F-40540

1962

UNION CARBIDE CHEMICALS COMPANY

VINYL CHLORIDE MONOMER F40540

TECHNICAL INFORMATION

VINYL CHLORIDE MONOMER

$CH_2 = CHCl$

RETURN TO RESEARCH DEPARTMENT
LIBRARY 701-3

RECEIVED
RESEARCH DEPARTMENT
AUG 19 1963
LIBRARY

This information is not to be taken as a warranty or representation for which we assume legal responsibility nor as permission or recommendation to practice any patented invention without a license. It is offered solely for your consideration, investigation and verification.

VINYL CHLORIDE MONOMER

GENERAL DESCRIPTION

Vinyl chloride is a colorless gas at standard temperature and pressure. It has a slightly sweet odor. The monomer is readily polymerized in the presence of peroxide type catalysts to form useful homopolymers and copolymers. In the absence of active catalysts the material is quite stable and is ordinarily shipped without an inhibitor. If an inhibitor is desired, 50 to 150 ppm. of phenol is generally used.

PHYSICAL PROPERTIES

Molecular Weight	62.50
Apparent Specific Gravity at 20/20°C.	0.9121
Δ sp. gr. / Δ t.	0.00186 per °C.
Boiling Point at 760 mm. Hg	−13.4°C.
50 mm. Hg	−63°C.
10 mm. Hg	−84°C.
Δ b.p./Δp.	0.026°C./mm. Hg
Vapor Pressure at 20°C.	2520 mm. Hg
Coefficient of Expansion at 20°C.	0.00203
Freezing Point	−153.8°C.
Solubility in Water at 20°C.	0.68% by weight
Solubility of Water in at 20°C.	0.09% by weight
Refractive Index, n_D at 20°C.	1.37
$\Delta n_D / \Delta t$	0.00080
Specific Heat at 20°C.	0.211 cal./g./°C.
Heat of Vaporization at 1 atm.	153 b.t.u./lb.
Heat of Polymerization	272 cal./g. (490 b.t.u./lb.)
Flash Point (open cup)	< 0°F.
Explosive Limits in Air	4 to 22% by volume

SHIPPING DATA

Pounds per Gal.	
20°C.	7.59
60°F.	7.66
Net Container Contents	
Cylinder	
Z	15 lb.
T (above 1198)	150 lb.
Labels Required	Red Gas
Cylinder Color Scheme	
Top	green
Bottom	black

UCC
049420

VINYL CHLORIDE MONOMER

SUSPENSION POLYMERIZATION OF VINYL CHORIDE

General Conditions

Reaction Temperature	40 to 60°C.
Pressure	75 to 125 psig
Agitator Speed	75 to 150 r.p.m.
Monomer Conversion	80 to 95 per cent

General Recipes

Monomer to Water Ratio	30/70 to 50/50
Suspending Agent (either (a) or (b) or both)	
(a) Colloid (CELLOSIZE WP-09, "Methocell",[1] or polyvinyl alcohol)	.05 to .15% of monomer
(b) Surfactant (TERGITOL 4 or 08, sodium lauryl sulfate, or "Aerosol" MA[2]	.05 to .15% of monomer
Catalyst (Benzoyl peroxide or diacetyl peroxide, etc.)	0.1 to 0.3% of monomer
Water	Deionized and Deaerated

(1) *Dow Chemical Company* (2) *American Cyanamid Company*

Comments

1. The same general conditions and recipies apply to copolymers with vinyl acetate and other monomers. The amount of comonomer that will react depends on the reactivity relative to vinyl chloride. About 25 per cent vinyl acetate is a practical limit.

2. The type and quality of resin produced is markedly affected by changes in conditions and formula ingredients. This can be minimized by adhering strictly to the same conditions in each reactant batch. Temperature, agitation, monomer conversion, and ingredients must be carefully controlled.

3. Resins for different end-uses require varied properties. These changes in properties can be attained by changes in the reaction conditions and formula ingredients. How to make these changes can only be developed through experience with a given production unit.

4. In preparing a suspension resin, add enough suspending agent to prevent coagulation of the resin during reaction and to control particle size within the desired range, but not enough to stabilize so that recovery of the resin is impeded. This is accomplished by balancing the agitation speed and concentrations of suspending agent and surfactant.

