Copy to BB
10-23-90

The Vinyl Institute

A Division of The Society of The Plastics Industry, Inc.

October 15, 1990

TO: Health, Safety and Environment Committee

RE: Publication Review

In 1986, we prepared the enclosed Technical Information Bulletin ("Recommended Guidelines For Vinyl Chloride: Storage, Shipping and Handling"). We would very much appreciate your review of this item so that we can have on hand information with a more current issue date.

Please complete the attached review sheet and return to me by November 16th.

Meredith

Meredith N. Scheck
Assistant Director

MNS/pmb

CTL018908

Wayne Interchange Plaza II • 155 Route 46 West • Wayne, NJ 07470 • (201) 890-9299 • Fax # (201) 890-7029

"RECOMMENDED GUIDELINES FOR VINYL CHLORIDE: STORAGE, SHIPPING AND HANDLING"

Check one of the following boxes and provide information requested:

( ) No changes are needed

( ) Minor revisions are needed

(If you check this item, please forward to me with this form your suggested changes.)

( ) Significant revisions are needed

(If you check this item, would you be willing to serve on a task force to revise the document? ( )Yes ( )No)

Responder: _____
(Name)

_____
(Company)

_____
(Telephone)

Please return by November 16th to:

M. Scheck
The Vinyl Institute
155 Route 46 West
Wayne, New Jersey 07470

HSE

The Vinyl Institute

TECHNICAL INFORMATION

RECOMMENDED GUIDELINES FOR VINYL CHLORIDE:

STORAGE, SHIPPING AND HANDLING

Prepared By:

The Vinyl Institute
Health, Safety & Environment Committee

Issued: August 1, 1986

TABLE OF CONTENTS

VINYL CHLORIDE: STORAGE, SHIPPING AND HANDLING

Introduction

Vinyl Chloride (VC) and its polymers (PVC) have been in commercial use for more than half a century. The Health, Safety and Environment Committee of the Vinyl Institute has prepared these guidelines from the experience gained during that period so that those handling vinyl chloride might share the benefits of that experience. The excellent safety record of the industry has been the result of strong and diligent efforts by the participants, and it should be useful to share the lessons which have been learned with others.

Some useful background information is presented first, then a discussion of factors to be considered in the design and operation of storage, shipping and handling facilities follows.

Physical and Chemical Properties

Relevant physical data are presented in Table I. Vinyl chloride is generally quite stable chemically, but it is important to realize that the formation of unstable peroxides occurs readily in the presence of oxygen, particularly when water, acid, iron salts, or certain organic impurities such as acetaldehyde are present. These peroxides can detonate upon heating or under friction, and can initiate polymerization under some conditions. One major producer has a limit of 1,000 ppm of oxygen in the vapor phase, which has been found satisfactory to avoid peroxide formation.

Table I

Selected Properties of Vinyl Chloride

		°F	°C
Boiling Point		7.9	-13.8
Freezing Point		-245	-154
Flash Point, Open Cup		-108	-78
Autoignition Temperature		882	472
Critical Temperature		314	158
Critical Pressure, psia	809		
Explosive Limits in Air, 1 atm, p 25°C, Volume Percent	3.6 to 33		

Liquid Density at °F, g/ml	0	0.983
	25	0.956
	50	0.930
	75	0.903
	100	0.880
	125	0.850
Vapor Pressure at °F, psig	0	-2.5
	25	7
	50	21
	75	41
	100	69
	125	106
	150	153
Vapor Cloud Explosion Yield (lb. to yield the equivalent of one ton of TNT)	24,305	

Fire and explosion remains the greatest single hazard potential in the use of VC. Constant efforts must be made to prevent leaks and spills and to avoid ignition if leaks do occur. The vapors are very easily ignitable, and are flammable over a wide range of concentrations. Many of the design criteria in subsequent sections are intended to minimize the probability of fires and explosions. Halogenated suppression agents are recommended for use in enclosed areas. Fires should not be extinguished unless the source of VC has been controlled.

