INDUSTRIAL HYGIENE SURVEY OF THE

Union Carbide Corporation
Polyvinyl Chloride Operations
South Charleston, West Virginia

SURVEY DATE
June 10-19, 1974

SURVEY CONDUCTED BY
James Jones
Howard Ludwig
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REPORT WRITTEN BY
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DATE OF REPORT
August, 1975

Environmental Investigations Branch
Division of Field Studies and Clinical Investigations
National Institute for Occupational Safety and Health
Cincinnati, Ohio

Place Visited:	Union Carbide Corporation P.O. Box 8004 South Charleston, West Virginia 25303
Date of Visit:	June 10-19, 1974
Persons Making Visit:	<u>NIOSH</u> DFSCI Phil Bierbaum James Jones Preston Rea Fred Wells Ralph Zumwalde DTS Howard Ludwig <u>Environmental Protection Agency</u> Larry Parker
Persons Contacted:	Art Ryrholm - Plant Manager John Carvajal - Assistant Plant Manager Bert Murray - Industrial Hygienist Bill Young - Industrial Hygienist James Copenhaver - International Association of Machinists and Aerospace Workers Local Union 598
Purpose of Visit:	To conduct an industrial hygiene survey of vinyl chloride polymerization operations.

INTRODUCTION

The National Institute for Occupational Safety and Health has underway an industrywide study of the vinyl chloride (VC) industry. As part of this study industrial hygiene surveys are being conducted to determine "typical" VC exposures at plants using each of the four production processes for making polyvinyl chloride (PVC).

As a result of information obtained during a preliminary visit to the plant March 19, 1974 by James Jones, it was decided to conduct an industrial hygiene survey at the plant. The reasons for selecting the plant were age and the types of processes used. On June 10, 1974 an initial meeting and a plant tour were attended by Phil Bierbaum, James Jones, Howard Ludwig, Preston Rea, Fred Wells and Ralph Zumwalde. Mr. Larry Parker of the EPA was also present. Sampling was then conducted June 11-19 by Messrs. Jones, Ludwig, Rea, Wells and Zumwalde.

During this visit, approximately 380 air samples were taken for evaluation of vinyl chloride exposures. In addition samples were taken to evaluate exposure to trichloroethylene and polyvinyl chloride dust. Noise and ventilation measurements also were made in selected areas.

On October 23, 1974, Messrs. Jones and Zumwalde revisited the plant to take additional polyvinyl chloride dust samples and to obtain additional process information.

DESCRIPTION OF THE FACILITY

The South Charleston plant is a large chemical producer with a wide variety of products. A listing of the major products is included as Attachment 1. In addition to these products a large number of custom produced specialty chemicals are manufactured here. The majority of the process equipment is located on an island in the Kanawha River with bulk storage tank facilities located on the north bank of the river. Materials stored in these tanks are piped under the river to the island. Service facilities, administrative offices, warehouses and some manufacturing operations are located on the south side of the river.

Our interest was in the polyvinyl chloride production operations and these were the only areas surveyed. At present VC is being used in three separate processes at this plant to make PVC; a solvent process, an emulsion process and a "Dynel" resin process.

The entire workforce of this plant is approximately 1800 persons with 150 of them involved in PVC operations. The PVC production areas generally run 3 shifts a day, 7 days a week. Production workers are members of Local 598 of the International Association of Machinists and Aerospace Workers.

HISTORY OF PVC OPERATIONS

The first commercially produced PVC made in the United States was produced in 1929 at the South Charleston plant, VC was also produced here beginning in 1928 by the caustic hydrolysis process. The original PVC process was a solvent process using heptane as the solvent. In 1933 they began making PVC copolymers and in 1936 changed solvents from heptane to ketones. In 1941 production of both emulsion and bulk process resins began. Also a fire destroyed the solvent process area which was rebuilt only to be damaged by another fire in 1943. Again it was rebuilt. During the period of 1942, VC production was changed from a caustic hydrolysis to an ethylene dichloride pyrolysis process. In 1947, Dynel resin production was begun. In 1949, bulk process operations were moved to Union Carbide's Texas City, Texas plant and suspension process operations took its place. Suspension process operations were also switched to Texas City in 1960. VC production was halted at the plant in 1968 and now all monomer is purchased from Dow Chemical.

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

This facility has an in plant dispensary with a full time Medical Director and an assistant. Nurses are on duty 24 hours a day. A pre-employment physical examination is required with re-examination every 1 to 2 years depending on age and department.

The safety department consists of a director and an assistant. There is also a person assigned to a respiratory protection program. Each production department has its own safety committee, which reviews safety practices, in addition to a central safety committee and a union safety committee.

Industrial hygiene matters are handled by the environmental protection group. They have 2 industrial hygienists and a technician plus men to take care of solid waste, water and air pollution. Industrial hygiene surveys for various hazards are conducted on a routine basis.

This plant also has a full time fire department which also handles rescue work. There is also a rescue squad made up of lab personnel trained in first aid.

DESCRIPTION OF THE PROCESSES

Solvent Process

This process is unique in the United States. The polymerization is carried out in an organic solvent in which both the reactants and products are soluble and the process is continuous. VC is pumped as a liquid under pressure to a reactor along with the solvent and catalyst. After the polymerization has reached the desired completion the solution is transferred to a stripping column where excess VC is removed and then recovered. The PVC is next precipitated, separated from solution in a centrifuge, washed, dried, screened and then packaged.

