

Chemical Safety Data Sheet SD-56

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Properties and Essential Information

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for
Handling and Use
of

VINYL CHLORIDE

Precautionary information, such as is presented in this Safety Data Sheet, should be provided to all persons who will use, handle, or otherwise be exposed to vinyl chloride.

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MCA

Manufacturing Chemists Association

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This Chemical Safety Data Sheet has been prepared for the guidance of plant engineering, operations and management, and for persons working with or handling vinyl chloride. The contents have been compiled from working experience and practical knowledge as provided by various manufacturers of vinyl chloride and from material on vinyl chloride appearing on scientific publications. While the Manufacturing Chemists Association believes these sources are reliable and represent the best opinions available on the subject as of 1978, the Association makes no warranty, guaranty or representation as to the correctness or sufficiency of any information or recommendation herein, and the Association assumes no responsibility in connection therewith; nor can it be assumed that all necessary warnings and precautionary measures are contained in this Chemical Safety Data Sheet, or that other or additional information or measures may not be required or desirable because of particular or exceptional conditions or circumstances, or because of applicable federal, state, or local law.

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CHEMICAL SAFETY DATA SHEET SD-56

VINYL CHLORIDE

Precautionary information, such as is presented in this Safety Data Sheet, should be provided to all persons who will use, handle, or otherwise be exposed to vinyl chloride.

PREFACE

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

Vinyl chloride is believed to be a carcinogen to man. Exposure of three animal species to vinyl chloride caused a higher frequency of angiosarcoma as well as other respiratory and digestive tumors than in the control groups. Workers in the manufacture of polyvinyl chloride resin have shown a higher incidence of angiosarcoma than expected after long exposure at relatively high concentrations. Acute overexposure affects the central nervous system producing intoxication and dulling of visual and auditory responses.

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. Appropriate regulations regarding vinyl chloride issued by OSHA, EPA and other regulatory agencies should be carefully reviewed before any work with or related to vinyl chloride.

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.

Outside Continental U.S., use (202) 483-7616 except in CANADA,
call Canadian Chemical Producers Association's TEAP
(Transportation Emergency Assistance Plan)

CHEMICAL SAFETY DATA SHEET SD-56

1. NAMES

Chemical Name: Vinyl Chloride
 Chemical Abstracts Registry Number: 000075-01-4
 Other Names: Chloroethylene, Chloroethene, Vinyl Chloride,
 Vinyl Chloride Monomer, VCM
 Formula: CH_2CHCl

2. PROPERTIES

2.1 Grade

Commercial, sometimes referred to as Technical or Polymerization.

2.2 Physical and Chemical Properties

National Fire Protection
 Association classification
 (Health, Flammability,
 Reactivity).....2-4-1

Physical StateGas at ordinary temperature and pressure. Liquid under pressure in cylinder or pressure vessel at room temperature.

Explosive Limits.....Lower 3.6%; upper 33% (by volume in air)

Flash Point (open cup).....-78°C (-108°F)

Ignition Temperature, Autogenous....472 °C (882°F)

Boiling Point at 101.3 kPa (1 atm)....-14°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 the corrosion of iron and of steel.

Critical Pressure.....5.34 MPa (775 psia)

Critical Temperature.....158 °C (317°F)

Hygroscopicity.....None

Vapor Density (air = 1)2.15

Density, Liquid	g/mL	lb/ft ³
4°C (39°F)	0.9121	56.93
21°C (70°F)	0.9085	56.71
40°C (105°F)	0.8712	54.38
46°C (115°F)	0.8601	53.69
54°C (130°F)	0.8428	52.61

Molecular Weight.....62.50
Light Sensitivity.....Uninhibited VCM is light
sensitive
Melting Point (freezing point).....-154°C (-245°F)
Odor.....Sweet smelling gas. In-
hibited VCM may have faint
phenolic odor.
Reactivity.....Polymerizes readily in pres-
ence of air, sunlight, oxygen
or heat. This behavior is due
to the presence of a double
bond. Otherwise vinyl chloride
is quite stable.
Vapor Pressure at 68°F.....35 psig

3. TRAINING AND JOB SAFETY

3.1 Employee Education and Training

3.1.1

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, with the Occupational Safety and Health Administration (OSHA) Standard for Vinyl Chloride (29 CFR 1910.1017) and with the Environmental Protection Agency (EPA) National Emission Standard for Vinyl Chloride (40 CFR 61.F). The handling and use of vinyl chloride are regulated by many governmental agencies but the regulations issued by OSHA and EPA directly affect the content of any training program for vinyl chloride workers. The supervisor should also seek supplementary information and assistance. One recommended reference is the MCA Accident Case Histories to learn of accidents and injuries that have occurred while handling or processing vinyl chloride. If the services of a safety specialist are available, the supervisor should consult with that specialist before finalizing a safety review of the operations involving vinyl chloride.

3.1.2

The OSHA Standard for Vinyl Chloride requires that each employee in vinyl chloride or polyvinyl chloride operations be provided training in a program that includes descriptions of the following:

- (a) Nature of the health hazards of vinyl chloride exposure.
- (b) Specific operations which could result in exposure to vinyl chloride in excess of the permissible exposure limit (PEL) and the necessary protective steps to be taken.
- (c) Purpose, proper use and limitations of respiratory protective devices.
- (d) Fire hazard and acute toxicity of vinyl chloride and the necessary protective steps to be taken.

- (e) Purpose and procedures of the monitoring program.
- (f) Purpose and procedures of the medical surveillance program.
- (g) Emergency procedures.
- (h) Specific information that enable the employee to recognize conditions that may result in the release of vinyl chloride.
- (i) A review of the OSHA Standard for Vinyl Chloride. This review must be presented during the employee's first training period and annually thereafter.

3.1.3

The EPA National Emission Standard for Vinyl Chloride requires that Standard Operating Procedures be prepared and implemented for:

- (a) Loading and unloading line emission control.
- (b) Slip gauge emission control.
- (c) Manual venting of gases.
- (d) Opening equipment emission control.
- (e) Sample taking, handling and disposition.
- (f) Leak detection and elimination.

3.1.4

In addition, employee training programs should include the following:

- (a) Process chemistry and objectives.
- (b) Basic process equipment and operating techniques.
- (c) Properties and safe handling procedures for the materials involved.

- (d) Detailed study of the process and process operation.
- (e) Standard operating procedures for the various plant jobs.
- (f) Modifications and additions to meet the foregoing EPA and OSHA requirements.

3.1.5

Completeness of standard operating procedures, with safety information, is essential in training new employees, providing guidance for older employees and in demonstrating compliance with regulations. An error by an untrained employee can be construed as negligence on the employer's part by a court or regulatory agency.

3.2 Safety Review

3.2.1

After becoming thoroughly familiar with the hazardous characteristics of vinyl chloride, the supervisor should review stepwise each procedure where the material is to be used and preferably do this with the assistance of the workers and first aid team members who are directly involved. During the review all potential hazards 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, but in addition with those which may be involved in handling containers and in operating equipment; any other hazards associated with the work also should be noted. The need for personal protective equipment should be determined, including its proper use as well as its limitations. Procedures for emergencies should be established including the location and operation of safety showers, fire extinguishers, alarms, etc. Any applicable governmental occupational safety and health regulations should be reviewed in order to insure compliance.

3.2.2

During the safety review of the operations it may become apparent that some hazards 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 both those who have developed the process and other knowledgeable persons. In chemical processing even a slight deviation might cause disastrous results.

3.2.3

In the standard operating procedures all potential exposures which require the wearing of personal protective equipment should be explained together with the precautions to be followed. Preferably, such 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 in one part of the standard operating procedure the need to take a sample and stating in another part "Wear eye protection when sampling."

3.2.4

If there are extremely critical steps in the process where, for example, overcharge of catalyst may cause an uncontrollable reaction, consider making these supervisory checkpoints. In such instances the standard operating procedure would specify that the employee must notify his or her supervisor before proceeding further. (In this example, notify the supervisor before 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. Similarly, if a process

variable is not or cannot be maintained within prescribed limits then the plant or process step should be shut down immediately and the supervisor consulted.

