

7.25

Chemical Safety Data Sheet SD-56

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

VINYL CHLORIDE

Chemicals in any form can be safely stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.

"The American Conference of Governmental Industrial Hygienists evaluated the most recent available industrial experience and toxicity data for vinyl chloride and revised the TLV from 500 ppm to 200 ppm. The Dow Chemical Company has an allowable time weighted average for industrial exposure to vinyl chloride of 50 ppm."

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MCA

MANUFACTURING CHEMISTS ASSOCIATION

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Chemical Safety Data Sheet

VINYL CHLORIDE

PREFACE

Vinyl chloride monomer is classified by the U.S. Department of Transportation as a flammable compressed gas. It is easily ignited, producing hazardous combustion gases largely composed of hydrogen chloride and carbon monoxide.

The primary health hazard of VCM is associated with excessive respiratory exposure. In acute overexposures the primary effect is on the central nervous system, producing intoxication and dulling of visual and auditory responses. Excessive chronic exposure may produce liver injury.

The full text of this chemical safety data sheet should be consulted for details of the hazards of vinyl chloride monomer and suggestions for their control.

FIRST AID—SEE PAGE 18.

For assistance in the event of any emergency involving this chemical in transportation, call MCA's Chemical Transportation Emergency Center.

CHEMTREC

(800) 424-9300 * (Use 483-7616 in District of Columbia)

Toll-free, day or night

* Use long distance access number if required.

**In CANADA, call Canadian Chemical Producers Association's TEAP
(Transportation Emergency Assistance Plan)**

R&S161934

VINYL CHLORIDE

1. NAMES

Chemical Names:	Vinyl Chloride Monomer Chloroethylene Chloroethene
Common Name:	Vinyl Chloride, VCM
Formula:	CH_2CHCl

2. PROPERTIES

2.1 GRADE: Commercial, sometimes referred to as Technical

2.2 IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES:

Boiling Point at 1 atm.	-13.8°C. (+ 7°F.)
Color	Colorless or water white
Corrosivity	Noncorrosive at normal atmospheric temperatures when dry (moisture free). In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron or steel.
Explosive Limits (Percent by Volume in Air)	Lower 3.6%; upper, 26.4%
Flash Point (Open Cup)	-78°C. (-108°F.)
Hygroscopicity	No
Critical Pressure, psia	775
Critical Temperature	158.4°C. (317°F.)
Ignition Temperature, Autogenous	472.22°C. (882°F.)
Light Sensitivity	Uninhibited VCM is light sensitive
Melting Point at 1 atm (Freezing Point)	-153.71°C. (-245°F.)
Molecular Weight	62.50
Odor	Sweet smelling gas. Inhibited VCM may have faint phenolic odor.
Physical State	Gas at ordinary temperature and pressure. Liquid under pressure in cylinder or pressure vessel at room temperature.
Reactivity	Polymerizes readily in presence of air, sunlight, oxygen or heat. This behavior is due to the presence of a double bond. Otherwise vinyl chloride is quite stable.
Specific Gravity of liquid @ 4°C. (Water = 1)	0.9121
Vapor Density of gas (Air = 1)	2.15
Vapor Pressure @ 68°F.	35 psia
Density, liquid, lb./cu. ft. at 70°F. at 105°F. at 115°F. at 130°F.	56.71 54.38 53.69 52.61
Threshold Limit Value (ceiling)	500 ppm or 1300 mg/M ³

3. HAZARDS

3.1 HEALTH HAZARDS (See Section 10 MEDICAL MANAGEMENT)

3.1.1 The primary hazard of vinyl chloride is associated with excessive respiratory exposure. Exposure to high levels may produce some lung irritation. Chronic overexposure may produce liver injury. When inhaled it acts primarily as an anesthetic. The odor is pleasant to most individuals and, therefore, acutely dangerous levels may be easily tolerated.

3.1.2 Warning Properties

The lowest concentration of VCM at which its odor can be detected is reported to be 260 ppm. Olfactory fatigue, however, may occur and the sense of smell cannot be relied upon as a warning for excessive low grade exposures.

3.2 FIRE AND EXPLOSION HAZARDS

3.2.1 Vinyl chloride is a gas at normal atmospheric temperature and pressure. The gas will burn very readily in proper mixtures of air or oxygen. An explosion hazard can exist when drawing samples or venting to the atmosphere. Open flames, local hot spots, friction, any spark producing equipment, and static electricity are to be avoided when handling this material.

3.2.2 Combustion Products of Vinyl Chloride Monomer

Analysis of a combustion gas sample obtained immediately above a flame of vinyl chloride monomer burning in air shows presence of hydrogen chloride (27,000 ppm), carbon dioxide (58,000 ppm), carbon monoxide (9,500 ppm) and phosgene less than

10 ppm. Only in the very near vicinity of a VCM fire would significant amounts of phosgene be present.

The main sources of danger to personnel result from the massive formation of hydrogen chloride gas and from carbon monoxide. However, the pungent odor of hydrogen chloride acts as a warning to clear the area or to obtain the necessary breathing apparatus before attempting any fire control measures. See MCA Chemical Safety Data Sheet, SD-39, Hydrochloric Acid (Aqueous) and Hydrogen Chloride (Anhydrous).

3.3 STABILITY HAZARDS

Vinyl chloride is shipped and used in both the inhibited and uninhibited state. In the uninhibited state, high purity must be maintained since contaminants may catalyze polymerization or cause decomposition of the VCM, liberating hydrogen chloride. Prior to shipment, uninhibited VCM should be tested for stability under shipping and storage conditions. Cleanliness of shipping containers is of prime importance when shipping uninhibited VCM.

Vinyl chloride may polymerize as a result of exposure to air, oxygen or sunlight at ambient or higher temperatures.

Vinyl chloride does not form peroxides by autoxidation as readily as many other monomers.

