



Centre Européen des Silicones

A Sector group of Cefic

**SAFE
HANDLING
OF
CHLOROSILANES**

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SAFE HANDLING OF CHLOROSILANES

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 West 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-Chemie. The CES Operating Safety Committee has produced this brochure.

The purpose of this brochure is to provide all persons who will use, handle, or otherwise be exposed to chlorosilanes with information about the safe handling and use of the eight main 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.

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

The full text of this publication should be consulted for information on the hazards of chlorosilanes 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. Start first aid immediately in all cases of contact with chlorosilanes (First aid - See Chapter III).

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 other safety information for his own particular situation.

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CHAPTER II 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, Chlorohydrogenomethylsilane, Chloro(hydrogen)methylsilane	$(\text{CH}_3)_2\text{HSiCl}$	1066-35-9	-
Methyltrichlorosilane	Trichloromethylsilane	CH_3SiCl_3	75-79-6	1250
Trimethylchlorosilane	Chlorotrimethylsilane	$(\text{CH}_3)_3\text{SiCl}$	75-77-4	1298
Methyldichlorosilane	Dichloromethylsilane, Dichlorohydrogenomethylsilane, 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	-
Chloropropylmethyldichlorosilane	Dichlorochloropropylmethylsilane	$\text{C}_3\text{H}_6\text{ClCH}_2\text{SiCl}_2$	7787-93-1	-
Vinyltrichlorosilane	Trichloroethenylsilane	$\text{CH}_2\text{CHSiCl}_3$	75-94-5	1305
Vinylmethyldichlorosilane	Dichloroethenylmethylsilane	$\text{CH}_2\text{CHCH}_2\text{SiCl}_2$	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	HSiCl_3	10025-78-2	1295
Silicon tetrachloride	Silicon chloride, Tetrachlorosilane	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.

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

CHAPTER III HEALTH FACTORS

3.1 GENERAL

Ingestion (swallowing) of liquid chlorosilanes may cause severe internal injury or death.

The chlorosilanes all react with moisture in the air or water to produce hydrogen chloride, the principal reaction product that can cause acute injury to any body tissue contacted.

The major acute health risks are potentially severe corrosive burns of the skin, eyes or respiratory tract.

Chronic health effects are not expected with these chemicals except as a result of severe acute injury. In any case a physician should be consulted.

First Aid - General principles

First aid should be started at once in case of contact with chlorosilanes in any form.

It is important to remove the injured person from the contaminated area as soon as possible.

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.

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 up to severe chemical burns that may result in total loss of sight.

First Aid and Medical Treatment

Irrigate eyes immediately with large amounts of water for a minimum of 15 minutes.

A physician should be called in attendance immediately. If the physician 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 physician, 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 physician. A physician should see all cases.

Clothing removed should be bagged and cleaned with appropriate precautions.

INHALATION

Inhalation of chlorosilane vapours or hydrochloric acid vapours or mist may cause damage of the respiratory tract.

Chlorosilane injury from inhalation 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, artificial respiration should be initiated immediately; oxygen should be administered but only by qualified personnel.

An injured person should be kept comfortably warm, but not hot.

Never attempt to give anything by mouth to an unconscious person.

GASTROINTESTINAL TRACT

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

First Aid and Medical Treatment

Any person ingesting liquid chlorosilanes must be evaluated and treated immediately on an emergency basis by a physician.

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 will cause irritant dermatitis.

Repeated inhalation of the mist will cause an inflammation of the upper and lower respiratory tract.

CHAPTER IV PERSONAL PROTECTIVE EQUIPMENT

4.1 GENERAL

Personal protective equipment is not an adequate substitute for good safe working conditions, adequate ventilation, and intelligent conduct on the part of employees working with chlorosilanes. In emergency situations and in certain operations involving chlorosilanes, full 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 worn.

4.2 PROTECTIVE EQUIPMENT

EYE AND FACE PROTECTION

Safety glasses

Safety glasses with unperforated side shields may be used where continuous eye protection is desirable, as in laboratories.

Spectacles 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

Chemical splash goggles should be worn whenever there is danger of chlorosilanes coming in contact with the eyes. Goggles should be properly fitted.

Face shields

Plastic shields (full length, 20 cm (8 in) minimum, with forehead protection) should be worn in addition to chemical splash goggles where face protection is desired.

Alternatively a gas mask can replace splash goggles and face shields.

Contact lenses

The wearing of contact lenses is not recommended where there is risk of exposure to chlorosilanes. Contact lenses 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

The 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. In all cases the apparatus should be equipped with a face piece that maintains positive pressure at all time. This will prevent any 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 never be used for emergency ingress or in areas of unknown vapour concentrations or oxygen content. The wearer must 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. Because of these limitations, only restricted use of cartridge respirators is considered appropriate.

BODY AND FOOT PROTECTION

Body Protection

Protective clothing will offer protection for a limited time only, but it will give the exposed person sufficient time to get clear of the contaminated area and reach a safety shower.