Dynel Process

This process is essentially an emulsion polymerization of VC and acrylonitrile. Fresh and recovered VC is batch mixed in closed tanks with acrylonitrile and the mix fed continuously to semi-batch stirred-tank type autoclaves, where the monomer is converted to polymer by a free-radical aqueous polymerization process. The reacted latex is then batch transferred to a set of parallel stripping tanks where unreacted VC is stripped from the latex and recovered. The stripped emulsion is batch-transferred to a pressurized storage tank and then fed continuously to two parallel resin recovery systems. In each system the emulsion is continuously coagulated to a paste, the paste diluted and heat hardened in a secondary tank at elavated temperature and pressure, and then flashed to atmospheric pressure. Resin in the slurry is continuously separated in a centrifuge and fed to a flash drying system. Dry powdered resin is collected from the cyclones in the drying system, blended, and packaged in either 50 pound bags or large cylindrical bins.

Dispersion Process

This process is an emulsion polymerization of VC and sometimes vinyl acetate. Fresh and recovered VC is batch mixed in a premix vessel with water, surfactants, and organic peroxide catalysts until a dispersion is formed. This dispersion is then fed to stirred-tank autoclaves, where the monomer is converted to polymer. When the polymerization is complete, the unreacted VC is stripped off and recovered. The PVC latex is then transferred to a large blend tank. When the blend tank is full, the latex is then fed to a spray dryer where the water is removed. The dryed resin is then fed through a rotary mill to a packaging bin and subsequently packaged in 40 pound bags.

INSPECTION OF PLANT

Potential Health Hazards

Potential health hazards observed during this survey were as follows:

1) respiratory exposure to vinyl chloride.
2) respiratory exposure to polyvinyl chloride dust in bagging operations.
3) respiratory exposure to acrylonitrile in Dynel resin area.

4) respiratory exposure to acetone in solvent resin area.
5) high noise exposures in various production areas.

Ventilation

General mechnical ventilation is provided by centrifugal fans in the solvent production area with air movement of approximately 15 air changes per hour. The other 2 production areas are outdoor operations.

The bagging stations are equipped with local exhaust ventilation with the air exhausting through a baghouse. Initial ventilation measurements on the dispersion bagging stations showed a capture velocity of only 200 to 300 feet per minute (fpm). The following week after the bags were cleaned, measurements were again made and showed capture velocities of 900 to 1300 fpm.

Housekeeping

Housekeeping in the plant appeared to be adequate in most areas.

SURVEY PROCEDURES

General

Air samples were collected in this plant for evaluating exposure to vinyl chloride, polyvinyl chloride dust and trichloroethylene. A noise survey was also conducted. The following paragraphs describe the method used to collect and analyze the air samples and take noise measurements.

Vinyl Chloride

Both personal and general area samples for vinyl chloride were collected in the PVC production areas using charcoal adsorption tubes. Area samples were collected mainly in control rooms or at operator's desks. Personal samples were collected on workers only when they left the control room. The samples were taken with Sipin SP-1 pumps at a flow rate of approximately 50 ml per minute for a maximum of 20 minutes. Standard Mine Safety Appliance (MSA) charcoal tubes were used. At the end of each day, all samples collected that day were packed in dry ice and shipped air mail to the NIOSH laboratory in Salt Lake City, Utah. There the samples were desorbed with carbon disulfide and analyzed by gas chromatography. Due to the large number of samples collected and the question of how long samples could be stored without VC migrating to backup sections, samples for the same man on the same day were combined for analysis. This necessitated far fewer analyses and enabled all samples to be analyzed within two weeks. Unfortunately, this method of combining samples masks any peak exposures that may occur.

Union Carbide personnel were also sampled for VC during our survey. Their sampling and analytical method is included as Attachment 2. It is also a charcoal tube adsorption method with GC analysis. A summary of the Union Carbide sampling results, both those taken during the survey and past sampling is shown in Tables 4, 5 and 6.

Trichloroethylene

Trichloroethylene area samples were taken using a Sipin SP-1 pump and MSA charcoal tubes. A flow rate of approximately 50 ml/min for 3-1/2 hours was used, and the sample was analyzed by gas chromatography at NIOSH's Salt Lake City, Utah lab.

Polyvinyl Chloride Dust

Personal samples for airborne PVC dust were collected in the bagging areas. These were total dust weight samples taken for approximately 3-1/2 hours at a flow rate of 2 liters per minute.

All samples were collected on 37mm diameter MSA polyvinyl chloride membrane filters with a 5μm pore size. Three piece Millipore filter holders were used with holder face in place but with the small plug removed (leaving a 4 mm diameter opening). An MSA Model G portable air sampling pump was used to pull air through the filter. All filters were tared and re-weighed on the 20 milligram "A" scale of a Cahn Gram Electrobalance.

Noise

In addition to air sampling, noise measurements were made in production areas. A General Radio Type 1565-A sound level meter calibrated with a Type 1562-A calibrator was used for all measurements. The meter response was set on the slow position and measurements made on the "A" weighting network.

