STORAGE AND PROTECTION OF MONOMERS

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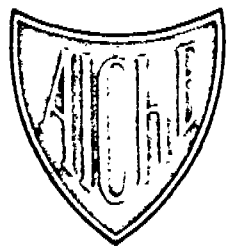

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Introduction.

In order to confine this discussion within the allotted time we have elected to discuss only two monomers which are manufactured, stored and handled in large volume by The Dow Chemical Company and others. These are styrene and vinyl chloride.

Styrene production in the U.S. in 1968 was in the order of 3.5 billion pounds and is expected to rise to 4.3 billion pounds by 1972. Individual locations producing from 500 million to one billion pounds of styrene monomer annually are not uncommon in the industry. Distribution from some of these plants is worldwide. Almost without exception, locations of major use are far removed from the producing points. This adds up to a lot of storage and handling. For example, Dow stores styrene at seven major locations in the U.S. and in perhaps ten foreign countries.

Vinyl chloride production in the U.S. in 1968 is in the order of 2.8 billion pounds and worldwide in excess of 10.0 billion pounds, and it is expected to rise in the U.S. to 4.5 billion pounds per year and worldwide to 13. billion pounds per year by 1970.

As with styrene, the location of VCM users is in most cases remote from the producing site, which makes large bulk storage and handling systems a necessary adjunct of the VCM production business, and in many instances requires some storage facilities at the user end as well.

Unlike styrene, vinyl chloride is a gas at N.T.P., and therefore requires pressure storage under its own vapor pressure, or as an alternate, refrigerated vapor recompression for low pressure storage systems.

Despite these storage requirements, the growing trend is to distribute vinyl chloride on a worldwide basis.

Styrene.

Characteristics: Styrene is a colorless non-corrosive, aromatic hydrocarbon liquid. Table I gives its more important properties as related to storage and handling.

TABLE I

SELECTED PROPERTIES OF STYRENE MONOMER

Chemical Formula	$C_6H_5CH{:}CH_2$
Density, lbs./gal. @ 77°F.	7.5
Vapor Pressure, mm Hg @ 77°F.	6.5
@ 104°F.	16.0
Boiling Point °F. @ 760 mm	293
Flash Point, Tag Closed Cup, °F.	94
Fire Point, Tag Open Cup, °F.	99
Explosive Limits in Air at Room Temperature %	1.1 to 6.1
Viscosity, Centipoise @ 77°F.	.71

In the development of techniques and equipment for the storage and handling of styrene three major objectives, and a few minor ones which will be developed as we go along, must be considered. These are personnel protection, protection of the quality and monomeric

status of the material under normal circumstances and protection against fire.

Personnel protection is accomplished primarily by training and a common sense approach. Styrene is low in acute oral toxicity but accidental ingestion cases should be referred to a physician immediately. A saline cathartic is the usual treatment. Vomiting should not be induced because of the possibility of aspiration of the monomer into the lungs.

Styrene in the eyes can be very painful but the likelihood of permanent damage is fairly remote. Eye protection should be worn where the possibility of eye contact exists as in sampling, transferring and maintenance activities. Washing immediately with water for 10 to 15 minutes is the recommended treatment. Again, medical attention should be obtained as soon as possible.

Casual skin contact normally causes little if any irritation. On the other hand, prolonged contact, as would result from continuing to wear clothing which had become soaked with styrene, will cause blistering and possibly swelling of the skin. Soap and water is the remedy. No case of absorption of styrene through the skin with resultant systemic effects is on record.

Vapor concentrations below about 100 ppm in air are neither harmful nor particularly objectionable to personnel. Concentrations above this level become increasingly more irritating to the nose and eyes.

In extreme cases an individual could be overcome, as by any other volatile hydrocarbon. Fresh air and rest should bring him back with no permanent effects.

Summing up, any styrene handling installation should be designed to minimize the probability of leaks and spills, provide adequate ventilation, and drainage to conduct any leaks or spills that do occur away from critical operating sites. Personnel should be well instructed as to the nature and hazards of the material and provided with safety goggles and ready access to a safety shower and eye bath.

Protection of quality. Styrene is marketed under the specification shown in Table II. For comparison, a typical analysis as manufactured is included.