In the absence of an initiator, VCM is chemically quite stable. Commercial VCM, uninhibited, is stored and shipped in steel containers under conditions which avoid exposure to air and sunlight. For large volume, long term storage, refrigeration is sometimes employed to maintain the temperature at about 20° C., maximum, to minimize the formation of haze, a condition caused by a small degree of polymerization.

4. ENGINEERING CONTROL OF HAZARDS

4.1 BUILDING DESIGN

Equipment and vessels containing VCM should preferably be isolated from other facilities by walls and floors of fire resistive construction.

Standard fire walls are recommended for the isolation of larger equipment and storage tanks, while partitions of plaster on expanded metal lath may be used to isolate smaller equipment from other combustible materials.

Not less than two means of exit should be provided from each separate room or building in which VCM

is stored, handled or used. No portions of such a room or building should be farther than 75 feet from the nearest exit. Additional exits should be provided depending upon the number of persons in the building. (See NFPA Standard #101, Life Safety Code.)

All exit doors should open out in the direction of travel and should be provided with panic hardware. Fire doors should open out in the direction of travel and be of an approved type.

Operations where large quantities of VCM are used should preferably be housed in one story buildings.

Explosion vents may be used to reduce destructive damage to buildings, ducts, mixers, blenders, driers and similar equipment in which flammable vapors are liable to concentrate.

Explosion venting windows, roof and wall panels, skylights, light windows, diaphragms, etc., may be used to minimize building damage due to explosion pressures.

Since the required area of explosion vents depends upon such factors as the intensity of an explosion, vapor temperature, type of structure, the type of vent closure, etc., the determination of vent ratios should be made by experienced engineers and safety and fire protection specialists. Consideration may be given to explosion suppression systems. (Reference: NFPA Fire Codes, Vol. 9-#68).

The question of adequate spacing of chemical storage buildings from other buildings and processing equipment should be considered.

A fire resistive stairwell with self-closing fire doors may be specified for hazardous operations on upper floors.

The need for segregating floor drains from sanitary or process sewer systems should be considered.

4.2 EQUIPMENT DESIGN

4.2.1 Processes should be designed so that operating personnel will not be exposed to direct contact with vinyl chloride or its vapor. The technical problems of designing equipment, providing adequate ventilation, and formulating operational procedures which promise maximum security and economy, can be handled best by engineers or other competent personnel. The manufacturers of vinyl chloride, and of the equipment in which it is to be used, are always prepared to help with these problems.

4.2.2 In the handling of vinyl chloride or operation of any type of vinyl chloride system, all valves, pipe lines, vents, safety devices, etc., should be so located that they can be readily inspected and repaired. They should always be in proper order and condition before the operation is started. All handling and storage equipment should be located away from any source of sparks, flames, heated surfaces and all sources of ignition which might cause fires or explosions. All charging and discharging pipes should enter through, or extend to, the bottom of all containers to minimize vaporization of the liquid. Use of excess flow valves and valves with fusible links should be considered on storage tanks and other large vessels in case of fires or leaks near these vessels.

4.2.3 It is essential for safety that equipment be used and maintained as recommended by the manufacturer and that a periodic test schedule of the equipment, including safety devices, should be fol-

lowed. All vent lines should extend outdoors to an area free of any source of ignition for discharge. Vents and vent lines should have flash arresters.

4.2.4 Material of copper or copper-bearing alloy should not be used in contact with vinyl chloride due to the possible presence of acetylene and the formation of explosive acetylides.

4.3 VENTILATION

4.3.1 Ventilation should be adequate to maintain exposures below the ceiling value of 500 ppm recommended by the U.S. Department of Labor.

4.3.2 If the workroom or operating area is separate from vinyl chloride storage or processing equipment, general ventilation is usually adequate. For emergencies, however, the area may be provided with mechanical exhaust ventilation to maintain concentrations below 500 ppm. Mechanical ventilators should be of the nonsparking or explosion-proof type and should have motors conforming to the National Electrical Code (Class I, Division I).

4.3.3 In the processing or storage area, if outside location is impracticable, special emergency equipment for ventilation is necessary under abnormal conditions, such as leaks or spills.

4.3.4 The most important consideration in ventilation is to ensure an adequate air flow away from the work area.

4.3.5 All ventilating systems should be inspected periodically and maintained in a safe and efficient working condition.

4.3.6 Under abnormal conditions, such as when leaks or spills occur, all available ventilation should be used.

4.4 AIR ANALYSIS

4.4.1 Analysis of the air for vinyl chloride in the work area will give a measure of the effectiveness of engineering control of the vapors. It may be performed to detect leakage of vapors from equipment and also to ascertain the order of magnitude of the health and fire hazard existing in work areas.

4.4.2 It should be kept firmly in mind that the use of the following instruments and test procedures for the detection of VCM in the air requires specially trained personnel.

4.4.3 Vinyl chloride vapor concentrations in the air near or within the explosive range are most easily determined by the use of a standard combustible gas indicator. The concentration of vapor may be read directly on the meter which is usually graduated in percent of the lower flammable limit. The above should not be used for the detection of health hazards.

4.4.4 A specially calibrated indicator is commercially available for vinyl chloride monomer determinations within the toxic range. Ampules which change color on exposure to VCM vapors are also commercially available and may also be employed for the detection of low level concentrations.

4.5 ELECTRICAL EQUIPMENT

All electrical equipment, motors, lights, and flashlights used in an area in which vinyl chloride is stored or handled should conform to the National Electrical Code.

5. EMPLOYEE SAFETY

5.1 EMPLOYEE EDUCATION AND TRAINING

5.1.1 Before undertaking any training of the employees who are engaged in handling or processing vinyl chloride the supervisor should be thoroughly familiar with the contents of this data sheet. MCA Case Histories describe accidents and injuries that have occurred while handling or processing vinyl chloride monomer. Safety specialists and suppliers may also be consulted.