RESULTS AND DISCUSSION

Vinyl Chloride Samples

Solvent Process - Results of each sample are given in Table 1 and are summarized in Table 4. The lowest personal VC concentration observed was none detected (ND) and the highest was 77.0 parts per million (ppm). Mean personal VC concentrations for the three shifts sampled ranged from 0.6 ppm to 8.1 ppm for solvent process workers.

Results of area sampling, done primarily in control rooms where workers spent a great deal of time, ranged from 0.2 ppm to 7.1 ppm. Mean area VC concentrations ranged from 0.7 ppm to 6.8 ppm.

Both the highest area and personal sample means occurring at the still operator's work location. He works in a building in which the stripping columns for the removal of excess VC are located. The B Autoclave Operator also has a high potential exposure when he draws quality control samples. But since he wears an air supplied respirator during this operation it was not included in his mean exposure.

Dynel Process - Results of each sample are given in Table 2 and are summarized in Table 5. The lowest personal VC concentration observed was ND and the highest was 4.2 ppm. Mean personal VC concentrations ranged from 0.2 ppm to 2.7 ppm.

Results of area sampling, done in the control room ranged from ND to 2.4 ppm with a mean concentration of 1.4 ppm.

Dispersion Process - Results of each sample are given in Table 3 and are summarized in Table 6. The lowest personal VC concentration observed was 0.1 ppm and the highest was 82.8 ppm. Mean personal VC concentrations ranged from 3.0 ppm to 43.7 ppm.

The dryer operator had the highest mean VC concentration. This was because his work location was in the same room with the VC compressors. These compressors developed leaks frequently and increased the dryer operator's exposure significantly. The utility operator, utility fitter and the laborer have potential for high exposure when they perform such operations as opening valves and autoclaves, cleaning filters and cleaning autoclaves. Each of these operations requires the use of an air supplied respirator. Prior to the institution of this procedure these workers would have been exposed to high levels of VC.

Results of area sampling, done in the control room, ranged from 1.2 ppm to 11.7 ppm with a mean concentration of 7.4 ppm.

Trichloroethylene

Two area samples for trichloroethylene were taken in the dispersion process. They were combined for analysis. A concentration of 1.2 ppm was found

Workers were not routinely exposed to trichloroethylene and this concentration is considerably below the OSHA standard of 100 ppm.

Polyvinyl Chloride Dust

Dust samples taken during the initial visit were unusable because of a mixup in the filters and cassettes used. They were old pre-weighed cassettes and we discovered that the tare weights for these filters were no longer available. Results of personal samples taken during the subsequent visit on October 23 are listed in Table 7. They ranged from 0.40 mg/m^3 to 15.27 mg/m^3.

The concentrations were consistently around 1 mg/m^3 except for the personal sample taken on the dispersion resin bagger. Dispersion resin is of a very small particle size (1-10 micron diameter) which are readily inhaled and make dust control difficult.

Noise Measurements

Solvent Area

Noise levels in Building 152 ranged from 68 dBA to 99 dBA. Areas with noise levels over 90 dBA were designated "noise areas" with required hearing protection. Building 153 noise levels ranged from 74 dBA to 76 dBA, Building 154 from 76 dBA to 86 dBA and Building 177 from 62 dBA to 91 dBA.

Dynel Area

Noise levels in this area varied from 65 dBA to 94 dBA. Again areas with levels over 90 dBA were "noise areas".

Dispersion Area

Noise levels in the dispersion area ranged from 60 dBA to 110 dBA. The highest levels were found in the mill room which was enclosed and required hearing protection to enter. Overall, high noise levels were either in areas that required hearing protection or areas where personnel spent little time.

CONCLUSIONS AND RECOMMENDATIONS

The sample results obtained during this survey were comparable to results obtained by Union Carbide (UC). The major differences were that the UC peak values were generally higher and average concentrations for certain job catagories were higher than the NIOSH results. The probable reason for the difference in peak concentrations was the fact that the NIOSH samples were combined for analysis. This would tend to average out any peaks. Also combining samples made it impossible to statistically compare NIOSH and Union Carbide results. For these reasons it is recommended that this procedure not be continued. The job catagories where major differences were noted were primarily types of jobs where exposure would be expected to be quite variable. The UC results for these jobs include more samples taken over a longer time frame, so that a larger percentage of the job activities would be covered.

The dispersion resin area showed higher VC exposure than the other areas. This was probably somewhat due to the higher production output with a commensurate amount of piping and reactors from which fugitive emissions emanate. The solvent process which had low concentrations of VC keeps the VC in solution which helps to lower VC emissions.

VC concentrations for the most part would not meet the OSHA standard of 1 ppm TWA.* The solvent and Dynel area VC concentrations were low enough that with enclosed control rooms with separate clean air supplies these TWA levels could be brought down. Again in the dispersion resin area lower VC levels in the control rooms would go a long way toward reducing exposures, especially to the dryer operator. Recommendations of this nature were made at the time of the survey and UC already was working on plans to accomplish this. At the time of the second visit in October these goals were partially accomplished. The dispersion area dryer operator's work area had been enclosed and air conditioned. This had succeeded in lowering the VC exposure considerably.

Further sampling being done to comply with OSHA requirements should show whether new control measures instituted were effective.

