

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

VINYL CHLORIDE

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BY:

R. N. WHEELER, JR.
JOHN T. BARR
ROBERT W. LAUNDRIE
P. J. SNYDER

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The information and recommendations contained in this memorandum were prepared for the guidance of plant engineering, operations and management, and for persons working with or handling vinyl chloride. The information was compiled from experience and information provided by various manufacturers of vinyl chloride, and from material on vinyl chloride appearing in scientific publications. While the authors believe these sources are reliable and represent the best opinions available on the subject as of April 1, 1977, neither they nor their companies make any warranty, guaranty or representation as to the correctness or sufficiency of any information or recommendation herein, and neither the authors nor their companies assume any responsibility in connection therewith; nor can it be assumed that all necessary warnings and precautionary measures are contained in this memorandum, nor that other or additional information or measures may 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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PROPERTIES AND ESSENTIAL INFORMATION
FOR
SAFE HANDLING AND USE
OF
VINYL CHLORIDE

Vinyl chloride monomer is classified by the United States Department of Transportation as a flammable compressed gas. It is easily ignited, producing hazardous combustion gases largely composed of 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 has 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 the visual and auditory responses.

The full text of this memorandum 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 associated agencies should be carefully reviewed prior to any work related to vinyl chloride.

FIRST AID - SEE PAGE 15

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 TEAP
(Transportation Emergency Assistance Plan)

PROPERTIES AND ESSENTIAL INFORMATION
FOR

SAFE HANDLING AND USE OF 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 or Polymerization.

2.2 IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES:

Boiling Point at 1 atm $-13.8^\circ\text{C. (+7}^\circ\text{F.)}$
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 33%
Flash Point (Open Cup). $-78^\circ\text{C. (-108.4}^\circ\text{F.)}$
Hygroscopicity. None
Critical Pressure, psia 775
Critical Temperature $158.4^\circ\text{C. (317}^\circ\text{F.)}$
Ignition Temperature, Autogenous . $472.22^\circ\text{C. (882}^\circ\text{F.)}$
Light Sensitivity Uninhibited VCM is light sensitive
Melting Point at 1 atm. $-153.71^\circ\text{C. (-245}^\circ\text{F.)}$
(Freezing Point)
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.

PROPERTIES AND ESSENTIAL INFORMATION
FOR
SAFE HANDLING AND USE OF VINYL CHLORIDE

Page Two

2.2 IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES: (cont.)

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

at 4°C. (Water = 1) 0.9121

Vapor Density of Gas (Air = 1) . . . 2.15

Vapor Pressure at 68°F 35 psig

Density, liquid, lb./cu. ft.

at 70°F 56.71

at 105°F 54.38

at 115°F 53.69

at 130°F 52.61

OSHA Permissible Exposure Limit. . . 5 ppm maximum (15 minute ceiling)
1 ppm eight-hour time weighted average

Section 3

TRAINING AND JOB SAFETY

3.1 Employee Education and Training

- 3.1.1 The supervisor should be thoroughly familiar with the contents of this data sheet, the Occupational Safety and Health Administration Standard for Vinyl Chloride (29CFR §1910.1017) and the Environmental Protection Agency's National Emission Standard for Vinyl Chloride (Part 61 Chapter I Title 40 CFR Subpart F) before undertaking any training of the employees who are engaged in handling or processing of vinyl chloride. Vinyl chloride handling and use are strictly 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 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 him before finalizing a safety review of his operations involving vinyl chloride.
- 3.1.2 The Occupational Safety and Health Administration Standard for Vinyl Chloride requires that each employee engaged in vinyl chloride or polyvinyl chloride operations shall be provided training in a program including:
- (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 and necessary protective steps.
 - (c) Purpose, proper use and limitations of the respiratory protective devices.
 - (d) Fire hazard and acute toxicity of vinyl chloride and necessary protective steps.
 - (e) Purpose and description of the monitoring program.
 - (f) Purpose and description of the medical surveillance program.
 - (g) Emergency procedures.
 - (h) Specific information to aid the employee in recognition of conditions which may result in the release of vinyl chloride.

3.1 Employee Education and Training (continued)

3.1.2 (i) A review of the OSHA standard for vinyl chloride. This review must be undertaken annually as well as at the employee's first training period.

3.1.3 The Environmental Protection Agency 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 The employee training program 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.

3.2 The supervisor should periodically review equipment, materials and procedures in current use. For maximum effectiveness, this review should include the participation or input from selected representatives of operations, maintenance, technical and other related activities. The results and recommendations from this review should be incorporated into employee training programs, standard operating procedures and equipment changes or revisions. All chemical processes and plants, particularly those working with reactive hazardous materials should be updated based on changes in process, changes in materials, past experience and new information.

All significant hazards should be explained together with the precautions to be followed in the standard operating procedures. For example, if eye protection is required while taking a sample, the standard operating procedure should read "Wear splash goggles and sample still number 000". This type of instruction is preferable to requiring that a sample be taken in one part of the standard operating procedure and requiring that goggles be worn in another part.

If there are extremely critical steps in the process where, for example, overcharge of catalyst may cause an uncontrollable reaction, consideration should be given to making these supervisory checkpoints. In a similar vein, if certain process variables are not or cannot be maintained within prescribed limits then the plant or process step should immediately be shut down and the supervisor consulted.

Complete standard operating procedures with safety information are essential to train new employees, to provide guidance for older employees and to demonstrate compliance in certain regulatory agencies. An error by an untrained employee is often regarded as negligence on the employer's part by the courts and by regulatory agencies.

Section 4 HEALTH HAZARDS - MEDICAL MANAGEMENT, FIRST AID AND
PROTECTIVE EQUIPMENT

4.1 Health Hazards

- 4.1.1 Vinyl chloride monomer is believed to be a carcinogen to man. Exposure of three animal species to vinyl chloride has 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 intermittent high concentration exposure have not been studied in animals and man.

Because of the evidence of carcinogenicity, the Occupational Safety and Health Administration and the Environmental Protection Agency have issued regulations that limit the emission of vinyl chloride to the air and the exposure of people to such emissions.

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

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

Vinyl chloride monomer in gaseous form has no distinctive warning odor in low concentrations nor is it irritating. High concentrations of vinyl chloride has a narcotic effect on the central nervous system and can produce anesthesia at high concentrations. Hazards may be related to impaired judgment or functional ability under these circumstances. The threshold of odor for vinyl chloride varies with purity of VCM and amount of exposure. A two-thousand ppm threshold of odor level has been observed.

4.1.2 Acute Toxicity

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

4.1 Health Hazards (continued)

4.1.2 Acute Toxicity (continued)

resembling mild alcohol intoxication in humans. Levels of approximately 16,000 ppm for the same length of time will 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 to VCM at concentrations of fifty ppm or greater has 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 most frequent among groups that were exposed to relatively high levels of VCM.

