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ETHYL CORPORATION

INTER-OFFICE

To Messrs. A. J. Haefner, F. C. Holmes, C. E. Major ADDRESS
FROM R. L. Johnson ADDRESS
SUBJECT Monsanto Technical Service Bulletin DATE September 18, 1964

Attached for each of you is a copy of a recent Monsanto Technical Service Bulletin on vinyl chloride monomer.

The section on Storage Life, page 2, is quite interesting.

R. L. Johnson
R. L. Johnson

RLJ:gr

Attachment

ETHYL CORP. CR&D			
SEP 21 1964			
	WEF	SEC	
	FEW	EDH	
	FC	FWF	
	AJH	JDJ	
	RLH	KLL	
	CWM	JRZ	
	AOW	NGA	
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	SMB	CRB	
	APG	AFL	
	HS	DOH	
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		GAS	
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FC 4403

TECHNICAL

SERVICE

BULLETIN

VINYL CHLORIDE
MONOMER

STORAGE AND HANDLING

INTRODUCTION

VINYL CHLORIDE MONOMER contains an aliphatic double bond which permits it to polymerize, copolymerize and undergo other chemical reactions. It is used chiefly in homopolymerization by the suspension and emulsion polymerization techniques. It should be noted, however, that commercial production of its copolymers is becoming quite significant, as is its use as a chemical intermediate to a lesser extent.

If a few simple precautions are observed, Vinyl Chloride Monomer can be used, stored, and handled safely in both large and small quantities.

Monsanto is a major producer of Vinyl Chloride Monomer, and our experience in storing and handling this material for the past several years is outlined briefly here. Monsanto will gladly provide technical assistance to customers in installing storage and handling facilities for Vinyl Chloride Monomer.

MATERIALS OF CONSTRUCTION

Steel is a completely satisfactory material for handling of Vinyl Chloride Monomer. Copper or copper-bearing alloys should never be in contact with either the liquid or vapor of Vinyl Chloride Monomer as it might result in the formation of explosive acetylides from acetylene which is a trace impurity in Vinyl Chloride Monomer.

STORAGE TANKS

Local and Underwriters regulations often specify certain features which affect actual installation of storage tanks. They should be consulted before the design of storage facilities has been completed.

The vapor pressure of Vinyl Chloride Monomer

at ordinary storage temperature necessitates special provisions for either storage under pressure or refrigeration. Refrigerated storage is not considered practical due to continuing operation and maintenance cost and due to the risk involved if the refrigeration system should fail.

The most common types of pressure tanks are long horizontal cylindrical tanks and spherical tanks. Spherical tanks are believed to be more economical for large tanks since less weight of steel is required to contain a given volume of material. Tanks should be of carbon steel plate and of all-welded construction. Cost evaluations should be run in each individual case to determine if spherical or cylindrical tanks would be more economical and also to determine the optimum size tanks to be installed.

Tanks and equipment should have a designed working pressure of from 100 to 150 psi and provisions should be made for either a water spray system to cool surfaces of tanks, or a suitable insulation such as foam glass to cover tanks. We strongly recommend a water spray system on the tank in any case to cool its surfaces in case of fire to prevent heat buildup.

Liquid fill lines for tanks may enter at the bottom of tanks, or they may enter at the top. In the latter case, they should extend to the bottom in order to prevent accumulation of static electricity while filling tanks. Liquid outlet lines may enter tanks at either the top, bottom or sides of storage tanks, but it is recommended that they be so fixed as to take material off at a point about six inches above the bottom of the tank. They should also be provided with check valves to prevent contamination of tank contents by backflow from the process lines.

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All tanks and filling equipment should be grounded to prevent sparking.

Tanks should be provided with temperature indicators near the bottom to enable observation of the liquid temperature. Pressure gages should be connected to the top of the tanks to measure vapor pressure within. The gages should be located at ground level to eliminate the need for climbing to the top of the tanks for taking readings.

