuum in the pressure drum or pressure cylinder; or when pressurising, avoid overpressures.

### ***Disconnecting***

When the pressure drum or pressure cylinder is empty, shut off the nitrogen at the station and at the pressure drum or pressure cylinder. Allow the pressure drum or pressure cylinder pressure to lower through the liquid line to the storage tank. Then shut off the product valve at the cylinder and storage tank before disconnecting the lines.

Use caution when disconnecting the chlorosilane unloading lines since there may be some residual liquid or vapour pressure. Replace the fittings on the liquid and vapour valves of the pressure drum or pressure cylinder and receiving station; close the cylinder fittings tightly.

## **BULK CONTAINER UNLOADING**

Bulk containers include road / rail tank cars and portable tanks.

The unloading area should be arranged so that any liquid spillage would drain away from both the bulk container and exposed structures and to a safe, contained area.

Appropriate barriers and signs should be used to ensure that the bulk container cannot be moved while it is connected to the unloading station.

The engine of any truck must be shut off before starting to unload and not restarted until the operation is complete.

Prior to unloading into a storage tank, check the level to make sure that the amount of material to be received will not overflow the storage tank. All vents should be connected to a vapour removal or recovery system.

Check the bulk container and all fittings and devices to make certain they are free of moisture or other contaminants and are in proper condition.

Before any connection or contact is made between a bulk container and unloading facilities, the bulk container should be electrically grounded. Any bulk containers should be properly bonded (electrically connected) and grounded before operations are started.

The unloading of chlorosilanes can be accomplished by pumping and/or pressure. Dry nitrogen should be used for liquid displacement or pressurising through a vapour-tight connection. Check the data plate to identify the working pressure.

The nitrogen line should be equipped with a regulator to control pressure, a non-return valve to prevent back-flow and a safety relief valve to prevent over pressuring the bulk container. Remote shut-off locations are recommended for the nitrogen supply and pump switch.

When pumping, avoid creating a vacuum in the system.

Should any hazardous conditions arise, unless contraindicated, immediately shut off the pump and /or nitrogen gas supply and vent the pressure from the bulk container. Close all valves, and other openings and then disconnect all unloading connections. Do not resume unloading until the hazardous condition has been eliminated. Remotely operated valves and safety trips designed, installed and maintained for the required integrity level as defined by the process risk assessment are recommended. The ability to isolate and then vent a bulk container during a hazardous condition may be a key to safety mitigation.

Empty transfer lines by purging with nitrogen after unloading. Do not close valves on both ends of a transfer line full of liquid chlorosilanes after unloading. Temperature changes could result in a hydrostatic pressure build-up with resulting leaks or piping failure.

When unloading is complete disconnect all lines with care since there may be some residual liquid or pressure. Plug or cap all fittings tightly and ensure the empty container is labelled in accordance with regulations.

## **UNLOADING – ROAD TANK CARS OR PORTABLE TANKS**

### ***Connecting up and unloading***

Check that the valves on the road tank car or portable tank are closed. Ensure that the liquid and gas transfer lines are free of moisture and foreign material.

To check for possible residual liquid between the valves and/or cap on the liquid line of the road tank car or portable tank, slowly loosen the fitting, being sure to use the proper personal protective equipment and clothing.

Connect the liquid and vapour lines of the road tank car or portable tank to the unloading station.

To start the transfer, slowly open the tank valves and check for leaks in the transfer line. Operate the pump or apply nitrogen pressure slowly until there is a normal flow of liquid into the storage tank. Monitor the storage tank level during the transfer.

### ***Disconnecting***

When the road tank car or portable tank is empty, shut off the nitrogen at the station and at the tank. Allow the transport tank pressure to lower through the liquid line to the storage tank. Then, shut off the product valve at the transport tank and storage tank before disconnecting the line. Use new gaskets and re-fit any caps, plugs and blanks.

## **UNLOADING - RAIL TANK CARS**

### ***Preparation of the Rail Tank Car for Unloading***

The unloading track should be level and the rail tank car positioned accurately for connection to the unloading system and unloading platform.

Unless the rail tank car is protected by a closed and locked switch or gate, place a derailer at one or both ends of the unloading track approximately one car length from the rail tank car being unloaded. Set the hand brakes, chock the wheels and ground the rail tank car.

A caution sign must be placed on the track or rail wagon to give the necessary warning to persons approaching the rail tank car. Display the sign until after the rail tank car has been unloaded and disconnected.

### ***Connecting up and unloading***

The loading swing bridge should extend to the centre of the rail tank car, should have handrail protection, and should be counterweighted or otherwise designed for case in raising and lowering. The rail tank car should be properly bonded and grounded.