4.2 Medical Management

4.2.1 Physical Examinations

The Occupational Safety and Health Administration Standard for (29CFR §1910.1017) 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. This program performed or under the supervision of a licensed physician as stated in the regulation is as follows:

(1) The the time of initial assignment, or upon institution of medical surveillance;

(i) A general physical examination shall be performed, with specific attention to detecting enlargement of liver, spleen or kidneys, or dysfunction in these organs, and for abnormalities in skin, connective tissues and the pulmonary system (See Appendix A).

(ii) A medical history shall be taken, including 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;

4.2 Medical Management (continued)

- 4.2.1 (D) Past history of blood transfusions, and
(E) Past history of hospitalizations.

(iii) A serum specimen shall be obtained and determinations made of:

- (A) Total bilirubin;
(B) Alkaline phosphatase;
(C) Serum glutamic oxalacetic transaminase (SGOT);
(D) Serum glutamic pyruvic transaminase (SGPT); and
(E) Gamma Glutamyl Transpeptidase.

(2) Examinations provided in accordance with this paragraph shall be performed at least:

(i) Every six months for each employee who has been employed in vinyl chloride or polyvinyl chloride manufacturing for ten years or longer; and

(ii) Annually for all other employees.

(3) Each employee exposed to an emergency shall be afforded appropriate medical surveillance.

(4) A statement of each employee's suitability for continued exposure to vinyl chloride including use of protective equipment and respirators, shall be obtained from the examining physician promptly after any examination. A copy of the physician's statement shall be provided each employee.

(5) If any employee's health would be materially impaired by continued exposure, such employee shall be withdrawn from possible contact with vinyl chloride.

(6) Laboratory analyses for all biological specimens included in medical examinations shall be performed in laboratories licensed under 42 CFR Part 74.

(7) If the examining physician determines that alternative medical examinations to those required by paragraph (1) of this section 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 of paragraph (1) of this section, if the employer obtains a statement from the examining physician setting forth the alternative examinations and the rationale for substitution. This statement shall be available upon request for examination and copying to authorized representatives of the Assistant Secretary of Labor for OSHA and the Regional OSHA Director.

4.2 Medical Management (continued)

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4.2 Medical Management (continued)

4.2.1 Physical Examinations (continued)

Appendix A - Supplementary Medical Information

When required tests under paragraph (1) of this section show abnormalities, the tests should be repeated as soon as practicable, preferably within three to four weeks. If tests remain abnormal, consideration should be given to withdrawal of the employee from contact with vinyl chloride, while a more comprehensive examination is made. Additional tests which may be useful:

- (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.

Records of such medical surveillance shall be available to the Assistant Secretary of Labor for OSHA and the OSHA Regional Director. Medical records shall be maintained for the duration of the employment of each employee of each employee plus twenty years or thirty years, whichever is longer.

4.2.2 Suggestions to Physicians

Treatment for vinyl chloride intoxication is symptomatic; no special procedures are required. In acute overexposures the primary effect is central nervous system depression. In chronic exposure the liver is the principal target with secondary effects possibly in the kidneys and lungs.

Note to Physicians: 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.

When breathing has ceased due to vinyl chloride narcosis, promptly initiate assisted respiration (e.g., mouth-to-mouth, 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.

4.2 Medical Management (continued)

4.2.2 Suggestions to Physicians (continued)

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 and exhalation pressure not exceed 4cm water. Masks providing for such exhalation pressures are available. 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 4cm 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 interruptions 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 over-exposed patients to a physician and give a detailed account of the accident (OSHA §1910.1017). Each employee exposed to an emergency shall be afforded appropriate medical surveillance.

4.3 First Aid

4.3.2 Contact with Skin

Vinyl chloride in liquid form is a skin irritant and can cause frostbite. All clothing that has become contaminated with vinyl chloride including shoes 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.

4.3.3 Contact with the Eyes

If liquid vinyl chloride has entered the eyes, they should be washed promptly with copious quantities of water for at least fifteen 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 the ingestion of significant quantities unlikely. Consult a physician in cases of suspected ingestion.

4.3.5 Inhalation

A worker who has been overcome by vinyl chloride must be carried at once into an uncontaminated atmosphere and if respiration has been slowed or stopped, effective artificial respiration must be initiated immediately. 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. 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.

Exposed persons showing signs of vinyl chloride intoxication should be led to an uncontaminated atmosphere promptly to prevent injury by falling, etc. All exposed persons are to be referred to a physician promptly 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 and 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 to the permissible level or to the extent feasible. Where such controls are not sufficient to reduce exposure to the permissible exposure limits, a written program shall be established and implemented to reduce employee exposure to the permissible limits or to the greatest extent feasible.

4.4.2 Protective Clothing

Clothing and gloves made of rubber or impervious material should be worn to protect the body skin from accidental contact with liquid vinyl chloride where applicable.

Protective garments are required for employees who are engaged in hazardous operations such as cleaning polyvinyl chloride residue on vessel walls. These garments shall be selected for the operation and possible exposure conditions when liquid vinyl chloride is not involved.

All protective garments shall be provided clean and dry for each use.

4.4.3 Foot Protection

Footwear with built-in steel toe caps are recommended for all industrial operations. For added protection against chemical contact and liquid vinyl chloride, safety footwear or overshoes worn over leather shoes are 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.

4.4 Personal Protective Equipment (continued)

4.4.4 Eye Protection (continued)

When there is danger of splashing or material is under pressure, splash goggles and/or plastic shields (full length, eight-inch minimum) with forehead protection should be worn where complete face protection is desirable.

Where liquid vinyl chloride is involved or there is likelihood of exposure to vinyl chloride at concentrations exceeding the permissible exposure limit, appropriate respiratory protection is required by OSHA. Use of a full-face piece respirator provides adequate eye protection without supplementary devices.

4.4.5 Respiratory Protection

Where employees are provided or are required to wear respiratory protective devices a respiratory protection program meeting the requirements of OSHA §1910.134 shall be established and maintained. Respirators selected for vinyl chloride shall be as follows:

<u>Atmospheric Concentration of Vinyl Chloride</u>	<u>Required Apparatus</u>
(i) Unknown, or above 3,600 ppm.	Open-circuit, self-contained breathing apparatus, pressure demand type, with full face-piece.
(ii) Not over 3,600 ppm	(A) Combination type C supplied air respirator, pressure demand type, with full or half face-piece and auxiliary self-contained air supply; or (B) Combination type C, supplied air respirator continuous flow type, with full or half face-piece, and auxiliary self-contained air supply.
(iii) Not over 1,000 ppm	Type C, supplied air respirator continuous flow type with full or half facepiece, helmet or hood.
(iv) Not over 100 ppm	(A) Combination type C supplied air respirator demand type, with full facepiece and auxiliary self-contained air supply; or

4.4 Personal Protective Equipment (continued)

4.4.5 Respiratory Protection (continued)

<u>Atmospheric Concentration of Vinyl Chloride</u>	<u>Required Apparatus</u>
(iv) Not over 100 ppm (continued).	(B) Open-circuit, self-contained breathing apparatus with full facepiece, in demand mode; or (C) Type C supplied air respirator, demand type, with full facepiece.
(v) Not over 25 ppm	(A) A powered air-purifying respirator with hood, helmet, full or half facepiece, and a canister which provides a service life of at least four hours for concentrations of vinyl chloride up to 25 ppm; or (B) Gas mask, front-or back-mounted canister which provides a service life of at least four hours for concentrations of vinyl chloride up to 25 ppm.
(vi) Not over 10 ppm	(A) Combination type C supplied-air respirator, demand type, with half facepiece and auxiliary self-contained air supply; or (B) Type C supplied-air respirator, demand type, with half facepiece; or (C) Any chemical cartridge respirator with an organic vapor cartridge which provides a service life of at least one hour for concentrations of vinyl chloride up to 10 ppm.