3.2.5

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

4. HEALTH FACTORS

4.1 Toxicity

4.1.1

Vinyl chloride monomer is believed to be a carcinogen to man. Exposure of three animal species to vinyl chloride caused a higher frequency of angiosarcoma, as well as other respiratory and digestive tumors than in the control groups. Workers in the manufacture of polyvinyl chloride resin have shown a higher incidence of angiosarcoma than anticipated after long exposure at relatively high concentrations. The long-term effects of short-term and of intermittent high concentration exposure have not been studied in either animals or man.

Both EPA and OSHA have issued regulations that limit the emission of vinyl chloride to the air and the exposure of people to such emissions.

Workers in the polyvinyl chloride, primarily reactor cleaners, have been found to have acroosteolytic changes in certain bones, particularly the distal phalanges of the fingers. This effect is largely reversible and has been associated only with high levels of exposure that have been experienced in the past. Certain skin changes suggesting scleroderma have been noted in some workers with occupational acroosteolysis.

Combustion and pyrolysis products of monomeric or of polymerized vinyl chloride include hydrogen chloride and other irritating gases. Exposure to these gases may cause severe irritation of the mucous linings of the respiratory tract; pulmonary edema and chemical pneumonitis may result.

Vinyl chloride monomer vapor has no distinctive warning odor at low concentrations nor is it irritating. The odor threshold for vinyl chloride varies with the purity and the amount of exposure. A 2,000 ppm odor threshold has been reported. High concentrations have a narcotic effect on the central nervous system and can produce anesthesia; judgment and functional ability can be impaired under these circumstances.

The permissible exposure limit (PEL) for vinyl chloride monomer is 1 ppm (eight-hour, time-weighted average) with a 5 ppm, 15-minute ceiling.* (Also see section 4.2.1).

*29 CFR 1910.1017.

4.1.2 Acute Toxicity

Concentrations of approximately 6,000 ppm for five minutes produce symptoms resembling mild alcohol intoxication in humans. Levels of approximately 16,000 ppm for five minutes produce varying degrees of intoxication, with lightheadedness, some nausea and a dulling of visual and auditory responses in most humans. Higher levels produce unconsciousness.

4.1.3 Chronic Toxicity

Long-term exposure of experimental animals at concentrations of 50 ppm or greater produced angiosarcoma of the liver and other evidence of the induction of malignant neoplasms. The incidence of hepatic angiosarcoma among workers exposed to vinyl chloride monomer has been in excess of the predicted incidence based upon control populations. The incidence appears to be dose related in that the disease is more frequent among groups that were exposed to relatively high levels of vinyl chloride monomer.

4.2 Medical Management

4.2.1 Physical Examinations

The OSHA Standard for Vinyl Chloride requires that all employees exposed to a vinyl chloride concentration of 0.5 ppm or more, without regard to the use of respirators, be provided a program of medical surveillance.* performed by or under the supervision of a licensed physician. An outline of the program required by OSHA follows:**

*29 CFR 1910.1017

**If the examining physician determines that medical examinations other than those required by OSHA regulations will provide at least equal assurance of detecting medical conditions pertinent to the exposure to vinyl chloride, the employer may accept such alternative examinations as meeting the requirements provided that the employer obtains a statement from the examining physician describing the alternate examinations and the reasons for substitution. This statement is to be made available for examination and copying to authorized representatives of the Assistant Secretary of Labor for OSHA and the Regional OSHA Director.

- (1) At the time of initial assignment, or upon institution of medical surveillance --
 - (i) Perform a general physical examination with specific attention to detection of enlargement of liver, spleen and kidneys, and to dysfunction in these organs, and for abnormalities in skin, connective tissues and the pulmonary system.

If any tests show enlargement, dysfunction or abnormalities, they should be repeated as soon as practicable, preferably within three to four weeks. If the results are repeated, consider withdrawal of the employee from contact with vinyl chloride, while a more comprehensive examination is made. Additional tests which may be useful include:

- (A) For kidney dysfunction: Urine examination for albumin, red blood cells and exfoliative abnormal cells.
 - (B) Pulmonary system: Forced vital capacity, forced expiratory volume at one second, and chest roentgenogram (posterior-anterior 14 x 17 inches).
 - (C) Additional serum tests: Lactic acid dehydrogenase, lactic acid dehydrogenase isoenzyme, protein determination and protein electrophoresis.
 - (D) For a more comprehensive examination on repeated abnormal serum tests: Hepatitis B antigen and liver scanning.
- (ii) Take a medical history; include the following topics:
 - (A) Alcohol intake;
 - (B) Past history of hepatitis;
 - (C) Work history and past exposure to potential hepatotoxic agents, including drugs and chemicals;

- (D) Past history of blood transfusions,
and
 - (E) Past history of hospitalizations.
- (iii) Obtain a serum specimen and determine:
- (A) Total bilirubin;
 - (B) Alkaline phosphatase;
 - (C) Serum glutamic oxalacetic transaminase
(SGOT);
 - (D) Serum glutamic pyruvic transaminase
(SGPT); and
 - (E) Gamma Glutamyl Transpeptidase.

OSHA regulations require that laboratory analyses for all biological specimens included in medical examinations be performed in laboratories licensed under 42 CFR 74.

- (2) Periodic examinations as described above should be performed at least annually for the first nine years of employment in vinyl chloride or polyvinyl chloride manufacturing and semiannually thereafter.
- (3) Each employee exposed to an emergency should receive appropriate medical surveillance.
- (4) Obtain a statement of each employee's suitability for continued exposure to vinyl chloride including use of protective equipment and respirators from the examining physician promptly after any examination and provide a copy of the statement to each employee.
- (5) Employee's whose health would be materially impaired by continued exposure should be withdrawn from possible contact with vinyl chloride.

OSHA regulations require that medical records be maintained for the duration of the employment of each employee plus 20 years or 30 years, whichever is longer. Such records should be available to the Assistant Secretary of Labor for OSHA and the OSHA Regional Director.

4.2.2 Suggestions to Physicians

Treatment for vinyl chloride intoxication is symptomatic; no special procedures are required. However, avoid the use of epinephrine or related drugs in treating acute overexposures; vinyl chloride may sensitize the heart to the arrhythmic action of these drugs.

The primary effect in acute overexposures is central nervous system depression. In chronic exposure the liver is the principal target with secondary effects possibly in the kidneys and lungs.

If breathing has stopped due to vinyl chloride narcosis, promptly initiate assisted respiration (e.g., mouth-to-mouth or mechanical resuscitation). Oxygen should be administered. Active ventilation is important to the maintenance of adequate tissue oxygenation and the removal of vinyl chloride to the exhaled air.

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 nonrebreathing 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 0.4 kPa (4 cm (1.5 in) of 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 0.4 kPa (4 cm (1.5 in) of water) 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.

4.3 First Aid

4.3.1 General

First aid should be started at once in the case of acute intoxication with vinyl chloride or in the case of contact with liquid vinyl chloride. Refer all overexposed patients to a physician and give a detailed account of the accident*. Each employee exposed to an emergency should receive appropriate medical surveillance; see section 4.2.

4.3.2 Contact with Skin

Vinyl chloride in liquid form is a skin irritant and can cause frostbite. All clothing including shoes that are contaminated with vinyl chloride should be removed immediately and not worn again until properly decontaminated. All affected body areas should be washed thoroughly with warm water and soap. The individual should be referred to a physician promptly.

*Required by 29 CFR 1910

4.3.3 Contact with the Eyes

If liquid vinyl chloride enters the eyes, wash promptly with copious quantities of water for at least 15 minutes. The eyelids should be held apart during washing to ensure contact of the water with all the surface tissues of the eye and lids. Prompt medical attention should be obtained.

4.3.4 Taken Internally

The gaseous nature of vinyl chloride makes ingestion unlikely. Consult a physician in cases of suspected ingestion.

4.3.5 Inhalation

At once, carry a worker who has been overcome by vinyl chloride into an uncontaminated atmosphere. Initiate artificial respiration immediately if respiration has been slowed or stopped. If oxygen inhalation apparatus is available, oxygen should be administered but only by a person authorized for such duty by a physician. The patient should be kept comfortably warm but not hot.

Stimulants will rarely be necessary where adequate oxygenation is maintained. Drugs for shock treatment should be given only by the attending physician. Never attempt to give anything by mouth to an unconscious person.