5.1.2 After becoming thoroughly familiar with the hazardous characteristics of vinyl chloride monomer, the supervisor should review each procedure where the material is to be used and preferably with the assistance of the workers directly involved. During the review all danger points should be identified and the precautionary measures determined. The review should not only be concerned with the dangers of contact or exposure to vinyl chloride monomer, but also those which may be involved in handling containers, operating equipment and other aspects of the work. Procedures for all foreseeable emergencies should be established including the location and operation of safety showers, fire extinguishers, alarms, etc. and the need for personal protective equipment.

5.1.3 During the safety review of the operations it may become apparent that some danger points can be eliminated. Possibly additional ventilation, machine guarding or modifying the method of handling the material or containers can avoid potential hazards. Process changes, however, should never be made without the approval of those who have developed the process and other knowledgeable persons. In chemical processing even a slight deviation might have disastrous results.

5.1.4 All significant hazards which cannot be satisfactorily guarded by rearrangement or other modification 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 instructions. For example, if eye protection is required while taking a sample the standard operating procedure might read, "Wear goggles and take sample from Still No. 000." This type of instruction is preferable to explaining to the worker the need to take a sample and in another part of standard operating

procedure having a notation to the effect that he is to wear eye protection when sampling.

5.1.5 If there are extremely critical steps in the process where, for example, over charge or under charge may cause uncontrollable reaction, considerations should be given to making these supervisory check points. In such instances the standard operating procedure should specify that the employee must notify his supervisor before proceeding further or as in this example, prior to charging the material to the reactor. It then becomes the supervisor's responsibility to verify that the employee has followed the proper procedure before undertaking the critical step.

5.1.6 The safety review described should be repeated periodically for all chemical processing operations and always following a significant change in the process.

5.2 PERSONAL PROTECTIVE EQUIPMENT

5.2.1 Availability and Use

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 VCM. It is, however, in some instances the only practical means of protecting the worker, particularly in emergency situations. One should appreciate that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area may be exposed to danger.

The effectiveness of personal protective equipment requires the training of workers in its proper use and care. The following personal protective equipment should be used when indicated:

5.2.2 Eye Protection

Chemical Safety Goggles

Cup-type plastic or rubber framed goggles, equipped with the approved impact resistant glass or plastic lenses, should be worn whenever there is danger of the material coming in contact with the eyes. Goggles should be carefully fitted.

5.2.3 Spectacle-Type Safety Goggles

Metal or plastic rim safety spectacles with side shields may be used where continuous eye protection

is desirable, as in laboratories. Spectacles, however, should not be used where complete eye protection is needed such as when handling bulk quantities, when there is danger of splashing, or when the material is under pressure.

5.2.4 Face Shields

Plastic shields (full length, 8" minimum) with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of material striking the eyes from underneath or around the sides of the face shield.

5.2.5 Respiratory Protection

5.2.5.1 Severe exposure to VCM may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection. Available types are described below:

NOTE: Respiratory protective equipment must be carefully maintained, inspected, cleaned and sterilized at regular intervals and always before and after use by another person.

(a) **Self-contained Breathing Apparatus** which permits the wearer to carry a supply of air compressed in the cylinder allows considerable mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air carried. *Compressed oxygen must not be used where there is danger of contact with flammable liquids, vapors, or sources of ignition, especially in confined spaces such as tanks or pits because of the increased fire hazard an oxygen rich atmosphere presents.*

(b) **Positive Pressure Hose Masks** which are supplied by blowers requiring no internal lubrication may be used. The wearer must be able to use the same route for exit as for entrance and must take precautions to keep the hose line free of entanglement. The air blower must be placed in an area free of contamination.

(c) **Air-line Masks**, supplied with clean compressed air, are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air piped to the area from a compressor. *It is imperative that the air supply is taken from a safe source and that it is not contaminated by oil decomposition from inadequate cooling at the compressor. The safer method is to use a separate compressor of the type not requiring internal lubrication. Pressure-reducing and relief valves, as well as suitable traps and filters, must be installed at all mask stations. An alternate arrangement*

ment frequently used is high pressure breathing air from standard (200 cu. ft.) cylinders, with a demand type valve and facepiece. This arrangement may also be used with 50-100 lb. clean piped plant air, and, as an additional precaution with the demand mask, a small cylinder of compressed air may be worn for use as an emergency escape from the area. Consult a reliable safety equipment dealer for details on the proper use of U.S. Bureau of Mines approved equipment.

(d) **Industrial Canister-Type Gas Masks**, equipped with full face pieces and approved by the U.S. Bureau of Mines, fitted with the proper canister for absorbing vapor, will afford protection against concentrations not exceeding 2 percent by volume when used in accordance with manufacturer's instructions. The oxygen content of the air must not be less than 16 percent by volume. The masks should be used for relatively short exposure periods only. They are not recommended for use in an emergency since, at that time, the actual vapor concentrations is unknown and an oxygen deficiency may exist. The wearer must be warned to leave the contaminated area immediately on detecting the odor of a chemical vapor. This may indicate that the mask is not functioning properly, that the vapor concentration is too high, that the canister is exhausted or that the mask is not properly fitted. Because of the limitations outlined, use of canister masks should be restricted.

NOTE: Where other gas having little or no odor may be encountered in addition to VCM the mask should be equipped with an "all purpose canister" and a "timing device" as approved by the U.S. Bureau of Mines.

(e) **Chemical Cartridge Respirators** may be used to avoid inhaling disagreeable but relatively harmless concentrations of VCM vapor. These respirators, however, are not recommended for protection where toxic concentrations may be encountered or where there may be oxygen deficiency.

CAUTION: Filter type respirators do not offer protection against gases or O₂ deficiency and are unsuitable for use when working with VCM.

5.2.6 Head Protection

Hard hats should be worn where there is danger from falling objects.

"Bump caps" are satisfactory in areas where there is little or no hazard from falling objects. They will give protection from liquid leaks and splashes.