Respirators shall be selected from among those jointly approved by NIOSH and MESA under the provisions of 30CFR Part 11.

Employee entry into unknown concentrations of vinyl chloride or concentrations greater than 36,000 ppm may be made only for life rescue. Entry into concentrations ranging from 3,600 to

4.4 Personal Protective Equipment (continued)

4.4.5 Respiratory Protection (continued)

36,000 may be made only for life rescue, firefighting or securing equipment so as to prevent a greater hazard.

When air purifying respirators are in use a continuous monitoring and alarm system must be provided when vinyl chloride concentrations may reasonably be expected to exceed the maximum allowable concentration for the devices in use. Such a system shall be used to alert employees that the vinyl chloride concentration exceeds that allowable for the respirator in use.

Where air purifying canisters or cartridges are used they shall be replaced prior to the expiration of their service life or at the end of the work shift in which they were used, whichever occurs first.

4.4.6 Head Protection

Hard hats are recommended for protection from falling objects, overhead liquid leaks and chemical splashes.

Section 5

FIRE HAZARDS AND FIRE FIGHTING

5.1 Fire Hazards

Vinyl chloride is extremely flammable. Its explosive limits are between 3.6 and 33% by volume in air for the vapor or gas. Vinyl chloride is most often handled as a liquid under pressure; thus, a one-gallon spill of liquid vinyl chloride quickly produces 45 cubic feet of flammable gas which produces over 1,000 cubic feet of explosive gas-air mixture. Vinyl chloride when burning produces carbon monoxide and hydrogen chloride. Burning is usually accompanied by the production of a dense black smoke.

The hazards of vinyl chloride with regard to fire are summarized as follows:

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

Explosion - Flammable vapor from a liquid spill if ignited cause a gas explosion hazard indoors, outdoors and sewers. Containers and/or tanks of liquid vinyl chloride may explode due to the heat from a fire.

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

5.2 Fire Fighting

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.

5.2 Fire Fighting (continued)

Followup 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 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 of this data sheet.)

Entry into 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.

Vinyl chloride is a reactive monomer and will undergo addition and polymerization reactions which are characteristic of the ethylenic double bond. Under normal conditions of handling and storage uninhibited vinyl chloride is relatively stable. Vinyl chloride polymerizes exothermally in the presence of light, air, oxygen or free radical initiators to yield polyvinyl chloride. To prevent polymerization in transit or storage it is important that the monomer be protected 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, though vinyl chloride will become hazy if stored for long periods at temperatures over 20°C indicating that some polymerization does take place.

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

Section 7

ENGINEERING CONTROL OF HAZARDS

7.1 Building Design

- 7.1.1.1 Equipment and vessels containing vinyl chloride should preferably be isolated from other facilities by walls and floors of fire resistive construction or by adequate spacing.
- 7.1.1.2 Standard fire walls are recommended for isolation of larger equipment and storage tanks, while partitions of plaster and expanded metal lath may be used to isolate smaller equipment from other combustible materials.
- 7.1.1.3 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 or OSHA Standard 28 CFR 1910 Subpart E).
- 7.1.1.4 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 an approved type.
- 7.1.1.5 For multistory buildings consideration should be given to the use of escape slides or external ramps instead of stairways or ladders from the higher levels. Most injuries have resulted from ignition of flammable vapor clouds or uncontrollable reactions. Escape from these hazards requires the utmost speed on the part of personnel.
- 7.1.2 In processes where large quantities of vinyl chloride are involved only those portions of the process requiring weather protection should be housed. Process vessels and storage tanks not requiring weather protection or close operating supervision should be located in the open.
- 7.1.3 Operations where large quantities of vinyl chloride are used should preferably be housed in one-story buildings or partially enclosed in critical areas only. Newer PVC plants with large reactors often have only the top portion of the reactors enclosed for a control room.
- 7.1.4 Explosion vents may be used to reduce destructive damage to buildings particularly those where a large leak or operating error could result in explosive concentrations of flammable vapors.

7.1 Building Design (continued)

- 7.1.4.1 Explosion venting windows, roof wall panels, skylights, light windows, diaphragms, etc. may be used to minimize building damage due to explosion pressures.
- 7.1.4.2 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 fire and safety protection specialists. (Reference NFPA Fire Codes Vol. 9-#68).
- 7.1.4.3 Vinyl chloride processing buildings equipped with internal water deluge and emergency ventilation systems controlled by flammable gas monitors are preferred for dissipation of flammable vapor clouds resulting from equipment failures within the building.
- 7.1.5 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 control of uninvolved equipment.
- 7.1.6 Fire resistive stairwells with automatic fire doors may be specified for hazardous operation on upper floors but these are less desirable than slides or ramps leading away from the building.
- 7.1.7 Floor drains and process drains should be segregated from sanitary sewer systems to minimize the sewer explosion hazard and to minimize the amount of waste water to be treated for vinyl chloride removal as required by the Environmental Protection Agency regulations.
- 7.1.8 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 as well as emergency showers and eye wash facilities.

7.2 Equipment Design

- 7.2.1 Materials of construction considered hazardous for equipment in vinyl chloride service are copper, zinc, aluminum and alloys containing these materials. Copper is excluded due to the possibility of traces of acetylene reacting to form explosive copper acetylides. Zinc and aluminum are excluded due to their reactivity 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 Equipment Design (continued)

7.2.2 Special Equipment and Design

The design of vinyl chloride piping and equipment is highly specialized because of the reactive, flammable and toxic properties of the material. Prior to the start of any plant or equipment design the Occupational Safety and Health Administration Standard for Vinyl Chloride (29 CFR §1910.1017) and the Environmental Protection Agency National Emission Standard for Vinyl Chloride (40 CFR 61f) as well as any other pertinent regulations should be thoroughly understood. The EPA Standard in particular requires specific equipment items. The technical problems of designing equipment, providing adequate ventilation and formulating operating procedures which ensure maximum safety and economy can be handled best by experienced engineers and safety and fire protection specialists.

7.2.3 In handling of vinyl chloride or the operation of any type of vinyl chloride system, all valves, pipelines, vents, safety devices, etc. should be located that they can be readily inspected and repaired. Consideration should be given to 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 these vessels. Bottom connections are to be avoided if practical.

7.2.4 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 have regularly scheduled testing and inspection.

