

SECRET

SL 090504

Fire and explosion

Vinyl chloride vapor is extremely flammable. Its explosive limits are between 3.6 and 33% by volume in air. Sufficient ventilation and the elimination of ignition sources are mandatory in areas having above average fire or explosion hazard. When a tank car is unloaded, the entire unloading system including pumps, tank car, rails, piping and storage tank must be electrically grounded, as described on page 20.

The major product of combustion is toxic and corrosive hydrogen chloride. Other products of combustion include carbon monoxide and carbon dioxide. Under certain conditions traces of phosgene may be produced. The main sources of danger to personnel result from carbon monoxide and from the extensive formation of hydrogen chloride gas, as well as from any unburned vinyl chloride vapor. Since a major combustion product is hydrogen chloride, any time its pungent odor is detected the area should be evacuated. Only persons properly protected should enter the area. Vinyl chloride vapor does not have any warning properties at low levels.

Carbon dioxide or dry chemical agents extinguish small fires effectively, but no entirely satisfactory extinguisher is known for large fires. Streams of water cannot extinguish a liquid vinyl chloride fire because the monomer does not mix with water and will float on top. Water may be sprayed to cool equipment, however. If the source of the vinyl chloride monomer leak has not been closed off, do not attempt to extinguish a large fire because hot metal can reignite an unburned vapor cloud. No one without proper protective respiratory equipment should enter an area where there has been a fire until the area has been thoroughly ventilated and checked to make sure the monomer concentration is below the level required by the Occupational Safety and Health Standard.

Chemical reactions

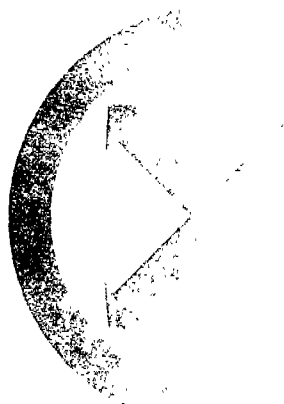
Contamination of uninhibited vinyl chloride monomer may catalyze polymerization, which is highly exothermic, or cause decomposition, which liberates toxic hydrogen chloride gas. The high purity of vinyl chloride must be maintained in shipment, transfer and storage.

Exposure to oxygen, air or sunlight can also catalyze polymerization.

Peroxides may also form.

Toxicity

The Occupational Safety and Health Standard on exposure to vinyl chloride published October 4, 1974, says: "Based on the demonstrated evidence of vinyl chloride monomer's carcinogenicity in three animal species (rats, mice and hamsters), and the substantial probability that vinyl chloride monomer had been the causal agent in the cases of liver angiosarcoma found in workers both here and abroad, OSHA . . . published a comprehensive proposal . . . to protect employees from hazards of exposure to vinyl chloride monomer."



Stated in this OSHA standard is the following "Permissible exposure limit":

(1) No employee may be exposed to vinyl chloride at concentrations greater than 1 ppm (part per million by volume) averaged over any 8-hour period, and

(2) No employee may be exposed to vinyl chloride at concentrations greater than 5 ppm averaged over any period not exceeding 15 minutes.

(3) No employee may be exposed to vinyl chloride by direct contact with liquid vinyl chloride.

In cases where these limits of exposure are exceeded, feasible engineering and work practice controls shall immediately be used to reduce exposures to or below the permissible exposure limit. Wherever feasible engineering and work practice controls are not sufficient, they shall nonetheless be used to reduce exposures to the lowest practicable level and shall be supplemented by the mandatory use of respiratory protection.

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

Besides the suspected carcinogenicity, vinyl chloride monomer vapor can produce immediate symptoms in persons exposed to high concentrations.

The odor of vinyl chloride monomer is sweetish and *the sense of smell cannot be relied upon as a warning*. High vapor concentrations may cause lung irritation, can cause dizziness and anesthesia, and may do other bodily damage in ways not yet ascertained. In all cases of overexposure, immediately remove the affected individual to fresh air and obtain medical attention.

Liquid vinyl chloride monomer may cause frostbite because it evaporates so fast. If a polymerization inhibitor is included, it may cause local skin burns. However, most vinyl chloride monomer shipped today is not inhibited.