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*It should be noted that, at the time of the survey, the OSHA temporary/emergency standard was 50 ppm peak concentration.

TABLE 1

SOLVENT RESIN AREA VINYL CHLORIDE SAMPLE RESULTS

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
1.	Area	6-15-74	Day	Bldg 152 - 3rd Floor Control Rm	3	2.6
2.	Area	6-19-74	Day	Bldg 152 - 3rd Floor Control Rm	5	0.3
3.	Area	6-19-74	Evening	Bldg 152 - 3rd Floor Control Rm	4	0.3
4.	Area	6-15-74	Day	Bldg 152 - 4th Floor Control Rm	2	1.5
5.	Area	6-19-74	Day	Bldg 152 - 4th Floor Control Rm	6	0.4
6.	Area	6-19-74	Evening	Bldg 152 - 4th Floor Control Rm	4	0.2
7.	Area	6-19-74	Day	Bldg 153	3	1.9
8.	Area	6-19-74	Evening	Bldg 153	3	1.3
9.	Area	6-19-74	Day	Bldg 154 - 3rd Floor	3	7.1
10.	Area	6-19-74	Evening	Bldg 154 - 3rd Floor	2	6.5
11.	Area	6-19-74	Day	Bldg 177 - 5th Floor	5	2.3
12.	Area	6-19-74	Evening	Bldg 177 - 5th Floor	4	0.9
13.	Personal	6-15-74	Day	B Autoclave Operator	2	ND
14.	Personal	6-15-74	Day	B Autoclave Operator (Resp. On)	1	77.0
15.	Personal	6-19-74	Day	B Autoclave Operator	4	2.6
16.	Personal	6-19-74	Evening	B Autoclave Operator	4	1.2

TABLE 1 (CONT'D)

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
17.	Personal	6-19-74	Day	Weighmaster	5	0.6
18.	Personal	6-19-74	Day	Weighmaster	5	1.1
19.	Personal	6-19-74	Day	Weighmaster	5	ND
20.	Personal	6-19-74	Day	Weighmaster	5	0.9
21.	Personal	6-19-74	Evening	Weighmaster	4	1.0
22.	Personal	6-19-74	Evening	Weighmaster	4	ND
23.	Personal	6-15-74	Day	Dispersator Operator	3	1.6
24.	Personal	6-15-74	Day	Dispersator Operator	1	5.4
25.	Personal	6-19-74	Day	Dispersator Operator	6	0.7
26.	Personal	6-19-74	Evening	Dispersator Operator	4	0.2
27.	Personal	6-15-74	Day	Flash Dryer Operator	3	2.4
28.	Personal	6-15-74	Day	Flash Dryer Operator	1	ND
29.	Personal	6-19-74	Day	Flash Dryer Operator	7	3.7
30.	Personal	6-19-74	Evening	Flash Dryer Operator	4	0.4
31.	Personal	6-15-74	Day	Varnish Blending Operator	1	ND
32.	Personal	6-15-74	Day	Varnish Blending Operator	1	2.9
33.	Personal	6-15-74	Day	Varnish Blending Operator	1	5.4
34.	Personal	6-19-74	Day	Varnish Blending Operator	7	0.9

TABLE 1 (CONT'D)

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
35.	Personal	6-19-74	Evening	Varnish Blending Operator	4	0.7
36.	Personal	6-15-74	Day	Operations Mechanic	1	1.3
37.	Personal	6-15-74	Day	Operations Mechanic	1	ND
38.	Personal	6-19-74	Day	Relief Operator	5	9.4
39.	Personal	6-15-74	Day	Truck Driver	3	2.3
40.	Personal	6-15-74	Day	Still Operator	3	5.4
41.	Personal	6-19-74	Day	Still Operator	4	11.1
42.	Personal	6-19-74	Evening	Still Operator	4	7.8
43.	Personal	6-15-74	Day	Transfer Operator	1	ND
44.	Personal	6-15-74	Day	Transfer Operator	2	ND
45.	Personal	6-19-74	Evening	Transfer Operator	4	8.8

TABLE 2

DYNEL RESIN AREA VINYL CHLORIDE SAMPLE RESULTS

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
1.	Area	6-18-74	Day	Bldg 209 - 1st Floor	3	1.4
2.	Area	6-13-74	Day	Bldg 209 - 2nd Floor Control Rm	3	ND
3.	Area	6-14-74	Day	Bldg 209 - 2nd Floor Control Rm	5	2.0
4.	Area	6-14-74	Day	Bldg 209 - 2nd Floor Control Rm	5	2.4
5.	Area	6-17-74	Day	Bldg 209 - 2nd Floor Control Rm	6	1.9
6.	Area	6-17-74	Day	Bldg 209 - 2nd Floor Control Rm	6	0.8
7.	Area	6-18-74	Day	Bldg 209 - 2nd Floor Control Rm	5	1.1
8.	Personal	6-13-74	Day	Production Supervisor	2	0.1
9.	Personal	6-14-74	Day	Production Supervisor	3	0.4
10.	Personal	6-13-74	Day	Autoclave Operator	1	4.0
11.	Personal	6-14-74	Day	Autoclave Operator	5	1.2
12.	Personal	6-17-74	Day	Autoclave Operator	4	1.6
13.	Personal	6-18-74	Day	Autoclave Operator	3	3.9
14.	Personal	6-13-74	Day	#1 Recovery Operator	2	2.4
15.	Personal	6-17-74	Day	#1 Recovery Operator	2	3.5
16.	Personal	6-17-74	Day	#1 Recovery Operator	3	ND

