GLOBAL SAFE HANDLING OF HEXAMETHYLDISILAZANE

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

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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 Hexamethyldisilazane (HMDZ) 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 HMDZ. This colorless liquid is hydrolytically unstable in the presence of moisture and upon contact with water is expected to form ammonia (CAS No. 7764-41-7) and trimethylsilanol (CAS No, 1066-40-6). HMDZ is a flammable liquid.

Face shields, full-face respirator, gloves, goggles, multi-purpose combination respirator cartridge (US), type ABEK (EN14387) respirator filter should be used. HMDZ is considered to be an irritant to the skin and respiratory tract.

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 HMDZ and suggestions for its safe handling and use. 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 HMDZ (First aid - See Chapter 3).

SEHSC, CES and SIAJ will strive to update this guide as significant new information becomes available regarding the handling of HMDZ. Readers are encouraged to submit suggestions for improvement to SEHSC[1]. Importantly, however, neither SEHSC, CES, SIAJ or 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.[2]

[1] Submissions should be made to Tracy Guerrero at tracy_guerrero@americanchemistry.com.

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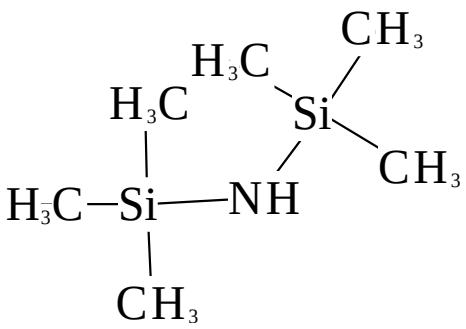
CHAPTER 2. HEXAMETHYLDISILAZANE NOMENCLATURE

This Guide is applicable to Hexamethyldisilazane:

CAS Numbers:	999-97-3
IUPAC Name:	1,1,1,3,3,3-hexamethyldisilazane (HMDZ)
Molecular Formula:	$C_6H_{19}NSi_2$
Structural Formula:	



Synonyms:	1,1,1-Trimethyl-N-(trimethylsilyl)silanamine
	Bis(trimethylsilyl)amine
	Disilazane, 1,1,1,3,3,3-hexamethyl-
	Hexamethyldisilazane
	Hexamethylsilazane
	HMDS
	HMDZ
	OAP
	Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-
	Dynasil HMDS
	Silazan HMN
	SEMICOSIL HMN-EL

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

CHAPTER 3. HEALTH FACTORS

3.1 GENERAL

HMDZ can be considered slightly to moderately toxic following acute oral, dermal, and inhalation exposure.

Studies of acute and short-term inhalation exposure to high doses have demonstrated respiratory tract irritation and CNS depression.

Under occlusive conditions, dermal necrosis has been observed.

Long term inhalation exposure is associated with neurotoxic effects of ataxia and decreased activity.

Medical advice should be obtained immediately after exposure to HMDZ.

First Aid and Medical Treatment

First aid should be started immediately after contact with HMDZ.

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 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 AND SHORT-TERM TOXICITY

EYES

Direct contact of HMDZ with the eyes of rabbits has resulted in trace conjunctival irritation. Based on several studies, it was determined that HMDZ was not irritating to the eye.

First Aid and Medical Treatment

Irrigate eyes immediately with large amounts of water for at least 15 minutes. Keep eyelids well open to rinse the whole eye surface and eyelids with water.

Seek medical advice immediately.

If it is necessary to transport the patient to a hospital or a physician’s office, irrigation of the eyes should be continued during transport.

SKIN

Skin contact under semi-occluded conditions caused minimal irritation with direct contact to 100% HMDZ in rabbits. However, studies conducted under occluded conditions with 100% HMDZ caused corrosion and in some cases ulceration and necrosis in rabbits.

Acute dermal studies in rabbits with high doses of HMDZ have indicated that this material can be absorbed and cause death and other treatment related effects. HMDZ is toxic via the dermal route of exposure.

No information is available on skin sensitization properties of this material.