Properly sized relief valves should be provided on the tops of tanks to provide for relief of excessive pressure. Monsanto's practice is to install on each tank two duplicate valves, each of which would allow for relief of the entire contents of the tank in case of fire. These are installed so that each may be blocked off from the tank by plug cock to allow for periodic removal and inspection of valves. If desired, rupture discs may also be placed between the tank and valves. Liquid level gages should be employed and liquid level should not exceed 90% of the total capacity of a tank.

Concrete or earth dikes of sufficient size to contain the contents of a tank should be constructed to contain any spillage that might result. Local or Underwriters regulations should be consulted concerning this and other safety aspects of storage facilities before installation of the facilities is begun.

New tanks should be free of all scale, dirt, grease, water or other foreign matter before receiving Vinyl Chloride Monomer. Before being put into service a tank should be purged with inert gas until free of air. Monsanto will gladly recommend cleaning procedures for new tanks or tanks converted from other use so as to insure that the quality of Vinyl Chloride Monomer remains good in storage.

Piping

Black steel pipe, ASTM A-53 has been found suitable for handling Vinyl Chloride Monomer. Fittings and connections for 1½" and larger pipe should be flanged or butt welded. Fittings and connections for 1" and smaller may be threaded and Best-O-Life No. 270 Joint Compound (I. H. Crancell Co., Los Angeles, California) or equivalent used.

Pumps

Centrifugal, positive displacement and gear type cast steel pumps are satisfactory for Vinyl Chloride Monomer service. Mechanical seals are recommended for use with them.

Valves

Standard steel gate and globe valves are satisfactory for Vinyl Chloride Monomer service. Blue African asbestos is suitable packing for valves. Lubricated steel plugcocks are satisfactory in Vinyl Chloride Monomer lines and may be designed to use:

Nordstrom 755 or P-55 lubricants
Stick or pressure lubricants
or equivalent.

Gaskets

Garlock No. 7021, 1/16" thick asbestos gaskets, or equivalent, are satisfactory for flanged connections. Teflon, Velumoid, lead and carbon are also suitable.

Filters

It is recommended that a filter be inserted between storage tanks and processing equipment.

A cartridge type filter with fine or medium replaceable cartridge is suggested. This can be a: Staynew ELS-7B

(Dollinger Corp., Rochester, New York)
Fulflow WXFDS-10-2

(Commercial Filter Corp. Boston, Mass.
or equivalent.

Filter cartridges should be inspected and renewed periodically.

Insulation

Tanks should be insulated with 2 to 4 inches of foamed glass brick, or equivalent, unless they are provided with water spray systems to cool surfaces of tanks. A suitable covering for insulation to protect it from the weather is:

Insulmatic No. 410
Asbestocite
or equivalent.

STORAGE LIFE

Vinyl Chloride Monomer is considered a stable monomer for storage purposes so long as it remains in contact with metallic iron. It is normally sold, shipped and stored in mild steel pressure vessels, and may be stored for periods of several months without change in quality in such containers. In vessels lined with glass or other materials which would prevent contact of Vinyl Chloride Monomer with metallic iron, polymerization may be expected to begin in 48 hours. Such polymerization in non-ferrous storage con-

tainers can be prevented by the addition to the Vinyl Chloride Monomer of phenol inhibitors in the range of 40-100 parts per million. It is necessary to remove the inhibitors before it can be used in polymerization reactions.

STORAGE IN CYLINDERS

Vinyl Chloride Monomer in cylinders of 5, 15 and 200 pound capacities are available from Monsanto. These should be stored in an upright position outside buildings in an isolated, well ventilated area which is protected from the sun's rays. Cylinders should be secured to prevent their falling over, and valves and safety devices should be protected from accumulation of grease, dirt, water, ice, snow or other foreign matter. All other safety precautions for storing and handling flammable, liquified gases in cylinders should be adhered to.

LOADING AND UNLOADING TANK CARS, TANK TRUCKS, AND CYLINDERS

There are several satisfactory methods for unloading tank cars and tank trucks of Vinyl Chloride Monomer. The user should consider the method he thinks most convenient and economical in view of his own particular situation.

