

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS

P. O. BOX 8004, SOUTH CHARLESTON, W. VA. 25303

24.

SOUTH CHARLESTON PLANT

December 2, 1974

Mr. John Stender
Assistant Secretary of Labor
for Occupational Safety and Health
U. S. Department of Labor
14th Street and Constitution Avenue
Washington, D. C. 20004

Re: Occupational Safety and Health
Standard for Exposure to Vinyl Chloride

Dear Mr. Stender:

The Occupational Safety and Health Standard for Exposure to Vinyl Chloride promulgated on October 4, 1974 applies to the transportation of vinyl chloride and polyvinyl chloride..... The broad application of this standard is such that all employees of distributive organizations must be monitored for exposure and trained in the hazards of vinyl chloride, and that records of those employees monitoring and training be maintained for thirty years. A four-ounce sample of polyvinyl chloride shipped by parcel post in a sealed can would require monitoring, training, and records for a mass of postal employees despite the fact that no significant exposure to vinyl chloride monomer could occur. A single, fifty-pound, paper bag of resin is essentially treated the same as a rail car containing fifty tons. In the case of the large bulk container - be it ship, rail car, or truck, adherence to the letter of the standard regarding monitoring, training, and record keeping is relatively easy and the transportation company has an economic incentive to transport the product. In the case of the single bag shipment, the multi-bag shipment, or the sample shipment, the logical move on the part of the transportation company is simply to refuse shipment to spare themselves the obvious expense involved in monitoring, training, and record keeping. The same applies to the public warehouse man and the terminal operator. Many of these distributive companies have indicated that they plan to handle direct truck load or rail car load shipments only of polyvinyl chloride.

Union Carbide Corporation owns and operates major polyvinyl chloride resin production facilities at South Charleston, West Virginia and at Texas City, Texas. Production facilities at these locations produce a variety of polyvinyl chloride resins by four different processes - suspension polymerization, bulk polymerization, emulsion polymerization, and solution polymerization. Only one of these polyvinyl chloride resin products, suspension resins,

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contains significant amounts of vinyl chloride monomer; this material is generally shipped by bulk and represents no considerable problem in distribution. Products from the other three processes are distributed world-wide via a network of warehouses and transportation companies. Of these resins, approximately one half or 100,000,000 pounds per year are ultimately delivered to about 1,500 customers in less-than-truck-load quantities. The average shipment is estimated to be 11,000 pounds. These less-than-truck-load shipments (9,500 per year) involve 41 public warehouses and up to 200 different common carrier trucking companies in the United States alone. The value of these sales to Union Carbide Corporation is approximately \$22,000,000 per year. A substantial number of trucking and warehouse companies have indicated they do not wish to handle these shipments in the future. Union Carbide Corporation thus finds itself with having to meet a very difficult standard in its production facilities and with being unable to supply many of its smaller customers. Other companies are faced with similar problems.

Union Carbide Corporation is also concerned about the distribution problem as it is related to its customers. Many of Union Carbide's customers are formulators of lacquers, plastisols, and organosols for coating and molding applications. These liquids are normally shipped in closed steel drums by common carrier truck. As required by the Standard, monitoring, training, and record keeping are needed. It is very hard to conceive how a vinyl resin containing no detectable vinyl chloride monomer, formulated into a coating material, and shipped in a sealed steel drum can be a hazard to a trucker or anyone else.

This problem was discussed with Mr. Grover Wren, Chief of Health Standards Development, by Dr. R. S. Brookman of Firestone Plastics Company, Mr. Wayne T. Brooks of Organization Resources Counselors, and me on November 26, 1974. The consensus of the discussion was that good monitoring studies of shipments correlated with type of PVC, weight of the shipment, vinyl chloride content of the PVC, the mode of shipment, and the resin container could be used to develop shipping rules, freight classifications, and resin containers to fulfill the spirit of the vinyl chloride standard without requiring all of the monitoring, et cetera burdens of the transportation company. With adequate guidelines for the shipper and the transportation company owners, application of the Standard's requirements for monitoring, training, and record keeping can be avoided without any sacrifice of employee safety.