Workers should wear eye protection and protective clothing to prevent skin contact with the liquid. If vinyl chloride gets on clothing or shoes, they should be removed immediately. If vinyl chloride contacts the skin, wash immediately with soap and water. If vinyl chloride contacts the eyes, the eyes should be washed immediately and thoroughly with water for at least 15 minutes. Get medical attention.



Workers should wear protective clothing and equipment when unloading shipments.

Work Practice Guidelines

PPG Industries has work practice guidelines used at its own plants to reduce exposure to vinyl chloride monomer during manufacture, storage and loading. Portions of the guidelines are reproduced here.

The OSHA and EPA standards for vinyl chloride appear after page 36.

Users of vinyl chloride monomer should observe the requirements of the appropriate regulatory agencies

I. Labeling and Posting

A. Signs

1. Entrances to the regulated areas¹ shall be prominently posted with legible signs bearing the following:

**DANGER!
CANCER-SUSPECT AGENT AREA
AUTHORIZED PERSONNEL ONLY**

2. Areas where hazardous operations² are performed or where an emergency currently exists shall be posted with legible signs bearing the following:

**CANCER-SUSPECT AGENT
IN THIS AREA
PROTECTIVE EQUIPMENT
REQUIRED
AUTHORIZED PERSONNEL ONLY**

NOTICE

The PPG guidelines and work practices described in this manual may not be applicable to the vinyl chloride monomer operations of individual customers. PPG recommends that customers develop work practice guidelines specifically designed for their individual operations

B. Labels for Monomer Containers

Vinyl chloride monomer in containers or vessels located outside the regulated area shall be labeled as follows:

VINYL CHLORIDE

**DANGER!
EXTREMELY FLAMMABLE
LIQUID AND GAS
UNDER PRESSURE
CANCER-SUSPECT AGENT
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 carbon dioxide.

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. Eliminate possible sources of ignition. Wear suitable respiratory protection.

C. Waste Material

Waste material removed from regulated area in closed containers for disposal shall have the following label:

**WASTE MATERIAL
DANGER!
MAY CONTAIN
VINYL CHLORIDE MONOMER
EXTREMELY FLAMMABLE
VINYL CHLORIDE IS
A CANCER-SUSPECT AGENT**

¹"Regulated area" means an area where vinyl chloride concentrations are in excess of the permissible exposure limit.

²"Hazardous operation" means any operation, procedure, or activity where a release of either vinyl chloride liquid or gas might be expected as a consequence of the operation or because of an accident in the operation, which would result in an employee exposure in excess of the permissible exposure limit

D Equipment

Process equipment, materials and clothing contaminated with vinyl chloride monomer shall not be removed from a regulated area unless it has been purged or placed in closed containers bearing the following legend:

DANGER!
CONTAMINATED WITH
VINYL CHLORIDE MONOMER
CANCER-SUSPECT AGENT

II. Appraisal of Employees

Each employee working in a regulated area shall be apprised of all known hazards, the consequences of over-exposure, appropriate emergency procedures, proper conditions for safe use and precautions to prevent exposure to vinyl chloride monomer. Each plant shall have prepared an operations manual detailing procedures for performing the work which contains specific safe work practices. These practices shall not contain inherent steps that result in exposure of the employee.

III. Medical

Medical surveillance shall be required or made available to workers covered by this Work Practice Guideline no less frequently than every 12 months. For employees who have worked over 10 years, this period shall be every six months. This medical program shall be considered the practical minimum and these examinations should be reviewed every three years for revisions and supplemental testing where indicated.

IV. Personal Protective Equipment and Clothing

A. Respiratory Protection

1. General

When the limits of exposure prescribed on page 13 under Toxicity cannot be met by limiting the concentration of vinyl chloride monomer in the work environment through feasible engineering means, the plant must establish and enforce a program of respiratory protection detailing the required protection of each job classification.

2. Non-Routine Operations

The requirements set forth in this section shall apply for non-routine operations such as brief exposure to concentrations as a result of maintenance or repair activities, emergency situations, or other short-time, non-standard work routines. A respiratory protection program meeting the general requirements outlined in the American National Standard, Practices for Respiratory

Protection, Z88.2-1969 shall be established and enforced. This program shall include instructions on the selection, fitting, use, testing for leakage, cleaning and maintenance of the respiratory protective device.