TABLE 2 (CONT'D)

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
17.	Personal	6-18-74	Day	#1 Recovery Operator	3	0.4
18.	Personal	6-13-74	Day	#2 Recovery Operator	2	<0.1
19.	Personal	6-14-74	Day	#2 Recovery Operator	1	4.2
20.	Personal	6-14-74	Day	#2 Recovery Operator	1	ND
21.	Personal	6-14-74	Day	#2 Recovery Operator	1	2.6
22.	Personal	6-14-74	Day	#2 Recovery Operator	1	3.0
23.	Personal	6-14-74	Day	#2 Recovery Operator	1	ND
24.	Personal	6-17-74	Day	#2 Recovery Operator	2	0.3
25.	Personal	6-17-74	Day	#2 Recovery Operator	5	ND
26.	Personal	6-13-74	Day	Utility Operator	2	0.1
27.	Personal	6-13-74	Day	Utility Operator	1	2.6
28.	Personal	6-14-74	Day	Utility Operator	1	ND
29.	Personal	6-14-74	Day	Utility Operator	1	ND
30.	Personal	6-14-74	Day	Utility Operator	1	2.7
31.	Personal	6-14-74	Day	Utility Operator	1	2.1
32.	Personal	6-17-74	Day	Utility Operator	4	1.2
33.	Personal	6-18-74	Day	Utility Operator	4	2.3
34.	Personal	6-13-74	Day	Insulator	2	0.2
35.	Personal	6-18-74	Day	Weighmaster	4	2.3

TABLE 3

DISPERSION RESIN AREA VINYL CHLORIDE SAMPLE RESULTS

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
1.	Area	6-11-74	Day	Bldg 190 - Control Room	5	11.1
2.	Area	6-12-74	Day	Bldg 190 - Control Room	4	5.6
3.	Area	6-13-74	Day	Bldg 190 - Control Room	6	11.7
4.	Area	6-18-74	Day	Bldg 190 - Control Room	4	1.2
5.	Personal	6-11-74	Day	Unit Foreman	2	3.6
6.	Personal	6-12-74	Day	Unit Foreman	1	22.0
7.	Personal	6-13-74	Day	Unit Foreman	2	0.3
8.	Personal	6-11-74	Day	Board Operator	1	5.3
9.	Personal	6-12-74	Day	Board Operator	4	6.2
10.	Personal	6-13-74	Day	Board Operator	5	22.9
11.	Personal	6-18-74	Day	Board Operator	2	9.4
12.	Personal	6-11-74	Day	Charge Operator	2	9.3
13.	Personal	6-12-74	Day	Charge Operator	4	15.1
14.	Personal	6-13-74	Day	Charge Operator	1	10.2
15.	Personal	6-18-74	Day	Charge Operator	3	29.8
16.	Personal	6-11-74	Day	Transfer Operator	2	12.9
17.	Personal	6-12-74	Day	Transfer Operator	3	7.6

TABLE 3 (CONT'D)

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
18.	Personal	6-13-74	Day	Transfer Operator	1	4.4
19.	Personal	6-12-74	Day	Dryer Operator	4	82.8
20.	Personal	6-13-74	Day	Dryer Operator	4	5.2
21.	Personal	6-11-74	Day	Utility Operator	2	29.4
22.	Personal	6-12-74	Day	Utility Operator	4	1.5
23.	Personal	6-13-74	Day	Utility Operator	2	0.1
24.	Personal	6-11-74	Day	Utility Fitter	3	19.2
25	Personal	6-11-74	Day	Utility Fitter	3	3.6
26.	Personal	6-11-74	Day	Utility Fitter	3	3.6
27.	Personal	6-12-74	Day	Utility Fitter	2	11.0
28.	Personal	6-12-74	Day	Utility Fitter	2	11.4
29.	Personal	6-13-74	Day	Utility Fitter	3	0.9
30.	Personal	6-13-74	Day	Utility Fitter	1	77.0
31.	Personal	6-18-74	Day	Utility Fitter	1	17.0
32.	Personal	6-18-74	Day	Utility Fitter	1	6.1
33.	Personal	6-11-74	Day	Weighmaster	7	9.6
34.	Personal	6-12-74	Day	Weighmaster	4	1.3
35.	Personal	-12-74	Day	Weighmaster	4	1.4

TABLE 3 (CONT'D)

	Types of Sample	Day	Shift	Location or Job Title	No. of Tubes Combined	V.C. Concentration ppm
36.	Personal	6-13-74	Day	Weighmaster	4	0.1
37.	Personal	6-13-74	Day	Weighmaster	4	2.6
38.	Personal	6-18-74	Day	Weighmaster	2	2.9
39.	Personal	6-11-74	Day	Laborer	2	6.6
40.	Personal	6-12-74	Day	Laborer	4	13.4
41.	Personal	6-13-74	Day	Laborer	4	0.7