Due to the diversity of the industry interests and the broad sweep of the vinyl chloride Standard in its safety objective, I think the Department of Labor should take the initiative in providing clear-cut rules and procedures for vinyl resin transportation and distribution. Certainly, a trucking company in

Mr. John Stender

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Des Moines, Iowa, hauling 2,000 pounds of solution polymerized VYHH resin containing no detectable vinyl chloride monomer, should not have to monitor its employee vinyl chloride exposure, train them in its hazard, and keep such records thirty years. A task force or committee, under the direction of the Assistant Secretary of Labor, should certainly be able to arrive at performance standards and rules for the distribution industry that achieve the objectives of the Standard. Union Carbide Corporation, Firestone Plastics Company, and many others would be willing to contribute data and alternative distribution technics to such a group. The formation of such a group could do much to clear up other questions regarding this Standard and to demonstrate that the Department of Labor considers employee safety a cooperative effort by all concerned.

Very truly yours,



R. N. Wheeler, Jr.

RNWJr/ra

RNW 0278

DETERMINATION OF RESIDUAL VINYL CHLORIDE
MONOMER IN VINYL RESINS

Method Number

WC-326-G-1

1 PURPOSE

Issue Page of
1 1 3

Date
January 20, 1975

A procedure for determining small amounts of residual vinyl chloride monomer present in vinyl resins is described. The resin sample is dissolved in a suitable solvent and is analyzed using a gas chromatographic technique utilizing a backflush mode. The method is applicable for use with poly(vinyl chloride), vinyl chloride-vinyl acetate copolymers and other vinyl resins in which there are no volatiles which interfere in the determination. The method resolves vinyl chloride from major impurities found in vinyl resins and can be quantitated with proper calibrations.

2 EQUIPMENT AND REAGENTS

- a) Gas chromatograph, Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with a hydrogen flame ionization detector.
- b) Backflush valve, Bendix 8-port sliding plate valve or equivalent.
- c) Tetrahydrofuran, reagent grade
- d) Balance with accuracy to 0.10 gram
- e) Fritted glass sparger, fine

3 INSTRUMENT PARAMETERS

Instrument	Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with hydrogen flame ionization detector
Column	20 feet x 1/8-inch stainless steel tubing packed with 20 percent TERGITOL E-35 on Chromosorb W AW, 60/80 mesh
Backflush valve	Bendix, 8 port sliding plate valve or equivalent
Temperatures	
Column	70°C isothermal
Injection port	100°C (maximum)
Detector	300°C
Carrier gas	helium
Flows	
Helium carrier gas	
a) inject	40 cc/minute
b) backflush	40 cc/minute
Hydrogen	20 psi at cylinder heat
Compressed air	40 psi at cylinder head
Sample size	40 microliters

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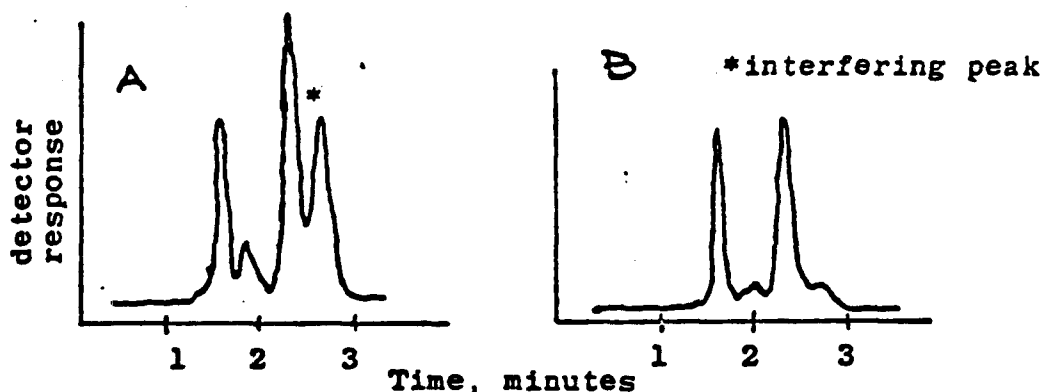
Electrometer
Range 1
Attenuation 8
Approximate elution time
vinyl chloride 2.8 minutes

- 4 SCHEMATIC OF FLOW SYSTEM A schematic of the flow system utilizing the Bendix 8-port sliding plate valve is attached as Figure 1.