References

"Vinyl Resins" – Smith (Reinhold Publishing)
"Vinyl and Related Polymers" – Schildknecht
U.S.P.2,492,087 to Monsanto Chemical Company, 1949
U.S.P.2,492,089 to Monsanto Chemical Company, 1949
U.S.P.2,245,742 to B.F. Goodrich, 1941

UCC
049421

VINYL CHLORIDE MONOMER

Reactivity of Monomers Relative to Vinyl Chloride

Vinyl Chloride	1.0	Methalkyl Chloride	2.3
Methyl Methacrylate	20	Methyl Acrylate	2
Styrene	15	Allyl Acetate	0.5
Methacrylonitrile	15	Allyl Chloride	0.4
Methyl Vinyl Sulfone	15	Vinyl Acetate	0.3
Vinylidene Chloride	9	Isopropenyl Acetate	0.3
Acrylonitrile	5	Vinyl Ethyl Ether	0.1

STORAGE AND HANDLING

Inhibited vinyl chloride monomer may be stored at normal atmospheric temperatures in steel pressure vessels. Uninhibited monomer may be stored either under refrigeration or at normal atmospheric temperatures in the absence of air, sunlight or other catalysts for relatively short periods of time. All tanks, piping, instrument leads, relief valves and equipment in contact with the monomer should be of steel and designed to have a working pressure of at least 138 psi. No copper or copper bearing alloys should be used in the storage facilities in contact with the monomer or its vapors. Cast iron is not recommended for use in flanges or fittings.

All liquid inlet lines should enter the bottom of the tanks or extend to the bottom of the tanks to prevent the accumulation of static charges on filling. In addition all tanks and filling equipment should be grounded.

The tanks should be equipped with a combination of a 138 psi frangible disk and pressure relief valve. In case excess pressure ruptures the safety disk, the pressure relief valve will prevent the loss of the entire contents of the tank after the excess pressure has been relieved. These tanks are designed for skin temperatures up to approximately 130°F. In localities where surface temperatures may go above this value, the tanks may be cooled with a water spray system. The tanks should not be filled to more than 90% of volume capacity. A blanket of inert gas or vinyl chloride vapor must be maintained in the tank at all times. No air should be allowed to enter the tanks at any time. Relief valve sizes may be determined by using A.S.M.E. Boiler Construction Code VA230 when the valve is designed to relieve all vapor formed without increasing the total pressure by more than 10%. Tanks may be gauged with nitrogen bubbler gauges.

Adequate diking and drainage should be provided under the tanks to confine and dispose of the liquid in case of vessel rupture. A water spray system is recommended as a method of keeping the metal tank cool in case of fire.

All outlet lines from storage tanks should contain check valves to prevent contamination of tank contents. Before a tank is put into vinyl chloride monomer service, it should be purged with an inert gas until free of air. Tanks of less than 30,000 gallons capacity are most economically constructed in the form of horizontal cylinders.

For detailed information on the storage and handling of vinyl chloride consult Manufacturing Chemists' Chemical Data Sheet SD-56. This bulletin mentions the following points as being necessary for safe handling.

1. Keep away from heat, sparks and open flame.
2. Provide adequate ventilation.

UCC
049422

3. Ground equipment and containers before discharging to reduce danger of ignition from static sparks.
4. In discharging do not heat containers above 50°C. (122°F.). No heat should be applied to tank cars.
5. All equipment should be of steel and have a designed working pressure of at least 100-150 psi.
6. In the event of accidental leaks, spills, or whenever excessive vapor concentrations may be encountered, only personnel equipped with approved respiratory protection should be permitted in the contaminated area.
7. Chemical safety goggles should be worn when discharging containers or tank cars or whenever there is a danger of the liquid or saturated vapor coming in contact with the eyes.
8. Waste disposal should be away from any source of ignition. Dilute phenolic residues before discharging to sewer.

In case of fire use carbon dioxide or dry chemical extinguishing equipment. In the event of contact with the liquid remove contaminated clothing immediately. For eyes flush immediately with large quantities of water for at least 15 minutes while medical attention is being sought.

TOXICOLOGICAL PROPERTIES

Practical observations indicate that breathing vinyl chloride vapors presents the greatest hazard. Because of the high vapor pressure of vinyl chloride, high vapor concentrations develop rapidly. These vapors have a typical anesthetic effect, first causing dizziness, weakness, mental confusion, and finally loss of consciousness. Removal from exposure brings about rapid recovery with only brief complaints of nausea and headache.