TABLE II

SPECIFICATION FOR STYRENE MONOMER

Property	Sales Spec.	Typical Anal.
Purity (by freezing point)		
% Minimum	99.5	99.73
Color		
APHA, Maximum	10	< 5
Saybolt, Minimum.	27	
Aldehydes (as benzaldehyde),		
% Maximum by wt.	0.020	.004
Peroxide (as H_2O_2)		
% Maximum by wt.	0.010	.0007
Sulfur (as S), %		
Maximum by wt.	0.0025	.0001
Chlorides (As Cl)		
% Maximum by wt.	0.01	.0001
Polymer Content		
Maximum - ppm	10	0

Polymer content and color are the most difficult qualities to maintain in storage, especially polymer content. Styrene has no significant value except as a polymer or copolymer with other monomers. It is in the latter field of use, especially when used as a co-monomer in the preparation of polyester resins, that small quantities of the homopolymer affect the quality of the finished product adversely. In addition to end use considerations, it is possible for the polymerization reaction, which is exothermic, to become self accelerating and result in an extremely dangerous situation, involving the development of high temperature and pressures in a container, as well as loss of the product. In short, styrene monomer is a heat sensitive perishable commodity and must be recognized and treated as such.

Polymerization in storage and shipping containers is controlled by the addition of an inhibitor. Although various compounds exhibit some degree of effectiveness the one almost universally used is para-tertiarybutyl catechol (TBC). Minimum effective concentration for prolonged storage is approximately 10 ppm. TBC also acts as an antioxidant and, strangely enough, is effective as a polymerization inhibitor only in the presence of oxygen. Table III gives a rough indication of the effectiveness of the TBC-oxygen system and clearly shows the effect of temperature on the system.

TABLE III

SHELF LIFE OF STYRENE MONOMER

EFFECT OF INHIBITOR AND OXYGEN AT VARIOUS TEMPERATURES

	12 to 15 ppm TBC		50 to 75 ppm TBC
Temp.	Saturated with Oxygen	Less Than 3 ppm Oxygen	Saturated with Oxygen
60°F.	5 to 6 mo.	10 to 15 days	More than 1 year
85°F.	1 to 2 mo.	4 to 5 days	3 to 4 months
110°F.	8 to 12 days	Less than 24 hrs.	Less than 30 days

Shelf Life as used here means time the monomer can be expected to remain within specification. This table is based on a combination of laboratory tests backed by many years of practical experience. From it several conclusions pertinent to quality protection in storage can be drawn: (1) the lower the temperature the better, (2) an adequate concentration of TBC must be maintained, and (3) an adequate concentration of oxygen must be maintained.

Although not absolutely necessary, Dow considers it good practice to insulate and refrigerate styrene storage in areas where average ambient temperature exceeds 80°F. for a substantial period. Refrigeration is external and the monomer is circulated as required to maintain the body of liquid in the tank around 70-75°F. Such an installation has the added advantage of tending to equalize day to night temperatures in the vapor space and thereby minimize condensation of monomer on the roof and sidewalls of the tank above the liquid level.

TBC is gradually depleted from styrene in the course of doing its job as an inhibitor. Fig. 1 shows this effect quantitatively.

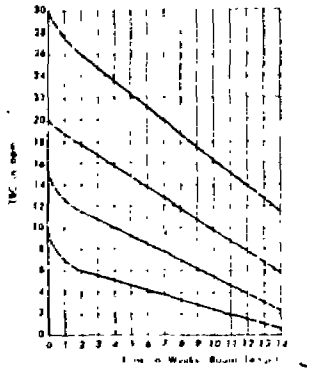

Fig. 1. Disappearance of TBC from Styrene Monomer in Storage

Concentration should never be allowed to fall below 10 ppm. System effectiveness can be maintained simply by adding TBC as required. Here again means of circulating the tank contents becomes important. TBC is added as a concentrated solution, say 15-20%, in monomer to achieve any desired increase in overall concentration. TBC content should be checked every few days in dead storage.