Exposed persons showing signs of vinyl chloride intoxication should be led to an uncontaminated atmosphere promptly to prevent injury by falling, etc. Refer all exposed persons promptly to a physician after exposure.

4.4 Personal Protective Equipment

4.4.1 Availability and Use

Personal protective equipment is not an adequate substitute for good, safe working conditions, adequate ventilation or intelligent conduct on the part of employees working with vinyl chloride. It is, however, in some instances the only practical means of protecting the worker, particularly in emergency situations.

The OSHA Standard for Vinyl Chloride specifically requires the use of engineering and work practice controls to reduce employee exposure to vinyl chloride either to the permissible level or to the extent feasible. Where such controls are not sufficient to reduce exposure to the permissible level, a written program is required to be established and implemented in order to reduce employee exposure to the permissible limits or to the greatest extent feasible.

4.4.2 Protective Clothing

All protective garments should be clean and dry before each use.

Clothing and gloves made of rubber or impervious material should be worn to protect against accidental skin contact with liquid vinyl chloride.

Employees engaged in hazardous operations such as cleaning polyvinyl chloride residue from vessel walls should wear protective garments selected for the operation.

4.4.3 Foot Protection

Safety footwear with built-in steel toe caps is recommended for all industrial operations. For added protection against chemical contact with liquid vinyl chloride, either safety footwear or overshoes (to be worn over leather safety shoes) made of chemical resistant material is recommended. It is important to thoroughly clean or discard contaminated footwear.

4.4.4 Eye Protection

Spectacle-type safety glasses meeting ANSI* Standard Z87.1 with metal or plastic frames are recommended as minimum protection against eye injuries from flying particles.

*American National Standards Institute.

If there is danger of splashing, or when material is under pressure, splash goggles should be worn; if complete face protection is desirable, use plastic shields (full length, 20 cm (8 in) minimum) with forehead protection in addition to splash goggles.

Where liquid vinyl chloride is involved or where there is likelihood of exposure to vinyl chloride vapor at concentrations exceeding the permissible exposure limit, appropriate respiratory protection is required by OSHA*. In such cases, the use of the required full-face piece respirator provides adequate eye protection without other supplementary devices.

4.4.5 Respiratory Protection

Establish and maintain a respiratory protection program wherever employees are provided with or are required to wear respiratory protective devices. The respiratory protective equipment that is used should be certified by the National Institute of Occupational Safety and Health (NIOSH) and carefully maintained, inspected, cleaned and sanitized at regular intervals and always before use by another person.

Except for life rescue, entry into concentrations greater than 36,000 ppm is prohibited by OSHA regulations; except for life rescue, firefighting, or prevention of a greater hazard, entry into concentrations between 3,600 and 36,000 is similarly prohibited. For various ranges of concentrations less than 3,600 ppm the required respiratory apparatus varies; see the regulations for details*.

When vinyl chloride concentrations may reasonably be expected to exceed the upper limit of the concentration range applicable to the respiratory apparatus in use, provide a continuous monitoring and alarm system to alert employees in the event that the concentration exceeds the allowable limit.

*29 CFR 1910

At the end of each work shift during which they are used, or sooner if their service life is about to expire, replace air purifying canisters or cartridges in respiratory protective devices.

4.4.6 Head Protection

NIOSH-approved hard hats are recommended for protection from falling objects, overhead liquid leaks and chemical splashes.

5. FIRE HAZARDS AND FIREFIGHTING

5.1 Fire Hazards

Vinyl chloride is extremely flammable. The explosive limits for the vapor lie between 3.6 and 33% by volume in air. Vinyl chloride is usually handled as a liquid under pressure; spilled liquid quickly vaporizes. A four liter (one gallon) liquid spill quickly becomes 1200 liters (45 ft³) of vapor. If mixed with double this volume of air, the upper explosive limit is reached; more air increases the volume of the explosive mixture; up to a volume of more than 30,000 liters (1,000 ft³) the vapor-air mixture will still explode if ignited.

Burning vinyl chloride, and the products of an explosion of vapor-air mixture also, produces carbon monoxide and hydrogen chloride (both toxic gases) and dense clouds of black smoke.

In summary:

Fire - Vinyl chloride is highly flammable. Vapors from a liquid spill spread quickly.

Explosion - Vapor from a liquid spill, if ignited, can cause a gas explosion indoors, outdoors and in sewers. Tanks and other containers of liquid vinyl chloride may explode due to the heat from a fire.

Health - Contact with the liquid may cause burns to skin and eyes. Vapors may cause dizziness or unconsciousness. Fire will produce irritating, poisonous gases.

5.2 Firefighting

Carbon dioxide or dry chemical agents extinguish small fires effectively, but no extinguisher is known to be suitable for large fires. Control of large fires is confined to eliminating the source of fuel and to reducing fire damage by cooling structures and tanks with water spray. Extinguishing a vinyl chloride fire from a major leak source such as a broken pipeline may lead to explosive reignition if all sources of spark and flame are not eliminated.

Some guidelines for major spills or fires are:

Immediate Action

Evacuate area.

Keep upwind. Define and isolate hazard area.

Wear self-contained breathing apparatus and protective clothing.

Eliminate all open flames, flares, smoking and internal combustion engines if there is a vapor cloud.

Continuing Action

Let fire burn unless leak or emission can be stopped immediately.

Cool tanks and containers with water from maximum distance until after fire is out. Use unmanned spray systems, monitor nozzles and hoses for major fires. Impound the water to prevent spread of the hazard. Do not let water enter the sewage collection system. Stay clear of tank and container ends. Evacuate immediately in case of a rising noise from a venting safety device.

5.3 Special Hazards

All persons exposed to vinyl chloride or its combustion products should be checked by a physician. (see section 4).

Entry into the fire area after the fire is out should be limited to persons wearing self-contained breathing apparatus until the absence of vinyl chloride, hydrogen chloride and other hazardous gases is confirmed by test.

6. INSTABILITY, REACTIVITY HAZARDS AND CONTROL

Vinyl chloride is a reactive monomer. It exhibits the addition and polymerization reactions characteristic of the ethylenic double bond. Under normal conditions of handling and storage uninhibited vinyl chloride is relatively stable but it polymerizes exothermally in the presence of light, air, oxygen or other free radical initiators. To prevent polymerization in transit or storage, protect the monomer at all times from contact with air, oxygen, moisture, catalytic impurities and light. Heat alone does not initiate hazardous polymerization until temperatures of 250°C or more are reached. However, if stored for long periods at temperatures over 20°C, vinyl chloride will become hazy, indicating some polymerization.

Vinyl chloride reacts with air or oxygen to form vinyl chloride polyperoxide which is shock sensitive, will detonate under some conditions, and will also catalyze polymerization of the monomer. In equipment where vinyl chloride is exposed to small amounts of air or oxygen such as recovery systems for vent gases, etc., polyperoxides have been found as a grey-white powdery mass. When the presence of polyperoxides is suspected, treatment with caustic solutions usually suffices for their destruction.

To stop polymerization or to prevent polymerization, small amounts of phenol, hydroquinones, phenothiazine, tert-butyl catechol, isoprene, styrene and styrene derivatives will act as inhibitors or short stops if thoroughly mixed with the vinyl chloride.

7. ENGINEERING CONTROL OF HAZARDS

7.1 Building Design

7.1.1 Isolation

Equipment and vessels containing vinyl chloride should be isolated from other facilities by walls and floors of fire resistive construction or by adequate spacing. Standard fire walls are recommended for isolation of larger equipment and storage tanks. Partitions of plaster and expanded metal lath may be used to isolate smaller equipment from other combustible materials.

Floor drains and process drains should be segregated from sanitary sewer systems to minimize sewer explosion hazards as well as the amount of waste water to be treated for vinyl chloride removal as required by Environmental Protection Agency regulations.

Adequate spacing of other process and service building from process buildings involving vinyl chloride is desirable to minimize damage from explosion and to insure the availability of critical services for fire-fighting and for control of uninvolved equipment.

7.1.2 Exit

Provide at least two means of exit 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 25 meters (75 feet) from the nearest exit. Additional exits should also be provided depending upon the number of persons in the building (see NFPA Standard #101 Life Safety Code and OSHA regulations, Title 28 CFR 1910). All exit doors should open out in the direction of travel and be provided with panic hardware.