5 PROCEDURE

Analyze the tetrahydrofuran (THF) prior to preparing any samples or calibration standards using the parameters listed in Section 3. A backflush valve has been incorporated into the system to facilitate the analysis. Four minutes after the sample injection, the column is backflushed and vented to the atmosphere thus preventing the solvent from reaching the detector. A backflush time of 10-15 minutes should be sufficient to elute the solvent. After the backflush period, return the valve to its original position. The base line should be allowed to equilibrate before injecting another sample.

Compare the THF chromatogram with those shown below. If the scan is comparable to A, the THF will have to be sparged with nitrogen at a medium flow rate for approximately 2 hours in an attempt to remove the interfering peak. Reanalyze the sparged THF to determine if it is acceptable. If the scan is comparable to B, the THF should be acceptable for use in the analysis.



Accurately weigh one gram of the resin to be analyzed into a 6-dram vial containing 9 grams of THF. Cap the vial and shake to effect solution. Analyze the sample using the parameters listed in Section 3 and follow the above instructions for the backflush.

Measure the peak height of the vinyl chloride peak in millimeters. The area can also be measured using an acceptable technique (e.g. planimeter, automatic integrator, computer, etc.).

6 CALIBRATION

Prepare solution mixtures in the THF of varying amounts of vinyl chloride to cover the expected ppm range of concentration. Obtain the gas chromatogram for each sample using the parameters listed in Section 3. Prepare a chart plotting the peak height (or area) obtained from the chromatogram of each sample versus the known concentration to establish a relative detector response. See Figure 2 for typical calibration curve.

7 CALCULATIONS

Determine the monomer content in the test solution from the calibration chart. Apply the peak height (or area) of the monomer obtained from the chromatographic scan of the test solution to the calibration curve and read the corresponding concentration in parts per million (ppm).

The concentration value obtained from the calibration curve is total monomer in the solution. In order to convert the data to monomer concentration based on total resin, the value must be multiplied by a factor of 10.

8 AS CHROMATOGRAM

A gas chromatogram is attached as Figure 3 showing the response for 1.3 ppm vinyl chloride.