5.2.7 Foot Protection

Leather or synthetic rubber safety shoes with built-in steel toe caps are recommended where there is danger of heavy objects falling on a workman's foot. Liquid vinyl chloride penetrates leather, and shoes wet with vinyl chloride should be (a) discarded

if the monomer is phenol inhibited, and (b) removed and not worn until thoroughly dry when handling uninhibited monomer.

5.2.8 Body, Skin and Hand Protection

5.2.8.1 Any work gloves, clothing or wearing apparel which becomes contaminated with VCM should be removed immediately, and the body should be thoroughly washed. All contaminated work gloves, clothing or wearing apparel should be thoroughly washed, and dried before reuse.

5.2.8.2 When cleaning, inspecting, or repairing tanks, safety equipment such as safety belts, rescue harness, lifeline, clothing and respiratory protective equipment should be worn as required by the specific nature of the work and the hazards involved.

5.2.8.3 Frequent inspections and necessary repairs should be made to all personal protective equipment so that it is always ready to give proper protection to the wearer.

5.2.8.4 Facilities for personal cleanliness should be provided.

6. FIRE FIGHTING

6.1 When vinyl chloride burns, the hazardous gases generated are mostly hydrogen chloride and carbon monoxide (See 3.2.2).

6.2 Emergency Measures (See 7.5.2)

6.3 Fire involving large quantities of spilled liquid are difficult to extinguish since vinyl chloride is not miscible with water and is lighter than water (will float on top of water). Most small fires can be extinguished with carbon dioxide or dry chemical

agents if properly applied. Adequate fire extinguishing equipment of carbon dioxide or dry chemical type, fixed and portable, should be provided. Water fog or spray is also satisfactory for cooling. Diking and/or draining should be provided for confining and disposing of the liquid in case of tank rupture or spills. Precautions should be taken to guard against VCM entering the general sewer system.

6.4 No one should be permitted to enter a fire area until it has been checked and approved for safe entry unless equipped with proper protective clothing and self-contained respirator.

7. SHIPPING, LABELING, HANDLING AND STORAGE

7.1 SHIPPING

7.1.1 DOT Classification and Regulations

Vinyl chloride monomer is classified by the U.S. Department of Transportation as a *flammable compressed gas*. When shipped by rail, water or highway, it must be packaged in authorized containers and shippers must comply with all DOT Regulations regarding packaging, loading, handling, labeling, marking and placarding.

7.1.2 Usual Shipping Containers— Type and Size

Cylinders—4B150, 4BA225, 4BW225, 3A150, 3AA150, DOT-25 and 3E-1800.

Cylinders with brazed seams are not permitted. Maximum permitted filling density—84%.

Cargo Tanks—MC330 and 331. Maximum permitted filling density—84%.

Tank Cars—DOT 106 500 X. Maximum filling density—84%.

DOT 105 200 W. Maximum filling density—87%.

DOT 112A 340 W. Maximum filling density—86%.

7.2 LABELING

7.2.1 DOT Requirements

7.2.1.1 Each container of vinyl chloride, including tank cars shall carry an identifying label.

7.2.1.2 The proper shipping name Vinyl Chloride, as shown in the commodity list (para. 172.5) must be used and shown on the outside shipping containers per para. 172.1(a) and 173.401(a).

7.2.1.3 Unless exempt, each individual container must bear the RED LABEL for FLAMMABLE GASES as described in para. 173.408(a)(1).

7.2.1.4 DOT 177.823(b) requires that tank motor vehicles transporting VCM shall be marked on both sides and at the front and rear, with letters at least 4" high, with the words "FLAMMABLE GAS" or "FLAMMABLE COMPRESSED GAS."

In addition, the name "VINYL CHLORIDE" must be displayed in letters at least 2" high. The words "FLAMMABLE GAS" must be displayed on other motor vehicles transporting 1000 lbs or more gross weight per para. 177.823(a).

7.2.1.5 Each railroad car must bear the "DANGEROUS" placard per para. 174.541(a)(1) and (3).

7.2.1.6 Para. 173.402(a)(13) specifies that an "EMPTY" label must be applied to containers which have been emptied and on which the old label has not been removed, obliterated, or destroyed. It

must be so placed on the container as to completely cover the old label.

7.2.1.7 Para. 174.562(b) specifies that a "DANGEROUS-EMPTY" placard shall replace or cover the "Dangerous" placard on the railroad tank car which has been emptied.

7.2.2. Precautionary Labeling

7.2.2.1 The Manufacturing Chemists Association recommends that all containers of VCM should bear a label as shown. The text is designed for the product as shipped for industrial use. It should be

VINYL CHLORIDE

**DANGER! EXTREMELY FLAMMABLE LIQUID AND GAS
UNDER PRESSURE**

HARMFUL IF INHALED

MAY POLYMERIZE VIOLENTLY UNDER FIRE

**CONDITIONS OF LOSS OR REMOVAL
OF INHIBITOR**

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid breathing vapor.

Avoid contact with skin.

Keep cylinder out of sun and away from heat.

Container should be grounded when being emptied.

Never drop cylinder.

FIRST AID: If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

In case of

Fire—Use water spray, dry chemical, or CO₂.

Spill or leak—For small spills, remove and allow to evaporate. For large spills or leaks, evacuate area. Dike or flush to ground and let evaporate. Do not flush to sewer because of explosion hazard.

MCA Chemical Safety Data Sheet SD-56 available.

used in addition to or in combination with any specific wording required by law. Since individual statutes, regulations, or ordinances may require that particular information be included in a label, that certain information be displayed in a particular manner, or that a specific label be affixed to a container, the use of this label text will not necessarily insure compliance with such laws. Such laws include the Federal Hazardous Substances Labeling Act; Federal Insecticide, Fungicide and Rodenticide Act; and similar state and municipal legislation.

7.3 CYLINDERS

7.3.1 Magnets or slings should never be used to unload cylinders. When transporting by crane or derrick a suitable platform, cradle, or boot should be used.