3. Vessel Cleaning, Draining, Charging or Maintenance

a. Where employees are engaged in cleaning, charging or maintenance inside vessels, respiratory protection shall be worn at all times. Where the concentration of vinyl chloride monomer inside the vessel has been purged below 25 ppm, and there is adequate oxygen content (19.5 volume %) to support life, an approved chemical canister mask which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm shall be worn.

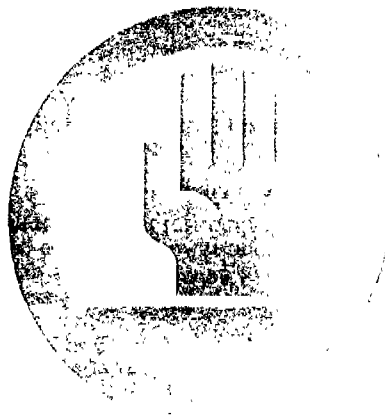
Whenever air-purifying respirators are used, the vessel shall be continuously purged with fresh air.

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

Apparatus prescribed for higher concentrations may be used for any lower concentration.

b. Where the concentration of vinyl chloride monomer cannot be brought below 25 ppm, the employees shall wear a Type C, supplied-air respirator, continuous-flow type, with full or half facepiece, helmet or hood (Type C per OSHA Standard page 35897, not over 1000 ppm).

c. Employees making the first break into a process line, storage line or vessel that contained or contains vinyl chloride monomer shall wear respiratory protection appropriate to protect the employee from exposure to vinyl chloride monomer.



4 Routine Operations

a. Workers loading or unloading tank cars, tank trucks, barges, ships, filling cylinders and other such similar operations where the facility does not have a closed system for vapor equalization, shall wear Type C respiratory protection during the above-mentioned operations.

b. Where there are loading and unloading operations which incorporate equalization lines, Type C respirators shall be located in the immediate area and worn in the event of spillage, leaks or emergencies. Only those employees properly protected with Type C respiratory protection shall attempt to correct an upset condition or emergency.

c. Employees engaged in loading, unloading and production shall have on their person a chemical cartridge respirator to be used for escape purposes.

d. Employees who collect samples for quality control purposes shall wear respiratory protection consisting of a chemical cartridge(s) type during the period when the sample is inserted and removed from the sampling line. Respiratory protection consisting of a chemical cartridge type shall be worn when gate and globe valves are operated.

e. Employees who monitor the workplace air shall have available appropriate respiratory protection in the event of leaks in equipment. These employees shall wear the respiratory protection when levels being measured exceed the permissible limit.



Self-contained breathing apparatus.

B. Clothing

1) Protective gloves, footwear or foot coverings, and protective head covering and protective eye wear shall be provided for use in regulated areas. This protective equipment shall be worn during maintenance and cleaning operations on or inside previously purged vessels, pipes, pumps and valves not removed from the regulated area.

2) For vessel cleaning, maintenance and changing charges, protective clothing shall be worn to prevent skin contact with liquid vinyl chloride monomer or other materials containing vinyl chloride monomer.

3) Employees making a break into a closed system line which contains or contained vinyl chloride monomer or other materials containing vinyl chloride monomer shall wear protective clothing.

V. Work Practices

A. Emergency Procedures

Specific emergency procedures shall be prescribed. The procedures shall be readily available, in writing, to the employees. The employees shall be familiarized with these procedures, and trained and rehearsed in their application.

B. Engineering Procedures

An engineering review procedure shall be established to incorporate design changes where feasible to minimize sources of vinyl chloride monomer vapors from processes, loading, unloading operations and maintenance procedures that contribute to employee exposures. Where local exhaust ventilation is used, it shall be designed and maintained to prevent the accumulation of or recirculation of vinyl chloride monomer vapor into a non-regulated area. Sample collection ports shall be so designed that during the sample collection period, the sample container is part of a closed loop system. Valves shall be located as close as practical to the end of the disconnecting line. Valves shall be located where their frequent closings are necessary to isolate equipment. Valves shall be made of high-quality type to prevent leakage of vinyl chloride monomer or liquid streams containing vinyl chloride monomer.

Blow-down and purge lines from equipment shall be designed to return to the process or to discharge to an emission control device such as an incinerator.