7.3 Ventilation

7.3.1 Good ventilation is essential in rooms or confined areas where vinyl chloride is handled to prevent the unsafe accumulation of toxic or explosive concentrations. Consideration should also be given to emergency ventilation to remove dangerous concentrations resulting from leaks and/or equipment failures. Good practice indicates that a normal ventilation system should yield at least fifteen air changes per hour for enclosed processing areas.

7.3 Ventilation (continued)

- 7.3.1 Many companies also provide emergency ventilation rates of thirty air changes per hour controlled by automatic analyzers in the work space air.

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 required one ppm or 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; i.e. under what conditions should it operate normally, when should it be off, when should emergency speed be used and should control 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 (40 CFR 61.60F) as a means of detecting and measuring emissions to the air. The standard requires a system which 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 (29 CFR 1910.1017) 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 complicated pieces of equipment and should be checked and maintained 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 the 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 should be ventilated and controlled to low concentrations of vinyl chloride. Flammable concentrations may exist only occasionally. Under normal condition, 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 is 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 all vessels and piping (bonding), by grounding all vessels and piping or by a combination of bonding and grounding.

Bonds or grounds for static electricity protection may be of any conductor size and 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 non-conductors 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.

Section 8

SHIPPING, LABELING AND HANDLING

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

(A) Vinyl chloride is a very volatile, toxic and flammable gas at normal atmospheric conditions. Vinyl chloride may be stored for reasonable periods of time (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.

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° and preferably between 0°C and 20°C.

Vinyl chloride, properly stored, uninhibited either under refrigeration or at normal atmospheric temperature, should be checked regularly for the presence of polymers.

(B) 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 100-150 psi conforming to the ASME code for unfired pressure vessels or any code applying to the locale of planned storage. Vapor recompression or refrigerated storage tanks can be designed, however, 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 150 psi. All welded construction is recommended to insure a

8.1 Storage (continued)

8.1.2 Conditions of Storage (continued)

leakproof integrity. Wherever possible, all liquid inlet lines should enter the bottom or extend to the bottom of the storage vessels. This contributes to the guarding against the accumulation of static electricity. All equipment should be properly grounded and bonded with resistance to ground never exceeding 25 ohms. The stand leg should have an opening in it near the top of the tank to act as a vacuum breaker and to help prevent blowback. All electrical wiring, lighting and equipment should comply with NEC requirements. Vinyl chloride tanks should be painted with white or other heat reflective paint.

(C) All storage areas should have installed an appropriate water spray system or automatic sprinkling system or other special fire extinguishing systems which are suitable for use with Class B fires. Portable fire extinguishers of the carbon dioxide or dry chemical type should be readily accessible to personnel in these areas. (See Section 5)

Diking and/or draining to a safe location should be provided in all storage areas to completely confine and dispose of the liquid in the event of a major spill or vessel rupture.

8.1.3 Isolation

Vinyl chloride storage areas should be selected and constructed in accordance with local codes or authorities having jurisdiction. Such highly volatile and flammable materials should be stored outside of buildings. Preferably, vinyl chloride storage tanks should be segregated away from major process units. Process units such as furnaces or reactors, which have a higher than average fire or explosion risk potential, should be situated as far from such storage tanks as practical. All potential ignition sources should be eliminated from such storage areas. Cylinders containing vinyl chloride should be stored in a vertical position, outside of buildings and 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" per OSHA.

8.1 Storage (continued)

8.1.4 Regulatory Aspects

(A) 20 CFR 1910.1017 outlines the scope, application and specific requirements of the Occupational Safety and Health Standard for Vinyl Chloride.

Specific sections of this standard provide for personnel exposure limits, regulating areas to authorized individuals, environmental monitoring, respiratory protection, labeling, etc. A vinyl chloride program must be established and comply with all the requirements of 29 CFR 1919.1017.

(B) 40 CFR Part 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 chloride plant.

8.1.5 Compatible and Dangerously Reactive Materials

Vessels used for vinyl chloride should be only used for vinyl chloride. They must be purged with a dry inert gas until free of oxygen ($<1,000$ ppm) prior to filling. VCM is generally non-corrosive 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 (acetylide) when exposed to copper or copper alloys.

8.2 Labeling and Identification

The statements and items listed below summarize the major labeling requirements; however, they are not necessarily complete or comprehensive. It is recommended that the Federal Code of Regulations be consulted for the specific details and labeling requirements of the Department of Transportation, OSHA and the Coast Guard.

8.2.1 Department of Transportation Requirements - Coast Guard.

8.2.1.1 Cylinder by Water, Land or Air

49 CFR 172.101 - Each container and overpacked cylinder containing vinyl chloride (including tank cars) shall carry a label "Flammable Gas" and a name "Vinyl Chloride" as shown on the outside of any shipping container and on any shipping papers.

8.2 Labeling and Identification (continued)

49 CFR 172-417 - Small cylinders should have a four-inch "Flammable Gas" label which is red in color and has black printing and cylinder marked with "Vinyl Chloride".

§172.417 FLAMMABLE GAS label.

(a) Except for size and color, the FLAMMABLE GAS label must be as follows:



(b) In addition to complying with §172.407, the FLAMMABLE GAS label must be red. The printing and symbol must be black.

49 CFR 173-306 - Exceptions from Department of Labor labeling requirements.

49 CFR 172.400 - General labeling requirements, placement of labels.

49 CFR 172.326 - Any portable tank (cylinder) containing more than 1,000 pounds of vinyl chloride must be marked in letters two inches or more in size with the shipping name "Vinyl Chloride" and have the Flammable Gas label affixed.

Any truck moving the portable vinyl chloride containing tank must be placarded on the two sides as well as front and rear with "Flammable Gas" placard. (Paragraph 172.515 and Appendix B)

The square on the point placard should be made from tagboard and have a size 10 3/4" by 10 3/4". It should withstand thirty days open weather exposure. The letters on this placard should be red in color with white lettering.

8.2 Labeling and Identification (continued)

8.2.1.2 Barge in Bulk

46 CFR 151.45-2 (e) Cargo Signs and Cards. Warning signs shall be displayed on the vessel, port and starboard facing outward without obstructions at all times except when the vessel is gas free

46 CFR 151.45-7 Shipping Papers. Each barge carrying dangerous cargo shall have on board a bill of lading manifest or shipping document giving the shipper, loading point location and the kind, grade and approximate quantity by compartment of each cargo in the barge

46 CFR 151.50-34 (h) The words "Cancer-Suspect Agent" must be added to the warning signs required by 46 CFR 151.45.2 (e).