7.3.2 Care should be exercised not to drop cylinders or otherwise handle them roughly.

7.3.3 Cylinders may be moved by tilting and rolling them on their bottom edge. Dragging and sliding them should be avoided.

7.3.4 When cylinders are transported by hand truck, they should be held securely in position by means of a locking clamp, chain or other suitable holding device.

7.3.5 Cylinders should never be used as rollers for moving any object or material.

7.3.6 Valve protection caps should always be kept in place except when the VCM containers are connected to piping, apparatus or equipment. As soon as a cylinder is disconnected the protective cap should be replaced.

7.3.7 Avoid disturbing the fusible plug. The safety device should be tagged in order to differentiate it from the discharge connection.

7.3.8 The area where the cylinder is connected should have adequate ventilation to prevent the build up of concentrations in the event of a leak.

7.3.9 Cylinders should be provided with pressure regulators as recommended by the supplier.

7.3.10 A water bath heated to a maximum of 50°C. (122°F.) may be used to empty cylinders by means of the vapor pressure of the vinyl chloride.

7.3.11 Check valves must be installed in feed lines from the cylinder to prevent the reactants from entering the cylinder.

7.3.12 When the cylinder is empty, the valve should be securely closed. Air must not be allowed to enter the container.

7.3.13 Cylinders must not be filled except by or with the consent of the owner, and then only in accordance with DOT Regulations.

7.3.14 Return of Cylinders

The cylinder valve protection cap or outlet cap must be securely replaced. The lower portion of the DOT shipping tag, if attached to the cylinder, must be removed. In other cases, applicable to DOT Regulations, compliance is essential. Bill of lading should give the cylinder identification number (which appears on the shoulder of cylinder) for each cylinder shipped, show name of consignee and indicate that the cylinders are empty.

Full or partly emptied cylinders should not be returned without permission of the supplier. Such cylinders must be shipped as full cylinders and correspondingly labeled and tagged. All empty cylinders should be returned promptly.

7.4 TANK CARS

7.4.1 Because of the flammable and toxic properties of VCM the unloading of tank cars is a hazardous operation. The supplier should be contacted for instructions and the instructions closely followed.

7.4.2 DOT Regulations, Para. 174.560 to 174.563 inclusive, contain instructions which must be observed.

7.4.3 Cars should be unloaded only on private sidings.

7.4.4 Shipper's instructions should always be followed and all caution markings on both sides of tank and dome should be read and observed.

7.4.5 No heat should be applied to the tank car. An inert gas line or compressed vinyl chloride gas line should be attached to vent connection of the tank car to provide a pressure for transfer of the liquid vinyl chloride from tank. Transfer may also be by pumping.

7.4.6 Cylinder nitrogen (inert gas) is often used as the pressuring medium in the event vinyl chloride gas is not available. Larger installations may have a suction line connected from the storage tank to a compressor which discharges compressed vinyl chloride gas to vent connection on tank car. The pressure on the car should never exceed the service pressure at which the safety valve is set to operate.

7.4.7 Return of Tank Cars

When a tank car is completely unloaded, all valves must be made tight, the unloading connections must be removed and all closures made tight. Air must not be permitted to enter the vessel. The inert gas used for the unloading procedures should be left in the vessel at a pressure not to exceed the service pressure for which the car was designed, but sufficient to prevent forming a vacuum in cold climates.

7.4.8 The DOT DANGEROUS placards on sides and ends of tank cars must be removed, or reversed (if in metal placard holders) by the party discharging the tank car. The empty car must be offered to the receiving carrier either without placards, or preferably with four (4) DANGEROUS—EMPTY placards.

7.5 TRANSPORTATION EMERGENCIES

7.5.1 Assistance Available

7.5.1.1 CHEMTREC (CHEMical TRANspor-tation Emergency Center)

This center, located in Washington, D. C. at the offices of the Manufacturing Chemists Association, is manned 24 hours per day, seven days a week, and provides, by telephone, immediate response/action information for police, fire-fighters and others concerned with the control of chemical transportation emergency situations. For assistance, dial

*(800) 424-9300 in the 48 contiguous States of the USA

483-7616 in District of Columbia

*(200) 483-7616 in Alaska

In Canada, call Canadian Chemical Producers Association's TEAP (Transportation Emergency Assistance Plan).

* Use long distance prefix if needed.

7.5.1.2 Company Mutual Aid

A number of vinyl chloride manufacturing companies voluntarily participate in a mutual-aid organization under which, in the event of a transportation accident, the closest company VCM plant will dispatch a qualified adviser to the scene of the accident if requested to do so by the shipper of the commodity.

7.5.2 Emergency Control

7.5.2.1 Personnel Attending Accident Scene

Shippers' representatives do not take charge of emergency operations. They are present as advisers only.

7.5.2.2 Recommended Emergency Kit

The following are considered essential:

- Explosion meter
- Self-contained air supply
- Wood plugs and wood mallet
- Data sheet and pencil
- Camera and film
- Flashlight (Bureau of Mines approved)

- Rubber gloves
- Slicker suit
- Rubber overshoes
- Safety lines (braided stainless, plastic covered) and harness
- Goggles
- Safety hat
- O-rings
- Strap wrench
- 10" adjustable wrench
- Screwdriver
- Ground continuity meter
- Large first aid kit and collapsible water container, approx. 50 gals. The water container should be filled at the emergency site and be available for eye wash or treatment of chemical skin contacts.

7.5.2.3 Recommended Procedures

Leaks of Vinyl Chloride

I. CONTROLLABLE LEAKS

- Small holes: Drive wooden plugs.
- Larger holes: Neoprene patch, bonded or chained to tank. Special rigs should be left to the judgment of the man at the scene.
- Jagged holes are difficult to close.
- Potassium bicarbonate will extinguish a vinyl chloride fire but reignition often occurs because it around valves if it appears that a leak can be subsequently controlled.