High volatility makes prolonged skin contact with the material improbable. However, contact with saturated clothing may cause skin irritation. There is some suggestion that skin penetration occurs and that the response given is an anesthetic one.

Injury to the eye would be similar to that caused by contact with liquid hand soaps. Eye protection is advisable, and in case of accidental contact wash the eye with clean water for fifteen minutes.

SPECIFICATION LIMITS

1. Acidity as Hydrochloric Acid	5 ppm., max.
2. Acetylene	2 ppm., max.
3. Aldehydes as Acetaldehyde	4 ppm., max.
4. Iron as Fe	0.4 ppm., max.
5. Phenol (Customer's Preference)	
Inhibited monomer	50 to 150 ppm.
Uninhibited monomer	2 ppm., max.
6. Ethylene	10 ppm., max.
7. Methyl Chloride	10 ppm., max.
8. Water	0.03% by wt., max.
9. Nonvolatile matter	0.01% by wt., max.
10. Color, Pt-Co.	20, max.
11. Appearance	Clear, free of suspended matter.

UCC
049423

TEST METHODS

1. ACIDITY

a) *Solvent mixture* Transfer 25 ml. of anhydrous methanol to a glass-stoppered 500-ml. volumetric flask containing approximately 250 ml. of ethylene dichloride and 15 ml. of a 0.1 per cent solution of thymol blue indicator in methanol. Dilute to the mark with additional ethylene dichloride,. stopper, and mix thoroughly.

b) *Procedure* Introduce 100 ml. of the solvent mixture into each of two 500-ml. glass-stoppered Erlenmeyer flasks by means of a suitable transfer graduate.

c) Chill the solutions to approximately −10°C. in a suitable cold bath.

d) Neutralize each solution with standard 0.005 N alcoholic potassium hydroxide to an orange end point.

e) Reserve one of the flasks as a blank.

f) Into the other flask introduce 100 ml. of the chilled sample by means of a suitable *chilled* transfer graduate. Insert a small piece of paper between the stopper and flask to prevent build-up of pressure and swirl the contents of the flask gently.

g) Remove the stopper and, using a 10-ml. buret, titrate with the standard 0.005 N potassium hydroxide to the same color as that of the blank, paragraph e.

h) *Caluclation*

A × 1.82 = acidity, ppm, as hydrochloric acid

A = ml. of 0.005 normal KOH required for the titration

2. ACETYLENE

a) *Erlenmeyer flask, 250-ml., specially prepared* Fit with a one-hole rubber stopper. Insert a 3-inch length of glass tubing into the hole and through the stopper so that approximately one-half of it extends above the top of the stopper. Attach 1.5 ft. of rubber tubing to the glass outlet tube.

b) *Gas scrubbing bottle* Fit a widemouth pint bottle with a two-hole rubber stopper. Into one hole fit a fritted cylinder gas dispersion tube so that it extends to within 1/4 inch of the bottom of the bottle; into the second hole insert a short piece of glass tubing.

c) *Ilsovay's solution – stock solutions*

Solution "A": Prepare by mixing the following: 200 ml. of 10% cupric nitrate, $CuNO_3 \cdot 3H_2O$; 80 ml. of 20% ammonium hydroxide, NH_4OH (710 ml. of c.p. reagent grade NH_4OH to 1000 ml.); 200 ml. of refined isopropanol, 91%; and 580 ml. of distilled water.

Solution "B": 15 per cent by weight hydroxylamine hydrochloride

Solution "C": 1.0 per cent by weight gelatin (Eastman Calfskin)

d) *Procedure*

CAUTION! Conduct the reaction part of the procedure under a suitable fume hood.

Transfer 110 ml. of Solution "A", 40 ml. of Solution "B", and 10 ml. of Solution "C" to each of the following containers: the gas scrubbing bottle and a 250-ml. glass-stoppered Erlenmeyer flask.

e) Reserve the solution in the flask as a blank.

f) Chill the specially prepared 250-ml. Erlenmeyer flask, paragraph a, and introduce 100 ml. of the chilled sample by means of a chilled 100-ml transfer graduate. *Make this transfer as quickly as possible.*

g) Stopper the flask with the stopper that is connected to the inlet tube of the gas scrubbing bottle by means of the rubber tubing.

h) Allow all of the sample to evaporate through the gas scrubbing bottle.