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)). Viton and similar synthetic rubber materials showed the best results. PVC and Nitrile Rubber can be used as a protective material (gloves, clothing and boots) for short term contacts in normal handling procedures to prevent severe burns of the skin. Latex rubber should not be used.

Hand Protection

To protect hands and arms, wear preferably long-sleeved gloves or gauntlets that cover the forearms and are arranged under the coat sleeves and properly sealed.

This will provide only limited protection.

Foot Protection

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

Head Protection

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

CHAPTER V TRAINING AND JOB SAFETY

Safety in handling 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 thoroughly familiar with the contents of the MSDS. In addition to being well acquainted with the hazardous characteristics of chlorosilanes 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 chlorosilanes.

After becoming thoroughly familiar with the hazardous characteristics of chlorosilanes, the supervisor should review each procedure step by step, preferably with the workers directly involved in the use and handling of chlorosilanes. 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 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 safety showers, fire extinguishers, alarms, etc.

The importance of water washing in the safety shower/eyewash for a minimum of 15 minutes after contact with chlorosilanes should be emphasised. Contaminated clothing and shoes must be removed before the person is washed under the safety shower. The assistance by another person to help remove clothing and, perhaps, to help hold eyes open in the eyewash may be necessary.

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.

CHAPTER VI FIRE HAZARDS AND FIRE PROTECTION

6.1 FIRE HAZARDS

Except for silicon tetrachloride, all of the chlorosilanes covered in this booklet 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 methylchlorosilane, 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).

Additional information on the fire hazards of the chlorosilanes (e.g., flash points and flammable limits) can be found in the appropriate MSDS.

6.2 FIRE PREVENTION

As with all flammable liquids, fire prevention is extremely important when using or storing chlorosilanes. This not only includes the provision of measures to minimise the potential for ignition, but also 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 dry nitrogen
- Control of 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, except for very small fires. Water can also 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.)

Sodium- and potassium-bicarbonate-based dry chemical fire extinguishers have proven effective to extinguish small chlorosilane fires, except those involving hydrogen-containing chlorosilanes such as trichlorosilane and methylchlorosilane, 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 generally 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.

Foam is the most effective agent overall for use on chlorosilane fires. However, a number of variables, most notably the chlorosilane involved, the foam concentrate, the concentration of the foam, the expansion ratio (final foam volume versus initial solution volume), the application equipment and the fire conditions, can have a significant impact on the effectiveness of foam on chlorosilane fires. Certain combinations of these variables can in fact produce less than satisfactory (and even adverse) results.

In general, though, alcohol-(polar) compatible AFFF (Aqueous Film Forming Foam) has proven to be an extremely effective foam type, and medium-expansion foam has been found to be the most effective foam expansion. Other foam types and expansions, however, can produce satisfactory results, especially on fires involving dimethylchlorosilane, trimethylchlorosilane and other heavily organic substituted chlorosilanes. For chlorosilanes containing Si-H (silicon-hydrogen) bonds, e.g., trichlorosilane and methylchlorosilane, alcohol-compatible AFFF and medium-expansion foam are highly recommended for maximum effectiveness.

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 significant amounts of corrosive vapours. In addition, hydrogen vapours can be released from hydrogen-containing chlorosilanes and may be trapped under the foam blanket. Extreme care should be taken not to disturb the foam blanket during and after foam application. (See Section 6.4 for more information on manual fire fighting.)

Other extinguishing agents that may be effective on small fires include dry sand and carbon dioxide. (Caution: When using carbon dioxide in enclosed spaces without adequate ventilation, an asphyxiation hazard can be created.)

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.

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, as appropriate, should be evacuated 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.)

As indicated in Section 6.3, foam has proven to be the most effective extinguishing agent on chlorosilane fires. When using foam, 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

Despite the chlorosilanes reactivity with water, water sprinkler systems are the most effective means of protecting buildings, equipment and building contents from chlorosilane fires. Foam-water sprinkler systems can also be used to provide additional extinguishing capabilities (such systems, however, are likely to have only limited effectiveness on trichlorosilane and methylchlorosilane fires).

In tank farms and other areas where spilled chlorosilanes would be relatively confined, a permanently installed medium-expansion foam system can be provided to extinguish any chlorosilane fires. An adequate number of hydrants and, where appropriate, monitor nozzles should be provided wherever chlorosilanes are stored, handled or processed.

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 accommodate the largest anticipated release of chlorosilanes as well as the quantity of water expected from fire fighting operations (including sprinkler systems, hoses, monitor nozzles, etc.).

In closed buildings CO₂ may be an adequate extinguishing medium.

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.

CHAPTER VII 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.

Full 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. 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 water.

LARGE SPILLS

For large spills provide diking or other appropriate containment. 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 could be an insoluble liquid or a solid.

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 requires 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 VIII **INSTABILITY AND REACTIVITY HAZARDS**

8. 1 INSTABILITY HAZARDS

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

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 gases.