First Aid and Medical Treatment

In cases of skin contact, remove contaminated clothing. Wash off with plenty of water and soap immediately for 10-15 minutes. In serious cases, use emergency shower.

Seek medical advice immediately.

Clothing removed should be bagged and cleaned with appropriate precautions.

INHALATION

Acute and short term inhalation exposure to HMDZ may cause respiratory tract irritation and CNS effects (like decreased activity and ataxia) based on studies in rats.

Short term inhalation studies in rats also showed the following treatment related effects that were not as severe and many resolved during the recovery period: decreased food consumption, decrease in body weight gain; changes in clinical chemistry and blood chemistry; and changes in increases in organ weights.

First Aid and Medical Treatment

If inhaled, remove person to fresh air.

If the victim is not breathing, artificial respiration should be initiated immediately; oxygen should be administered but only by qualified personnel.

If unconscious, place individual in a stable sideways position. Protect individual against loss of body heat. Never attempt to give anything by mouth to an unconscious person.

Seek medical advice immediately.

GASTROINTESTINAL TRACT

Acute oral studies in rats with high doses of HMDZ have indicated that this material can cause death; CNS effects; and redness of the gastrointestinal tract. HMDZ is considered harmful via the dermal route of exposure.

First Aid and Medical Treatment

If swallowed, do not induce vomiting. If vomiting does occur, lean the individual forward.

Rinse mouth thoroughly with water.

Never give anything by mouth to an unconscious person.

Seek medical advice immediately.

3.3 REPRODUCTIVE/DEVELOPMENTAL TOXICITY

In a reproductive screening study, HMDZ via the inhalation route did not elicit any treatment related effects for the reproductive and developmental endpoints evaluated in the study.

3.4 SUBCHRONIC AND CHRONIC TOXICTY

There are no chronic studies available for HMDZ.

A subchronic inhalation study also indicated the same type of CNS effects observed in acute and short term studies (decreased activity and ataxia) from inhalation exposure to HMDZ. There were also similar treatment related effects that were observed in the short term studies: decreased food consumption, decrease in body weight gain; changes in clinical chemistry and blood chemistry; and changes in increases in organ weights.

3.5 GENOTOXICITY

HMDZ did not demonstrate genotoxicity/mutagenicity when evaluated in short-term assays.

CHAPTER 4. PERSONAL PROTECTIVE EQUIPMENT

4.1 EYE AND FACE PROTECTION

Chemical splash goggles

Tightly fitting chemical splash goggles should be worn when handling HMDZ.

Face shields

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

A full-face respirator can replace splash goggles and face shields.

Contact lenses

The use of contact lenses should be prohibited where there is risk of exposure to HMDZ because they may trap material between the lens and eye.

4.2 RESPIRATORY PROTECTION

Employees who are subject to HMDZ exposure above recommended industrial hygiene thresholds should be provided with proper respiratory protective equipment and trained in its use and care.

Full face respirator

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

Full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) cartridges may be used as back up to engineering controls. 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.

4.3 BODY AND FOOT PROTECTION

Body Protection

Complete chemical resistant protective suit will offer short term protection.
Protective clothing should be flame retardant and antistatic.

Hand Protection

For full contact of HMDZ, long-sleeved nitrile rubber gloves with 0.4 mm minimum layer thickness should be used. For splash contact of HMDZ, long-sleeved nitrile

rubber gloves with 0.11 mm minimum thickness may be used. To eliminate chance of dermal exposure, gauntlets should be worn to cover forearms and be arranged properly under protective clothing.

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/bump 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 5. TRAINING AND JOB SAFETY

Safe handling and use of HMDZ depends upon effective employee education, proper training in safe practices and the use of safety equipment, and knowledgeable supervision.

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

Procedures for all foreseeable emergencies should be established, including the location and operation of eye wash stations, safety showers, fire extinguishers, alarms, and manual activation points for fixed fire protection.

Before undertaking training of the employees who are engaged in handling or processing HMDZ, the supervisor should be familiar with the contents of the SDS and the hazardous characteristics of HMDZ and the precautions explained in the SDS. Before handling, supervisors need to determine whether any regulatory requirements will be triggered by the planned use and/or handling of HMDZ, which may include provisions for specific risk analysis, emergency planning, process control, and training.