II. UNCONTROLLABLE LEAKS—No Fire

- Isolate area.
- Remove sources of ignition.
- Control spread of vapors by water spray.

III. UNCONTROLLABLE LEAKS—FIRE

- Evacuate and isolate area.
- Keep adjacent cars cool, if possible, with water spray.
- Keep unofficial personnel away.
- Treat a non-burning tank car in vicinity of fire as if it is about to rupture.

- e. If vinyl chloride gets to a sewer, evacuate area and flush sewers with fire hoses.

7.5.2.4 Spilled Vinyl Chloride

Spilled vinyl chloride should not be deliberately ignited.

7.5.2.5 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and extent of car damage, VCM may be recoverable, but recovery should *not* be the determining factor in controlling the situation.

- a. If car condition permits, transfer contents to empty tank car using nitrogen pressure.
- b. If car is ruptured, attempt to use pump with flooded suction.
- c. If pumping is impractical, use water or oil to float out remainder of VCM.
- d. Fill empty tank with water or nitrogen.
- e. If a vinyl-ice mixture forms, keep a water stream to the tank until it dissipates.
- f. Handling of vinyl chloride in a damaged car can be influenced by weather conditions. At low temperatures, since vaporization is reduced, patch tank, if possible, so that it can be moved.

7.5.3 Marine Emergencies

7.5.3.1 U.S. Coast Guard regulations require that a cargo information card for vinyl chloride be carried aboard the tank barge mounted near a warning sign and in such a position as to be easily read by a man standing on the deck of the barge. The cargo information card shall also be carried on the bridge or in the pilot house of the towing vessel. Copies are available from the Manufacturing Chemists Association.

7.5.3.2 Special Safety Equipment

In addition to normal safety equipment provided at the dock, the following special items should be available:

- a. Self-contained breathing equipment (at least two spare bottles).
- b. Explosimeters.
- c. Ground continuity meter.
- d. Water with an appropriate number of nozzles.
- e. Dry chemical fire extinguisher.

- f. MCA Chemical Safety Data Sheet SD-56 and Cargo Information Card CIC-80.

7.5.3.3 Recommended Emergency Procedures

7.5.3.3.1 Leaks of Vinyl Chloride

I. GENERAL—ACTIVATE ALARM

II. CONTROLLABLE LEAKS—NO FIRES

- a. Isolate leak from source.
- b. Eliminate ignition source.
- c. Control spread of vapors by water fog.
- d. Attempt to repair leak using adequate safety protection procedures.

III. UNCONTROLLABLE LEAKS OR RUPTURES—NO FIRES

- a. Isolate area.
- b. Remove all sources of ignition.
- c. Use water spray to prevent accumulation of liquid and to dissipate vapor cloud. It is not recommended that the ship's fire water supply be hooked into the city water supply.)

IV. UNCONTROLLABLE LEAKS—FIRE

- a. Isolate area.
- b. Evacuate area except for emergency personnel.
- c. Use water fog on fire and fumes (do not extinguish fire unless leak can be controlled).
- d. Use copious amounts of water to keep adjacent areas cool.
- e. Treat adjacent tanks as if about to rupture.

- f. Make provisions to minimize the mixing of air with VCM vapor in confined spaces and the burning tanks or line (water, N₂ or inert gases).

7.5.3.3.2 Spilled Vinyl Chloride

Spilled VCM should not be deliberately ignited.

7.5.3.3.3 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and the extent of the tank damage VCM may be recoverable

but provisions must be made to keep air out of the tank.

- a. If tank condition permits, transfer contents to an empty tank or back to shore.
- b. If tank cannot be patched and it does not have a deep well pump or the deep well pump cannot be used, sparge heated nitrogen into the bottom of the tank to vaporize the VCM.
- c. Fill empty tank with water or inert gas.

7.6 STORAGE

7.6.1 VCM should always be handled with full recognition of its flammability. Precautions should be taken both to keep the material enclosed and to eliminate sources of ignition.

7.6.2 Corrosion

VCM is noncorrosive at normal atmospheric temperatures when dry (moisture free). In contact with water at elevated temperatures VCM accelerates corrosion of iron or steel.

7.6.3 Volatility

VCM is very volatile and is a gas at normal atmospheric conditions. Containers used for handling VCM at ambient temperature are usually under pressure.

7.6.4 Temperature Requirements

Uninhibited VCM may be stored either under refrigeration or at normal atmospheric temperature in the absence of air or sunlight. Regular checks should be made for the presence of polymers.

7.6.5 Conditions of Storage

7.6.5.1 Type of Construction

All piping (including instruments, leads), storage tanks, galleys, devices and equipment employed to handle VCM should be of steel and designed to have a working pressure of at least 100-150 psi with a safety factor conforming to the A.S.M.E. code for unfired pressure vessels or any code applying to locale of planned storage. Shut-off valves and control valves should be of steel or a suitable alloy not bearing copper, designed for working pressures of 150 psi or over. All welded construction is preferred to riveted construction. It is recommended wherever possible that all liquid inlet lines enter the bottom or extend to the bottom of the vessel. This aids in guarding against the accumulation of static electricity. All equipment should be properly grounded and bonded with resistance to ground never exceeding 25

ohms. Electrical lighting, wiring and equipment should conform to NEC. An efficient water spray system should be installed or made available. Adequate diking, and/or draining should be provided under tank area to confine and dispose of the liquid in case of vessel rupture. Cylinders used to store VCM must meet DOT Specifications.

7.6.5.2 Isolation

Storage areas should be selected in accordance with local codes or authorities having jurisdiction. For highly volatile and flammable material, storage should be located outside of buildings. Cylinders containing VCM should be stored always in a vertical position, outside of buildings, and in an isolated and well-ventilated area. It is preferable to store cylinders in the open, but provision should be made to shield them from the direct rays of the sun and prevent accumulation of dirt, snow, water, or ice on valves or safety devices.