UCC
049424

i) Transfer a portion of the sample and blank solutions to the respective 20-mm. cells of a Beckman Model B spectrophotometer and determine the absorbance of the sample solution at a wavelength of 540 millimicrons based on a reading of 0 for the blank. For a complete description of the instrument and its operation refer to Beckman Bulletin 206-B.

j) From the previously prepared calibration curve, paragraph m, read the ppm. of acetylene corresponding to the absorbance of the sample at 540 millimicrons. Duplicate determinations must agree within 1 ppm.

k) *Calibration curve* Prepare a series of acetylene standards from 1 to 6 ppm., inclusive, by adding known amounts of acetylene to acetylene-free vinyl chloride.

l) Determine the absorbance for each of the synthetics by following the procedure given in paragraphs d to i, inclusive.

m) Plot a calibration curve of absorbance versus ppm. acetylene using the values obtained in paragraph l.

3. ALDEHYDES

a) *Fuchsin reagent* Weigh 0.500 g. of Fuchsin reagent (rosanilin hydrochloride) in a small weighing dish and transfer to a 1000-ml. volumetric flask containing 490 ml. of distilled water. Add 11 ml. of a saturated (at 25° C.) solution of sulfur dioxide in distilled water. Stopper the flask, mix well, and allow to stand overnight. At the end of this period dilute the contents of the flask to the mark with distilled water. Add approximately one g. of powdered activated carbon and mix until the solution is decolorized. Filter the solution by gravity to remove the activated carbon. The reagent should be clear and have no more than a trace amount of pink color.

b) *Standard aldehyde solution* Accurately weigh 1.386 g. of acetaldehyde-ammonia (Eastman Catalogue No. 560-T) in a small weighing dish and transfer to a 100-ml. volumetric flask containing 50 ml. of distilled water. By means of a buret add 22.7 ml. of standard 1.0 N or 45.4 ml. of 0.5 N sulfuric acid, dilute to the mark with distilled water, and mix thoroughly. Allow the solution to stand overnight. Before use, verify the presence of acetaldehyde odor in the solution. This solution should be prepared fresh each time a new calibration curve is prepared.

c) *Purity of primary standard* The purity of the primary standard should be determined each time a new standard aldehyde solution is prepared. Using a weighing dish, introduce 0.6 to 0.8 g. of the Eastman acetaldehyde-ammonia weighed to the nearest 0.1 mg. into each of two 500-ml. glass-stoppered Erlenmeyer flasks containing 50 ml. of distilled water and swirl to effect solution. Add 50 ml. of distilled water to a third flask and reserve as a blank. Pipet two ml. of 0.04 per cent solution of bromophenol blue indicator in methanol into each sample and blank flask and carefully neutralize the contents to the indicator with standard 0.5 N aqueous hydrochloric acid. Add exactly 5.0 ml. of the 0.5 N acid in excess. Pipet 50 ml. of 0.5 N aqueous hydroxylamine hydrochloride reagent into each flask and allow the flasks to stand at room temperature for 60 minutes. Titrate the contents of each flask to a grayish-blue end point with standard 0.5 N aqueous sodium hydroxide.

Calculation:

$$\frac{(A-B)N \times 6.108}{\text{g. acetaldehyde-ammonia}} =$$

= acetaldehyde-ammonia, % by weight

A = ml. of N normal NaOH required for the sample.

UCC
049425

B = ml. of N normal NaOH required for the blank.

d) *Procedure* Assemble the apparatus as shown in Figure 1. NOTE: All equipment used in the performance of this test must be cleaned with dichromate cleaning solution, rinsed with water, then methanol, and air-dried. The test must be performed under a flame-free fume hood and in an aldehyde-free room.

e) Transfer 12 ml. of distilled water to each of six impingers. Insert the impinger tubes and place in beakers of wet ice as shown in Figure 1. Connect the rubber tubing between the impingers in such a manner as to have two series of three impingers.

f) Using a graduate that has been previously chilled with solid carbon dioxide, introduce 100 ml. (100 g.) of the sample into each of two previously chilled 125-ml. flasks.

g) Connect the sample flasks to respective series of three impinger tubes. Place a small piece of cork or wood under each flask and allow the sample to evaporate to dryness.

h) When the samples have evaporated completely, disconnect the rubber tubing, and remove the impinger tubes. Allow the tubes to drain by touching the tips against the insides of the respective impingers.