FIGURE 1
SCHEMATIC OF FLOW SYSTEM UTILIZING THE
BENDIX 8-PORT SLIDING PLATE VALVE

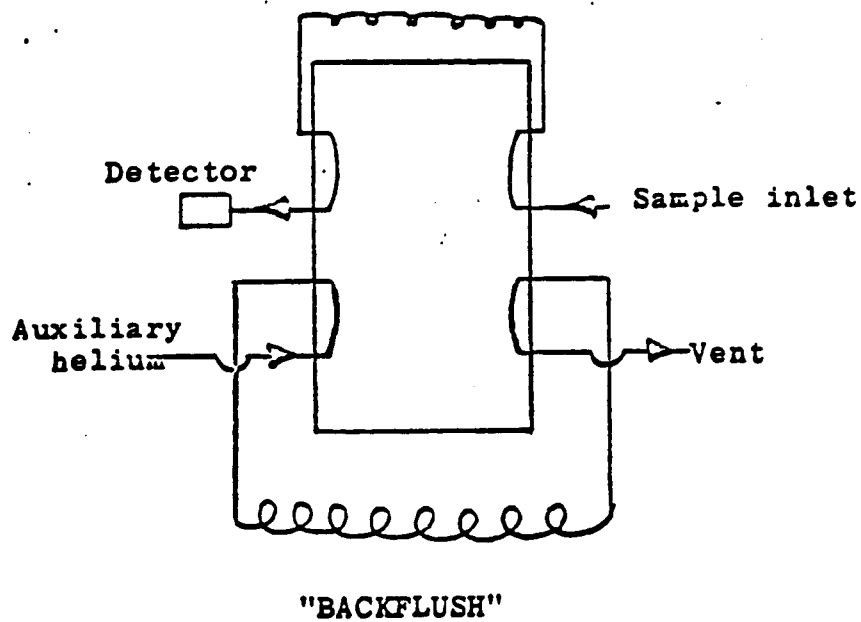