TABLE 4

SOLVENT RESIN AREA VINYL CHLORIDE SAMPLING SUMMARY

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range		Percent of Time on Job	8 Hr. TWA ppm
			Low	High		
NIOSH Bldg 152 - 3rd Floor Control Rm	1.1	1.3	0.3	2.6		
UC	<1		<1	1		
NIOSH Bldg 152 - 4th Floor Control Rm	0.7	0.7	0.2	1.5		
UC	1	0.7	<1	2		
NIOSH Bldg 153	1.6	0.4	1.3	1.9		
UC	—	—	—	—		
NIOSH Bldg 154 - 3rd Floor	6.8	0.4	6.5	7.1		
UC	2	1.8	<1	3		
NIOSH Bldg 177 - 5th Floor	1.6	1.0	0.9	2.3		
UC	—	—	—	—		
NIOSH B Autoclave Operator	1.9	1.0	ND	77	20	1.7
UC	19	21.8	<1	79		
NIOSH Weighmaster	0.6	0.5	ND	1.1	65	1.0
UC	<1	—	<1	<1		
NIOSH Dispersator Operator	2.0	2.4	0.2	5.4	45	1.5
UC	2	1.2	1	5		

TABLE 4 (CONT'D)

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range Low	Range High	Percent of Time on Job	8 Hr. TWA ppm
NIOSH Flash Dryer Operator	1.6	1.7	ND	3.7	20	0.7
UC	2	1.8	<1	4		
NIOSH Varnish Blending Operator	2.0	2.2	ND	5.4	30	1.4
UC	9	4.7	4	15		
NIOSH Operations Mechanic	0.6	0.9	ND	1.3		
UC	42	51.6	5	78		
NIOSH Relief Operator	9.4	—	—	—		
UC	10	8.8	<1	25		
NIOSH Truck Driver	2.3					
UC	4					
NIOSH Still Operator	8.1	2.9	5.4	11.1	100	8.1
UC	<1		<1	<1		
NIOSH Transfer Operator	2.9	5.1	ND	8.8	50	2.2
UC	<1					

TABLE 5

DYNEL RESIN AREA VINYL CHLORIDE SAMPLING SUMMARY

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range Low	Range High	Percent of Time on Job	8 Hr. TWA ppm
NIOSH Bldg 209 - 1st Floor	1.4	—	—	—		
UC	1	—	—	—		
NIOSH Bldg 209 - 2nd Floor Control Rm	1.4	0.8	ND	2.4		
UC	2	1.4	<1	4		
NIOSH Production Supervisor	0.2	0.2	0.1	0.4	100	0.2
UC	—	—	—	—		
NIOSH Rigger	—	—	—	—		
UC	82	—	—	—		
NIOSH Pipe Fitter	—	—	—	—		
UC	23	22.7	4	48		
NIOSH Insulator	0.2	—	—	—		
UC	2	—	—	—		
NIOSH Utility Operator	1.4	1.2	ND	2.7	15	1.4
UC	18	36.9	<1	115		
NIOSH No. 2 Recovery Operator	1.3	1.7	ND	4.2	10	1.4
UC	2	1.6	<1	6		

TABLE 5 (CONT'D)

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range		Percent of Time on Job	8 Hr. TWA ppm
			Low	High		
NIOSH No. 1 Recovery Operator	1.6	1.7	ND	3.5	10	1.4
UC	2	1.2	<1	4		
NIOSH Autoclave Operator	2.7	1.5	0.1	4.0	10	1.5
UC	14	13.4	<1	43		
NIOSH Weighmaster	2.3	—	—	—		
UC	—	—	—	—		

TABLE 6

DISPERSION RESIN AREA VINYL CHLORIDE SAMPLING SUMMARY

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range Low	Range High	Percent of Time on Job	8 Hr. TWA ppm
NIOSH Bldg 190 Control Room	7.4	5.0	1.2	11.7		
UC	7	4.0	2	12		
NIOSH Utility Fitter	16.6	23.5	0.9	77.0	50	12.1
UC	91	160.0	<1	803		
NIOSH Weighmaster	3.0	3.4	0.1	9.6	100	3.0
UC	16	11.8	<1	35		
NIOSH Charging Operator	16.1	9.5	9.3	29.8	25	9.6
UC	13	13.5	<1	39		
NIOSH Operations Mechanic	—	—	—	—		
UC	10	6.6	3	18		
NIOSH Operations Foreman	8.6	11.7	0.3	22.0	100	8.6
UC	8	0.0	8	8		
NIOSH Transfer Operator	8.3	4.3	4.4	12.9	25	7.6
UC	14	18.2	2	62		
NIOSH Dryer Operator	43.7	54.0	5.2	82.8	100	43.7
UC	39	72.5	<1	357		

TABLE 6 (CONT'D)

Location or Job Title	Mean Concentration ppm	Standard Deviation	Range		Percent of Time on Job	8 Hr. TWA ppm
			Low	High		
NIOSH Board Operator	11.0	8.2	5.3	22.9	10	7.8
UC	16	25.9	2	88		
NIOSH Utility Operator	10.3	16.5	0.1	29.4	20	8.0
UC	24	25.2	2	71		
NIOSH Laborer	6.9	6.4	0.7	13.4	50	7.2
UC	47	54.4	4	203		