Fire doors should open out in the direction of travel and be an approved type.

Fire resistive stairwells with automatic fire doors may be specified for hazardous operation on upper floors. However, for multistory buildings consider the use of escape slides or external ramps instead of stairwells or ladders as a means of emergency egress from higher levels. Most injuries result from uncontrollable reactions or from ignition of flammable vapor clouds. Provision for prompt escape from such hazards is desirable.

7.1.3 Housing

In processes involving large quantities of vinyl chloride only those portions of the process requiring weather protection should be housed, preferably in one-story buildings or partially enclosed in critical areas only. Other process vessels not requiring weather protection or close operating supervision and other equipment such as storage tanks should be located in the open.

7.1.4 Explosion Vents

Explosion venting windows, roof wall panels, skylights, light windows, diaphragms, etc. may be used to minimize building damage due to explosion pressures. To reduce destructive damage to buildings particularly where a large leak or operating error could result in explosive concentrations of flammable vapors, use explosion vents.

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. Hence, determination of vent ratios should be made by experienced engineers and fire and safety protection specialists (see NFPA Fire Code #68).

7.1.5 Other Provisions

For dissipation of flammable vapor clouds that may result from equipment failures within the building, equip processing buildings with internal water deluge and emergency ventilation systems controlled by flammable gas monitors.

The vinyl chloride process building design should include a breathing air supply system for respirators, an open head automatically controlled fire water sprinkler system and an adequate forced ventilation system (also see section 7.3) as well as emergency showers and eyewash facilities.

7.2 Equipment Design

7.2.1 Materials of Construction

Materials of construction considered hazardous for equipment in vinyl chloride service are copper, zinc, aluminum and alloys containing these materials. Copper is excluded since traces of acetylene in vinyl chloride could form explosive copper acetylides. Zinc and aluminum react with vinyl chloride. Other materials such as steel, stainless steel, nickel, glass, Teflon, compressed asbestos and ceramics are acceptable. Most elastomers swell and lose strength in vinyl chloride service.

7.2.2 Special Equipment and Design

7.2.2.1

The design of vinyl chloride piping and equipment is highly specialized because of the reactive, flammable and toxic properties of the material. Before initiating any plant or equipment design the Occupational Safety and Health Administration Standard for Vinyl Chloride (see 29 CFR 1910) and the Environmental Protection Agency National Emission Standard for Vinyl Chloride (see 40 CFR 61) as well as any other pertinent regulations should be thoroughly understood. The EPA Standard in particular required specific equipment items. The technical problems of designing equipment, providing adequate ventilation and formulating operating procedures that ensure maximum safety and economy can be handled best by experienced engineers and safety and fire protection specialists.

7.2.2.2

In the handling of vinyl chloride and in the operation of any type of vinyl chloride system, all valves, pipelines, vents, safety devices, etc., should be located so that they can be readily inspected and repaired. Consider using redundant facilities in critical areas. All handling and storage equipment should be located away from any source of sparks, flames, heated surfaces and other sources of ignition. The use of excess flow valves, valves with fusible links and remotely operated valves should be considered on large tanks in the case of fires or major leaks near such vessels. Bottom connections are to be avoided if practical.

7.2.2.3

Safety requires that equipment be used and maintained as recommended by the manufacturer or within design limits such as the ASME Pressure Vessel Code. All process equipment including safety devices should be tested and inspected on a regular basis.

7.3 Ventilation

7.3.1 General and Emergency Equipment

Good ventilation (at least fifteen air changes per hour for enclosed processing areas) is essential in rooms or confined areas where vinyl chloride is handled to prevent the unsafe accumulation of toxic or explosive concentrations.

Emergency ventilation (thirty changes of air per hour, controlled by automatic analyzers in the work space air) should be available to remove dangerous concentrations resulting from leaks or equipment failures.

Pressurized control rooms or buildings with ventilation air intakes located upwind or some distance from sources of contamination can be used to provide a "safe" area for operating personnel where respirators need not be worn.

Good ventilation is a valuable tool in achieving the permissible exposure limit or a lower concentration in the work space air, but it is effective only when used in conjunction with good equipment and process design and proper equipment maintenance. In the design of a good mechanical ventilation system, consideration should be given to employee comfort and to control of the system; for example, under what conditions should it operate normally, when should it be off, when should emergency speed be used and when or whether control should be automatic or manual.

7.3.2 Air Analysis-Monitoring

Analysis of the air for vinyl chloride in the work area is required by the EPA Standard (Title 40 CFR 61) as a means of detecting and measuring emissions to the air. The standard requires a system that obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromatography or by alternative methods. The OSHA Standard (see Title 29 CFR 1910) requires that when employees are wearing air purifying respirators a continuous monitoring and alarm system be in use if there is a likelihood of exceeding the vinyl chloride concentration allowable for the respirator in use. In addition, these analyzers are invaluable in providing data for work in meeting the OSHA permissible exposure limits.

Flammable gas detectors are also used to indicate danger from fire or explosion and may activate water deluge as well as mechanical ventilation systems.

Automatic analyzers are complex. This kind of equipment should be checked and maintained on a regular basis to meet the EPA standard requirements as a minimum.

The OSHA standard also requires monitoring employee exposures to vinyl chloride on a specific basis. Sampling and analysis may be done in any fashion so long as acceptable levels of accuracy are achieved. This type of monitoring requires consultation with a trained industrial hygienist.

7.4 Electrical Equipment

7.4.1

Vinyl chloride is normally handled in closed systems and all work areas are ventilated and controlled to low concentrations of vinyl chloride. Flammable concentrations may exist in emergency cases. Under normal conditions, electrical equipment approved for Class I Division 2 locations may be used.

The selection of electrical equipment for a plant requires skilled evaluation by a competent process engineer as well as an electrical engineer. All equipment and wiring should be purchased and installed to meet the appropriate sections of the National Electric Code.

7.4.2

Separate power supply to lights, analyzers and automatic control systems is provided by many companies in their plants. These separate power supplies are often backed up by auxiliary generators or batteries for critical control items.

7.4.3

Static electricity may be generated when vinyl chloride or polyvinyl chloride flows through or is discharged from a pipe. To drain off static charges and avoid spark discharges, a continuous path from the point of generation to ground should be provided. This is best accomplished by electrically interconnecting (bonding) all vessels and piping, by grounding all vessels and piping or by a combination of bonding and grounding.

Bonds and grounds for static electricity protection may be of any conductor size. Any ground that is adequate for power or lightning protection is more than adequate for grounding static electricity. Ground wiring should be of sufficient size to provide reasonable protection against physical wear. Periodic checks of continuity to ground should be made. Systems using nonconductors such as glass, plastic and ceramic piping or coatings should be carefully checked for continuity. Some types of Teflon-lined plug valves have required electrical bonds between the plug and the body to reduce sparking.

For a more complete discussion of static electricity see NFPA #77.

8. STORAGE, LABELING AND PLACARDING, SHIPPING

8.1 Storage

8.1.1 General

Vinyl chloride storage areas should always be selected to comply with all applicable local codes and regulations, especially those involving occupational health, environmental control, hazardous materials and fire prevention. Organizations such as the National Fire Protection Association, the National Board of Fire Underwriters and the Factory Insurance Association can be consulted about proper site selection.

8.1.2 Conditions of Storage

8.1.2.1

Vinyl chloride is a very volatile, toxic and flammable gas at normal atmospheric conditions. Vinyl chloride may be stored for reasonable periods of time (up to one year) without danger from the hazardous decomposition or polymerization of vinyl chloride when kept in contact with ferrous materials and in the absence of air, oxygen, water, light or excessive heat. However, uninhibited vinyl chloride in storage, either under refrigeration or at normal atmospheric temperature, should be checked regularly for the presence of polymers.

Containers and vessels used for handling vinyl chloride at ambient temperatures are usually under pressure. Nitrogen blanketing may be employed to increase the storage pressure in order to facilitate tank pumping operations. Refrigeration can be used to maintain the storage temperature within an acceptable range - below 50°C and preferably between 0°C and 20°C.