Toxicological Properties

The most significant acute toxicological property of vinyl chloride is its anesthetic capacity. This effect becomes important at about 8,000 ppm and can cause death after a short time at the low percent level. Cardiac arythmia has been seen in dogs anesthetized with vinyl chloride.

Reversible liver enlargement was reported in rodents after exposures as low as 50 ppm for a few weeks. Angiosarcoma (ASL) of the liver has been seen in mice after a lifetime exposure at that same concentration, and in other mammals at higher levels. Workers exposed to concentrations approaching a few thousand ppm for several years also have developed ASL. Some 32 deaths in the U.S. and about 115 in the free world have been reported from this cause. Acroosteolysis, a degenerative disease of the bone ends, also was seen in highly exposed reactor cleaners in the past, but no new cases have been reported since exposure reduction steps were taken in the 1960's.

Vinyl chloride has a relatively high heat of vaporization, and thus large spills will vaporize relatively slowly. This presents a hazard of frostbite to workers, as well as increasing the fire danger.

The odor of vinyl chloride is too mild to be useful as a warning of its presence. Most persons cannot detect less than 1,000 ppm.

Regulatory Status

Only a brief summary of the regulations pertaining to VC will be given here. Each manufacturer or user should become familiar with the details of the rules and regulations as they are relevant to each specific activity.

Occupational Health and Safety Administration (OSHA) - Vinyl chloride is regulated as a carcinogen at 29CFR1910.1017. Extensive work practices, training, labeling, and recordkeeping requirements are detailed there. Some of these are discussed in later sections. The labeling requirements at 1910.1017 take precedence over the Hazard Communication Rule requirements at 1910.1200, but both rules must be followed:

Environmental Protection Agency (EPA) - Standards for VC manufacturing and polymerization facilities are found at 40CFR61.60 et seq. Specific work practices are outlined and non-emergency relief valve emissions are prohibited. Many states have assumed the enforcement authority for this rule.

A recommended maximum concentration limit (RMCL)in drinking water has been set at zero (40CFR141.50), and an enforceable maximum concentration limit (MCL) of 1 ppb has been proposed.

Vinyl chloride and certain of the wastes from its manufacture are listed as hazardous wastes under RCRA at 40CFR261.

The interim statutory Reportable Quantity (RQ) for reporting a spill under Superfund is 1 lb. (40CFR302.4). The final RQ value has not been set. The statute exempts "federally permitted" releases from the reporting requirements, but the EPA has not yet defined that term.

Food and Drug Administration (FDA) - Polymers and copolymers of vinyl chloride currently are Generally Regarded as Safe (GRAS) for many food-contact applications and are formally approved at a number of places in 21CFR172, 175, 177, 179, and 181 when manufactured and processed in accordance with appropriate procedures. The FDA has proposed to establish limits of 5-50 ppb for residual vinyl chloride in the polymer used for such purposes.

Department of Transportation (DOT) - Vinyl chloride is listed as a hazardous material. Railcars for bulk shipping must conform to the specifications of types 105 or 112, including head shields, shelf couplers, and sheathed insulation. Details can be found in 49CFR173 and 179. Full and empty cars must be placarded, as is discussed in a later section.

Storage Considerations - Vinyl chloride storage areas should be selected and designed to comply with all applicable local codes and regulations. 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. Adequate separation between tanks and other structures is a primary concern.

Storage Conditions - Vinyl chloride may be stored for reasonable periods of time without danger from hazardous decomposition or polymerization when kept in contact with ferrous materials and in the absence of air, oxygen, water, light or excessive heat.

Nitrogen blanketing may be required under some conditions to increase the storage pressure in order to facilitate tank pumping operations. Significant amounts of the nitrogen will dissolve in the liquid under these conditions. Refrigeration can be used in hot climates in order to maintain the storage temperature within a desirable range -- preferably between 0°C and 20°C. In a few instances, vinyl chloride is stored as a cryogenic liquid.

Storage Construction - Steel is the preferred material of construction for handling vinyl chloride. Stainless steel often is used for conditions where water may be present, such as in recovery and recycle operations. It has been reported that 316L is preferred in this service to prevent chloride-induced stress corrosion at weld lines, particularly if the services is about 40°C and polymer deposition may occur.