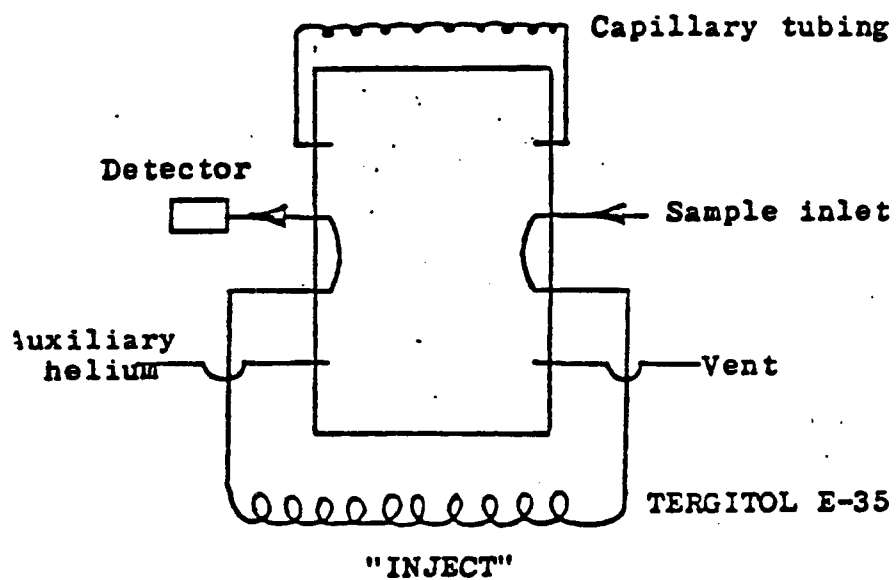
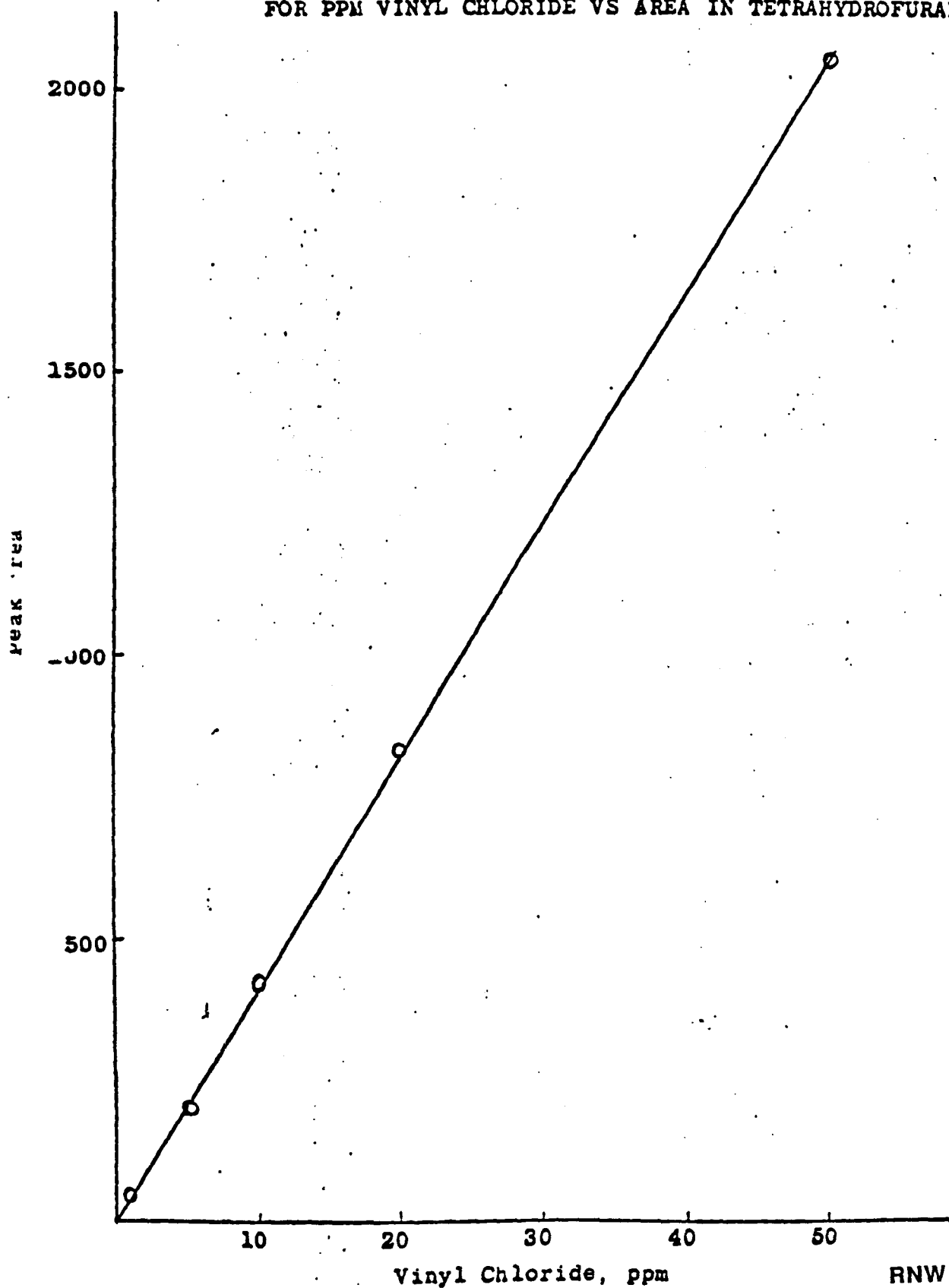
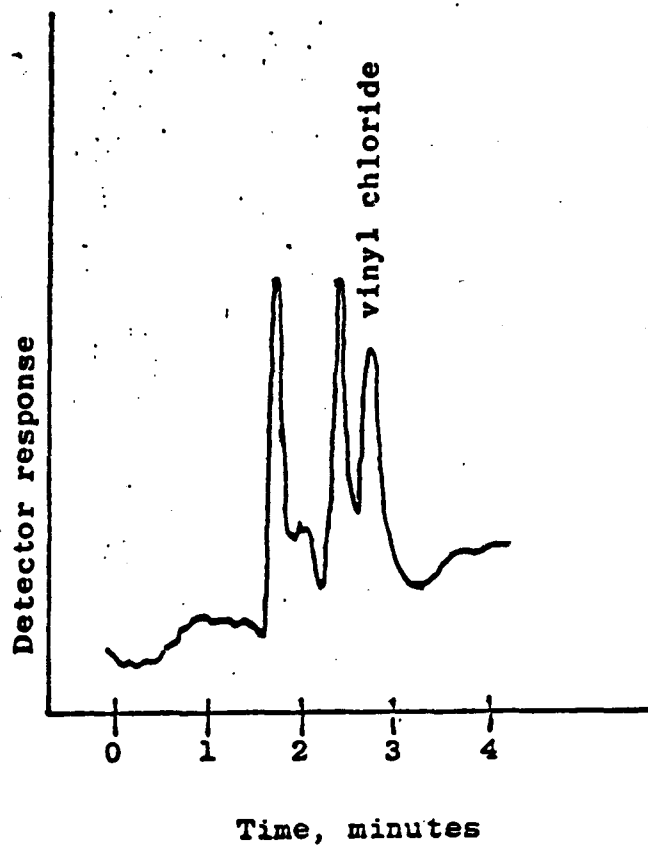