7.6.5.3 Compatible and Dangerously Reactive Materials

Tanks in VCM service should be used only for the storage of VCM. Before VCM is placed in a tank, the vessel should be purged with a dry inert gas until free of oxygen. VCM is generally noncorrosive at normal atmospheric temperatures when dry (moisture free). However, mild to appreciable corrosion has been noted when wet, even at ordinary temperatures. This may be due to the presence of impurities. In contact with water at elevated temperatures VCM accelerates corrosion of iron or steel. Acetylene as an impurity in VCM may form an explosive compound (acetylide) when exposed to copper or possibly copper alloys.

7.7 REPACKAGING

7.7.1 Only clean, DOT Specification cylinders should be used.

7.7.2 Adequate ventilation should be provided and all sources of ignition removed from transfer areas.

7.7.3 Proper personal protective equipment should be used. Transferring VCM from cylinders by the use of an uncontrolled heating method is not recommended. Temperatures of over 50°C (122°F) should not be applied to any part of a cylinder containing compressed gas. Excessive heating weakens the structural characteristics of the metal and may seriously damage the cylinder. Low melting safety devices may reach the fusing point by the application of excessive heat to a cylinder. Never apply direct flame to a cylinder. A definite fire hazard is created. For recommended practice to transfer contents of a cylinder see 7.3.

8. TANK AND EQUIPMENT CLEANING AND REPAIRS

(See MCA Safety Guide SG-10 "Entering Tanks and Other Enclosed Spaces")

8.1 JOB EVALUATION AND PREPLANNING

8.1.1 Because vinyl chloride monomer has physical and chemical properties which generate hazards of a toxic and flammable nature, tank and equipment cleaning and repairs should be conducted in such a manner as to eliminate or minimize the hazards. (See 10.1.1 Health Hazards—Note concerning Acroosteolysis.)

8.1.2 Equipment and tank cleaning and repair should be under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of the work. All precautions pertaining to education, protective equipment, and health and fire hazards should be reviewed and understood.

8.1.3 The hazardous nature of tank inspection, cleaning, and repair requires that the foreman and crew be selected, trained, and drilled carefully. They should be fully familiar with the hazards and the safeguards necessary for the safe performance of the work. The preparation of a stepwise work procedure for the entire job, recognizing all possible hazards as they might occur, developing safe procedures and designating suitable protective equipment, has been found to be particularly effective in maintaining work safety.

8.1.4 A written work permit must be prepared before tank preparation and entry. It must describe work procedures to be used, hazards which may be encountered and procedures and equipment to be used to nullify these hazards. It must be prepared, reviewed and signed by the supervisor to whom the tank is assigned after they have satisfied themselves that tank entry and repair work can be done safely.

8.2 TANK OR EQUIPMENT CLEANING

8.2.1 Tanks and equipment, pumps, lines and valves should normally be drained and thoroughly cleaned before being repaired. Workmen should never be allowed to attempt to repair equipment while it is in operation and the lines in service unless special precautions are used such as "Hot Tap" work.

8.2.2 Smoking, use of open flames, and the presence of unauthorized personnel should be prohibited.

8.2.3 All lines, which may contain hazardous substances, entering or leaving the tank should be blanked. After draining, the tank should be flushed with water to remove any remaining VCM liquid. The tank should then be steamed to remove residual VCM. Water and steam lines and nozzles should be

grounded to minimize hazards of static electricity. The tank should then be cooled by filling with water and draining. Finally, the tank should be purged with fresh air and then tested for VCM by an approved method. It should also be tested for oxygen sufficiency. The controls for all agitators, pumps and other electrical equipment connected to the tank should be padlocked by the worker entering the tank.

8.3 ENTERING TANK

8.3.1 No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the vessel has been properly prepared, tested and found to be safe.

8.3.2 No workman should enter a tank or vessel that does not have a manhole opening large enough to admit a person wearing a safety harness, lifeline and emergency respiratory equipment.

8.3.3 Forced air ventilation is recommended during the entire time men are cleaning, repairing or inspecting the tank. Ventilation can be accomplished by exhausting or removing vapors from the bottom of the tank either through a bottom opening or through a large flexible duct. Blowers should be sparkproof and should not be allowed to overheat and thus provide a source of ignition. All men who enter the tank should wear a safety harness and lifeline.

8.3.4 When a tank car or storage tank is being cleaned or repaired one man on the outside of the tank should keep the men in the tank under observation. This man should not leave his post or enter the tank without first obtaining a substitute. Another man should be available nearby to aid in rescue if any of the men in the tank are overcome.

8.3.5 Suitable respiratory protective equipment, together with rescue harness and lifeline, should always be located outside the tank for rescue purposes.

8.3.6 During the course of the work, frequent air samples should be taken to see that the concentrations are within safe range.

8.3.7 If repair work is interrupted, the tank atmosphere should be tested and a new work permit issued before work is resumed.

8.4 EMERGENCY RESCUE

8.4.1 A rescuer should not enter a confined space without wearing approved respiratory protective equipment, a safety harness and an attached lifeline. Another employee should be immediately

for a minimum of 15 minutes with water is required. The presence of skin and eye washing equipment in the areas where vinyl chloride is used is necessary.

Washing supplies and equipment should be maintained and always immediately available.

10.2.3 Physical Examinations

Preplacement examinations should be made on all workers having potential exposure to vinyl chloride, with particular emphasis placed upon liver and kidney functions.

10.3 SUGGESTIONS TO PHYSICIANS

Treatment for vinyl chloride intoxication is symptomatic; no special procedures are required. It should be recognized that the principal target of chronic exposures is the liver, with secondary effects, particularly in acute exposures, to the kidney. In acute overexposures the primary effect is on the central nervous system.

NOTE TO PHYSICIAN: Avoid use of epinephrine or related drugs in treating acute overexposure cases, since vinyl chloride may sensitize the heart to the arrhythmic action of these drugs.