Oxygen content is adequately maintained when styrene is stored under air. The equilibrium concentration of oxygen in the liquid is around 50 ppm at room temperature. Under air is always the simplest and generally most satisfactory way to store styrene where the tank is designed to minimize polymer accumulation on the roof and turnover

is frequent enough to eliminate any problems arising from build-up of aldehydes and other oxygenated compounds. Shelf life as shown in Table III applies.

Storing under air can, however, create problems as well as solve them. Since TBC is a high boiling compound, monomer vapors above the liquid level in a tank are uninhibited. Normal temperature swings result in a continuous cycle of vaporization and condensation on any structure in the vapor space including the roof and sidewalls of the tank. Droplets will adhere to any rough or porous surface. In the presence of air these droplets polymerize readily into a highly discolored and oxidized product. Polymer "icicles" develop and continuation of the refluxing action disolves the material and carries it back into the bulk of the liquid. If allowed to proceed indefinitely these icicles will grow to tremendous size and eventually fall into the tank, generally throwing the entire contents off specification. The photographs, Fig. 2 and Fig. 3 illustrate the condition that develops.

Fig. 2. Icicle growth in an air atmosphere on the unlined roof and supporting structure of a 70' x 24' high tank after 125 days service. Sidewalls had been sandblasted to white metal and lined before placing in service. The roof structure was sandblasted to bright metal but not lined. Color problems were encountered.

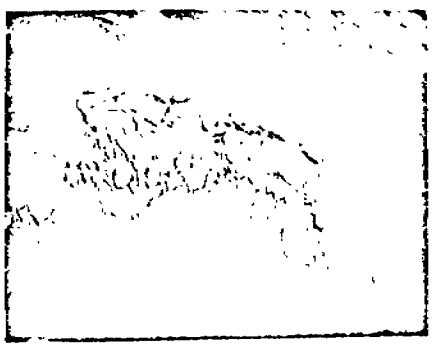

Fig. 3. 10 ft. x 36 ft. horizontal steel tank in process of being cleaned after four years in styrene service.

The situation just described has been found to occur to a harmful degree only in uncoated steel tanks having internal roof supporting structures such as the tank shown in the photograph. Rusty steel and complicated structure seems to be the preferred enviornment for polymer build-up. A non-porous smooth surface provides no sites for the retention of the uninhibited monomer and, even in the presence of air, little polymer build up can be expected. All modern styrene storage is designed to provide such a surface within the bounds of reason. Self supporting dome roofs are employed. API 650 tanks having a dome radius equal to 0.8 the diameter of the tank are satisfactory, and can be constructed in sizes up to at least 70 feet in diameter. The roof and sidewalls down to within about two feet of the bottom are coated with one of a number of suitable coatings. For large tanks, of course, a coating which will cure at atmosphereic temperature is the most practical. Several epoxy types fall within this category. The bottom and lower two feet of wall is coated with a rust resisting inorganic zinc silicate material such as the Dimetcotes. The purpose here is to permit static charges in the liquid to drain off through the tank ground. The photograph, Fig. 4, demonstrates the effectiveness of the coating.

Fig. 4. Epoxy coated 10 ft. x 36 ft. tank (looking up) after six months in styrene service. Inspection after 3-1/2 years showed no change.

In situations where it is necessary to continue to use uncoated tanks, particularly those containing internal structures, for styrene storage the best solution to polymer formation in the vapor space is to pad the tank with an inert gas such as nitrogen or natural gas. The latter is usually cheaper and just as satisfactory. In the absence of oxygen, polymer formation is retarded to the extent that a tank may remain in service from five to ten years without having to be cleaned. However, under this condition the oxygen in the liquid is rapidly depleted and polymerization will proceed as indicated in Table III. A serious quality problem is created unless the tank is subject to rapid turnover as, for example, a day tank. The solution is straightforward, but requires careful control if a flammable pad gas is used. You simply pump enough air into the liquid periodically or continuously to maintain a minimum of 10 ppm oxygen in the liquid phase.

If styrene is to be stored within or near a chemical complex wherein halogens, particularly bromine, are used or produced, a tank breathing to the atmosphere creates an untenable situation with respect to air pollution. Styrene concentrations in air as low as a few parts per billion will form an extremely potent lachrymator when contacted by bromine in sunlight. Only slightly higher concentrations will do the same thing with chlorine. Where this situation exists as, for example, in Dow's Texas Division all styrene tanks within range of a probable halogen containing atmosphere are vented through an independently fueled flare. Such precaution is necessary regardless of the storage atmosphere.