Cast iron is not recommended for piping, pumps, or valves because of its very brittle nature. Aluminum is not recommended for use with any chlorinated materials. Copper and its alloys are acceptable for instrumentation parts, but stainless steel tubing is preferred for major tubing runs because of its superior mechanical properties.

All-welded construction is recommended whenever possible, except for connections to vessels, where flanges are preferred. If flanged construction is needed, as in lines subject to polymer build-up, adequate electrical bonding and grounding is necessary. The resistance to ground should not exceed 25 ohms. Threaded fittings (except for instrument connections) are not recommended, and if used, should not be less than 1-1/2 inches in size. There should be no threaded connections on storage tanks.

With either bottom- or top-entering inlet and outlet connections, there should be remote actuated shut-off fire-safe valves at the tank connection. A section of plastic instrument air tubing and an air-to-open valve adds to the ability to assure rapid closure in case of a fire. All other tank connections should have a manual valve mounted directly on the tank flange. Excess flow valves cannot be relied on as a adequate protection in either tank cars or storag tanks. The valve under the relief assembly must not close off all relief devices at one time.

The ability to flood a tank with water from the bottom would give added protection against vinyl chloride releases in the case of mechanical failures in bottom-connected lines.

Storage Protection - Storage tanks should be painted with light-reflective coatings to reduce heat absorption. Support legs and at least the lower part of the tank should have fire-resistant coverings. The area should be diked to contain any liquid spillage, but sloped so that the pool is not held beneath the tank. Design of the diked area should contemplate the volume of water or other firefighting liquid or foam which may be added.

Consideration should be given to a remote method of ignition of a pool should it develop. Storage tanks should have automatic sprinkler/deluge systems of a type approved by the applicable local and national codes and actuated by temperature rise and/or vapor detection.

Turret nozzles are especially useful for localized cooling in case of a fire. Liquid vinyl chloride would tend to float on any water or ice, and the rapid vaporization from contact with the warmer water will increase the rate of vaporization of the vinyl chloride, which then will freeze large quantities of water with considerable trapped vinyl chloride vapor.

Storage Design - Adequate separation should be allowed between storage tanks for effective maintenance or firefighting, and to prevent excessive heat transfer in case of fire. Maximum feasible separation should be provided from sources of ignition such as furnaces, maintenance areas, or non-enclosed electrical stations.

A design working pressure of about 150 psig is advised for non-refrigerated systems. All pump casings and piping sections which could be isolated by valving off from the main storage vessel should have hydraulic relief valves or equivalent protection. Pumps are required by EPA to have pressurized double mechanical seals, to be sealless, or to have some other equivalent leak prevention system. High temperature rise protection is desirable for the pump casing. Adequate pressure relief valves for fire conditions should be placed on the main vessel. Dual systems with a 3-way transflo valve on the tank which cannot close off both systems at the same time are useful for maintenance. The EPA air standard requires that a rupture disk be present before all pressure relief valves which are not vented into a recovery or abatement system. Such venting can be useful for hydraulic relief valves which will be called on to vent only small volumes, but should never be used on primary storage vessel relief systems. There the relief valve tail pipe should be as short as possible, with no more than one elbow.

Storage tanks must be labeled as required by the OSHA standards, as well as meeting any local rules.

Wiring in the storage area must meet all applicable national and local codes, and should conform to Class I, Group D, Division I as a minimum. Other areas generally qualify for Class I, Division II.

Panel-mounted sight glasses with light-absorbant glass are preferred to the stand-off tubular type gauges. If the latter are used, the check valves and glasses should be inspected regularly. Remote indicating (redundant) metal systems are preferable to either glass type. Redundant flowmeters of a reliable type are very useful in preventing accidental overfilling of tanks and reactor.

A detailed preventative maintenance program should be developed which assures routine bench testing of relief valves, pressure gauges, level indicators, and other such critical devices used in the handling of VC. A testing program for pressure vessel wall integrity and for major rotating equipment also is valuable. A written record should be maintained of all inspections and tests which are performed.