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 hydrogen chloride. Trichlorosilane and methyldichlorosilane reacted with water can also produce hydrogen. Hydrogen can further be generated when hydrochloric acid reacts with some metals.

ALCOHOLS

Primary alcohols react with chlorosilanes almost as rapidly as does water, forming hydrogen chloride; secondary and tertiary alcohols react less rapidly.

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.

9.1 BUILDING DESIGN

Process installations should be built outdoors. Chlorosilanes are best processed in open structures with good access for mobile fire fighting and spill equipment.

Storage vessels should be located 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.

Firewalls are necessary for the isolation of larger volumes of chlorosilanes when outside storage is not possible.

When it is necessary to handle chlorosilanes within buildings, all rooms should be provided with exhaust ventilation at floor level since the vapours are denser than air.

Fire protection should be incorporated 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.

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

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 to ensure maximum security and economy can best be handled by experienced 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 with 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 only dry nitrogen, 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 should never be used. They are more readily corroded and many, in case of fire, have low melting points.

Cast iron, due to its brittleness, must not be used to contain chlorosilanes; cast steel and forged steel can be used.

Plastics should not be used in chlorosilane service due to incompatibility and reactivity of this material.

VESSELS

Storage vessels should 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, the storage vessels may be equipped 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 or after 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. "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.

Vessel supports should be made of reinforced concrete or structural steel. Fire-protective coatings shall be used if the stored chlorosilane is flammable.

PIPING

Carbon steel piping is recommended.

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 (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 are preferred when maximum fire resistance is desired.

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.

Remotely controlled valves are recommended 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. Use flanged or union connections. Do not use quick disconnect couplings.

PUMPS

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

INSTRUMENTATION

Best available equipment should always be used.

Modulating leak-tight control valves are recommended. Remote control of all-important valves should be installed.

Stainless steel diaphragm pressure switches and pressure and differential pressure transmitters are recommended.

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 national legal requirements.

Area classifications should be established for all areas in which chlorosilanes are handled or stored. It is recommended that vapour-tight and corrosion-resistant electrical equipment is used 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 is best accomplished by electrically interconnecting (bonding) all vessels and piping and grounding all vessels and piping.

Ground wiring should be sufficient size to provide reasonable protection against physical wear. Periodic checks of continuity to ground should be made.

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 should be purged with dry nitrogen before filling with a flammable chlorosilane. Generally purging with dry nitrogen before filling with any kind of chlorosilane is always recommended to suppress 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.

CHAPTER X

SHIPPING, LABELLING AND MARKING

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

CHAPTER XI **HANDLING OF BULK CONTAINERS, DRUMS, PRESSURE DRUMS AND PRESSURE CYLINDERS**

GENERAL CONSIDERATIONS

All safety and other precautions documented in other sections of this manual must be observed 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.

All shipping containers should be inspected for leaks before they are allowed to enter or leave the plant.

Care must be taken to ensure moisture and air are excluded at all times.

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

All operations should be continuously attended and the shippers 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 at 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.

At all times, valves, piping and the interior and exterior of protective valve housings should be kept 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 local emergency services should be notified and the public warned to stay away. Notify the manufacturer of the chlorosilane immediately.

DRUMS

The following equipment should be available at 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 make 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.

Defective or Leaking Drums

When handling leaking drums of chlorosilanes, full 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

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. Ensure liquid and vapour valves are in closed position; then carefully remove the threaded plugs. Be aware of potential valve leakage upon plug removal.

Ensure the unloading transfer line and vapour line connections are clean and dry; 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, care should be taken to 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. Drainage should be directed 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 take care to avoid creating a vacuum in the system.

Should any hazardous conditions arise, 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.

Transfer lines should be emptied 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.

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. This sign must be displayed 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 ease 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; the liquid valve, 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 XII WASTE DISPOSAL

Customer treatment and disposal of chlorosilanes should be limited to emergencies since routine treatment and/or disposal could require regulatory permits and specialised equipment.

If the chlorosilane to be disposed of is uncontaminated and in its original undamaged packaging unit, it may be possible to return the product to the supplier, subject to the supplier's approval prior to shipment.

Incineration of chlorosilanes is the recommended disposal practice, with highly specialised equipment being required. The incinerator must be equipped with emission controls capable of handling silicone dioxides and hydrogen chloride.

Whenever there is a chance to dispose of the chlorosilane or chlorosilane mixture (safe transport provided) by incineration this should always be done. Disposal of chlorosilanes at the customer's place should always be done in close consultation with a specialist of the supplier. The feasibility of the chosen process should always 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 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.

CHAPTER XIII EQUIPMENT CLEANING AND REPAIRS

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

The preparation of a check-list work procedure for the entire job recognising all possible hazards as they might occur, has been found to be particularly effective in maintaining work safety.

The tank or equipment to be cleaned must first be completely emptied 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.

Tanks and equipment used for the first time for chlorosilane service or after maintenance must be cleaned of any contaminants including rust, dried carefully and thoroughly purged with dry nitrogen.



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