i) Prepare a blank for the reagent by adding 20 ml. of distilled water to a 25-ml. glass-stoppered graduate.

j) Pipet 5 ml. of the Fuchsin reagent into the blank. Stopper the container, mix thoroughly, and place in a water bath maintained at 25 ± 0.5°C. for 35 ± 2 minutes.

k) Repeat step j with each sample impinger, diluting it to 25 ml. with distilled water after the addition of Fuchsin reagent. Stopper, mix, and place each container in the water bath, noting its starting time, before adding reagent to the next one. This automatically spaces the starting times approximately 2 minutes apart.

l) Remove each container from the bath after 35 ± 2 minutes, and transfer a portion of the solution to one of two matched one-cm. cells. Determine the

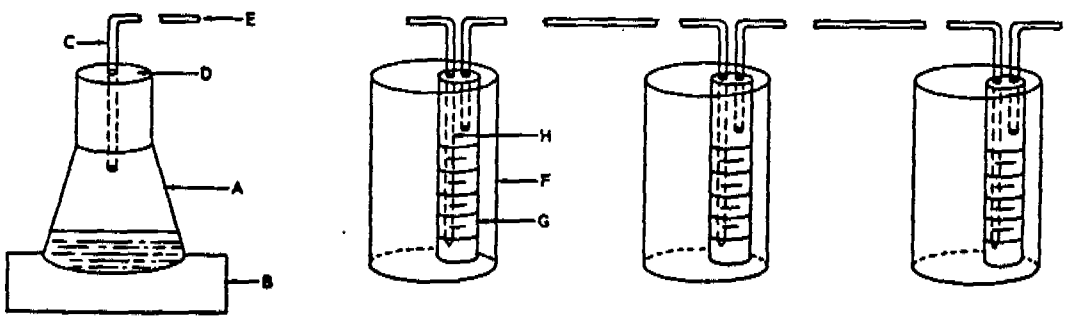


Figure 1

ASSEMBLY FOR ALDEHYDE DETERMINATION

A – 125-ml. flask
B – Cork ring
C – Glass tubing
D – Rubber stopper
E – Rubber tubing
F – Beakers for wet ice and large enough to hold two impingers.
G – Midget dust impinger, (Fisher 59, Catalog No. 9-258A)
H – Dust impinger tube, (Fisher 59, Catalog No. 9-258B)

A minimum of duplicate sets of apparatus are required.

UCC
049426

absorbance of each solution at 560 millimicrons using a Beckman Model B spectrophotomer and distilled water as the reference solution. Deduct the absorbance due to the blank from each of the sample solutions.

m) Calculation

$$\frac{A \times 1000}{\text{g. sample}} = \text{acetaldehyde, ppm.}$$

A = total mg. of acetaldehyde. Determine from the calibration curve, paragraph q, the mg. of acetaldehyde corresponding to the net absorbance due to the solution in each impinger. A = the sum of these values.

n) *Calibration curve* Pipet one ml. of the primary standard, paragraph b, into a 100-ml. volumetric flask containing 50 ml. of distilled water. Dilute to the mark with distilled water, stopper, and mix thoroughly.

o) Prepare a series of standards by pipetting 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 ml. of the diluted primary standard into respective 25-ml. glass-stoppered graduates. These standards contain 0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, and 0.50 mg. acetaldehyde, respectively, depending on the purity of the original acetaldehyde-ammonia.

p) Dilute the contents of each graduate to the 20-ml. mark with distilled water and determine the absorbance of each standard as described in paragraphs j through l. Deduct the absorbance of the zero standard from the absorbance of each of the standards to find the net absorbance of the standards.

4. IRON

a) *Standard iron solution* Dissolve 0.2809 g. of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in 50 ml. of distilled water contained in a 1000-ml. glass-stoppered volumetric flask. Slowly and with constant swirling add 10 ml. of concentrated c.p. nitric acid and heat to boiling. Cool and dilute to the mark with distilled water. A 1.0-ml. aliquot of this dilution is equivalent to 0.4 ppm, iron, as Fe, when using a 100-ml. sample.

b) *Sodium acetate, 2 molar* Dissolve 164 ± 0.01 g. of c.p. sodium acetate in 1000 ml. of distilled water.

c) *Alcohol-water solution* Measure 25 ml. of S.D.2-B alcohol into a 100-ml. glass-stoppered graduate containing 30 ml. of distilled water. Stopper and mix thoroughly.