8.1.2.2

All piping, instrument leads, storage tanks, relief devices and other equipment employed to handle vinyl chloride should be constructed of recommended materials (see section 7.2). This equipment should be designed to withstand a full vacuum, if practical, or a working pressure of at least 700-1100 kPa (100-500 psi) conforming to the ASME Code for unfired pressure vessels or other code applying to the locale of planned storage. However, vapor recompression or refrigerated storage tanks can be designed for lower operating pressures.

Shut-off valves and control valves should be of steel or a suitable alloy not containing copper, and these valves should be designed for working pressures of at least 1100 kPa (150 psi). To insure leakproof integrity all welded construction is recommended.

All equipment should be properly grounded and bonded with the resistance to ground 25 ohms or less. To further minimize the accumulation of static charge, liquid inlet lines should either enter the bottom or extend to the bottom of storage vessels. All electrical wiring, lighting and equipment should comply with NEC requirements.

The stand leg should have an opening near the top of the tank to act as a vacuum breaker and to help prevent blowback. Vinyl chloride tanks should be painted with white or other heat reflective paint.

8.1.2.3

All storage areas should have installed an appropriate water spray system, an automatic sprinkling system, or other special fire extinguishing system that is suitable for use with Class B fires. Portable fire extinguishers, carbon dioxide or dry chemical, should be readily accessible to personnel in these areas (see section 5).

In all storage areas provide for diking or for draining to a safe location for both, to completely confine and dispose of the liquid in the event of a major spill or vessel rupture.

8.1.3 Isolation

Highly volatile and flammable materials such as vinyl chloride should be stored outside of buildings. Vinyl chloride storage areas should be selected and constructed in accordance with local codes or the regulations of authorities having jurisdiction. Preferably, vinyl chloride storage tanks should be segregated from major process units.

Process units that have a higher than average fire or explosion risk potential, such as furnaces or reactors, should be situated as far from storage tanks as practical. All potential ignition sources should be eliminated from storage areas.

Cylinders containing vinyl chloride should be stored in a vertical position, outside of buildings in an isolated and well-ventilated area. It is best to store cylinders in the open, but provision should be made to shield them from the sun's direct rays and to prevent the accumulation of dirt, snow, water or ice on their valves or safety devices. Vinyl chloride storage areas should be restricted to authorized personnel only and are often classified as "regulated areas" (see pertinent OSHA regulations).

8.1.4 Regulatory Aspects

Title 29 CFR 1910.1017 outlines the scope, application and specific requirements of the Occupational Safety and Health Standard for Vinyl Chloride. This standard provides for personnel exposure limits, individuals authorized to enter an area, environmental monitoring, respiratory protection, labeling, etc.

Title 40 CFR 61 "The National Emission Standards for Hazardous Air Pollutants" outlines the rules and regulations governing vinyl chloride emissions that have been established by the Environmental Protection Agency. The provisions of this standard should be complied with by the owner or operator of a vinyl chlorid plant.

8.1.5 Compatible and Dangerously Reactive Materials

Vessels used for vinyl chloride should be used only for vinyl chloride. They should be purged with a dry inert gas until free of oxygen ($\leq 1,000$ ppm) prior to filling. Vinyl chloride monomer is generally noncorrosive at normal atmospheric temperatures when dry (moisture free). However, mild to appreciable corrosion has been reported when vinyl chloride is wet even at ordinary temperatures. This may be due to the presence of impurities. In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron and steel. Acetylene as an impurity in vinyl chloride may form an explosive compound (acetylides) when exposed to copper or copper alloys.

8.2 Labeling and Placarding, Shipping

All federal regulations regarding labeling and placarding must be followed. Department of Transportation (DOT) regulations can be found in 49 CFR; see 46 CFR for U. S. Coast Guard (USCG) regulations concerning shipments by barge; see 29 CFR for labeling and other requirements promulgated by OSHA.

8.2.1 Precautionary Labeling

It is recommended that containers of vinyl chloride bear a label containing at least the information shown here. The text is designed for the product as shipped for industrial use. It should be used in addition to or in combination with any specific wording required by law. Individual statutes, regulations, or ordinances may require that particular information be included in the 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 will not necessarily insure compliance with such laws. Such laws include the Federal Hazardous Substance Labeling Act; Federal Insecticide, Fungicide and Rodenticide Act; and similar state and municipal legislation.

VINYL CHLORIDE

DANGER!

CANCER HAZARD
EXTREMELY FLAMMABLE LIQUID AND GAS
UNDER PRESSURE
HARMFUL IF INHALED
MAY POLYMERIZE VIOLENTLY UNDER FIRE
CONDITIONS OR 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 rounded 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.

Fire: Use water spray, dry chemical or CO₂.

Spill or Leak: For small spills, evacuate area and permit 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.

For additional safety and health information, see
MCA Chemical Safety Data Sheet SD-56*.

*Or cite equivalent reference.

8.2.2 Shipping

Vinyl chloride is classified by the DOT as a flammable gas. When shipped by rail, water or highway it must be packaged in authorized containers and shippers must comply with DOT regulations regarding packaging, loading, handling, labeling, marking and placarding.

Each container and overpacked cylinder containing vinyl chloride, including tank trucks and cars, must carry a "FLAMMABLE GAS" label and show the name "VINYL CHLORIDE" on the outside of the shipping container and on the related shipping papers. See the appropriate regulations for information concerning the size and color of required labels and their lettering, the number of labels and placards, the composition and durability of placards, cargo signs and cards required, warning signs, "EMPTY" labels, and related matters.

8.3 Nonbulk Containers

8.3.1 General

In many of the steps involved in the handling, loading, sampling and processing of vinyl chloride, there are points of potential employee exposure to vinyl chloride monomer. Such potential exposure points should be identified and engineering, work practice and personal protective controls provided as required by the OSHA vinyl chloride standard to control employee exposures within the permissible exposure limit.

8.3.2 Cylinders

Full or partially empty cylinders should not be returned without permission of the supplier. Partially empty cylinders are required to be shipped as full vinyl chloride cylinders and correspondingly handled, labeled and tagged.

In shipping vinyl chloride cylinders, the bill of lading should give cylinder identification number. For each cylinder shipped, show the name of the consignee and indicate whether the cylinder is empty or full.

Valve protection caps should always be kept securely in place except when the vinyl chloride containers are connected to piping, apparatus or equipment. Replace the cap as soon as a cylinder is disconnected. Empty vinyl chloride cylinders should be securely closed and capped; do not allow air to enter the cylinder.

Magnets, slings, hooks, or tongs should never be used to unload cylinders. When transporting by crane or derrick a suitable platform, cradle or boot should be used. Exercise care, do not drop, bump, drag, or slide cylinders or otherwise handle them roughly. Do not use cylinders as rollers for moving other objects or materials. Do not disturb the fusible plug; tag it in order to distinguish it from the discharge connection.

Cylinders transported by hand truck should be held securely in position by means of a locking clamp, chain or other suitable holding device.

Areas where cylinders are connected or stored should have sufficient ventilation to prevent vinyl chloride concentrations from exceeding the OSHA permissible exposure limit.

Use pressure regulators recommended by the supplier. Install check valves in feed lines from cylinders to prevent other reactants from entering.

Cylinders should be filled only with the consent of the owner and in accordance with applicable DOT and OSHA regulations.

8.3.3 Sample (Bomb) Cylinders

Where applicable, the recommendations set forth for cylinders in the preceding section also apply to sample bombs.

Stainless steel sample pressure bombs used to take vinyl chloride monomer samples should be dedicated to vinyl chloride service and should conform to DOT requirements. In order to minimize the venting of vinyl chloride to the atmosphere, a closed loop sampling system designed to include the sample container is preferred. Emission to the atmosphere during sampling must be controlled within the limits prescribed by EPA. Sampling containers should be routinely inspected to assure the integrity of the valves and to check for leakage.

Persons directly involved in the collection or analysis of vinyl chloride samples for quality control purposes should wear NIOSH/MESA-certified respiratory protection consistent with the requirements of the OSHA vinyl chloride standard. The type of respiratory device utilized should reflect actual or reasonably anticipated vinyl chloride exposure levels.

All quality control testing and analyzing should be performed in a laboratory equipped with a chemical laboratory hood having a capture velocity adequate to collect vinyl chloride vapors under conditions prevailing in the laboratory. The discharge from the laboratory hood and from the analytical test instruments shall be designed so that vinyl chloride vapors do not re-enter a nonregulated area.