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

After becoming familiar with the hazardous characteristics of HMDZ, 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 or exposure to HMDZ, but also with the dangers that may be involved in handling containers, in operating equipment, possible electrostatic charge accumulation 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. Operating and handling instructions may include the proper PPE for each step where such protection is deemed appropriate; the addition of PPE pictograms in the documentation may also be helpful.

If there are critical steps in the process where, for example, overcharge, undercharge or incompatible material charge 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.

Employees should be thoroughly familiar with the flammability hazard of HMDZ, and the site-specific installations and procedures in place to minimize ignition. Such considerations may include proper grounding and bonding of equipment and containers, and the use of non-sparking tools. Material transfer rates may be limited to minimize electrostatic charge accumulation. Flame resistant clothing may be considered.

To the extent practicable, the employee should understand the chemistry and chemical reactions of the process, as well as the hazards of any potential cross-contamination resulting in the equipment or common shared equipment. For example, contact with water or moisture may result in ammonia.

Employees should also be aware of specific chemicals used and/or stored in the processing area, which could react violently with HMDZ (i.e. strong acids, strong bases). Training should include measures to prevent inadvertent mixing, proper

response in the event of accidental mixing (such as a leak, operational error or other incident), and awareness of other chemicals in the processing area, like strong acids which might react violently with HMDZ. Consider regular safety reviews with employees; annual reviews for HMDZ processing operations, and before there is any change made to the process or equipment. Detailed and 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

Hexamethyldisilazane (HMDZ) is a highly flammable liquid and vapour.

HMDZ liquid is lighter than water and may float on water, spreading material during fire fighting. Leaking material or fire runoff to sewer may create fire or explosion hazard.

HMDZ vapours are heavier than air and can accumulate to form explosive concentrations. The vapours may also spread a considerable distance to a source of ignition, and flash back towards the source.

HMDZ reacts with water to form ammonia.

HMDZ is a non-conductor and, therefore, can accumulate static electrical charges when processed, handled or dispensed.

HMDZ's flash point is 52 to 53 ^{o}F, closed cup, for "pure" material. Additional information on the physical and chemical properties of HMDZ, including numerical values for flash point, boiling point and flammable limits, can be found in the appropriate SDS.

Burning Characteristics

Burning HMDZ evolves carbon oxides, nitrogen oxides, and silicon oxides, and various other combustion by-products.

In a fire or if heated by radiant heat, a pressure increase may occur in closed containers of HMDZ; the container may burst, with the risk of a subsequent explosion.

6.2 FIRE PREVENTION

As with all flammable liquids, fire prevention is extremely important when using or storing HMDZ. This not only includes the provision of measures to minimize the potential for ignition, but also the design of equipment and facilities to prevent the release of HMDZ**.**

Fire prevention measures similar to those typically recommended for flammable liquids are necessary when storing or using HMDZ. 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 gas 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
- Provisions to control static charge accumulation and static discharge, including controlled transfer rates and use of dip-tubes (see section 9.5 for more information)

6.3 EXTINGUISHING AGENTS

Water is not an effective extinguishing agent for HMDZ fires. However, water fog can be used to knock down the vapour cloud to protect personnel by dispersing and diluting the vapour cloud. The vapour cloud may contain ammonia, which is generated from HMDZ reaction with water.

3% Alcohol Resistant Aqueous Film Forming Foam has been effectively used to extinguish small and large HMDZ fires.

Dry Chemical fire extinguishers may be used to extinguish small HMDZ fires. Expect to use much larger quantities of dry chemical than would be required to extinguish a similar hydrocarbon fire. Dry chemical is not considered effective on large fires because an adequate amount of agent cannot normally be delivered quickly enough.

CO_2 fire extinguishers can be used on small fires. CO_2 is not effective on large fires. Please note that the use of CO_2 in an enclosed area can create an asphyxiation hazard.