Vinyl Chloride Monomer tank cars may be unloaded by applying inert gas pressure to the gas inlet lines. This forces liquid out the liquid outlet line of the car and into the storage tank. Cylinder nitrogen may be used for this purpose. A variation of this is to pump Vinyl Chloride gas from the gas line on the storage tank into the gas line of the car. The difference in pressures effected by this operation will cause the flow of liquid from the car to the tank. It should be pointed out that care must be taken not to exert pressure within the car in excess of its rated working pressure.

Another method of unloading tank cars is to connect a line from the gas line of the car to the gas line of the storage tank to maintain equal vapor pressures between the two vessels. Liquid monomer can then be pumped from the carrier to the storage tank. This procedure can also be used without the vapor equalization line; however, care must be taken that heat and pressure in the storage tank do not become excessive.

Vinyl Chloride Monomer tank cars should always be left with a positive pressure inside them after unloading. Air must never be allowed to enter these tank cars, and the cars must never have heat applied to them to accelerate unloading. The

same provisions for unloading tank cars apply to the unloading of tank trucks.

Vinyl Chloride Monomer cylinders may be discharged by placing them in a water bath which is at a temperature of 50°C. (122°F.) to increase vapor pressure. Heat should not be applied to cylinders by other means. Air should never be allowed to enter cylinders, and they should always be returned with positive pressure in them. Users should not attempt to refill cylinders.

More detailed instructions for the unloading of tank cars containing flammable liquids is contained in MCA Manual Sheet TC-4 and in ICC regulations, Sec. 74-560 to 74-563 inclusive. Monsanto will also assist in any technical problems concerning unloading of Vinyl Chloride Monomer.

SAFETY PRECAUTIONS

Vinyl Chloride Monomer has explosive limits of 4 to 22% by volume in air and a flash point of -108.4°F. (open cup). It is classified by the Interstate Commerce Commission as a flammable liquified gas. In general, all precautions for the storage of flammable liquified gases should be observed for Vinyl Chloride Monomer.

Vinyl Chloride Monomer has a sweet characteristic odor; however, its irritating effect may not be sufficient to warn of the presence of dangerous concentrations. It is generally recommended that concentrations for an eight-hour work day not exceed 500 parts per million by volume in air. In cases where concentration of vapors may be excessive, only persons with approved respiratory equipment should be allowed to enter.

Vinyl Chloride Monomer cylinders may be heated by means of a 50°C. (122°F.) water bath to facilitate discharge of monomer by its vapor pressure; however, heat should not be applied by any other means. Heat should never be applied by any means to a Vinyl Chloride Monomer tank car or storage tank.

Air should never be allowed to enter cylinders, tank cars or storage tanks. Cylinders and tank cars should always be left with a positive pressure after unloading.

All equipment handling Vinyl Chloride Monomer at normal temperatures should have a designed working pressure of 100-150 psi. Any system which may be closed at anytime with Vinyl Chloride Monomer in it should have duplicate relief valves installed. All equipment should be of steel, and no copper or copper-bearing alloys

should be allowed to contact Vinyl Chloride Monomer either in its liquid or vapor form as highly explosive copper acetylides may be formed.

All cylinders, tank cars, fill lines, storage tanks, etc. handling Vinyl Chloride Monomer should be grounded.

Vinyl Chloride Monomer should be handled in well ventilated areas removed from dangers of open flames, heaters, sparks, and other sources of ignition. In carrying out operations around storage facilities, only explosion-proof motors and non-sparking tools should be used. Buildings housing processing facilities should be completely explosion-proof. Fire-fighting equipment should be available to persons working in those areas. Carbon dioxide and dry chemical extinguishers are suitable.

Vinyl Chloride Monomer itself is not absorbed by the skin; however, the phenol inhibitor is absorbed by the skin and may cause severe skin irritation and burns if portions of the skin exposed to the liquid monomer are not flushed profusely with water. Protective equipment, including face goggles, should be worn where handling may result in spillage. Clothing or bandages contami-

nated with the liquid monomer should be immediately removed to prevent freezing of the skin or frostbite caused by evaporation of the monomer in contact with the skin and to prevent the irritating effect of the phenol in contact with the skin.