8.2.1.3 Ship in Bulk

46 CFR 35.30-1 (b) General Safety Rules. A sign shall be displayed to warn persons approaching the gangway while a vessel is moored or anchored unless it is empty and gas-freed. The sign shall state in letters not less than two inches high substantially as follows:

WARNING

NO OPEN LIGHTS

NO SMOKING

NO VISITORS

46 CFR 151.45-2 (e) 3 A cargo Information Card for each cargo regulated by this subchapter shall be carried on the bridge or in the pilot house of the towing vessel readily available for use by the person in charge of the watch

46 CFR 40.15-1 (b) and (c) The words "Cancer-Suspect Agent" must be added to the warning sign required by 46 CFR 35.30-1 (b). Signs bearing the legend:

Cancer-Suspect Agent in This Area

Protective Equipment Required

Authorized Personnel Only

must be posted whenever hazardous operations, such as tank cleaning, are in progress.

8.2.1.4 Portable Tanks. Portable tanks are not authorized for use with vinyl chloride.

8.2 Labeling and Identification (continued)

8.2.2 MCA Recommended Label

8.2.2.1 The Manufacturing Chemists Association recommends that all containers of vinyl chloride should bear a label as shown. The text of the label 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. 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 will not necessarily insure compliance with such laws.

VINYL CHLORIDE

**DANGER! 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 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, 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.

MCA Chemical Safety Data Sheet SD-56 available.

8.2 Labeling and Identification (continued)

8.2.3 OSHA Labeling Requirements

8.2.3.1 The Occupational Safety and Health Administration (OSHA) is authorized by the Occupational Safety and Health Act of 1970 to establish occupational safety and health standards.

29 CFR Part 1910.1017 lists all the requirements for the control of employee exposure to vinyl chloride. The requirements of this health standard include environmental monitoring, the establishment of regulated areas, training and use of specific signs and labels.

8.2.3.2 Entrances to regulated areas* shall be prominently posted with legible signs bearing the legend:

Cancer-Suspect Agent Area

Authorized Personnel Only

8.2.3.3 Areas containing hazardous operations or where an emergency** currently exists shall be posted with legible signs bearing the legend:

Cancer-Suspect Agent in This Area

Protective Equipment Required

Authorized Personnel Only

8.2.3.4 Containers of polyvinyl chloride resin waste from reactors or other waste contaminated with vinyl chloride shall be legibly labeled:

Contaminated with Vinyl Chloride

Cancer-Suspect Agent

8.2.3.5 Containers of polyvinyl chloride shall be legibly labeled:

Polyvinyl Chloride (or Trade Name)

Contains

Vinyl Chloride

Vinyl Chloride is a Cancer-Suspect Agent

*Regulated areas means any area where vinyl chloride concentrations may be in excess of the permissible exposure limit.

**Emergency means any occurrence such as, but not limited to, equipment failure or operation of a relief device which is likely to or does result in massive release of vinyl chloride.

8.2 Labeling and Identification (continued)

8.2.3 OSHA Labeling Requirements (continued)

8.2.3.6 Vinyl chloride shall be legibly labeled either

Vinyl Chloride

Extremely Flammable Gas Under Pressure

Cancer-Suspect Agent

or in accordance with 49 CFR Parts 170-189 with the additional legend applied near the label or placard

Cancer-Suspect Agent

8.2.3.7 No statement shall appear on or near any required sign, label or instructions which contradicts or detracts from the effect of any required warning, informations or instructions.

All transportation equipment (tank trucks, tank cars, barges or ships) not subject to labels as specified above shall be labeled in accordance with the requirements set forth in applicable Department of Transportation and United States Coast Guard regulations.

Department of Transportation Requirements - Each container of vinyl chloride including tank cars shall carry an identifying label.

The proper shipping name, Vinyl Chloride, as shown in the commodity list (172.101) must be used and shown on the outside shipping container per paragraph 172.300.

Unless excepted each individual container must bear the FLAMMABLE GAS label as described in paragraph 172-417.

Department of Transportation 172.328 requires that tank motor vehicles transporting vinyl chloride shall be marked on both sides and at the front and rear with letters at least four inches high with words "Vinyl Chloride". The words "Flammable Gas" must be displayed on other motor vehicles transporting 1,000 pounds or more gross weight per paragraph 177.823 (a).

Each railroad car must bear the "Flammable Gas" placard per paragraph 177.823 (a).

Paragraph 173.29 (f) 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 to completely cover the old label.

8.2 Labeling and Identification (continued)

8.2.3 OSHA Labeling Requirements (continued)

8.2.3.7 Paragraph 172.510 (c) specifies that a "Flammable Gas-Empty" placard shall replace or cover the "Flammable Gas" placard on the railroad tank car which has been emptied.

The labels used should also conform with all other Federal, State and Local regulations relating to vinyl chloride such as the Federal Insecticide, Fungicide and Rodenticide Act; The Federal Hazardous Substances Act; The Federal Food, Drug and Cosmetic Act and other similar state and local legislations.

8.2.3.8 The Manufacturing Chemists Association also provides cards (Chem-Cards) containing information concerning the material as well as suggestions for safety precautions and emergency procedures. A copy of such a card is shown. These are of particular value accompanying bulk shipments.

VINYL CHLORIDE

Compressed, liquefied gas; sweet odor. Gas is heavier than air.

HAZARDS

(CANCER SUSPECT AGENT)

FIRE

Extremely flammable. May be ignited by heat, sparks or open flame. Burning releases hydrogen chloride gas which is extremely irritating and corrosive. Fire may cause violent rupture of tank.

EXPOSURE

Vapor harmful. Liquid may cause skin or eye injury similar to frostbite.

IN CASE OF ACCIDENT

IF THIS HAPPENS



For assistance, phone

CHEMTREC

toll free, day or night

800-424-9300

DO THIS



SPILL or LEAK

Shut off ignition. No smoking or flares. Keep people away. Keep upwind. Shut off leak if without risk. Wear self-contained breathing apparatus and full protective clothing. Flush area with water spray. Run-off to sewer may create explosion hazard; notify authorities.

FIRE

Do not put out fire until leak has been shut off. On small fire use dry chemical or CO₂. On large fire use water spray. Wear self-contained breathing apparatus. Tanks in massive flame contact may rupture violently unless cooled by straight streams of water. Use unmanned monitor nozzle. Apply from side. Keep clear of tank ends. Otherwise, withdraw from area and let fire burn.

EXPOSURE

Remove to fresh air. If unconscious, call a physician. If not breathing, apply artificial respiration, oxygen. In case of contact with liquid, thaw frosted parts with water. In case of exposure to gas from fire, administer oxygen if breathing is difficult.

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8.3 Non-Bulk Containers

8.3.1 General

In many of the specific steps involved in the handling, loading, sampling and process of vinyl chloride, there are points of potential employee exposure to vinyl chloride monomer. Each facility working with vinyl chloride should identify what potential exposure points may exist and perhaps be peculiar to their individual plant operations. When necessary, engineering, work practice and personnel protective controls must be provided as outlined by the OSHA vinyl chloride standard to control employee exposures to, at or below the permissible exposure limit.

8.3.2 Cylinders

8.3.2.1 Cylinders should not be filled except with or by the consent of the owner and then only in strict accordance with the applicable Department of Transportation and OSHA regulations.