Color development in storage can be one of the most exasperating quality problems with styrene. This is because the reason is usually not immediately apparent and is sometimes never determined. One cause, discussed above, is the extraction of color bodies from oxidized polymer attached to structures within the tank. Another is a compound which sometimes is formed by the reaction of TBC, moisture, and iron oxide (rust). Still another is prolonged contact with copper bearing alloys such as brass and bronze. Copper reacts with styrene to impart a characteristic blue-green color to the monomer, and should not be used in styrene handling equipment. (All other common metals such as aluminum, stainless steel, galvanized steel, etc. are suitable).

Assuming the system is adequately designed to maintain overall quality as previously discussed, the best defense against color problems is

the avoidance of contamination by strict adherance to high standards of cleanliness. For example, styrene which has been laying in a line for a week or so, especially an exposed line, should never be flushed into a storage tank without prior inspection. If a batch of styrene turns up off-color it can usually be restored by contact with activated alumina in a fixed-bed filter. TBC will also be removed and must be replaced immediately.

Particulate matter can be extremely detrimental in some styrene end-uses, another reason for cleanliness. It is standard practice to filter the monomer between bulk storage and shipping containers. Many users filter again immediately prior to use. Cartridge type filters, capable of removing 10 micron particles, are commonly used. Fig. 5, is a photograph of loading pumps and filters in a Dow plant. Note especially the canopy for shading the area.

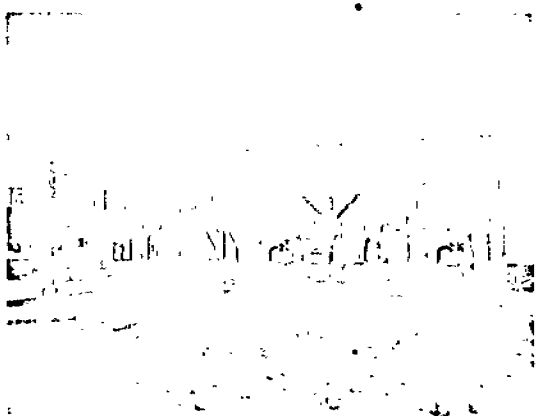

Fig. 5. Styrene loading pumps and filters.

Fire Protection. Although styrene is classified as a Reactive flammable liquid, it is a relatively low hazard material with respect to fire protection. Fig. 6 is a plot showing the range of temperature and pressure at which an explosive mixture with air will occur in a confined vessel.

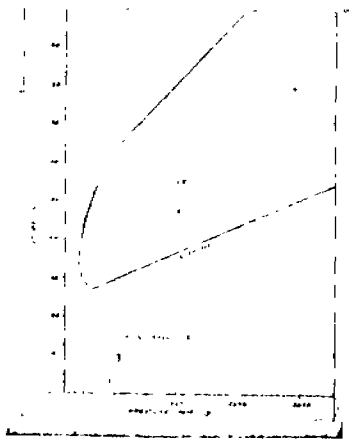

Fig. 6. Conditions for explosive mixture with styrene under air.

Sources of ignition should be eliminated from styrene storage areas, no smoking rules adhered to, and totally enclosed electrical equipment used. Explosion proof equipment is recommended only in confined areas. Static electricity is probably one of the more important ignition hazards. All tanks, pumps, etc. should be adequately grounded and submerged filling practiced.

Styrene tanks should, in general conform to the Flammable Liquids Code NFPA-30. Tanks of over 10,000 bbls. capacity should be individually diked, the dike having 100% of tank capacity. Dike drains are kept normally closed but with valve accessible under emergency conditions. Pumps should be located outside the dike. Distance between tanks should be a minimum of one half the sum of their diameters.

From the standpoint of polymer build-up the number of roof nozzles on a tank should be the minimum. A flame arrestor and vacuum-pressure relief are usually mounted on the same nozzle. Emergency relief is combined with a manhole*. A gauge hatch is the only other necessary opening, but we frequently provide for a float operated tape level indicator. Flow line and drain valves adjacent to the tank must be steel (preferred) or ductile iron as per API 604.