d) *Procedure* Transfer 25 ml. of the alcohol-water solution to a 250-ml. glass-stoppered Erlenmeyer flask.

e) Into the flask introduce 100 ml. of the chilled sample by means of a suitable *chilled* transfer graduate.

f) Gently swirl the contents of the flask, remove the stopper, and allow the vinyl chloride to evaporate under a fume hood. Swirl the flask to remove the last trace of vinyl chloride.

g) Filter the remaining alcoholic solution through a Gooch crucible fitted to a 250-ml. filtering flask and connected to a suitable vacuum system.

h) Quantitatively transfer the filtrate to one of two, 100-ml. glass-stoppered volumetric flasks, rinsing the filtering flask with five 5-ml. portions of distilled water.

i) To the second volumetric flask add 25 ml. of the alcohol-water solution and introduce 1.0 ml. of the standard iron solution by means of a suitable measuring pipet. Reserve as a blank.

j) To each flask add 2 drops of concentrated c.p. hydrochloric acid and 2 drops of 0.1 per cent bromo-phenol blue indicator in ethanol.

k) Add the 2 molar sodium acetate solution dropwise to each flask until each solution turns a faint blue.

l) To each flask add 4.0 ml. of 10 per cent hydroxylamine hydrochloride solution in water and 10.0 ml. of 0.12 per cent solution of o-phenanthroline in water.

UCC
049427

m) Dilute each solution to the mark with distilled water, stopper the flasks, and mix each thoroughly.

n) Allow the solutions to stand at room temperature for at least 20 minutes.

o) Transfer the sample and blank solutions to respective 100-ml. matched tall-form Nessler tubes.

p) Compare the colors of the sample and blank solutions visually in transmitted light. If the color of the sample is more reddish-orange than that of the blank, the iron content of the sample is in excess of 0.4 ppm., as Fe.

5. PHENOL

a) Weigh 25 g. of the sample, chilled in a solid carbon dioxide-acetone mixture, to the nearest 0.1 g., into a *chilled* 100-ml. glass-stoppered volumetric flask.

b) Place the flask in room temperature water and allow the vinyl chloride to evaporate under a fume hood. Do not agitate until nearly dry and then do so to drive off any remaining vinyl chloride.

c) Allow the flask to warm to room temperature and dilute to the mark with methanol, specification 1-6A1-1.1 or equivalent. Stopper the flask and mix thoroughly.

d) Introduce 20 ml. of this dilution into a second 100-ml. glass-stoppered volumetric flask by means of a suitable transfer pipet and dilute to the mark with additional methanol. Stopper and mix thoroughly.

e) Determine the ultraviolet absorbance on a portion of this dilution using a Beckman Model DU spectrophotometer, a wavelength near 271 millimicrons, and 1.00-cm. silica cells.

f) Prepare a series of synthetic samples containing from 5 to 30 ppm. phenol in anhydrous methanol and determine the absorbance of each as described in paragraph e using methanol as a blank.

g) Plot the absorbance of the synthetic samples against their respective concentrations.

h) Using the absorbance value obtained, paragraph e, determine the phenol content of the sample by reading from the calibration curve, paragraph g, and calculating as follows:

i) *Calculation*

C × 20 = phenol, ppm., in original sample

C = ppm. phenol obtained from curve, paragraph g

j) *Note:* Nonvolatile aromatics, i.e., hydroquinone and diphenylamine, will interfere with this determination.

6. ETHYLENE AND METHYL CHLORIDE

a) *Sample handling and special precautions*

All samples must be taken from a liquid sampling point into evacuated cylinders to prevent fractionation and loss of the more volatile components. Fill the cylinder to approximately 90 per cent of capacity, and drain off 10 per cent from the liquid phase to prevent possible rupture of the cylinder.

Equip the gas handling system of the gas chromatograph with a conventional vacuum system as described in 58C-9C1-V6.3.