6.4 MANUAL FIRE FIGHTING

~~Prevent extinguishing agents from entering a container or vessel that contains HMDZ. If the container or vessel is subsequently sealed, the resulting ammonia vapours may over-pressurise the container or vessel, resulting in a sudden rupture of the container or vessel.~~

IMPORTANT:

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 HMDZ fire, as appropriate, should be evacuated to a safe area.

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

Even though direct water spray or water jet SHOULD NOT be used to fight HMDZ fires, water may be used to protect personnel, nearby containers, structures and equipment from radiant heat. Water can also be used to disperse and dilute vapor clouds and combustion effluents. (NOTE: The resulting water runoff may be slightly basic in pH, so provisions should be made for the collection and neutralisation of this water.)

6.5 FIXED FIRE PROTECTION

A fixed fire protection system that is capable of delivering Alcohol Resistant Aqueous Film Forming Foam (AR-AFFF) (3%) with medium expansion nozzles has been shown effective in fighting HMDZ fires.

Application of only water to a HMDZ fire is generally ineffective. If water alone is used, then the fire will likely continue until all the fuel is consumed. Water application can provide effective cooling to adjacent containers, tanks and structures, to protect from the effects of the fire.

The provision of adequate spill control facilities is important to safely drain away burning HMDZ 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.

CHAPTER 7. SPILL CONTAINMENT AND ENVIRONMENTAL IMPACT

An accidental spill or release of HMDZ may form an explosive mixture with air and upon contact with water or humid air will form ammonia, which should be minimized or controlled as quickly as possible. The HMDZ vapors can also present a flash fire or deflagration risk.

Full protective equipment is needed for individuals who must work in an ammonia vapour cloud.

Evacuate personnel to safe areas. Remove all ignition sources and ensure all tools/equipment used when handling the product are spark-proof tools and explosion-proof equipment. Ground and bond containers when transferring material. Absorb spill with inert material (e.g. dry sand or earth), then transfer to a chemical waste container. The resulting material should then be properly packaged and disposed of. Clean contaminated surface thoroughly.

(For details on waste disposal see Chapter 12).

CHAPTER 8. INSTABILITY AND REACTIVITY HAZARDS

8.1 INSTABILITY HAZARDS

HMDZ is stable in the absence of air, moisture, oxidizing agents, and acids.

Due to the low flash point and high vapour pressure of HMDZ, a flammable or explosive environment can be easily obtained in the presence of air. HMDZ's flash point is 52 to 53 ^{o}F, closed cup, for "pure" material. . It is very important to understand the physical properties and safe handling requirements on the SDS prior to handling a HMDZ. Inerting, grounding, and bonding of equipment are key in mitigating these hazards.

When HMDZ is exposed to moisture in the air, the HMDZ and water will react to form ammonia. Precautionary measures should be used to avoid contact between water and/or moisture when handling HMDZ. Reference the SDS for proper personal protective equipment and ventilation when handling HMDZ.

8.2 REACTIVITY HAZARDS

AIR

HMDZ is flammable and can form explosive mixtures with air. Moisture in air causes hydrolysis; ammonia will be generated.

WATER

Water reacts with HMDZ, forming ammonia.

CHAPTER 9. MINIMUM ENGINEERING CONTROL OF HAZARDS

9.1 BUILDING DESIGN

The following points are provided as considerations, not requirements. Each installation must be evaluated versus company-specific requirements, local conditions, local building codes, governmental requirements and professional engineering guidance documents.

Consider building process installations in open structures with good access for mobile firefighting and spill equipment.

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

The building's structure should have a permanent, reliable electrical bonding and earthing system that meets appropriate codes. The system should also be part of a preventive maintenance program that includes periodic inspection and testing to ensure earth ground.

Incorporate appropriate fire protection in the building or open structure. Fixed foam suppression systems may be appropriate.

When it is necessary to handle HMDZ within buildings, consider providing exhaust ventilation at floor level since the vapours are denser than air. Reference documents, such as NFPA 30 for specific design considerations.

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 HMDZ storage when outside storage is not possible.

Plan and practice personnel evacuation routes or means of exit.