Fixed foam protection is the recommended provision for extinguishing styrene tank fires. The foam chamber is separated from the tank by a frangible such as aluminum foil or glass to prevent polymer accumulation. Inspection is at least annually. Provision should be made to supply liquid foam solution at a rate of 0.1 gallon per minute per square foot of surface.

In September of 1967 Dow, in conjunction with National Foam Systems Inc., conducted an experimental test to determine the feasibility of subsurface foam injection for extinguishing fires in tanks containing styrene. Essentially the method consists of pumping a foam solution into the tank through a product line. As the foam enters the tank, it rises to the liquid surface, providing a fire smothering blanket. It has generally been acknowledged that such a system, if effective, would offer cost, maintenance and reliability advantages over the

* An excellent paper entitled "Practical Way to Size Safety Disks" by E. Diss, H. Karam and C. Jones of The Dow Chemical Company appeared in the September 18, 1961 issue of CHEMICAL ENGINEERING.

commonly used foam chamber systems which require a separate, external piping system arranged to discharge foam on the liquid surface inside the tank. Admitting the foam through a swing line, placing it near the liquid surface and also near the center of the tank, provides a particularly desirable situation.

The test tank was approximately 11 feet in diameter and contained 6 ft. 3 in. (about 3,400 gallons) of styrene. The foam used was National Foam Systems, Inc. Aero-O-Foam XL-3 liquid, a foam containing fluorinated compounds. The foam was applied in 4% concentration and admitted to the center of the bottom of the tank, having passed through an aeration device, or "foam maker". Foam was started five minutes and fifteen seconds after light-off at a rate of approximately 0.1 gallon per minute per square foot of liquid surface. Results of this test are tabulated below:

TIME	DESCRIPTION
0'0"	Light off
5'15"	Foam injection started (valve opened)
5'32"	Sound of foam on hot tank walls
6'0"	Fire very low - mostly around edges
6'20"	Fire around edge only
7'15"	Fire controlled - small flickers only
7'45"	Fire nearly out - two small flickers
8'25"	Fire extinguished
8'56"	Foam stopped

The test was considered successful on all counts. Other than the extinguishment of the fire, original areas of concern included the possibility of undesirable reactions or degradation of the monomer from the foam and the extent of entrainment of monomer in the foam. Neither of these proved to be of consequence. The styrene was very simply reprocessed to a salable product and entrainment proved to be substantially less than that experienced with gasoline and hexane.

Before moving on to a discussion of vinyl chloride I would like to present two more slides, Figs. 7 and 8, which illustrate a schematic and a photograph of a typical styrene storage tank as recommended by The Dow Chemical Company.

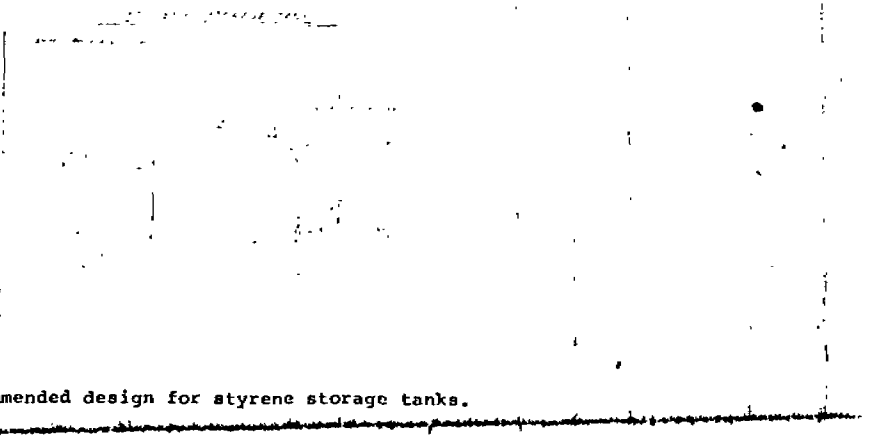

Fig. 7. Recommended design for styrene storage tanks.

Vinyl Chloride.