FIGURE 2
TYPICAL GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR PPM VINYL CHLORIDE VS AREA IN TETRAHYDROFURAN



RNW 0283

FIGURE 3
GAS CHROMATOGRAM OF VINYL RESIN
WITH 1.3 PPM VINYL CHLORIDE MONOMER



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25

RNW 0285



MATERIAL SAFETY DATA SHEET

EFFECTIVE DATE: March 15, 1981

004-029



PRODUCT NAME: UCAR® Solution Vinyl Chloride-Vinyl Acetate																							
CHEMICAL NAME:		CHEMICAL FAMILY: Vinyl chloride-vinyl acetate maleic acid terpolymer																					
FORMULA: $\left(\text{CH}_2 - \text{CH} \right)_n \left(\text{CH}_2 - \text{CH} \right)_m \left(\text{CH}(\text{COOH}) - \text{CH}(\text{COOH}) \right)_k$		MOLECULAR WEIGHT: $\bar{M}_n \approx 8000$ to 22 000																					
SYNONYMS:																							
DEPARTMENT OF TRANSPORTATION	HAZARD CLASSIFICATION		None																				
	SHIPPING NAME		None																				
CAS # 25085-82-9 CAS NAME Acetic acid ethenyl ester, polymer with chloroethene and 2,5-furandione.																							
MELTING POINT Not applicable																							
DENSITY 1.34 ± 0.005 grams per cc at 20/20 °C																							
PER CENT VOLATILES BY VOLUME Nil																							
APPEARANCE AND ODOR Fine, white, powdered solid; very slight, pleasant odor.																							
<table border="1"><thead><tr><th>MATERIAL</th><th>%</th><th>TLV (Units)</th><th>HAZARD</th></tr></thead><tbody><tr><td>Vinyl chloride-vinyl acetate resin</td><td>>97</td><td>Not established</td><td>None currently known</td></tr><tr><td>Hydrogen chloride</td><td><0.0001</td><td>1 ppm</td><td>Carcinogen</td></tr><tr><td>Water</td><td><2</td><td></td><td></td></tr><tr><td>Solvents</td><td><0.5</td><td></td><td>Flammable. Toxic</td></tr></tbody></table>				MATERIAL	%	TLV (Units)	HAZARD	Vinyl chloride-vinyl acetate resin	>97	Not established	None currently known	Hydrogen chloride	<0.0001	1 ppm	Carcinogen	Water	<2			Solvents	<0.5		Flammable. Toxic
MATERIAL	%	TLV (Units)	HAZARD																				
Vinyl chloride-vinyl acetate resin	>97	Not established	None currently known																				
Hydrogen chloride	<0.0001	1 ppm	Carcinogen																				
Water	<2																						
Solvents	<0.5		Flammable. Toxic																				
AUTOIGNITION TEMPERATURE		725 °F, ASTM D 1929																					
EXTINGUISHING MEDIA		Use water spray, carbon dioxide, dry chemical, or alcohol-type or universal-type foams. Apply by manufacturer's recommended technique.																					
SPECIAL FIRE FIGHTING PROCEDURES		Use supplied breathing air and protective clothing.																					
UNUSUAL FIRE AND EXPLOSION HAZARDS		Hydrogen chloride will form under fire conditions.																					



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304/744-3487

This number is available days, nights, weekends, and holidays.

While Union Carbide Corporation believes that the data contained herein are factual and the opinions expressed are those of qualified experts regarding the results of the tests conducted, the data are not to be taken as a warranty or representation for which Union Carbide Corporation assumes legal responsibility. They are offered solely for your consideration and use of these data and information must be determined by the user to be in accordance with applicable Federal, State, and local laws and regulations.

AV AT SOURCE: None established for vinyl resin by ACGIH or OSHA. Vinyl chloride:
1 ppm, OSHA 29 CFR § 1910.1017, exemption (b) (6).

ACUTE EFFECTS OF OVEREXPOSURE

SWALLOWING	None currently known. May cause some nausea.
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SKIN ABSORPTION	None currently known.
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INHALATION	None currently known.
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SKIN CONTACT	None currently known.
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EYE CONTACT	None currently known.
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CHRONIC EFFECTS OF OVEREXPOSURE	OSHA has classed vinyl chloride as a carcinogen. Substance is exempt under (b) (6) of the standard.
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OTHER HEALTH HAZARDS	ACGIH has a TLV for nuisance and respirable dusts and OSHA regulates both under 29 CFR § 1910.1000, Table Z-3. Powdered vinyl resins can contribute to nuisance dusts and may contribute to respirable dusts.
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EMERGENCY AND FIRST AID PROCEDURES:

SWALLOWING	Give two glasses of water and induce vomiting by putting finger down throat.
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SKIN	Flush with water.
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INHALATION	No emergency care anticipated.
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EYES	Flush with water.
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NOTES TO PHYSICIAN

This is a relatively innocuous substance not expected to cause harm.
Any treatment that might be required for overexposure should be
directed at the control of symptoms and the clinical conditions. There
is no specific antidote.