The sequence of removing pipe caps and handling the valves is particularly important. The vapour valve should be opened first so pressures can be equalized as the liquid is removed. If the liquid is removed without equalization, atmospheric pressure may cause the walls of the tank car to collapse. The liquid valve should be opened last.

### ***Disconnecting***

When the rail tank car has been completely unloaded, close all valves and disconnect the unloading and vent lines. Remove grounding connections. Plug or cap all fittings tightly.

Remove wheel blocks, derailleurs, caution signs and locks from switches and tracks. Return the empty rail tank car in accordance with transport regulations.

## **CHAPTER 12. WASTE DISPOSAL**

Customer treatment and disposal of chlorosilanes must comply with regulatory permits. Routine treatment and/or disposal may require permits and/or specialized equipment.

If the chlorosilane to be disposed of is uncontaminated and in its original undamaged packaging unit, contact the supplier.

Chlorosilanes are typically incinerated for disposal, with highly specialised equipment generally being required to handle silicon dioxide and hydrogen chloride.

To dispose of chlorosilanes at the customer's place consult with a specialist of the supplier. The feasibility of the chosen process should be tested first with a small amount of chlorosilane.

In general, disposal of chlorosilanes can be accomplished by controlled introduction into water (hydrolysis) or neutralisation with aqueous alkaline (basic) compounds such as lime, soda-ash or caustic or sodium bicarbonate. To prevent the evolution of acidic vapour, the quantity of water or alkaline neutralisation agent must be sufficient to absorb all of the hydrogen chloride that will be formed.

The exothermic and corrosive nature of the reaction should be considered in selecting materials of construction for the equipment used in this procedure. Adequate ventilation should also be provided to handle any vapour evolution in a safe manner. Foam treated chlorosilane should be disposed in a similar way (hydrolysis, neutralisation).

The final reaction products formed depend on the nature of the chlorosilane treated (i.e. number of hydrolysable Si-Cl bonds). Liquid siloxanes, solid silicic acid, aqueous siliconates or rubbery material may be produced. Aqueous acid is always a by-product of hydrolysis with pure water. Trapped chlorosilane and residual acid in the reaction products require additional treatment (washing) prior to disposal by incineration (liquids, solids) or land-filling (solids).

### **SPECIAL CASE OF HYDROCHLOROSILANES.**

The disposal of hydrochlorosilanes (such as trichlorosilane, methyldichlorosilane, etc.) should be conducted with extreme care due to the potential generation of hydrogen gas. Hydrogen gas is extremely flammable and can cause a rapid pressure build-up unless properly vented. The formation of explosive oxyhydrogen gas must be prevented by purging with nitrogen.

These hydrochlorosilanes should be hydrolysed with water only to minimise the potential for hydrogen generation. The resultant reaction mixture may then be neutralised with additional precautions because under alkaline conditions hydrogen is evolved. Sodium bicarbonate is recommended for neutralisation.

Silicic acid, which is formed, contains Si-H bonds. Therefore, the solid residue represents a hazard too and must be handled with care. Especially when dry self-ignition may occur.

See the 2016 Global SiH manual for more details.

## CHAPTER 13. EQUIPMENT CLEANING AND REPAIRS

One possible procedure is provided for illustrative purposes; other procedures may be more appropriate given a facility's particular circumstances and design.

Cleaning, repair and entry of chlorosilane equipment should be under the direction of trained personnel who are familiar with the hazards. All precautions should be reviewed and understood by all personnel working on the equipment.

Consider the preparation of a check-list work procedure for the entire job recognising possible hazards as they might occur.

Empty the tank or equipment to be cleaned of all liquids.

Pipelines into or out of the tank, or other apparatus should be shut off and disconnected by installing a blank flange on the open end to protect against human error and unsuspected leaks. Valves and previously installed blank flanges in the pipeline should not be relied on unless checked.

The tank or equipment should be purged through the vent system with dry nitrogen.

After purging, open all top openings and fill the vessel rapidly with water; then, while vented, drain the water out to a safe location as rapidly as possible.

Measure the pH of the liquid remaining. If it is acidic, neutralise with sodium bicarbonate.

In case of solid residues continue to flush with water until all solids are removed. Insertion of a steam hose to boil the water or the application of a high pressure water jet may help to loosen solids.

When the tank is completely free of visible solids, steam it out to vaporise any minute residue. Then drain the tank and allow it to dry.

Prior to any vessel entry or hot work the equipment and surrounding area should be checked for proper oxygen levels, flammability levels and toxicity (HCl) levels to ensure a safe work area. Pay close attention to where hydrogen may have been trapped in the head or top nozzles of equipment.

Tanks and equipment used for the first time for chlorosilane service or after maintenance must be cleaned of any contaminants including rust, dried completely and thoroughly purged with dry nitrogen. Depending on the use and application a flush of the system with the chlorosilane may be required to prevent product discoloration and metal contamination.