Characteristics: Vinyl Chloride Monomer (VCM) at normal ambient temperature and pressure is a colorless gas with a faint sweet odor. VCM is stored and shipped as a liquid under pressure and the greatest hazards in the handling of this material are the dangers of fire and explosion.

Table IV gives the more important properties of VCM as related to storage and handling.

TABLE IV
SELECTED PROPERTIES OF VINYL CHLORIDE MONOMER

Chemical Formula	CH_2:CHCl
Boiling Point (760 mms.), °F.	7.2
Melting Point, °F.	-244.4
Vapor Pressure at 77°F.	~56 psia
Flash Point (Cleveland Open Cup), °F.	-108.4
Explosive Limits Vol. % in Air	3.6-26.4
Liquid Density grams/ml. 77° F.	0.9013
-4° F.	0.9834
Liquid Viscosity cps @ 77° F.	0.185

The same three major objectives which apply for styrene monomer also apply for the development of technique and equipment for safe handling and storage of vinyl chloride monomer; plus some techniques peculiar to VCM due to its high vapor pressure and extreme flammability.

The major objectives are:

a. Personnel Protection

b. Protection of Quality and Monomeric Status

c. Protection against Fire and Explosion

Personnel Protection. Adequate training in the potential hazards of the material and the proper personnel protection equipment and techniques for safe handling of the material are essential to the safety of all personnel handling VCM.

VCM is moderately toxic, with a threshold limit value (TLV) of 500 ppm for repeated 7-8 hour daily exposures.

Concentration above this TLV can cause dizziness, disorientation and "drunkenness", and concentrations approaching the lower explosive limit (3.6 vol. % in air) can cause helplessness and unconciousness in a very short exposure (anesthetic).

Thus operating areas must be designed with adequate drainage and ventilation, equipment selected to minimize the possibility of leaks and spills and operating personnel equipped with and trained in the proper use of respiratory equipment.

~~Canister type masks approved by the M.C.A for vinyl chloride may be used for short exposures where the concentration of VCM is known to be less than 2% by volume in the air, and the oxygen content is greater than 16 vol. %, or either such condition likely to develop.~~ No. Self contained breathing apparatus must be used by adequately trained personnel to handle such an emergency.

Liquid VCM spilled on the skin can cause frostbite due to rapid evaporation, and moderate chemical burns can occur to the skin due to liquid exposure, particularly with inhibited VCM, since the most commonly used inhibitor is phenol.

Skin areas splashed with VCM should be immediately washed copiously with water; eye exposures must be immediately washed with water for 15 minutes minimum, and medical attention obtained immediately.

Clothing, gloves, boots, etc. contaminated with vinyl chloride should be removed immediately to avoid prolonged skin contact.

Trained operating personnel must be fully aware of the flammable and explosive characteristics of VCM to preclude the possibility of human error causing a major spill, or providing an ignition source for minor leaks or spills.

Summing up, VCM storage systems should be designed to minimize leaks and spills; with adequate ventilation and drainage to conduct any leaks or spills away from critical operating areas; and the storage and process areas treated strictly as hazardous areas both from an engineering and operating procedural standpoint.

All personnel involved should be well trained in the nature and hazards of the monomer and in the proper handling procedures and equipped with chemical safety goggles, adequate respiratory equipment for emergency use, and provided with ready access to an eye wash and safety shower.

Protection of Monomer quality. Vinyl chloride is marketed under the specification shown in Table V. For comparison, a typical analysis as manufactured is included.

TABLE V

SPECIFICATION FOR VINYL CHLORIDE MONOMER

Property	Sales Specification	Typical Anal.
Acetylene, ppm	2 maximum	< 1
Acidity as HCl, ppm	5 maximum	< 0.5
Aldehyde, ppm	5 maximum	nil
Iron, ppm	0.5 maximum	< 0.5
Non Volatile Matter (% by weight)	0.05 maximum	< 75
Phenol, ppm	25 minimum	25-75
Inhibited	100 maximum	
Uninhibited	2 maximum	nil
Sulfur (as S), ppm	5 maximum	< 5
Water (% by weight)	0.03 maximum	< 100

Until 1956, essentially all VCM was inhibited as produced with 50-100 ppm of phenol to preclude the possibility of spontaneous polymerization during handling and storage.