The emissions of vinyl chloride vapor are stringently regulated in monomer- and polymer-producing plants. These regulations, published in the Federal Register on October 21, 1976 (41FR46559) can also be found in the Code of Federal Regulations 40CFR61 Subpart F. These regulations should be consulted before implementing engineering procedures.

C. Laboratory Procedures

1) All quality control testing and analyses shall be performed in a laboratory equipped with a chemical laboratory hood having a capture velocity adequate to collect vinyl chloride monomer vapors under conditions prevailing in the laboratory. The discharge from the laboratory hood shall be designed so that vinyl chloride vapors do not reenter other non-regulated areas.

2) All full sample containers (bombs) shall be stored inside the laboratory hood pending analysis. Sample bombs empty or practically empty of liquid shall not be stored in the laboratory unless the storage space is properly ventilated and under negative pressure. Sample bombs may be stored outside the laboratory building provided the storage location meets safety requirements.

The unused portion of sample remaining after analysis must be discharged back to process or to a suitable emission control device. Discharge to atmosphere is not permitted.

3) Analytical test instruments such as a gas chromatograph, that are located inside the laboratory but outside the laboratory hood, shall have their purge and bypass lines discharge into the laboratory hood.

4) All quality control sampling containers (bombs) shall be periodically checked to assure the integrity of the valves, to inspect for leakage, and to verify that they are labelled as required in section (1) of the OSHA Standard. Screw caps shall be provided for all sample bombs and used when the bomb is not in service.

5) No glassware containing vinyl chloride shall be removed from the laboratory hood.

D. General Housekeeping

1) To prevent airborne contamination and accidental skin contact with vinyl chloride monomer, emphasis shall be placed upon periodic inspection, prompt repair of equipment and leaks, and proper handling, storage and disposal of materials.

2) An initial air monitoring survey and atmospheric sampling tests shall be made in accordance with applicable standards. There shall be periodic tests for leaks at pumps, valves and flanges and for emission of vinyl chloride monomer. The frequency of these tests shall be such to verify the integrity of equipment and adherence to proper work practices and shall comply with the EPA monitoring requirement 40CFR61.65(b)(8).

3) For waste material and contaminated equipment handling, see Section I (C) and (D) on Labeling and Posting.

E. Special Precautions

Vinyl chloride monomer is a gas at ambient temperatures. Therefore, waste materials, equipment and other sources of the monomer in closed containers shall not be placed in areas of excessive temperature or sunlight where buildup of internal pressure may result in rupture of the container, fire or explosion.

F. Vessel Entry

1) A vessel entry procedure shall be developed. Employees shall be familiarized with the procedure in writing, and shall be trained and rehearsed in the techniques provided for in the procedure.

2) Atmospheres within the vessel shall be purged to where vinyl chloride monomer contained therein is below 25 ppm and the oxygen content contained therein is sufficient for supporting life. The purged material must be routed to an emission control device until the vinyl chloride monomer concentration within the vessel reaches 2% by volume. Then the vessel may be opened to atmosphere and purging continued until the 25 ppm level is reached. Where either the vinyl chloride monomer concentration cannot be reduced below 25 ppm or where there is insufficient oxygen or where other toxic materials may be present in concentrations dangerous to life, an air-supplied respirator (Type C) and protective clothing, as stated in Section IV of this Work Practice Guideline, shall be provided by the plant and used by the employee. In vessels which have been purged to below 25 ppm, respiratory protection outlined in Section IVA3 shall apply.

3) All piping to and from the vessel shall be blanked or otherwise isolated prior to entry.

G. Blow-Down Procedure

Whenever any equipment which contains or contained vinyl chloride monomer is to be purged or blown-down, there shall be a written procedure established to prevent the worker from being exposed. This can be accomplished by returning the blow-down stream to the process through equalizing lines or to an emission control device. If these systems are not feasible, Section IV of this Guideline shall be followed.

H. Tank Car, Tank Truck, Barge and Ship Loading and Unloading

Each unloading line and each vapor equalizing line shall be equipped with vent connections permitting, at the completion of unloading, pressure to be vented, and the hose purged with an inert gas back to the process or to an emission control device. The EPA vinyl chloride regulation 40CFR61.65(b)(1) should be consulted for details on loading lines.

VI. Sanitation

A. General

Storage or consumption of food, storage or use of containers of beverages, application of cosmetics or smoking are prohibited in regulated areas.