10.3.1 Oxygen Administration

Oxygen has been found useful in the treatment of inhalation exposures of many chemicals, especially those capable of causing either immediate or delayed harmful effects in the lungs.

In most exposures, administration of 100% oxygen at atmospheric pressures has been found to be adequate. This is best accomplished by use of a face mask having a reservoir bag of the non-rebreathing type. Inhalation of 100% oxygen should not exceed one hour of continuous treatment. After each hour, therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

Some believe that superior results are obtained when exposures to lung irritants are treated with oxygen under an exhalation pressure not exceeding 4 cm. water. Masks providing for such exhalation pressures are obtainable. A single treatment may suffice for minor exposures to irritants. It is believed by some observers that oxygen under pressure is useful as an aid in the prevention of pulmonary edema after breathing irritants.

In the event of an exposure causing symptoms or in case of a history of severe exposure, the patient may be treated with oxygen under 4 cm. exhalation pressure for one-half hour periods out of every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruption appear.

CAUTION: It may not be advisable to administer oxygen under positive pressure in the presence of impending or existing cardiovascular failure. The use of adrenalin is not recommended because some chlorinated hydrocarbons can increase the risk of ventricular fibrillation after adrenalin therapy.

11. FIRST AID

11.1 GENERAL PRINCIPLES

First aid should be started at once in case of acute intoxication with vinyl chloride. Immediately remove the affected individual to fresh air. Refer all injured individuals to a physician and give a detailed account of the incident.

11.2 CONTACT WITH SKIN AND MUCOUS MEMBRANES

Vinyl chloride, in concentrated form, is a skin irritant. All contaminated clothing should be removed at once; and this clothing, including shoes, if there is any evidence of contamination, should not be worn again until thoroughly dry. All affected skin areas should be thoroughly washed with warm water and soap. The individual should be referred to a physician.

11.3 CONTACT WITH EYES

If vinyl chloride has entered the eyes, prompt

washing with copious quantities of water for at least 15 minutes should be instituted immediately. It is advisable to irrigate the eyes gently with water at room temperature in order to minimize additional pain and discomfort. Prompt medical attention should be obtained.

11.4 INHALATION

Promptly remove the affected individual from exposure to fresh air. If breathing has ceased effective artificial respiration should be started immediately. If oxygen inhalation equipment is available, oxygen should be administered, provided a person authorized for such administration by a physician is available. The patient should be comfortably warm but not hot. Stimulants will rarely be necessary where adequate oxygenation is maintained. Any such drugs for shock treatment should be given only by the attending physician. *Never attempt to give anything by mouth to an unconscious patient.*

available to man the lifeline and to assist in the rescue if needed. The rescuer should be in view of the outside attendant at all times or in voice communication with him.

8.5 EXTERIOR REPAIR WORK

All outside welding, burning or spark-producing work on tanks or equipment which have contained

VCM should be done after the container has been thoroughly cleaned of VCM vapors. Purging should be tested by a competent person to see if it is free of VCM. It is not recommended that air be used to purge a vessel.

If the repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

9. WASTE DISPOSAL (See 7.5)

9.1 All Federal, State, and Local regulations regarding health and pollution should be observed. Disposal of waste material, however, depends to a great extent upon surroundings, weather conditions and the emergency making disposal necessary.

9.2 When it becomes necessary to dispose of VCM as such, it is preferable to do so as a vapor, venting to an area free of any source of ignition.

9.3 When a waste disposal problem arises as a result of a major spill or equipment rupture, only properly protected and qualified personnel should remain in the area.

9.4 Waste mixtures containing VCM should not be allowed to enter drain or sewers as serious explosions in such systems may result.

10. MEDICAL MANAGEMENT

10.1 HEALTH HAZARDS

10.1.1 Vinyl chloride monomer does not present a serious industrial health hazard provided workers are adequately supervised and observe the proper means of handling it. Under the Occupational Safety and Health Act, the U.S. Department of Labor has set a 500 ppm Ceiling Value on permitted employee exposures. Based upon animal and human observations, this level provides considerable margin of safety for industrial exposures.

NOTE: A syndrome termed occupational acro-osteolysis, characterized primarily by Raynaud's phenomenon and osteolytic changes in certain bones, particularly the distal phalanges of the hands, has been noted among certain workers in vinyl chloride polymerization operations. The specific cause of this disease, and particularly any role played by vinyl chloride, is unknown.

Recent research studies reported from Italy indicate that repeated, long-term high level exposures of rats to vinyl chloride monomer vapor can result in the development of malignant tumors. However, many years of industrial experience with human exposures to concentrations frequently far above current standards have not demonstrated any carcinogenicity to humans.

10.1.2 Acute Toxicity

Levels on the order of 6,000 ppm for five minutes exposure are required to produce minimal

symptoms resembling mild alcohol intoxication in humans. Levels approximately 16,000 ppm for the same length of time will produce varying degrees of intoxication, with light-headedness, some nausea, and a dulling of visual and auditory responses in most humans.

10.1.3 Chronic Toxicity

The liver is the principal target resulting from excessive chronic exposure. The currently recommended ceiling level (OSHA) of 500 ppm is well below a level producing any signs or symptoms of toxicity.

10.2 PREVENTIVE MEASURES

10.2.1 All operations in which vinyl chloride is used should be regularly evaluated, and atmospheric concentrations kept, at all times, below 500 ppm. Sophisticated air sampling techniques are required. This includes gas chromatography. Processes must be closed or ventilated sufficiently to achieve a concentration control low enough so that respiratory protection devices are needed only on an emergency basis.

10.2.2 Personal Hygiene

Vinyl chloride should be kept off the skin and out of contact with the eyes. If accidental contact to the skin occurs, immediate washing with soap and water is necessary; if to the eyes, immediate irrigation

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Betanaphthylamine _____	(1949) SD-32	Isopropylamine _____	(1968) SD-72	Sodium and Potassium Dichromates _____	(1952) SD-46
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