Ensure eyewashes and safety showers are located in appropriate locations.

9.2 EQUIPMENT DESIGN

The design of piping and equipment for HMDZ is somewhat specialised because of the flammable and corrosive properties of the substance. These special concerns are briefly mentioned in this and following subsections.

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

GENERAL

The equipment system, such as lines, pumps, valves, vessels, etc., must be thoroughly dried with an inert gas and no trace of water remaining before introducing HMDZ. Contact with moisture may cause a chemical reaction resulting in product degradation and ammonia formation.

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

Totally enclosed systems should be used. Atmospheric openings or vents will allow moisture to enter the system, potentially causing a reaction with HMDZ and the formation of ammonia.

Use dry nitrogen (or other dry inerting gases such as helium 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

Stainless steel, carbon steel and glass-lined steel are satisfactory for piping and other equipment used to contain HMDZ.

Non-ferrous metals and alloys such as aluminium, bronze, copper, zinc or magnesium are more readily corroded and not recommended.

Plastics are generally not recommended in HMDZ service, primarily due to concerns with static build-up.

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 controled nitrogen supply and shut down systems which avoid dangerous underpressure. The storage tank design pressure is dependent on the overall process system design, in conjunction with the physical properties of HMDZ. Generally vessels should have emergency vents that satisfy the requirements stated in the local regulations.

Vessels equipped with pressure safety valves to relieve excess internal pressure due to fire or other pressurising causes should have a non-fragmenting-type rupture disk ahead of the relief valve. Appropriate vent systems must be designed to recover HMDZ released by pressure safety valves.

A preventive maintenance program should be established to regularly inspect and test pressure relief systems.

Vessel supports should be made of appropriate materials which may include reinforced concrete or structural steel. Fire-protective coatings should be considered.

PIPING

Consider stainless steel (316L) or carbon steel piping. Glass-lined steel is compatible, however may not be preferred because of concerns with electrostatic charge accumulation.

Welded and flanged piping connections are preferred 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 HMDZ (such as non-asbestos compressed materials) must be used to provide a leak-tight joint. Fully fluorinated elastomers, such as polytetrafluoroethylene, are compatible options. Spiral-wound metallic gaskets or metal/graphite gaskets should be considered for fire resistance.

Prior to use, all piping must be checked for tightness by pressurising with nitrogen and holding for a set period of time. An acceptable pressure change (increase or decrease) should be pre-determined for a successful check. 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 storage tanks and 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 or seamless, braided flexible metal hose. Consider using flanged or union connections. Do not use quick disconnect couplings because they may be inadvertently released. If braided, flexible metal hoses are used, they should be included in a routine visual inspection program with hydraulic pressure test and/or replacement schedule.

PUMPS

Pump selection should be based on the process requirements in conjunction with HMDZ fluid properties. Centrifugal style pumps, either seal-less or mechanically sealed, are good to consider.

INSTRUMENTATION

Modulating leak-tight control valves and remotely operated valves will help to limit operator exposure in the event of an incident.

Flanged connections are recommended to minimize possible leak paths.

Temperature devices should be sealed such as with a sleeve welded to the equipment to avoid leaks and inconsistent positioning.

Level indication with a high-level alarm is recommended on all vessels and tanks. Feed and bottom discharge valves of HMDZ storage tanks should be remotely controlled, as should pumping equipment. The remote operation should be integrated with emergency shutdown switches or interlock sequences to automatically stop filling when the tank is at risk of overfilling.

9.3 VENTILATION

Enclosed processing buildings should be ventilated at a rate that ensures the atmosphere remains below the lower explosive limit (LEL) for HMDZ. If mechanical ventilation is used, the electrical equipment must meet legal requirements.

9.4 ELECTRICAL EQUIPMENT

All electrical equipment must conform to applicable legal requirements.

Area electrical classifications should be established for all areas in which HMDZ is handled or stored. Consider vapour-tight and corrosion-resistant electrical equipment in areas where HMDZ is stored and handled.