8.4 Bulk Transport

8.4.1 General, Loading/Unloading

Shipper's plants and procedures vary; the design of bulk transport facilities varies. Unloading procedures are usually specified by the supplier; obtain instructions before proceeding. Shipper's or owner's instructions should always be followed; observe all caution markings on the sides and dome of a tank.

In many of the handling, sampling and unloading steps there are potential points of exposure to vinyl chloride monomer. Consult the technical service staff of the supplier for assistance in identifying monomer unloading exposure points. Also check for other exposure points. See section 8.3.3 for precautions pertaining to sampling.

8.4.1.1

Loading and unloading of bulk containers should be considered a hazardous operation. OSHA regulations regarding signs, barricades and respirator use should be followed.

8.4.1.2

Leaking bulk containers or bulk containers delivered with defective valves or other defective equipment should be held pending instructions from the owner. Take only action to provide for control of immediate safety problems such as obvious leaks and spills: Wear NIOSH/MESA-certified air supplied respirators. Remove all sources of ignition. Keep people away. Control the leak by plugs, valves or patches to control the immediate hazard. (Also see sections 4, 5 and 9).

8.4.1.3

Use only material recommended for vinyl chloride handling as packing and lubricant for valves and piping.

Pumps and compressors should be equipped with double mechanical seals on packing glands. Vent the space between the seals to an EPA-accepted control device or purge the space with a pressurized fluid so that there is no external leakage of vinyl chloride.

Unloading or loading piping should be provided with excess flow check valves to control spills in the event of a line break. All unloading or loading piping should be attached to an EPA-accepted control system to control emissions to the atmosphere within allowed limits. The use of slip gauges is prohibited unless EPA-accepted control devices are provided to control the emissions within allowed limits.

8.4.1.4

The operating mechanism for unloading valves should have a secondary control, remote from the fill openings and discharge valve for emergency use in the event of a fire or other accident.

The control mechanism should have a fusible section which will permit valves to close automatically in case of fire.

8.4.1.5

Where access to the top of the tank car or truck is needed, the spot should be provided with stairs and a platform of noncombustible construction. Overhead piping and equipment should be counterbalanced for ease in handling.

8.4.1.6

Prohibit vehicular traffic in the area during transfer, if possible. Otherwise, minimize and control traffic by temporary road blocks.

8.4.1.7

An emergency shower and eyewash should be provided directly accessible to and within 8 meters (25 ft) of a loading or unloading spot. A hose should be connected and ready for emergency use and the emergency shower and eyewash tested before proceeding with loading or unloading. Other sources of water should be available for washdowns.

8.4.1.8

Before any sample is taken, or a connection or contact is made between the tank truck or car and the unloading line or other unloading equipment, the truck or car should be electrically grounded.

8.4.1.9

Only after a qualified representative authorized by the consignee has thoroughly checked the transfer connections for proper alignment and has verified that the storage tank will accommodate the contents of the tank truck or car, should transfer be initiated. Similar coordination should precede disconnecting.

8.4.1.10

If a spill or overflow should occur during a transferring operation, the pump or supply should be stopped, valves shut off and the spill cleaned up before other actions are taken. See section 4, 5 and 9.

8.4.2 Transportation Emergencies

If a tank truck becomes damaged enroute and cannot proceed safely to destination, every effort should be made to park it where it will not endanger traffic or property, if possible in a vacant lot and away from populated areas. If a tank car is damaged similarly, spot it where people, property and traffic will not be endangered. The police and fire department should be notified and the public should be restricted from the area. Follow MCA chem-card precautions as available or contact producer for safe disposal instructions. Emergency information is also available from CHEMTREC by calling (toll-free) 800-424-9300.

8.4.3 Tank Trucks

8.4.3.1

Tank trucks should be visually inspected for leaks and to confirm the contents before they are allowed to enter the plant. Unloading or loading should be performed only during daylight unless the working areas are adequately lighted.

8.4.3.2

Truck loading and unloading facilities should be level and paved so that the truck can be easily and safely maneuvered to and from the working area. The pad should be of sufficient length and width to allow minimum clearances of 1.2 meter (4 ft) at each end and 0.6 meter (2 ft) on each side. The pad should be sloped to drain spills away from the truck and exposed structures. The engine should be

stopped and wheels blocked and brakes set to prevent movement during loading or unloading. The driver should be out of the cab. If the tractor must be separated from the trailer, place an adequate brace under the front end and separate before making any connections.

8.4.3.3

Because of the hazard of backing equipment into roadways and the possible need to move a truck quickly from the unloading spot, the position of nearby objects and structures should be arranged so that the truck can be driven off the pad in a forward direction. If a drive-through arrangement is used, a chain, gravity-swing guard gate, or equivalent, should be provided across the truck entrance to the driveway when the entrance is not in use.

8.4.3.4

A sign should be placed near the truck stating in effect, "DANGER - UNLOADING VINYL CHLORIDE", to caution others to stay away from the operation.

8.4.3.5

On completion of the operation, loading or unloading hoses must be evacuated as noted previously and wheel blocks removed.

8.4.3.6

The truck engine should be started and the truck removed only after all connections are severed and the absence of flammable gases confirmed by test.

8.4.4 Tank Cars

Tank cars are the most commonly used bulk container for vinyl chloride shipment. All are unloaded from the top through one or both of the liquid eductor tubes. A third valve provides access to the vapor space of the car for purposes of padding or pressurizing the car to prime the unloading pump.

8.4.4.1

The car unloading track should be level and the engine crew should accurately spot the car at the unloading lines.

8.4.4.2

Set the tank car brakes and block the wheels prior to hookup of the pipelines. Unless the car is protected by a closed locked switch, derails should be placed approximately one car length from each end of the car.

8.4.4.3

Place caution signs and warning lights prescribed by Department of Transportation regulations at the derails on the track to warn persons or trains approaching the car from open end or ends of the siding. These should remain in place until the car is ready to be moved.

8.4.4.4

The contents of the car should be verified by checking the car number with the shipping papers. Many companies also sample the contents for analysis. Failure to verify the car contents might lead to serious and hazardous mixing of reactive chemicals.

8.4.4.5

Tank cars of vinyl chloride are filled with liquid up to 86 percent of the water weight capacity of the tank. Vinyl chloride vapor occupies the space above the liquid. To prevent formation of a flammable mixture or premature polymerization, do not introduce air or oxygen during unloading or storage. Before hooking up, purge all lines thoroughly with nitrogen containing no more than 10 ppm oxygen. Nitrogen purging can be minimized by sealing the line and alternately pressurizing with nitrogen, then bleeding off to a remote recovery system or to an incinerator.

Remove the threaded pipe plugs on the liquid and gas valves cautiously and connect the liquid unloading line and the vapor padding line. The vapor pressure is needed to prime the centrifugal forwarding pump, if one is used. To reduce pressure drop, locate the pump as close to the tank car as possible. Some installations have a compressor on the vapor line from the storage tank in addition to the pump. In warm climates, a compressor may be used alone without a pump, but in cold weather a pump is usually needed - with or without the compressor - to facilitate unloading. The vapor pressure used for padding should not exceed 80 percent of the relief valve setting. Never apply heat to accelerate the unloading of a vinyl chloride tank car.

For flexibility in the unloading system, either stainless steel hose or steel pipe with flexible joints can be used. The flow of vinyl chloride from the tank car should be regulated by a valve in the transfer line. If the discharge rate suddenly becomes too great, an excess flow check valve in the tank car will close. To reopen this valve, close the unloading connection valve until the pressure is equalized.

Start unloading by slowly opening the vapor padding connection valve to the car. If it is necessary to discontinue unloading for any reason, close all valves tightly and disconnect all unloading connections.

8.4.4.6

Check the storage tank frequently to determine when the tank car is almost empty. Note the reading of the pressure gauge on the unloading line to determine when all the liquid has been emptied from the tank car. Unload liquid completely from the tank car but leave at least 35-70 kPa gauge (5-10 psig) of vinyl chloride vapor pressure in the empty tank car being returned after closing and sealing all openings. This is necessary to prevent air from entering the car.

After the car is emptied, stop the transfer pump. Close the padding connection valve and then the unloading connection valve at the top of the car. After this, close all other valves in the vinyl chloride line.