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

8.3.2.3 Valve protection caps must always be kept securely in place except when the vinyl chloride containers are connected to piping, apparatus or equipment. As soon as the cylinder is disconnected the protective cap must be replaced. Empty vinyl chloride cylinders must be securely closed and capped. Air must not be allowed to enter the vessel.

8.3.2.4 Full or partly emptied cylinders should not be returned without permission of the supplier. Such cylinders must be shipped as full vinyl chloride cylinders and correspondingly handled, labeled and tagged.

8.3.2.5 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.

8.3.2.6 Department of Transportation approved cylinders containing vinyl chloride shall be legibly labeled in accordance with the requirements of OSHA and the Department of Transportation. (See Section 8.2)

8.3.2.7 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.

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

8.3 Non-Bulk Containers (continued)

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

8.3.2.10 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.

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

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

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

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

8.3.3 Sample (Bomb) Cylinders

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

8.3.3.1 Stainless steel sample pressure bombs meeting the requirements of Department of Transportation regulation 3B-400 should be used to take quality control vinyl chloride monomer samples. Samples must be taken in bombs that are dedicated to vinyl chloride service. A closed loop sampling system which is designed to include the sample container is preferred in order to minimize the venting of vinyl chloride to the atmosphere.

8.3.3.2 Person(s) directly involved in the collection or analysis of vinyl chloride samples for quality control purposes should wear NIOSH/MESA approved 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.

8.3.3.3 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.

8.3.3.4 All quality control sampling containers (bombs) should be routinely inspected to assure the integrity of the valves and for leakage.

8.4 Bulk Transport

8.4.1 General

In many handling and unloading steps there are potential points of exposure to vinyl chloride monomer. Consult with the technical service staff of the supplier regarding where monomer unloading exposure points may be in your plant. Check also for other exposure points that are peculiar to individual plant operations.

Design of bulk transport facilities varies and unloading procedures are usually specified by the supplier. Complete understanding between the supplier and the user with regard to equipment and procedures is essential to safety of the transfer operation.

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

1. EPA does not approve control devices. The control device used must meet the emission levels.
2. Allow no vehicular traffic in the area during transfer. If this cannot be done, minimize and control traffic by temporary road blocks.
3. If a sample is required before transfer for testing purposes, a stainless steel sample bomb meeting the Department of Transportation's requirements and dedicated to vinyl chloride service should be used. A closed loop sampling system is preferred. The operator taking the sample must use a suitable respirator and appropriate personnel protective equipment during the period of sampling.

Bulk containers delivered with defective valves or other equipment should be held pending instructions from the owner. Only such actions should be taken that will provide for control of immediate safety problems such as obvious leaks and spills.

8.4 Bulk Transport (continued)

8.4.1 General (continued)

In these cases remove sources of ignition. Keep people away. Control the leak by plugs, valves or patches to the extent that the immediate hazard is controlled. Personnel potentially exposed to vinyl chloride vapor should wear NIOSH/MESA approved air supplied respirators.

8.4.2 Miscellaneous Items

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

An emergency shower and eye bath should be directly accessible and within twenty-five feet of the loading or unloading spot.

Fittings - The packing and lubricant for valves and piping must be of a material recommended for vinyl chloride handling.

Pumps and compressors must be equipped with double mechanical seals on packing glands. Space between the seals must be vented to an EPA-approved control device or purged 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 must be attached to an EPA-approved control system to limit atmosphere emissions to 0.13 FT^3 at STP for each disconnect.

The use of slip gauges is forbidden unless EPA-approved control devices are provided to control the emissions.

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 The tank truck pad should provide two feet clearance on each side of the truck and four feet at each end. The pad should be sloped to drain spills away from the truck and exposed structures. Tank truck wheels should be blocked and brakes set to prevent movement during loading or unloading and the engine stopped. If the tractor must be separated from the trailer, this must be done before making any connections and place an adequate brace under the front end.

8.4 Bulk Transport (continued)

8.4.3.3 Static electricity is often generated by the tank truck in transit or it may be generated by the loading or unloading operation. All piping, tanks and structures should be electrically bonded by conductors that are adequate for power or lightning protection before any work is initiated. (See NFPA #77).

8.4.3.4 All sampling must be done with EPA-approved systems to minimize vinyl chloride emissions to the atmosphere.

8.4.3.5 Unloading or loading operations should conform to the owner or operators instructions. 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. Sampling slip gauging and unloading hose emissions are subject to the same EPA limitations noted for tank trucks.

8.4.4.1 Shippers and/or owners instructions should always be followed and all caution markings on both sides of the tank and dome should be read and observed. If inspection shows the car has faulty equipment or is leaking, the shipper should be contacted for instructions. Shippers' plants and procedures vary; thus, instructions should be obtained regarding loading or unloading a vinyl chloride tank car.

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

8.4.4.3 The tank car brakes must be set and the wheels blocked 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.

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

8.4 Bulk Transport (continued)

8.4.4.5 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 can lead to serious and hazardous mixing of reactive chemicals.

8.4.4.6 Typical Unloading Situation

Tank cars of vinyl chloride are filled with liquid up to no more than 86% of the water weight capacity of the tank. Vinyl chloride vapor occupies the space above the liquid. Air or oxygen must not be introduced during unloading or storage to prevent formation of a flammable mixture or premature polymerization. Purge all lines thoroughly with nitrogen before hooking up. Use nitrogen with a maximum of ten ppm oxygen. Nitrogen purging can be minimized by sealing the line and alternately pressurizing with nitrogen and bleeding off the nitrogen to a remote recovery system or 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 225 psig. Never apply heat to accelerate the unloading of a vinyl chloride tank car.

To obtain flexibility in the unloading system, either stainless steel hose or steel pipe with flexible joints can be used. The flows 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 re-open 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.

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

8.4 Bulk Transport (continued)

8.4.4.6 Check the storage tank frequently to determine when the tank car is almost empty. Completely unload the tank car; it should not be used for storage.

A pressure gauge on the unloading line is the best way to indicate when all the liquid has been emptied from 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 so the vinyl chloride monomer vapor in those lines is transferred to the recovery system.

Check the vinyl chloride monomer concentration to make sure there are no invisible leaks from valves. Wear respiratory protection if there is any leakage. Take care of leaks as recommended.

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".

IMPORTANT Leave at least 5-10 psig of vinyl chloride vapor pressure in the empty tank car being returned after closing and sealing all openings. The pressure is necessary to prevent air from entering the car.

8.5 Shipping

8.5.1 Department of Transportation Classification and Regulations

Vinyl chloride is classified by the United States Department of Transportation as a flammable gas. When shipped by rail, water or highway it must be packaged in authorized containers and shippers must comply with Department of Transportation regulations regarding packaging, loading, handling, labeling, marking and placarding. (R. M. Graziano's Tariff No. 31, 1977 is a source of condensed Department of Transportation Regulations for Hazardous Materials.)

8.5 Shipping (continued)

8.5.2 Shipping Containers - Type and Size
Title 49 CFR Transportation Part 173.304

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

Cylinders with brazed seams are not permitted.