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STABILITY		CONDITIONS TO AVOID	None
UNSTABLE	STABLE		
--	✓		
INCOMPATIBILITY (materials to avoid)		None	
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS		Burning and elevated temperatures can produce hydrogen chloride, carbon monoxide, and/or carbon dioxide.	
HAZARDOUS POLYMERIZATION		CONDITIONS TO AVOID	None
May Occur	Will not Occur		
--	✓		
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED		Sweep up; collect in a suitable container for disposal.	
WASTE DISPOSAL METHOD		Bury in a landfill where permitted under appropriate Federal, State, and local regulations.	
RESPIRATORY PROTECTION (specify type)		Dust respirator in high dust concentrations.	
VENTILATION	General room ventilation should be adequate. Supplement with local exhaust equipment, should dusting conditions prevail.		
PROTECTIVE GLOVES	Substantial leather work gloves	EYE PROTECTION	Safety glasses
OTHER PROTECTIVE EQUIPMENT	Eye bath and safety shower		
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING			
Breathing dust may be harmful. Avoid breathing dust.			
FOR INDUSTRY USE ONLY			
OTHER PRECAUTIONS			
Limit the amount of dust available by appropriate handling and processing. Eliminate static electricity by proper procedures and by effective grounding.			

LEVEL AND SOURCE:

None established for vinyl resin by ACGIH or OSHA. Vinyl chloride:
1 ppm, OSHA 29 CFR § 1910.1017, exemption (b) (6).

ACUTE EFFECTS OF OVEREXPOSURE

SWALLOWING	None currently known. May cause some nausea.
SKIN ABSORPTION	None currently known.
INHALATION	None currently known.
SKIN CONTACT	None currently known.
EYE CONTACT	None currently known.

CHRONIC EFFECTS OF OVEREXPOSURE

OSHA has classed vinyl chloride as a carcinogen.
This resin is exempt under (b) (6) of the standard.

OTHER HEALTH HAZARDS

ACGIH has a TLV for nuisance and respirable dusts and OSHA regulates both under 29 CFR § 1910.1000, Table Z-3. Powdered vinyl resins can contribute to nuisance dusts and may contribute to respirable dusts.

EMERGENCY AND FIRST AID PROCEDURES:

SWALLOWING	Give two glasses of water and induce vomiting by putting finger down throat.
SKIN	Flush with water.
INHALATION	No emergency care anticipated.
EYES	Flush with water.

NOTES TO PHYSICIAN

This is a relatively innocuous substance not expected to cause harm.
Any treatment that might be required for overexposure should be directed at the control of symptoms and the clinical conditions. There is no specific antidote.

RNW 0289



MATERIAL SAFETY DATA SHEET

EFFECTIVE DATE: March 15, 1981

4-002

INS-3

IDENTIFICATION

PRODUCT NAME: UCAR® Solution Vinyls	
CHEMICAL NAME:	CHEMICAL FAMILY: Vinyl chloride-vinyl acetate copolymers
FORMULA: $\left(\text{CH}_2-\text{CH}(\text{Cl}) \right)_x \left(\text{CH}_2-\text{CH}(\text{O}_2\text{CCH}_3) \right)_y$	MOLECULAR WEIGHT: $\bar{M}_n \approx 8\,000$ to 35 000
SYNONYMS:	
DEPARTMENT OF TRANSPORTATION	HAZARD CLASSIFICATION: None
	SHIPPING NAME: None
CAS # 9003-22-9	CAS NAME: Acetic acid ethenyl ester, polymer with chloroethene

MELTING POINT	Not applicable
DENSITY	1.35 to 1.39 grams per cc at 20/20 °C
PER CENT VOLATILES BY VOLUME	Nil
APPEARANCE AND ODOR	Fine, white, powdered solid; very slight, pleasant odor.