Bulk Transport

Bulk transport vehicles should be inspected for mechanical integrity and to insure the identity of their contents before they are connected to the loading/unloading station. The station equipment should be inspected carefully before each use. Defects should be reported at once, and no attempt should be made to load or unload until the defect is remedied. The Department of Transportation requires loading and unloading operations to be performed under constant surveillance.

Bulk vessels should be dedicated to vinyl chloride service, and should be maintained under positive pressure at all times to prevent entry of air. If nitrogen padding is used to assist unloading in very cold weather, the supplier should be informed of that fact before the vessel is returned. No container should be filled to more than 85% liquid full.

The design of the loading/unloading station should provide sure footing for the operator in all types of weather, and conform to OSHA standards for elevated work platforms. Proper counterbalancing and support of the hoses and connectors should be provided to reduce operator effort and to assure tight connections. Hammer-type unions or flanged connections have been found more satisfactory than quick-disconnect couplings. Top unloading vessels should be used. Consideration should be given to the drainage of any massive spill away from the major operating area. The location of the station should provide adequate separation from other operating areas, and minimize the pipe runs to storage. It should be as far away from major traffic areas as feasible. The preventative maintenance program should include the loading arms as well as the other equipment in this area.

Many employers require the use of appropriate protective gear while connecting and disconnecting loading lines, pumps, and during other operations where high concentrations of VC could occur. OSHA requires such protection (29CFR1910.1017) where liquid may be encountered. A safety shower/eye fountain should be located within easy access of all loading/unloading stations.

CHEMTREC should be notified immediately at 1-800-424-9300 of any transportation or other emergency involving vinyl chloride. The National Response Center (800-424-8802) should be notified of any spills or releases to the environment which are above the reportable quantity or are not "federally permitted".

Railcars - Accumulation or storage of railcars containing vinyl chloride, either full or empty, in areas accessible to the public should be minimized, if for no other reason than to avoid public concern.

The Compressed Gas Association (CGA) has developed an emergency dome repair kit for field use when leaks develop in that area. Pamphlet P-10 is available from the CGA in Washington, D.C. Shippers and users should become familiar with the nearest location of a kit. Many VC producers also have developed emergency capping kits and field valve change-out procedures. Each user of VC should establish with its suppliers the procedures and facilities available for emergency situations. Many Vinyl Institute members participate in CHEMNET, a mutual aid organization that will provide advice and suggestions for obtaining field assistance, if needed in transportation emergencies. CHEMNET can be contacted through CHEMTREC at 800-424-9300.

The selection of a disposal method for vinyl chloride from cars involved in serious train accidents should be done on a case-by-case basis. Several recent events have been resolved safely by piercing the derailed car with a shaped charge, followed by ignition of the venting gas.

Derail devices or a locked switch and warning signs must be in place whenever railcars are connected to the station. Brakes must be set and the wheels blocked whenever the car is connected.

Bulk Trucks - It is particularly important to observe the electrical grounding and chocking rules for trucks during their loading and unloading. If the tractor unit is to be moved, it should be done before the operation begins and not returned until the connectors are removed.

Clearances of at least two feet on each side and four feet on each end of the trailer are desirable. The station should have a level, smooth pad that is curbed and drained away from the trailer and pump station.

Marine Movements - Coast Guard rules apply to shipments by water. The principles for safe handing are not substantially different for this than for rail or truck movements. The larger quantity involved calls for a proportional degree of care being applied.

Cylinders - Cylinders should not be filled with vinyl chloride or any other substance without expressed permission from the owner. Cylinders for shipping vinyl chloride are regulated by the DOT under rules found at 49CFR173.304. The outlet valve(s) must have a suitable protective cap. Cylinders with brazed seams are not permitted; seamless cylinders are preferred. Maximum allowed fillage is 84%. The same general labeling requirements apply to cylinders as to other containers. Cylinders whose inspection expiration date has been passed must be tested and inspected before the next refilling. Only pressure reducers designed for VC and having the proper threads should be used. Manifolds or piping systems should have proper pressure relief devices and an effective check valve so that other materials cannot be backpressured into the cylinders.