Maximum filling density - 84%.

Title 49 CFR Transportation Part 173.315
Requirements for Compressed Gases in Cargo Tanks
MC-330 and 331.

Maximum filling density - 84%.

Title 49 CFR Transportation Part 173.314
Requirements for Compressed Gases in Tank Cars
DOT 106A500X

Maximum filling density - 84%.

DOT 105-200W

Maximum filling density - 87%.

DOT 112A340W

Maximum filling density - 86%.

DOT 114A340W

Maximum filling density - 86%.

8.6 Transportation Emergencies

8.6.1 Assistance Available

8.6.1.1 CHEMTREC (CHEMical Transportation
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.

8.6 Transportation Emergencies (continued)

8.6.1 Assistance Available (continued)

8.6.1.1 CHEMTREC (continued)

For assistance, dial:

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

*(800) 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.

8.6.1.2 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 vinyl chloride plant will dispatch a qualified adviser to the scene of the accident if requested to do so by the shipper of the commodity.

8.6.2 Emergency Control

8.6.2.1 Personnel Attending Accident Scene

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

8.6.2.2 Recommended Emergency Kit

The following are considered essential:

- a. Explosion meter
- b. NIOSH/MESA approved self-contained breathing apparatus
- c. Wood plugs and wood mallet
- d. Data sheet and pencil
- e. Camera and film
- f. Flashlight (Bureau of Mines approved)
- g. Rubber gloves
- h. Slicker suit
- i. Rubber overshoes
- j. Safety lines (braided stainless, plastic covered) and harness

8.6 Transportation Emergencies (continued)

8.6.2 Emergency Control (continued)

8.6.2.2 Recommended Emergency Kit (continued)

- k. Goggles
- l. Safety hat
- m. O-rings
- n. Strap wrench
- o. Ten-inch adjustable wrench
- p. Screwdriver
- q. Ground continuity meter
- r. Large first aid kit and collapsible water container, approximately fifty gallons. The water container should be filled at the emergency site and be available for eye wash or treatment of chemical skin contacts.

8.6.2.3 Recommended Procedures

Leaks of Vinyl Chloride

I. Controllable Leaks

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

II. Uncontrollable Leaks - No Fire

- a. Evacuate area and isolate.
- b. Remove sources of ignition.
- c. Control spread of vapors by water spray.

III. Uncontrollable Leaks - Fire

- a. Evacuate and isolate area.
- b. Keep adjacent cars cool, if possible, with water spray.
- c. Keep nonessential personnel away.
- d. 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.

8.6 Transportation Emergencies (continued)

8.6.2 Emergency Control (continued)

8.6.2.4 Spilled Vinyl Chloride

Spilled vinyl chloride should not be deliberately ignited.

8.6.2.5 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and extent of car damage, vinyl chloride 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 vinyl chloride.
- d. Fill empty tank with water or nitrogen.
- e. If a vinyl-ice mixture forms, keep a water stream on 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.

8.6.3 Marine Emergencies

8.6.3.1 United States Coast Guard regulations (reference Vinyl Chloride Coast Guard Standard, i.e. Parts 40, 151, and Chapter 1 of Title 46 CFR. . .) 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.

8.6.3.2 Special Safety Equipment

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

- a. NIOSH/MESA approved self-contained breathing equipment (at least two and two spare bottles).
- b. Explosimeters.
- c. Ground continuity meter.

8.6 Transportation Emergencies (continued)

8.6.3 Marine Emergencies (continued)

8.6.3.2 Special Safety Equipment (continued)

- 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.

8.6.3.3 Recommended Emergency Procedures

8.6.3.3.1 Leaks of Vinyl Chloride

I. General - Activate Alarm

II. Controllable Leaks - No Fires

- a. Evacuate area of nonessential personnel and 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. Evacuate area of nonessential personnel and 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 fires 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 vinyl chloride vapor in confined spaces and the burning tanks or line (water, N₂ or inert gases).

8.6.3.3.2 Spilled Vinyl Chloride

Spilled vinyl chloride should not be deliberately ignited.

8.6 Transportation Emergencies (continued)

8.6.3.3 Recommended Emergency Procedures (continued)

8.6.3.3.3 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and the extent of the tank damage vinyl chloride 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 vinyl chloride.

Section 9

WASTE DISPOSAL GUIDELINES
AND SPILL CONTROL

9.1 Waste Disposal Regulations

9.1.1 Federal, state, interstate 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 must be given to air, water (surface and ground) and land pollution potential. MCA Technical Guides SW-1 (Landfill), SW-2 (Contract Disposal) and SW-3 (Incineration) may be helpful in fulfilling environmental responsibilities.

9.1.2 Discharges into Navigable Waters

Discharges are controlled by regulations (State, Interstate, Local or Federal) 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 EPA Standard for emission of Vinyl Chloride (see 40 CFR Part 61 Sub-part F) stipulates as a work practice that in process waste water that contains over ten ppm of vinyl chloride must be stripped to ten ppm or less before:

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

Any vinyl chloride stripped from such waste waters must be directed to a primary control device that emits less than ten ppm 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

Under the authority of Section 112 of the Federal Clean Air Act (see 42 U.S.C. 1857 et seq.), the Federal

9.1 Waste Disposal Regulations (continued)

9.1.4 Air Emissions (continued)

Environmental Protection Agency declared that vinyl chloride was a hazardous air pollutant and promulgated a National Emission Standard for Vinyl Chloride (see 40 CFR Part 61 Sub-part F). Essentially, the standard regulates the equipment and work practices to be used to meet:

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

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

9.1.5 Land Application

At the present time environmental regulations for other than air and water pollution control are of a non-federal nature; however, Federal guidelines have been promulgated in some instances (land fill and incineration) and strict compliance with those and local, state and regional requirements is necessary.

9.2 Spill and Leak Control

9.2.1 General

Prevention of leaks and spills must be the keynote in the 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 making control of a polymerization a major objective in any emergency.

Large spills of liquid vinyl chloride are especially hazardous. The heat of vaporization keeps a great deal of the material liquid so that it penetrates porous fill, runs into sewers and depressions where it can generate large volumes of flammable gas. (Ten gallons of liquid

9.2 Spill and Leak Control (continued)

9.2.1 General (continued)

vinyl chloride will produce a flammable cloud fifty feet in diameter.) In designing plants, consideration should be given to this fact. Handle large spills of liquid vinyl chloride with extreme caution.

9.2.2 Control of Leaks and Spills

The National Emission Standard for Vinyl Chloride (see 40 CFR Part 61 Sub-part F) delineates much of the equipment and practices considered by the Environmental Protection Agency to be the best available control technology (BACT). Among recommended practices of the standard are:

1. The use of sealless pumps, double mechanical seals on pumps, or the equivalents.
2. A proscription against manual discharge valve and relief 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 volume of vinyl chloride in vessels prior to opening of such vessels and directing such vinyl chloride gas or liquid to a control device.
6. The use of leak patrols on a periodic basis.
7. The incorporation of a leak detection program into the standard operating procedures.