MATERIAL	%	TLV (Units)	HAZARD
Vinyl chloride-vinyl acetate resin	>97	Not established	None currently known
Hydrochloric acid	0.00001	4 ppm	Carcinogen
Water	<2		
Solvents	<0.5		Flammable, Toxic

AUTOIGNITION TEMPERATURE	734 °F, ASTM D 1929
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EXTINGUISHING MEDIA	Use water spray, carbon dioxide, dry chemical, or alcohol-type or universal-type foams. Apply by manufacturer's recommended technique.
SPECIAL FIRE FIGHTING PROCEDURES	Use supplied air and protective clothing.
UNUSUAL FIRE AND EXPLOSION HAZARDS	Hydrogen chloride will form under fire conditions.

RNW 0290

304/744-3487

This number is available days, nights, weekends, and holidays.

While Union Carbide Corporation believes that the data contained herein are factual and the opinions expressed are those of qualified experts regarding the results of the tests conducted, the data are not to be taken as a warranty or representation for which Union Carbide Corporation assumes responsibility. They are offered solely for your consideration, investigation, and verification. Any use of these data and information must be determined by the user to be in accordance with applicable Federal, State, and local laws and regulations.

UNION CARBIDE CORPORATION • COATINGS MATERIALS DIVISION • OLD FIDGEBURY RD. DANBURY, CT 06817

004 002

SAFETY DATA			
STABILITY		CONDITIONS TO AVOID	None
UNSTABLE	STABLE		
--	✓		
INCOMPATIBILITY (materials to avoid)		None	
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS		Burning and elevated temperatures can produce hydrogen chloride, carbon monoxide, and/or carbon dioxide.	
HAZARDOUS POLYMERIZATION		CONDITIONS TO AVOID	None
May Occur	Will not Occur		
--	✓		
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED		Sweep up; collect in a suitable container for disposal.	
WASTE DISPOSAL METHOD		Bury in a landfill where permitted under appropriate Federal, State, and local regulations.	
RESPIRATORY PROTECTION (specify type)		Dust respirator in high dust concentrations.	
VENTILATION	General room ventilation should be adequate. Supplement with local exhaust equipment, should dusting conditions prevail.		
PROTECTIVE GLOVES	Substantial leather work gloves	EYE PROTECTION	Safety glasses
OTHER PROTECTIVE EQUIPMENT	Eye bath and safety shower		
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING			
Breathing dust may be harmful. Avoid breathing dust.			
FOR INDUSTRY USE ONLY			
OTHER PRECAUTIONS			
Limit the amount of dust available by appropriate handling and processing. Eliminate static electricity by proper procedures and by effective grounding.			

RNW 0291

USE AND SOURCE:

None established for vinyl resin by ACGIH or OSHA. Vinyl chloride:
~~1 ppm.~~ OSHA 29 CFR § 1910.1017, exemption (b) (6).

ACUTE EFFECTS OF OVEREXPOSURE

SWALLOWING	None currently known. May cause some nausea.
SKIN ABSORPTION	None currently known.
INHALATION	None currently known.
SKIN CONTACT	None currently known.
EYE CONTACT	None currently known.
CHRONIC EFFECTS OF OVEREXPOSURE	OSHA has classed vinyl chloride as carcinogen. The resin is exempt under (b) (6) of the standard.
OTHER HEALTH HAZARDS	ACGIH has a TLV for nuisance and respirable dusts and OSHA regulates both under 29 CFR § 1910.1000, Table Z-3. Powdered vinyl resins can contribute to nuisance dusts and may contribute to respirable dusts.

EMERGENCY AND FIRST AID PROCEDURES:

SWALLOWING	Give two glasses of water and induce vomiting by putting finger down throat.
SKIN	Flush with water.
INHALATION	No emergency care anticipated.
EYES	Flush with water.

NOTES TO PHYSICIAN

This is a relatively innocuous substance not expected to cause harm. Any treatment that might be required for overexposure should be directed at the control of symptoms and the clinical conditions. There is no specific antidote.