9.5 STATIC ELECTRICITY

HMDZ is an electrically insulating (low conductivity) liquid having a relatively low minimum ignition energy (MIE) of < 0.1 mJ, both characteristics that can increase the potential electrostatic ignition hazard. Static electricity discharges can ignite HMDZ vapour. Inerting the whole system in which HMDZ is transferred, with dry nitrogen, is therefore of utmost importance.

Static electricity may be generated when the material flows through or is discharged from a pipe or falls freely through space. Splash filling is particularly hazardous and should be avoided. Once generated, electrostatic charge is more difficult to dissipate in HMDZ because the material is non-conductive, with a conductivity of less than 10 picosiemens per meter (pS/m).

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

Ground wiring should be of sufficient size and construction 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 existance of an effective connection.

To dissipate electrostatic 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, and grounding all vessels and appropriate piping.

Personnel who perform HMDZ packaging operations should also be electrically grounded to limit the accumulation of electrostatic charge. The use of antistatic footwear in combination with antistatic flooring is one method of electrically grounding personnel. Only non-sparking tools should be used.

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 HMDZ. Purging with dry nitrogen before filling also 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.

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

All safety and other precautions documented in other sections of this manual must be observed when unloading HMDZ. It is particularly important that appropriate personal protective equipment is used. Normal procedures for handling ammonia 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 HMDZ 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 HMDZ shipping container.

All 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 at the unloading area.

All devices (fittings, pumps, hoses, etc.) must be suited for use with HMDZ. These devices should be used only for HMDZ, 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 HMDZ 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 HMDZ immediately.

DRUMS

The following equipment should be available at HMDZ drum unloading stations: emergency eyewash and shower, dry-chemical fire extinguisher, and 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 HMDZ

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

HMDZ 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 HMDZ) 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 HMDZ by gravity or to feed a pump. Application of pressure to a drum is not recommended.

Handling Empty HMDZ Drums

Empty drums should be isolated and thoroughly rinsed inside and out with water before disposal in accordance with local regulations. Water washing creates ammonia, therefore make sure drums are thoroughly drained of HMDZ before flushing to avoid dangerous pressure rise inside the drum.

Defective or Leaking Drums

When handling leaking drums of HMDZ, 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 HMDZ 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. . Tank contents should be double checked that they do not have any additional chemicals inside prior to pumping HMDZ. 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 HMDZ 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. 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 is a key safety mitigation.

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 HMDZ 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. 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 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; 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, derailers, 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 HMDZ should be limited to emergencies since routine treatment and/or disposal could require regulatory permits and specialised equipment.

If HMDZ 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 HMDZ is the recommended disposal practice, with highly specialised equipment being required. The incinerator must be equipped with emission controls capable of handling silicon dioxide and ammonia.

HMDZ waste should be segregated in hazardous waste area to prevent undesirable reactions with other waste products.

Whenever there is a chance to dispose of HMDZ (safe transport provided) by incineration, this should always be done. Disposal of HMDZ 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 HMDZ.

CHAPTER 13. EQUIPMENT CLEANING AND REPAIRS

Cleaning, repair and entry of equipment with residual HMDZ 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 recognizing 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 physically disconnecting the pipeline or 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 into the equipment with dry nitrogen to a safe pressure (below the rated pressure of the equipment, typically your relief valve lift pressure) and venting off the equipment to a safe location (for example scrubber, incinerator, etc.). Typically, it is recommended to do three purge and vent cycles. Then begin to test the vented material to determine if HMDZ is still present, this can be done through a purge valve to atmosphere to obtain a reading of the material to indicate no flammability or toxic vapors.

After purging, open all top openings and fill the vessel with water or pressure wash the equipment; then, while purging with dry nitrogen, drain the water out to a safe location. Then drain the equipment and allow it to dry. Precautions should be taken due to open equipment with oxygen deficient atmosphere.

Perform an additional check for proper oxygen levels, flammability levels and toxicity (ammonia) levels to ensure a safe work area.

Prior to any equipment entry or hot work the equipment and surrounding area should be checked for proper oxygen levels, flammability levels and toxicity (ammonia) levels to ensure a safe work area.

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