During the late 1950's it became apparent to most major producers that uninhibited VCM could be stored and handled safely under the proper conditions.

Since the deletion of the inhibitor makes the inhibitor removal system at the users plant site unnecessary, a considerable capital and operating expense incentive exists to do so, and thus a major proportion of VCM is now manufactured, stored and shipped in the uninhibited state, although some users still specify phenol inhibited monomer.

Since large volumes of VCM are now stored and handled in the uninhibited state, the proper design, maintenance and operating procedures for VCM storage systems to protect the quality and monomer status of the stored VCM are absolutely essential to safety and loss prevention.

Coincidentally these same steps also optimize the conversion to and quality of the end use product.

Like styrene, the only significant end use for VCM is as polyvinyl chloride (PVC) or as a co-polymer with other monomers.

The impurities or monomer characteristics which affect the polymer quality adversely are mainly color, oxygen, homopolymer in the monomer, iron content, and unsaturated hydrocarbon impurities which produce variable polymerization rates and polymer quality. High water content is also undesirable.

These characteristics can all be controlled within specification limits by the proper engineering and operating control of the final stages of the VCM finishing train and storage facilities.

Materials of construction of the system can all be carbon steel, indeed all equipment, instruments, guages etc. must be scrutinized to exclude the use of copper and copper bearing alloys due to the possibility of trace acetylene reacting with the copper to form copper acetylides. Aluminum and aluminum alloys must also be excluded due to the reactivity of this metal with VCM.

All valves, direct connecting instrument cases, pumps, casings, etc. must be carbon steel or equivalent, not cast iron or ductile iron, to preclude the possibility of major spills due to equipment fracture or breakage.

Stainless steels are acceptable but unnecessarily costly for this service due to the size of most systems and in view of the suitability of carbon steels. It is mentioned here only because some minor specialty items such as instruments may be more available in stainless steel.

For ambient condition storage systems, design pressure of the storage tanks should be 100 psig, with 150 psig flanges, fittings, etc. used throughout the system. Horizontal cylindrical tanks are generally used for relatively small installations, 50,000 gallons or less. For larger installations, up to multimillion pounds, spheres are preferred.

In the case of vapor recompression and refrigerated systems, lower design pressures can be used for the storage tanks, but pumping and piping systems should still adhere to the 150 pound design.

For safety reasons as well as monomer quality preservation, the oxygen content of stored vinyl chloride vapor phase must be maintained below 1000 ppm by volume. Thus storage tanks must be cleaned, dried and inerted to remove oxygen prior to introducing VCM into the system. Experience has indicated that the best way to remove atmospheric oxygen from a system is to pad and depad the system, (including tanks, lines, pumps, etc. as a unit) with nitrogen until the oxygen content reaches the desired level. For example, padding a system originally containing one atmosphere of air to 30 psig with nitrogen, depadding to atmosphere and repeating until the pad-depad procedure has been done 5 times will reduce the oxygen content of the system to 0.082 volume percent.

Experience has indicated strongly that vinyl chloride which is produced on the alkaline side, 0.2-0.5 ppm alkalinity as NaOH, has a more stable storage life and it is recommended that VCM which is to be stored or handled for any period more than a few hours be processed on the alkaline side. This can be achieved by pumping to storage via flake NaOH traps.

It is also recommended that flake NaOH traps be installed in the tank farm with the necessary piping systems to load bulk VCM shipments via these NaOH beds. It is essential to protect VCM against contamination by air, water, or any oxidizing chemicals, (peroxides or peroxide precursors in particular), to preclude the degradation of the monomer quality. Steps to achieve this are obvious, i.e., do not permit tie-ins of any of these deleterious compounds to VCM systems.

VCM should not be exposed to sunlight, and storage temperatures should be maintained as low as possible. Sight glasses if used should be suitably rated reflex type glasses with actinic proof shields. However, Dow recommends the use of non-glass devices for level indication. A DP cell located at the bottom of the tank with steam traced vapor leg connected to the top of the tank is quite satisfactory. Tanks should be painted white or any other heat reflective paint system used to protect the monomer quality. In tropical and subtropical locations it is recommended that vapor recompression systems be used to maintain storage tank temperatures low enough to protect the monomer quality.