Sample Containers - Sample containers that are to be shipped in interstate commerce must meet the conditions referred to in the preceding paragraphs. Cylinders for local use should be of no less quality, but will be lighter and generally smaller. Double-valved cylinders are preferred in order to be suitable for the pass-through sampling system required by the EPA standard.

Samples not exceeding 300 pounds may be shipped by cargo plane, but not in passenger planes, or as luggage. See 49CFR172.101 and relevant current air freight regulations for details.

Labels - Labeling requirements of the DOT can be found at 49CFR172.101(e). Each container must have on it a label or placard identifying the contents as VC, a flammable gas, and using the identification number UN1086. "Empty" tank cars must have a placard reading "Residue" and giving the UN1086 identifier. See 49CFR172.203, et. seq.

OSHA requires (29CFR1910.1017) that all areas where exposure may exceed 0.5 ppm on a eight-hour average be posted with "Cancer-Suspect Agent Area, Authorized Personnel Only" signs, and all stationary containers of VC labeled "Vinyl Chloride, Extremely Flammable Gas Under Pressure, Cancer Suspect Agent." Shipping containers must be labeled in accordance with 49CFR170.189, and "Cancer Suspect Agent" added near the placard.

Emergency Response

The first action in case of an emergency outside a manufacturer's our user's facility should be to notify CHEMTREC at 800-424-9300 and the local authorities, most often the state police, in order to set in motion the extensive assistance mechanisms which are available. Releases which are regulated under Superfund should be reported to the National Response Center at 800-424-8802.

Inside a regulated facility there is required to be in place a detailed emergency response program. This should be initiated as quickly as an emergency is recognized.

OSHA forbids entry into areas with concentrations over 36,000 ppm (23.6% - the lower explosive limit) except for rescue, even with full protective gear. This prevents some response actions that may have been considered acceptable in the past such as plugging small holes or changing a valve "on the fly". Real emergencies seldom involve such small occurrences, and broader actions usually are required.

While awaiting professional assistance, some actions can be begun:

1. Injuries - Injured persons should be removed as far from the site as the injuries allow.

2. Traffic Control - Set-up barriers to prevent entry by untrained persons to the site.

3. Evaluation - Consideration should be given to warning or evacuating at least a quarter to a half mile radius around a railcar or bulk truck to avoid flying fragments in case of an explosion. Geographic, weather, or other site-specific conditions may suggest other distances as more desirable.

4. Response Headquarters - A safe but usable site for response headquarters should be selected and responders directed to it.

5. Fact Collection - An effort should be made to preserve as much information on the cause and results of the incident as is feasible.

6. Authority - As response develops, it is important that one person be given the overall authority. The official function of that person will vary from state to state, and conflicting activity must be avoided. Neither consignees nor shippers usually take a decision-making position, but can be valuable advisors.

Persons responding should have, as a minimum, the following equipment:

1. Protective clothing and NIOSH-approved self-contained breathing gear.

2. Vapor detection devices usable in the ppm and percent ranges.

3. Appropriate outdoor clothing.

4. Ropes, traffic warning devices.

5. First aid gear.

6. Portable radio.

7. Portable lighting.

8. Capping or plugging equipment.

Anyone responding should be prepared to stay several hours at the site, and should have replacement or back-up personnel assigned.

Every event must be evaluated on a case-by-case basis, thus relevant experience is of great value. Hazards presented by other containers or vehicles involved in the accident can be of great significance. Concealed damage may be a problem not recognized at once. For example, a damaged or overturned car may have its relief valve blocked so that it no longer is capable of relieving pressure adequately. Water may be useful to cool equipment, but is not an effective fire control medium, and may only spread other substances involved. Fires should never be extinguished unless the source of the fuel has been controlled. Flashback from reignition at hot surfaces is a real danger at the fire scene, and it is very probable that if a vapor cloud is allowed to escape it will find a source of ignition, with the resultant major damage from such an explosion.

If there is danger of a loaded car rupturing from external heat, or if it does not appear possible to right the car or transfer its contents to other vessels safely, serious consideration should be given to deliberate piercing of the shell and simultaneous ignition of the contents. This has been used successfully in several instances.