TABLE 7

POLYVINYL CHLORIDE DUST SAMPLING RESULTS

Date	Location	Job	Dust Concentration mg/m^3
10-23-74	Bldg. 190	Area Sample in Middle of Bagging Line	1.02
10-23-74	Bldg. 190	Fork Truck Operator in Bagging Area	0.82
10-23-74	Bldg. 190	Weighmaster Operating Middle Bagger	15.27
10-23-74	Bldg. 177	Weighmaster	1.62
10-23-74	Bldg. 177	Weighmaster	.40

ATTACHMENT 1

List of Major Chemicals Produced in South Charleston Plant, UCC Chemicals and Plastics

2 Ethyl hexaldehyde
Methyl amyl alcohol
Diacetone alcohol
Mesityl oxide
Propylene glycol
Hexylene glycol
Di propylamine
Misc. specialty amines and glycol ethers
Morpholine
Pentanedione
Vinyl ethyl ether
Propionic acid
Valeric acid
2 Ethyl butyric acid
2 Ethyl hexoic acid
Ethyl acetate
Butyl CELLOSOLVE acetate
Butyl acetate
Glycol diacetate
Glyceryl triacetate
FLEXOL plasticizer 3GH
2 Ethyl hexyl tallate
Hexylene glycol diacetate
NIAX catalyst A-99
NIAX polyols (most of UCC product line)
Butyl chloride
UCON lubricants (most of UCC product line)
Fiber resin NYGS-2
Dynel fiber
Solvent vinyl resins (VAGD, VAGH, VYHD, VYHG)
Dispersion vinyl resins (QYOH, QYKV, QYNV, QYJV)

ATTACHMENT 2

ENVIRONMENTAL HEALTH LABORATORY
RESEARCH AND DEVELOPMENT DEPARTMENT
UNION CARBIDE CORPORATION, SOUTH CHARLESTON, W. VA.

VINYL CHLORIDE

DETERMINATION IN AIR BY ADSORPTION ON ACTIVATED CHARCOAL AND ANALYSIS BY GAS CHROMATOGRAPHY

1 PURPOSE AND LIMITATIONS This paper describes a procedure for measuring the exposure of personnel to vinyl chloride in the working environment. The method describes the preparation of standards which will determine vinyl chloride in the range of 9 to 90 parts per million by volume in air, based on a 4-hour sample at a flow rate of 28 ml per minute. Lower or higher ppm ranges can be determined by preparing additional standards to cover the range desired. (Vinyl chloride can be determined to at least 0.05 ppm by volume in air by this procedure, using more dilute standards.)

2 PRINCIPLE The sample is collected by passing air through a glass tube containing activated charcoal which adsorbs any vinyl chloride vapors present. The vinyl chloride is then desorbed from the charcoal by carbon disulfide extraction and analyzed by gas chromatography.

3 INSTRUMENT PARAMETERS

Chromatograph	AID (Analytical Instrument Development, Inc.) Portable Chromatograph, Model 511, or equivalent chromatograph, with flame ionization detector.
Column	Six-foot x 1/8-inch stainless steel packed with 10% di(2-ethylhexyl) sebacate on Chromasorb P, 80/100 mesh, NAW.
*Column temperature	100°C isothermal
Injection temperature	100°C
Detector	flame ionization detector
Carrier	helium or nitrogen
Hydrogen flow rate	23 cc per minute
Air flow rate	133 cc per minute
Sample size	2 µl solvent flush technique
Retention time	0.5 minute (adjust carrier flow until vinyl chloride elutes at this time)

*Note: If this column is used in a conventional chromatograph, better separation of vinyl chloride from other light boiling impurities will be obtained by operation of the column oven near ambient temperature ≅30°C. The AID portable chromatograph cannot be used at ambient temperature without modification since the heat from the flame ionization detector will cause the temperature in the column oven to rise to 60 to 70°C.

Alternate Column - Better Resolution

Instrument	Hewlett-Packard 5750 gas chromatograph - dual column, or equivalent.
Column	25-foot x 1/8 inch stainless steel packed with 25% by weight 75% CO880/25% Tergitol E-35 on 40/60 mesh rescreened Chromosorb P.
Detector	flame ionization
Column temperature	40° to 100°C at 4°C per minute
Detector temperature	125°C
Injector temperature	125°C
Carrier gas	helium, 30 ml per minute
Air flow	350 ml per minute
Hydrogen flow	30 ml per minute
Sample size	10 µl
Approximate elution time	6.5 minutes

4 REAGENTS AND APPARATUS

a) Personal sampling pump. MSA Model G or Bendix Micronair. Insert an in-line orifice made from a cut-off and restricted (pinched) hypodermic needle in the sampling line to the pump in order to obtain a 28 cc per minute flow on these pumps.

b) Hypo-vials, 15-ml size, Cat. No. 12911; Neoprene septa, Cat. No. 13233; alumina seals, Cat. No. 13214; and hand crimper, Cat. No. 13212, Pierce Chemical Company, Rockford, Illinois.