Protection against fire and explosion. Vinyl chloride storage systems should be located in a segrated area well separated from the major process unit and engineered as a Class I Group D Division I area and treated procedurally as such.

Any sections of the process, or any adjacent process which has a higher than average fire or explosion hazard, such as reactors or furnaces should be located as far away from a VCM storage facility as is practical.

The VCM storage system should be designed to eliminate and/or minimize the possibility of leaks or spills by paying close attention to design pressures, safety valve settings, selection of valves, instruments and design temperatures.

VCM should not be allowed to "free fall" from top entries into tanks. Inlets should be into the bottom of tanks or, if top inlets are used, grounded dip pipes should be provided. In addition, all tanks, pipelines and auxiliary equipment such as pumps and compressors must be grounded to preclude ignition of leaks due to static electricity.

A major VCM storage facility should be equipped with its own lightning rod.

All operating equipment in a process unit and/or storage system must be inerted to preclude oxygen contamination prior to commissioning, and the obvious steps taken to preclude the introduction of slugs of oxygen during service must be routinely followed.

Example: Loading tank cars, tank trucks, barges, etc. - the receiving container vents back to the storage tank, therefore these receiving vessels must be inerted to remove oxygen, preferably by padding up and down as outlined above.

It is also important that loading containers be electrically grounded during the loading operation.

It is desireable where possible to have shipping containers returned from customers with a "heel" of say 5 psig vinyl chloride vapor in them to preclude the possibility of atmospheric air leaking into the container in transit.

It is a good precaution to analyze the heel of VCM vapor in returned shipping containers for oxygen content prior to reloading them with VCM.

Storage tanks of greater than 10,000 USG capacity should be diked inside a concrete dike with a capacity to contain the entire contents of the storage tank, or tanks, if more than one tank is involved. Also the diked area must have an underground drain equipped with block valves. This drain should not lead into the main plant sewer system as the danger exists of flooding the entire plant, including ignition source areas with flammable VCM-air mixtures. Since vinyl chloride is lighter than and essentially immiscible in water it will float on top of a flowing sewer.

The VCM storage dike drain should discharge to a separate underground sewer preferably leading to a remote disposal or recovery sump. The drain block valve should be accessible from outside the dike wall, and left normally in the closed position; checked each day and opened when necessary to drain casual water from the diked area.

Pumps and where possible block valves, level gauges, etc. associated with the storage tanks should be located outside the dike wall.

Major storage installations, say greater than 50,000 USG, should be equipped with an open head water deluge invoked by heat actuated devices and/or manually invoked remotely to provide emergency flushing in the event of major spills or fires.

Water alone will not effectively extinguish or control large VCM fires due to its lighter than water character, and water may even spread the fire by floatation, but will serve to protect the tanks and contents from overheating while the fire is being brought under control by chemical means. In the event of a VCM fire a point to remember is that one of the products of combustion is HCl gas. It is recommended that in areas where mobile fire fighting rigs equipped with foam or powder capabilities are not readily accessible, fixed foam facilities be installed adjacent to the storage system and piped permanently inside the dike at required points to control and extinguish fires at any point within the dike area.

Summing up: the best way to provide safety in VCM storage and handling facilities is to engineer the installation to minimize spills and leaks;

preclude any ignition source for minor leaks and spills that might occur; provide a drain, deluged, dike area, guard against contamination of the system with air or oxidating chemicals and train people thoroughly in the proper safe procedures for handling the product.

Figures 9 and 10 show a schematic and a photograph of typical VCM storage facilities.

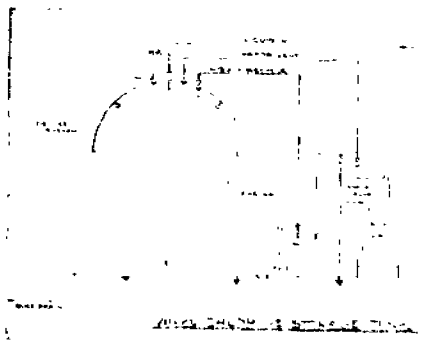

Fig. 9. Schematic Diagram of a Typical Vinyl Chloride Storage System.