9.2.3 Handling Vinyl Chloride Leaks and Spills

The greatest danger from vinyl chloride leaks is:

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

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

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

1. The use of proper protective clothing (see 4.4.2, 4.4.3, 4.4.4) and appropriate respiratory equipment (see 4.4.5).

9.2 Spill and Leak Control (continued)

9.2.3 Handling Vinyl Chloride Leaks and Spills (continued)

2. The sounding of a gas alarm and evacuation of all but personnel required to preserve life and property.
3. The use of emergency ventilation.
4. The valving off of the sources of the leak (isolation).
5. The use of the 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 because it may create an explosion hazard.
6. The shutting down of all ignition sources in the immediate area - such as autos, switch engines, trucks, electrical switchgear, boilers, etc. No ignition sources within twenty yards of the vapor cloud should be permitted.
7. The warning and evacuation of the public that may be in the path of a vapor cloud. Evacuation should be upwind and 2,000 feet from the sources if possible.

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

Section 10

TANK AND EQUIPMENT CLEANING AND REPAIR

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. All work should be done in compliance with an adequate vessel entry procedure that provides for training, the use of suitable protective equipment, health safeguards and a written checklist or work practice guideline for each step.

10.2 Preparation of the Tank or Equipment

10.2.1 The Environmental Protection Agency regulation (40 CFR Part 61 Sub-part F) on vinyl chloride has sharply restricted the allowable emissions to the environment from vessel openings. Vessels over 25-gallon capacity are allowed to release no more than 2% of the vessel volume as vinyl chloride vapor or 25 gallons upon opening, whichever is greater. Reactors are limited to twenty pounds of vapor per million pounds of product. Therefore, special control methods must be used.

10.2.2 Any liquid vinyl chloride should be transferred to another suitable vessel insofar as possible. 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 moving the final effluent to less than ten parts per million concentration of vinyl chloride. The model method recommended by EPA is to use water to displace the vapor to a recovery or abatement system. The water so used becomes contaminated and must be stripped to less than ten ppm vinyl chloride concentration before release to the environment. Alternate methods are repeated evacuation and repressurization with an inert gas or 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 less than 2% of the standard volume of the vessel or 25 gallons it may be opened to the atmosphere and further action is not regulated by EPA, but OSHA rules still apply. (See 40 CFR Part 61, Sub-part F).

10.2.3 Peroxide residues should be assumed to exist if the vessel has contained recovered vinyl chloride or if there has been any possibility that oxygen and moisture have been present.

10.2 Preparation of the Tank or Equipment (continued)

10.2.3 Sufficient 10% sodium hydroxide should be added to cover any solid deposits in the lower section of the vessel and this should remain in contact for three to six hours. This time may be shortened to two hours if the temperature can be raised above 60°C (145°F). This should be done before an attempt is made to disconnect any lines on the bottom of the vessel to avoid detonation of this sensitive material. Care should be taken in handling, removing and disposing of this solution to prevent caustic burns. Refer to the MCA Data Sheet Number SD-9 on sodium hydroxide for recommended precautionary measures.

10.2.4 All process piping should be disconnected, slip blanket or blinded so that there is no opportunity of process materials or utilities re-entering the vessel. Local regulations regarding the method of installing blinds should be followed. It is not sufficient to valve off these lines or to only insert blinds in the line. An open section should exist between the vessel and the line if there is any question as to the integrity of the blinds.

10.2.5 As soon as the vessel is open to the atmosphere, positive ventilation should be applied to remove the remaining vinyl chloride vapor. 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. Care should be taken that all dead spots are eliminated and 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 one is assured that no liquid vinyl chloride remains in the vessel or its associated piping and should wear suitable NIOSH/MESA approved 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 the interior of the vessel should be washed as free as possible of wall fouling or loose debris to prevent desorption of vinyl chloride back into the work atmosphere.

10.3 Vessel Entry

10.3.1 General [Consult OSHA Regulations 1910.1017(h)]

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

10.3 Vessel Entry (continued)

10.3.1 General (continued)

to be used to protect against these hazards. The permit must be prepared, reviewed and signed by the supervisor to whom the tank is assigned after he has satisfied himself that tank entry and repair work can be done safely and applicable regulations met.

As a minimum this permit procedure must assure that proper protective equipment is used, mechanical and electrical lockout procedures followed, the vessel atmosphere has been tested, and adequate rescue capabilities are available. A new authorization or permit is required at each shift change.

10.3.2 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.

10.3.3 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 10% 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.

10.3.4 The electrical supply to any agitation within the vessel, and to any moving equipment nearby shall be locked out in the off position according to local codes and the key kept in the possession of the man inside the vessel or his 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.

10.3.5 Danger signs should be prominently placed to indicate when workmen are in the tank.

10.3 Vessel Entry (continued)

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, life line 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 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 men 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 life line. Another person should be on guard during the inspection.

10.3.8 Workers entering vessels should wear boots or rubbers over safety shoes, eye protection, hard hat and a NIOSH/MESA approved supplied air respirator. Impermeable clothing is needed if the walls are fouled with polymer. A wrist harness and safety line are also required and at least one other person similarly equipped for vessel entry should be stationed at the entrance of the vessel at all times. At least one other employee must be within audible hailing distance at all times.

10.3.9 All ladders, scaffolds or other large equipment shall be tied off properly and secured to prevent slipping or falling during the work assignment. Care must be taken 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. Refer to 29 CFR 1910.309 (OSHA regulation).

10.4 Emergency Rescue

10.4.1 It is essential that one or more attendants be present at the point of entry whenever another person is in the tank, depending upon the mechanical aids provided for removing a man from the tank. If work is being done in an isolated area, arrangements should be made to have additional assistants available at all times. Each person entering a tank should wear an approved safety harness or wristlets with a rope attached. An individual rope must be provided at the manhole cover for each person.

10.4 Emergency Rescue (continued)

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

10.4.2 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 life line or before he has summoned additional assistance.

10.4.3 If a workman is overcome by fumes, he 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 No repairs should be attempted until the vessel has been completely freed of polymer and peroxide residues. Care should be taken to avoid any exposure to vinyl chloride that may be entrapped in the solids. Protective foot, head and hand covering shall be required as a minimum, in addition to the previously recommended air-supplied respirators, while engaged in cleaning.

10.5.2 Any burning or welding may cause the formation of hydrogen chloride due to the decomposition of polymer. Adequate respiratory protection shall be used and sufficient ventilation is supplied to compensate for the oxygen demand of the welding operation.

10.5.3 No burning, welding, grinding or other operation that provides a potential source of ignition shall be allowed until

10.5 Cleaning and Repairs (continued)

10.5.3 (continued)

a hot-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 must be considered. Continued testing of the work space must be done as described in Section 10.3.3.

10.5.4 All repairs to a vessel must be done in accordance with the appropriate ASME codes.

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

REFERENCES AND OTHER DATA SOURCES

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3. OSHA Exposure to Vinyl Chloride (29 CFR 1910.1017).
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