High concentration of Vinyl Chloride Monomer vapors can cause dizziness and anesthesia. Persons displaying those symptoms should be immediately removed to an uncontaminated area and the appropriate first aid treatment given. A physician should be called at once.

Areas where Vinyl Chloride Monomer is handled or stored should be plainly posted as fire hazard areas, and employees should be thoroughly indoctrinated in the safe handling and fire fighting procedures for Vinyl Chloride Monomer and in first aid procedures to be performed in cases where persons are splashed with liquid monomer or show signs of being affected by high vapor concentrations. These first aid procedures and handling and fire fighting procedures are rather thoroughly outlined by the Manufacturing Chemists' Association in their Chemical Safety Data Sheet SD-56, and it is recommended by Monsanto that all users of Vinyl Chloride Monomer follow those procedures.

FD 4407

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DATA

SHEET

VINYL CHLORIDE MONOMER

Chemical and Physical Data

Structural Formula: $\text{CH}_2=\text{CHCl}$

Molecular Weight: 62.50

Physical State: Gas at ordinary temperature and pressure; Liquid in cylinders or other pressure vessels at room temperature

Color of Gas: Colorless

Odor of Gas: Pleasant, sweet

Reactivity: Polymerizes in presence of air, sunlight, oxygen, or heat, otherwise quite stable

Corrosivity: Non-corrosive at normal temperature when free of moisture. Accelerates corrosion in contact with H_2O at elevated temp.

Boiling Point: -13.9°C . (7.0°F .)

Hygroscopicity: None

Critical Pressure: 52.7 atm.

Critical Temperature: 158.4°C . (317°F .)

Entropy: $S^\circ = 63.06 \text{ cal}/^\circ\text{C}/\text{mol}$

Explosive Limits: 4-22% by volume

Flash Point: -78°C . (-108.4°F .)

Freezing Point: -153.71°C . (-245°F .)

Heat of Combustion (Gross):

Gas: 262.6 kcal/mol (constant pressure)

Heat of Formation:

$\Delta H_f^\circ = 7.5 \text{ kcal/mol}$ (gas at 25°C .)

4.1 kcal/mol (liquid at 18°C .)

Heat of Fusion:

$\Delta H = 1.131 \text{ kcal/mol}$ at -159.7°C .

Heat of Vaporization:

$\Delta H = 5.5 \text{ kcal/mol}$ at 13.9°C .

Estimated Latent Heats of $\text{C}_2\text{H}_3\text{Cl}$

Temp. $^\circ\text{C}$.	Latent Heat (Clapeyron's Equation)	
	cal/g	kcal/mol
-20	83.4	5.52
0	81.4	5.07
20	77.7	4.85
50	70.1	4.38

Ignition Temperature, autogenous:

472.22°C . (882°F .) (Vapors above at -60°C .)

Index of Refraction: 1.38 at 15°C .

Vapor Density: 2.15 (Air = 1.00)

Liquid Density:

Temp. $^\circ\text{C}$.	Liquid Density g/cc
-12.96	0.9692
1.32	0.9443
13.49	0.9223
23.11	0.8955
39.57	0.8733
43.20	0.8555
59.91	0.8310

$d \text{ (g/cc)} = 0.9471 - 0.001746t \text{ (}^\circ\text{C)} - 0.00000324t^2$

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Solubility:

Solubility in:

Water	Slightly Soluble
Alcohol	Soluble
Ether	Very Soluble
Kerosene	Soluble
"Heavy Solvent"	Soluble

Dichloroethane and Ethyl Alcohol:

Press. mm Hg	C ₂ H ₄ Cl ₂ g/100 g	C ₂ H ₅ OH of solvent (0°C.)
400	23.2	17.2
300	18.7	12.1
200	10.5	8.05
100	5.25	3.78

Specific Heat of Liquid:

0.27 cal/g/°C. or BTU/lb./°F.