The lines leading from the unloading connection valve and the padding connection valve should be purged with nitrogen so the vinyl chloride monomer vapor in those lines is transferred to the recovery system.

Do not allow tank car to stand with unloading connections attached after unloading has been completed. Remove all lines from the car and disconnect grounding wires. Reverse the "FLAMMABLE GAS" placard on the car so that it reads "FLAMMABLE GAS - EMPTY."

8.4.4.7

For additional information see MCA Technical Bulletins TC-7, "Tank Car, Approach Platforms", and TC-29, "Loading and Unloading Flammable Liquid Chemicals, Tank Cars".

9. WASTE DISPOSAL GUIDELINES AND SPILL CONTROL

9.1 Waste Disposal Regulations

9.1.1

Federal, state and local regulations governing waste disposal make it essential for the producers and users of vinyl chloride to be fully aware of viable alternatives for the safe ultimate disposal of waste vinyl chloride and to select and practice a disposal method or process which assures compliance with all applicable regulations. Consideration should be given to air, water (surface and ground) and land pollution potential. MCA Technical Guides SW-1 "A Guide for Landfill Disposal for Solid Waste", SW-2 "A Guide for Contract Disposal of Solid Waste", and SW-3 "A Guide for Incineration of Chemical Plant Wastes", may be helpful in fulfilling environmental responsibilities.

9.1.2 Discharges into Navigable Waters

Discharges are controlled by regulations (Federal, state or local) promulgated under the Federal Water Pollution Control Act (Public Law 92-500). Point source discharges must be in compliance with the effluent limitations set forth in the NPDES permit for that point source.

The Federal Standard for emission of vinyl chloride (see 40 CFR) stipulates as a work practice that process waste water that contains more than the allowed maximum concentration of vinyl chloride must be stripped of the excess before:

- (a) Being exposed to the atmosphere.
- (b) Being discharged to a waste treatment plant.
- (c) Being discharged untreated as a waste water.

Vinyl chloride stripped from such waste waters must be directed to a primary control device that does not emit more than the allowed maximum concentration of vinyl chloride to the atmosphere.

9.1.3 Discharges to Municipal Sewage

Vinyl chloride or waste waters contaminated with vinyl chloride should never be discharged to public or private sewage treatment plants.

9.1.4 Air Emissions

The EPA has declared vinyl chloride to be a hazardous air pollutant and has promulgated a National Emission Standard for Vinyl Chloride (see 40 CFR). Essentially, this standard regulates the equipment and work practices to be used to meet:

- (a) Point source discharges.
- (b) Mass emission levels.

Although the EPA has preempted the regulation of vinyl chloride emission, states may also regulate vinyl chloride emissions as long as their regulations are at least as restrictive as the Federal regulations.

9.1.5 Land Application

At the present time there are no federal environmental regulations for other than air and water pollution control. However, federal guidelines have been promulgated in some instances (land fill and incineration) and strict compliance with those and with local and state requirements is necessary.

9.2 Spill and Leak Control

9.2.1 General

Prevention of leaks and spills should be the keynote in handling of either liquid or gaseous vinyl chloride. Nothing takes the place of carefully designed and well-maintained equipment operated by competent, trained and skilled operators. Standard safe startup, operating and shutdown procedures should be spelled out and their use enforced.

The prevention of spills, leaks and emissions should not result in operating procedures or plant designs that in any way interfere with the proper operation of emergency venting either by rupture disc, relief valve or manual vent. The polymerization of vinyl chloride can be rapid and highly exothermic. Hence, control of a polymerization is a major objective in any emergency.

Even small spills of liquid vinyl chloride are especially hazardous. Due to its large heat of vaporization, liquid spills of vinyl chloride monomer remain liquid long enough so that it often penetrates porous fill, runs into sewers or partially fills depressions where it then evaporates generating large volumes of flammable gas. (Forty liters (ten gallons) of liquid vinyl chloride monomer can become a flammable cloud (15 meters (50 feet) in diameter.) Plant design should be handled with extreme caution.

9.2.2 Control of Leaks and Spills

The Federal Standard for emission of vinyl chloride delineates much of the equipment and practices considered by the EPA to be the best available control technology (BACT). Among recommended practices of the standard are:

- (1) The use of sealess pumps, double mechanical seals on pumps, or equivalents.
- (2) A proscription against manual discharge valve discharges except as a last resort in emergency situations.
- (3) The use of add-on devices to control vinyl chloride discharges - possibilities suggested include incinerators, absorbers, refrigerated vents, strippers, recovery units and gasholders.
- (4) The use of continuous sequential monitoring for leaks and emissions in stacks and buildings.
- (5) Provision for reducing the volume of vinyl chloride in vessels prior to opening such vessels and provisions for directing any released vinyl chloride gas or liquid to a control device.
- (6) Provision for leak patrols on a periodic basis.
- (7) The incorporation of a leak detection program into standard operating procedures.

9.2.3 Handling Vinyl Chloride Leaks and Spills

Hazards from vinyl chloride leaks include:

- (a) The damage that results from a fire and/or explosion.
- (b) The exposure of plant personnel and the public to the effects of inhalation.

The explosion limits for vinyl chloride are 3.60 percent to 33.00 percent volume in air.

Practical considerations in the event of a leak of vinyl chloride should include:

- (1) Use proper protective clothing and appropriate respiratory equipment (see section 4).
- (2) Sounding a gas alarm and evacuating all personnel except those required to preserve life and property.
- (3) Use emergency ventilation.
- (4) Valve off sources of the leak (isolation).
- (5) Use a deluge system or other source of water mist to dilute the atmosphere. Such water should be drained to open ponds or diked areas, not to underground sewage collection systems; otherwise it may create an explosion hazard.
- (6) Shut down all ignition sources in the immediate area - such as autos, switch engines, trucks, electrical switchgear, boilers, etc. No ignition sources within 20 yards of the vapor cloud should be permitted.
- (7) Warn and evacuate the public that may be in the path of a vapor cloud. Evacuation should be upwind for at least 60 meters (2,000 feet) from the source, if possible.

When the immediate danger from a leak or spill has been controlled each incident should be carefully investigated and medical surveillance provided for those involved. Federal and state regulations should be consulted and the required reports promptly made to regulatory agencies.

10. TANK, EQUIPMENT CLEANING AND REPAIRS

10.1 Preparation for the Job

The inherently hazardous nature of vessel entry is increased by the flammability and toxicity of vinyl chloride and by the possibility of the presence of peroxide residues in a vessel that has contained vinyl chloride. Only experienced and trained workers should be assigned this duty and then only under the direct supervision of an experienced foreman. Each person should be thoroughly familiar with all of the hazards and safeguards necessary for the safe performance of work inside a tank. All work should be done in compliance with an adequate vessel entry and work procedure that provides for training, for the use of suitable protective equipment, for health safeguards and for a written checklist or work practice guideline for each step. The preparation of a stepwise work procedure for the entire job, rec-

ognizing 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.

10.2 Preparation of the Tank or Equipment

10.2.1

The EPA regulations on vinyl chloride limit allowable emissions to the environment from vessel openings. (See 40 CFR for details). Special control methods should be used to keep the emissions within the prescribed limits.

10.2.2

Before opening a tank, transfer all possible liquid vinyl chloride to another suitable vessel. The remaining heel should then be evacuated or allowed to evaporate to a lower pressure system which leads eventually to a recovery or emission abatement system capable of lowering the final effluent concentration to or below the limiting value prescribed by EPA. The EPA recommends the use of water to displace the vapor to a recovery or to an abatement system. The water so used is contaminated and must be stripped to a lower concentration that meets the EPA requirements before it is released to the environment. Alternate methods include repeated evacuation and repressurization with an inert gas and continual purging with inert gas or steam with the exhaust gas being treated by recovery or abatement equipment in either case. When the vinyl chloride content has been reduced to meet the EPA requirements the vessel may be opened to the atmosphere and further action is not regulated by EPA, but OSHA rules still apply.

10.2.3

Peroxide residues should be assumed to exist if the vessel has contained recovered vinyl chloride or if there is any possibility that oxygen or moisture were present at any time.