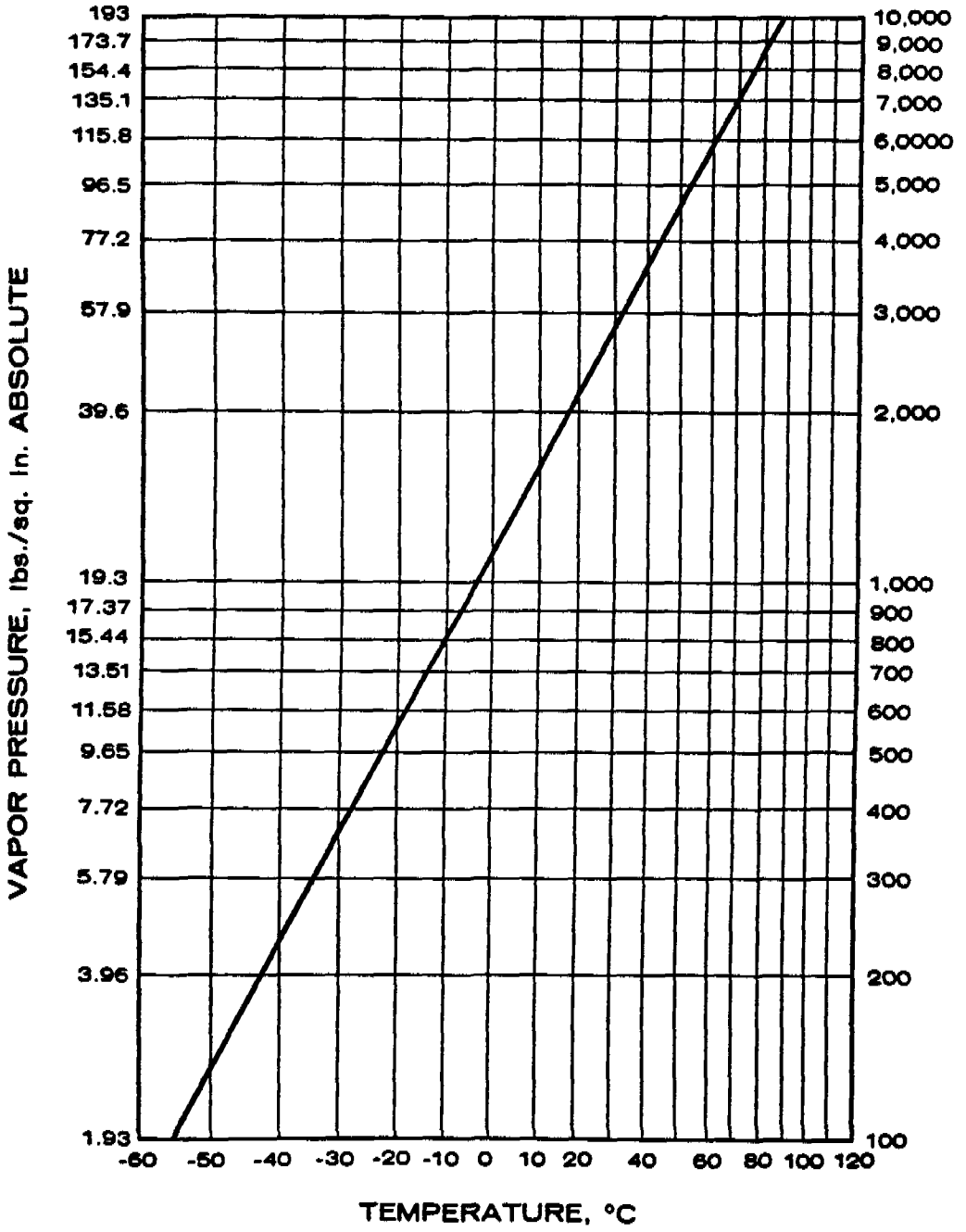
b) *Instrument parameters*

Instrument – Beckman GC 2A Gas Chromatograph or equivalent
Recorder – Brown, 0-1 mv., with integrator from Disc Instruments, Inc.
Column – 25-ft, 1/4-inch O.D. tubing packed with 25 per cent hexadecane on 60 to 80 mesh Chromosorb W
Column temperature – room temperature (25° C.)
Eluting gas – helium
Pressure – 35 psig
Flow (measured at outlet at room temperature) – 100 c.c. per minute.
Filament current – 300 ma
Sample volume – 10 c.c. (gas)
Total elution time – 20 minutes

UCC
049428

VINYL CHLORIDE MONOMER

VAPOR PRESSURE OF VINYL CHLORIDE AT VARIOUS TEMPERATURES



UCC
049429

UNION CARBIDE CHEMICALS COMPANY
DIVISION OF UNION CARBIDE CORPORATION
270 Park Avenue, New York 17, N. Y.

Printed in U.S.A.

F-40540