B. Showers and Hand-Washing Facilities

Showers and hand-washing facilities shall be available to all vinyl chloride workers.

C. Clothing

Clothing saturated with vinyl chloride monomer or with other process streams containing vinyl chloride monomer shall be promptly removed and replaced with uncontaminated clothing.

VII. Monitoring and Record-Keeping Requirements

A. Workplace Areas

1) Concentrations of vinyl chloride monomer in the regulated area shall be monitored at strategic sampling points. Adequate summary records of these concentrations shall be maintained and held available for inspection for a period of 30 years.

2) a. Sampling frequency and patterns shall be adequate to represent the regulated area environment and to demonstrate proper work practices and the integrity of the equipment.

b. As required by the EPA vinyl chloride standard 40CFR61.65(b)(8) and 40CFR61.6, a monitoring program must be established to insure control of fugitive emissions. Vessel environments shall be periodically monitored at frequent intervals for vinyl chloride monomer concentrations during the times they are occupied by an employee. Summary records of these measurements shall be maintained for 30 years.

3) Where the manufacturing process is located out-of-doors, a sampling station should be located downwind of the operations. Multiple sampling points may be necessary.

B. Personal Monitoring

1) Sampling shall be of such frequency and pattern as to represent levels of exposure of employees to vinyl chloride monomer. Provisions set forth in the OSHA standard for vinyl chloride monomer shall be followed. Summary records shall be maintained for 30 years for all sample schedules to include the sampling data, analytical methods, type of respiratory protection in use (if applicable) and the concentrations of vinyl chloride monomer. Job summary records shall be maintained so that they may be classified by employee.

2) Each worker shall have access to the sample results as they pertain to his occupational exposure.

3) Within ten working days after monitoring which discloses that any employee has been exposed beyond the OSHA standard, each such employee shall be notified in writing of the results of the overexposure. An evaluation of the incident shall be made and corrective action outlined.

VIII. Emission Restrictions

Section 112 of the Clean Air Act requires EPA to control "hazardous air pollutants." The federal regulatory response to the law is found in the Code of Federal Regulations, 40CFR61, National Emission Standards for Hazardous Air Pollutants (NESHAPS). EPA has reserved this regulatory tool for those substances in wide use that are known to cause serious impairment of human health at very low concentrations. So far, mercury, asbestos, beryllium and vinyl chloride have been regulated in this category.

The Standard for Vinyl Chloride was published in the Federal Register on October 21, 1976, and became effective for existing sources 90 days thereafter. It represents one of the most sophisticated regulations EPA

has yet published to control a single material or single industry. It is a technology-based regulation, prescribing both allowable emissions and allowable engineering and operating practices to secure the maximum possible reduction in vinyl chloride emissions. The regulation does not specify permissible ambient air concentrations.

The regulation applies to both vinyl chloride monomer and polymer plants. Specific emission limits are established for various emission sources. These sources include formation and purification equipment in vinyl chloride monomer plants. They also include reactors, strippers, mixing and weighing equipment, monomer-recovery equipment and all other sources following the reactor or stripper in a vinyl chloride polymer plant.

In addition to emission limits, operating procedures and/or engineering standards are specified to control relief valve discharges, loading and unloading line disconnection losses, slip gage emissions, seal leakage from pumps, compressors and agitators, relief valve leakage, emissions resulting from losses due to opening of equipment and taking and handling of samples. Other sources of fugitive leakage are addressed by requiring the installation and operation of a leak detection and elimination system. This includes both stationary and portable monitoring equipment and operating procedures designed to detect and locate other sources of leakage (such as valve stems and flanges) and to initiate repair.

Emission tests to demonstrate the performance of emissions control equipment are required. Continuous monitoring of control device emissions and of all uncontrolled source emissions is required to assure continuing compliance with the standard.

Because of its complexity, a careful study of the exact text of the regulation, including test procedures, should be undertaken prior to the engineering of any new vinyl chloride equipment. It should also be noted that preconstruction approval of additions or modifications to vinyl sources must be obtained from the applicable authority.

As of the date of publication of this manual, several states have been granted implementation and enforcement authority for NESHAPS regulations. In addition, many states are considering the adoption of state laws and regulations which may place more stringent standards on vinyl chloride than the federal standards. Contact with both state and federal pollution control agencies is advised to obtain up-to-date regulatory information.