Specific Heat of Vapor:

Temp. °C.	Specific Heat cal/g/°C.
25	0.208
127	0.249
227	0.285
327	0.314
427	0.337
527	0.353

Specific Volume:

Estimated Specific Volume of Saturated Vapor of Vinyl Chloride

Temp. °C.	Specific Volume cc/g
-30	635
-20	418
0	199
20	105.4
40	60.3
60	38.2

Vapor Pressure:

Temp. °C.	Press. cm Hg	Press. atm
-28.73	39.58	0.52
-18.61	67.78	0.89
-1.57	122.48	1.61
5.53	153.20	2.03
25.72	302.70	3.98
39.72	449.60	5.91
60.34	759.50	9.99

$$\log p = 0.3420 - 1150.9/T + 1.75 \log T - 0.002415T$$

p = atm. absolute

T = temp. °C. absolute

Viscosity:

Liquid: 0.281 centipoises at -20°C.
0.263 centipoises at -10°C.

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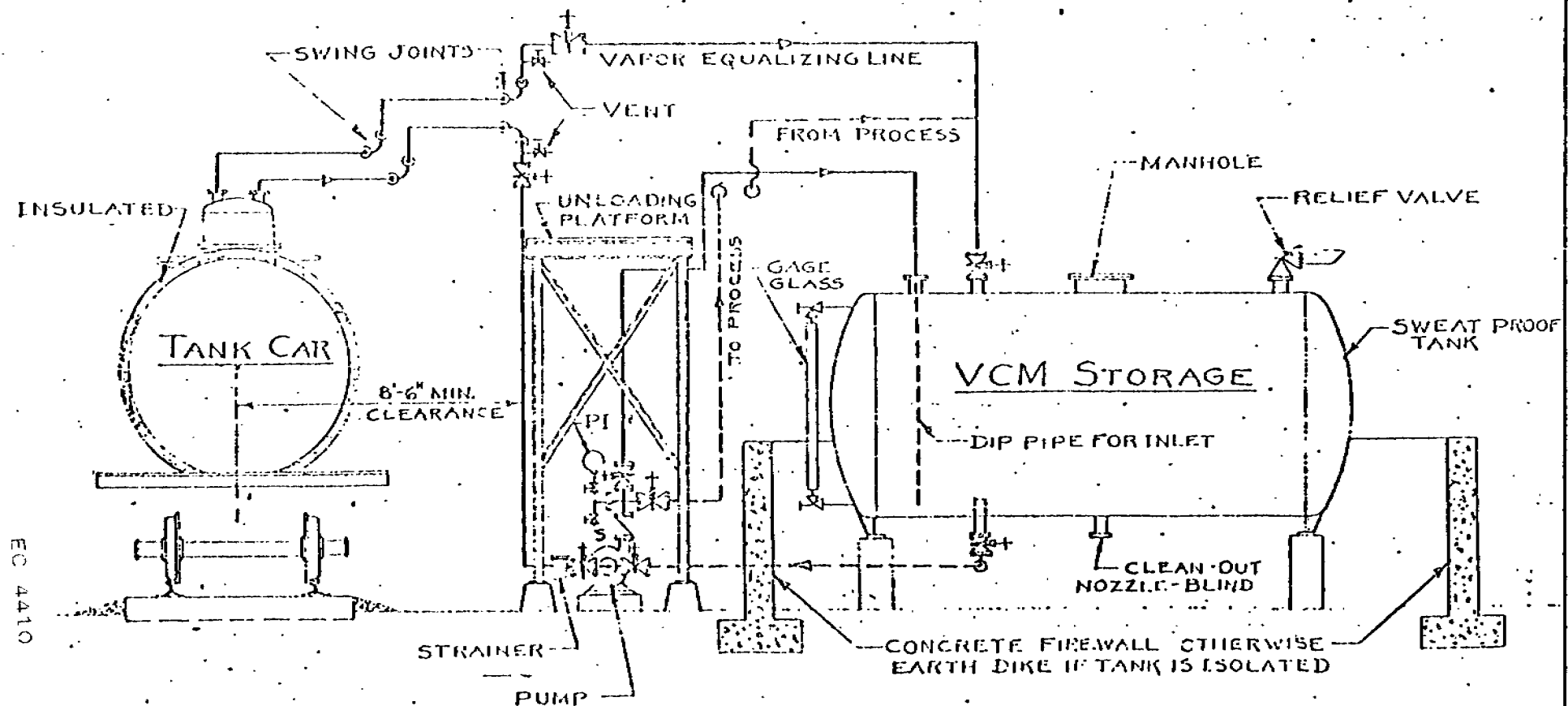
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VCM UNLOADING & STORAGE DIAGRAM