c) Carbon disulfide, spectrophotometric grade

d) Activated charcoal, Cat. No. 580-26, Barnebey-Cheney, Columbus, Ohio

e) Soap film flow meter, 10-ml size

f) Stop watch

5 PREPARATION OF THE ACTIVATED CARBON ADSORPTION TUBE

a) Prepare the activated charcoal by placing the charcoal on a 40-mesh sieve and wash with demineralized water until no visible fines appear in the washings.

b) Dry the carbon in a drying oven at 110°C until dry and free flowing (overnight). Store in a screw-top, glass bottle until needed.

c) Cut 8-mm O.D. x 6-mm I.D. Pyrex glass tubing into 6-inch lengths and fire polish the ends.

d) Insert a Pyrex glass wool plug two-thirds of the distance into the glass tubes. The longer section of tubing will be designated as the primary end, while the shorter side of the tubing is the back-up end.

e) Pack the tubes with the activated carbon, using a length of 60 mm in the primary section and 35 mm in the back-up section. Retain the carbon with glass wool plugs.

f) Seal the tubes with a red rubber septum or parafilm until ready for use.

6 SAMPLING PROCEDURE

a) Remove the seals from the charcoal tube and attached the back-up section to a portable pump by means of a length of 1/4-inch Tygon tubing.
b) Set the flow rate at 28 ml per minute through the tube with a calibrated rotameter. (NOTE: The 10-ml soap bubble flow meter can be used to obtain a more precise reading of the air flow through the tube if desired).
c) Record the time the air sampling was started and the time when the sampling is completed. A four-hour sample may be taken with this system.
d) After sampling, recheck the flow rate and reseal the ends of the charcoal tube. Return the tube to the laboratory for analysis.
e) Record the temperature and barometric pressure at the sampling site.

7 ANALYTICAL PROCEDURE

a) Make a small hook at the end of a piece of wire and remove the glass wool plug from the primary end of the charcoal tube. Make sure that no charcoal particles adhere to the glass wool plug.
b) Pour the charcoal into a 10-ml glass-stoppered volumetric flask and cool the flask and carbon in a wet-ice bath.
c) Pipet 3 ml of carbon disulfide (CS_2) into the cooled flask and stopper securely. (CAUTION: Carbon disulfide is toxic and should be handled under a hood.)
d) Agitate the flask periodically for at least 30 minutes.
e) Solvent Flush Injection Technique. This injection technique is designed to eliminate difficulties arising from blow-back or distillation with the needle of the microliter syringe.
f) Flush a 10-µl syringe with CS_2 several times to wet the barrel and plunger.
g) Draw 2 µl of CS_2 into the syringe and remove the tip of the needle from the solvent. Withdraw the plunger an additional 0.5 µl to separate the CS_2 from the sample with a pocket of air.
h) Dip the needle into the sample solution in the volumetric flask and withdraw the plunger until the air bubble between the solvent and the sample has passed the 2-µl mark on the syringe.
i) Remove the tip of the needle from the sample solution and adjust the volume in the syringe until the meniscus of the air bubble rests on the 2-µl mark. Remove the excess sample solution from the tip of the needle.
j) Pull the plunger back an additional 0.5 µl to prevent the sample solution from evaporating from the tip of the needle.
k) Inject the entire contents of the syringe into the chromatograph.
l) Measure the peak height and determine the vinyl chloride content from a previously prepared calibration curve.

8 CALIBRATION CURVE

a) Pipet 10 ml of carbon disulfide (CS_2) into each of five 15-ml hypo-vials. Cap the vials with the Neoprene septa and aluminum seals, using the hand crimper.

b) Place the hypo-vials in wet ice to reduce the vapor pressure of CS_2.

c) Cap one of the valves on a steel sample cylinder containing vinyl chloride with a 1/8-inch Swagelok tubing nut which has a chromatographic septum installed in the nut.

d) Insert a hypodermic needle through the septum on the cylinder, open the valve and allow the vinyl chloride to vent through the needle for about 10 seconds to purge the air from the system. Remove the needle.

e) Using the appropriate gas-tight syringe fitted with a number 27 gauge hypodermic needle, insert the needle through the septum on the cylinder and allow the pressure of the vinyl chloride to displace the volume of the syringe. Flush the syringe two times to remove any air which may have been trapped in the needle.

f) Into the respective hypo-vials, inject 0.2, 0.3, 0.5, 1.0, and 2.0 cc of vinyl chloride from the syringe.

g) Shake the hypo-vials for one minute to put the vinyl chloride in solution. These standards will contain 56, 82, 133, 260, 515 µgm of vinyl chloride per ml. (NOTE: These calculations are corrected for the dead space in the gas syringe needle. The cold CS_2 solutions in the hypo-vials are under slight negative pressure. Measurements have shown that the dead space in the syringe needle amounts to 0.04 cc, and 0.02 cc of this volume is pulled into the hypo-vial by the negative pressure.)

h) Allow the standards to warm up to room temperature, then inject these standards into the chromatograph using the procedure described in Section 7, paragraphs e through k. Shake the hypo-vials each time just prior to withdrawing a sample.

i) Plot peak height versus micrograms of vinyl chloride per ml.

9 CALCULATION

$$\frac{A \times 3 \times 24.5}{L \times 62.5} = \text{vinyl chloride, ppm by volume at 25°C and 760 mm}$$

A = µgm per ml of vinyl chloride read from calibration curve
L = total liters of air sample (flow rate x time)