To avoid detonation of this sensitive material and before any lines are disconnected from the vessel, add sufficient ten percent sodium hydroxide solution to cover any solid deposits in the vessel allowing it to remain in contact for three to six hours. The time may be shortened to two hours if the temperature can be raised above 60°C (145°F). Care should be taken in handling, removing and disposing of this solution to prevent caustic burns; see Chemical Safety Data Sheet SD-9, Sodium Hydroxide.

10.2.4

All process piping should be disconnected, slip blanket or blinded so that there is no opportunity for process materials or utilities to re-enter the vessel. Local regulations regarding the method of installing blinds should be followed. It is not sufficient to valve off these lines nor to only insert blinds in the line. An open section should exist between the vessel and the line if there is any question about the integrity of the blinds. If pipe sections are to be removed and flanges opened, the lower bolts should be loosened first and, although the lines have been cleaned, care should be taken to avoid personal contact with any liquid draining or dripping from the equipment.

10.2.5

If the vessel is to be opened to the atmosphere, sources of ignition should be eliminated from the work area until tests show that the concentration throughout the area and inside the vessel are well below the flammable limits. Positive ventilation should be applied to remove the remaining vinyl chloride vapor. Care should be taken to eliminate all dead spots and to insure that the exhaust gases are dispersed adequately.

10.2.6

All persons in the work area during the vessel preparation steps should be equipped with impermeable clothing until it is assured that no liquid vinyl chloride remains in the vessel nor in its associated piping. Personnel should wear suitable NIOSH/MESA-certified air-supplied respirators until tests have shown that the vinyl chloride concentration has been reduced to the point where other methods of protection are adequate.

10.2.7

After adequate dispersion of vinyl chloride vapors from the interior of the vessels it should be washed as free as possible of wall fouling and loose debris in order to prevent the desorption of vinyl chloride from such materials into the work atmosphere.

10.3 Vessel Entry

10.3.1

Prepare a written work permit before tank preparation and entry. The permit should describe work procedures to be used, hazards that may be encountered and procedures and equipment to be used to nullify these hazards. It should be prepared and reviewed by the supervisors to whom the tank is assigned and approved after they are satisfied that tank entry and repair work can be safely performed and that the requirements of applicable regulations are met. (See 29 CFR).

As a minimum the preparation of a work permit should insure that proper protective equipment is used, proper mechanical and electrical lockout procedures are followed, that the vessel atmosphere has been tested, and that adequate rescue capabilities are available.

If the work extends beyond one shift or interrupted, a new work permit should be issued before resumption of work.

10.3.2

No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested and found to be safe. Before directing workers to enter a tank, an inspection of the interior should be made by the foreman who should be equipped with a positive pressure (or continuous flow) air-line mask or self-contained breathing apparatus, together with rescue harness and lifeline. Another person should be on guard during the inspection.

10.3.3

Special ventilation providing a continuous supply of fresh air is required during the entire time personnel are inside the tank.

It is preferable that vapors be exhausted from the bottom of the tank with fresh air being admitted at the top. In the case of the tanks having a top opening only this can be accomplished by extending a flexible air duct to the bottom of the tank. Care must be taken to avoid recycling exhaust gases into the tank.

10.3.4

During the course of the work, frequent tests should be made to determine that the atmosphere in the tank is being maintained within the safe range. This precaution is necessary because residues not completely removed by washing may recontaminate the tank atmosphere.

If flammable vapors are detected over ten percent of the LEL, the cleaning process should be repeated until the tank or vessel is free of vapor. The air should also be tested for oxygen content.

10.3.5

The electrical supply to any agitation within the vessel, and to any moving equipment nearby should be locked out in the off position according to local codes and the key kept in the possession of the worker inside the vessel or the foreman. The starting switch should be activated to be sure the proper circuit has been deactivated. The switch may also be disabled by a rod or lock in the "off" position, although this should not be the only lockout protection. See SG-8, "Electrical Switch Lockout, Tag and Try Procedure".

10.3.6

No one should enter a tank or vessel that does not have a manhole opening large enough to admit him while wearing his safety harness, lifeline and respiratory protective equipment. It should be ascertained that the tank or vessel can be left by the original entrance. In some cases, it is advisable to have a block and tackle positioned on a tripod or otherwise fastened above the manhole.

10.3.7

It is essential that one or more attendants be present at the point of entry whenever another person is in the tank; the number of attendants depends upon the complexity of the mechanical aids provided for removing a worker from the tank. If work is being done in an isolated area, arrangements should be made to have at least two additional attendants available at all times. The attendants should observe the interior operations, from outside the tank, continuously.

10.3.8

All person entering vessels should wear boots or rubbers over safety shoes, eye protection, hard hat and a NIOSH/MESA-certified supplied air respirator. Impermeable clothing is also needed if the walls are fouled with polymer. Each person should wear an approved safety harness or wristlets with a rope attached. Provide an individual rope at the manhole cover for each person.

10.3.9

All ladders, scaffolds or other large equipment should be tied off properly and secured to prevent slipping or falling during the work assignment. Take care to avoid tangling of air hoses and rescue lines with other equipment.

10.3.10

Any lights or electrically powered tools shall be inspected for proper insulation and grounding, and local codes shall be followed in regard to the permissible voltage to be used inside vessels. See 29 CFR. Welding equipment used within a tank should be provided with a quick shut-off under the control of an attendant outside the tank.

10.3.11

Danger signs should be placed suitably to indicate that workers are in the tank.

10.4 Emergency Rescue

10.4.1

Emergency procedures should be established in advance for summoning an ambulance, a physician, or other agency, so that such assistance can be enroute to the location while the rescue is underway.

10.4.2

Additional supplied-air respirators (hose mask) or self-contained breathing apparatus, together with rescue harness and lifeline should always be located outside the tank entrance for rescue purposes regardless of the type of respiratory equipment or air supply provided for employees inside the tank. The air intake of the hose mask should be located in an uncontaminated area.

10.4.3

The attendant or attendants stationed on the outside of the tank should keep the workers in the tank under observation and other workers should be nearby and instantly available with self-contained breathing apparatus and necessary equipment to aid in the rescue if a person in the tank is overcome. Protective clothing should be worn by the whole crew, if required.

10.4.4

Under no circumstances should a rescuer enter a tank to remove a victim of overexposure without proper respiratory protection (canister respirators are not proper equipment), a safety harness and an attached lifeline.

The free end of the lifeline should be manned by an attendant located outside the tank. An adequate number of attendants should be immediately available to assist in the rescue if needed. At all times the rescuer should be in view of or in constant communication with the outside attendant.

10.4.5

If a person is overcome by fumes, they should be removed to fresh air immediately. Artificial respiration should be applied if breathing has stopped and a physician or ambulance summoned at once.

An injured worker should leave the vessel under his own power, if possible, but if not he may be assisted by the attendant lifting on the rescue line or by means of the block and tackle. Only as a last resort should one person try to carry another up a ladder or out of a manway. Victims of a fall who have a suspected back or neck injury should only be moved in a basket litter.

Refer to section 4 for treatment of overexposure to vinyl chloride.

10.5 Cleaning and Repairs

10.5.1

Repairs to interiors or exteriors of tanks or equipment including repairs to steam coils, cutting, riveting and welding, should be permitted only after a work permit has been issued by an authorized person. No work permit should be issued until the vessel has been completely freed of polymer and peroxide residues (see section 10.2).

10.5.2

No burning, welding, grinding or other operation that provides a potential source of ignition shall be allowed until a work permit has been issued by a responsible supervisor who has determined that the work can be done safely. Both the conditions in the work area and the possibility of flammable vapor from adjacent areas should be considered. Also, burning or welding may cause the formation of hydrogen chloride due to decomposition of polymer residue; use adequate respiratory protection. Provide sufficient ventilation to compensate for oxygen demand of a welding operation.

10.5.3

Take care to avoid any exposure to vinyl chloride that may be entrapped in the solids. Protective foot, head and hand covering is necessary in addition to air-supplied respirators while engaged in cleaning.

10.5.4

Test the work space frequently as described in section 10.3.3.

10.5.5

Carry out repairs to a vessel in accordance with the appropriate ASME Codes.

10.5.6

Careful attention should be given to the condition of interior nozzles and flanges, especially those bearing safety relief devices. All residues and build-up should be removed while the vessel is open.

10.5.7

At shift changes and in all other cases when repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resuming work.

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