LEGEND:

EV	DENOTES	GATE VALVE
XI	"	GLOBE "
S	"	CHECK "
PI	"	DIAL TYPE PRESSURE INDICATOR
S	"	SAMPLING POINT
----	"	TRANSFER LINE TO PROCESS



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4.3.5 Valve protective caps should be kept in place on cylinders except when the cylinders are connected for discharge.

4.3.6 Cylinders must not be filled except by or with the consent of the owner, and then only in accordance with the Regulations of the Interstate Commerce Commission.

4.3.7 No attempt should ever be made to mix gases or liquids in a cylinder.

4.4 Tank Cars

4.4.1 Applicable instructions for unloading tank cars containing flammable liquids are set forth in MCA Manual Sheet TC-4. (Also see ICC Regulations, Sec. 74.560 to 74.563 inclusive, for unloading tank cars.)

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

4.4.3 In the event of a tank car fitting failure or leak, the shipper should be telephoned or wired immediately for instructions (See 6.3).

4.4.4 Tank cars should be electrically grounded to dissipate static or induced lightning charges.

4.4.5 No heat should be applied to the tank car. An inert gas line or compressed vinyl chloride gas line should be attached to vent connection of the tank car to provide a pressure for transfer of the liquid vinyl chloride from tank car to receiving tank.

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

4.4.6 Some tank cars in vinyl chloride service are equipped with excess flow check valves. A too rapid opening of the discharge valves will cause the check valves to close. If this should occur, the outlet valve should be closed until the pressure is equalized and the excess flow valve opens.

4.4.7 Positive vinyl chloride or inert gas pressure should be left in car. No air should be allowed to enter car (See 3.3.3).

5. STORAGE

5.1 Hazards (See 8. Health Hazards and Their Control)

5.1.1 Aside from the risk of fire and explosion, vinyl chloride presents no other very serious problem in general handling. The presently accepted upper limit of safety as a health hazard is 500 ppm.

5.1.2 Vinyl chloride should always be handled with full recognition of its flammability. Precautions should be taken both to keep the material enclosed and to eliminate sources of ignition. If there should be any unavoidable leaks, reliance must be placed upon the elimination of all sources of ignition and on the provision of sufficient ventilation to keep escaping vapors at nonflammable levels (See 6.2).

5.1.3 CORROSION

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

5.1.4 VOLATILITY

Vinyl chloride is very volatile and is a gas at normal atmospheric conditions. Containers used for handling vinyl chloride at atmospheric temperature are always under pressure.

5.1.5 TEMPERATURE REQUIREMENTS

Inhibited vinyl chloride may be stored at normal atmospheric conditions in suitable pressure vessel.

Uninhibited vinyl chloride may be stored either under refrigeration or at normal atmospheric temperature in the absence of air or sunlight but only for a duration of a few days. If for longer periods, regular checks should be made for the presence of polymers.

5.2 Conditions of Storage

5.2.1 TYPE OF CONSTRUCTION

All piping (including instrument leads), storage tanks, relief devices and equipment employed to handle vinyl chloride should be of steel and designed to have a working pressure of at least 100-150 psi with a safety factor conforming to the A.S.M.E. code for unfired pressure vessels or any code applying to locale of planned storage. Shut-off valves and control