

BFG TECHNICAL DOCUMENT

BFG Goodrich

Chemical Division

RESEARCH AND DEVELOPMENT REPORT

Vinyl Chloride Monomer Concentration in
Working Environments as Related to the Residual
Vinyl Chloride Monomer Concentration in Stripped Latex Products

By
D.E. Weaver - R.E. Shaffer
P. Dmyterko

Project No. 3696-61 Report Type R&D Closure
Profit Center Latex R&D Date February 16, 1981
Copy Approval Authority E.J. Leeson/ E. J. Leeson

FULL COPY

J. C. Healy
CTF-ALTC (4)
R&D File BRDC (2)
R. J. Meyer/Int'l. (4)
E. J. Leeson
D. E. Weaver (10)
G. E. Eilbeck-R.Y. Garrett

EXECUTIVE SUMMARY ONLY*

BRECKSVILLE

R. J. Fawcett
D. E. Ley-C.H. Lufter
G. E. Thompson

CLEVELAND

J. L. Hobey-E.B. Osborne
W. C. Holbrook-R.K. Hinderer
D. H. Hall-F. J. Donat
W. C. Niederst
M. E. Roha-G.A. Lindsay

ALTC

L. B. Crider
C. E. Fleming-R.M. Kreager
R. D. Hardesty
R. L. Bowles-H.S. Haller-D.E. Farley

AKRON

J. Hughes Powell, Jr.

OTHERS

R. J. Grahek - LGCP
J. C. Meck - ALGCP

*If full copy required-request from author.

EXECUTIVE SUMMARY

OBJECTIVE

Develop technical informaion to support a business decision to remove cancer hazard labels from vinyl latex products.

SIGNIFICANT RESULTS

Test data were used to relate ambient vinyl chloride monomer (AVCM) concentrations to residual vinyl chloride monomer (RVCM) levels in stripped latex products. Worst case conditions were simulated. It was determined that exposure of workers to AVCM concentrations above the OSHA action level is unlikely in real workplace situations.

CONCLUSIONS

1. In a typical Geon 576 compounding operation the AVCM concentration is estimated to be well below the OSHA action level.
2. Under worst case conditions at Rhineland Paper Company, who use Geon 576 latex in a clear coating operation, the AVCM concentration is estimated to be well below the OSHA action level.
3. In a double coating operation at Sanitas, who use compounded Geon 580X52, the AVCM concentration is estimated to be well below the OSHA action level.
4. Personnel monitoring data by two different labs at Rhineland Paper Company confirmed that the AVCM concentration there is well below the OSHA action level.

ACTION TAKEN

E. B. Osborne, Vice President and General Manager, Latex, has issued a letter to latex customers informing them that vinyl chloride warning labels are no longer attached to vinyl latex products. No further action is needed.

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY.....	ii
Objective.....	ii
Significant Results.....	ii
Conclusions.....	ii
Action Taken.....	ii
List of Tables.....	iv
List of Figures.....	v
Summary.....	1
Discussion.....	3
I. Introduction.....	3
II. Residual Vinyl Chloride Monomer (RVCM) -- Stripped Latex Products.....	4
III. Experimental Plan.....	7
IV. Procedure - R.E. Shaffer.....	7
V. Testing-Air Sample Tubes - Peter Dmyterko.....	13
VI. Data Analysis.....	24
VII. Translation of Critical RVCM Data to Other Vinyl Latex Products.....	25
VIII. Diffusion Rate Estimate.....	28
IX. AVCM Estimate for a Typical Compounding Operation.....	33
X. Paper Coating Operation at Rhineland Paper Company.....	34
XI. Scrim Coating Operation at Sanitas.....	36
APPENDIX.....	39
List of References.....	40
Statistics and Computer Applications Report..... D.E. Farley-H.S.Haller	41
Standard Sampling Procedure No. 2800-A..... BFGoodrich Chemical Group	49
Standard Test Procedure No. 1021-A..... BFGoodrich Chemical Group	59
Vinyl Chloride in Air-Method No. P&CAM 178 NIOSH	73
Results of Area Monitoring at Rhineland Paper Co. 83 1) BFGoodrich Corporate Environmental Health Lab85 2) Wausau Insurance Company.....	87

LIST OF TABLES

	<u>Page</u>
I. Plant Data-RVCM, mg/kg - Major Products.....	6
II. Test Data: RVCM and AVCM, Closed Room Experiments.....	12
III. Gas Chromatography Conditions for the Thermal Desorption VCM Analysis.....	16
IV. Chromatography Conditions for VCM Analysis by the CS ₂ Desorption Technique.....	19
V. Blanks: Background VCM Concentration in Air, ppm.....	21
VI. Critical Levels of RVCM in Vinyl Latexes-Closed Room with No Ventilation.....	24
VII. Correlation Constants: Vapor Liquid Equilibria.....	25
VIII. Calculated Critical RVCM Levels in Vinyl Latexes Based on Equilibrium Partial Pressure.....	27
IX. AVCM Calculated from RVCM Loss Data.....	29

LIST OF FIGURES

	<u>Page</u>
1. Schematic Diagram of Experimental Apparatus.....	10
2. AVCM Concentration vs. Latex RVCN Concentration--Raw Data.....	22
3. Measured AVCM Concentration as Related to AVCM Calculated from Latex RVCN Loss During the Test.....	30
4. AVCM vs. Equilibrium VCM Partial Pressure.....	32
5. Ventilation Requirement for OSHA Compliance During a Typical Geon 576 Compounding Operation.....	35

BFG32155

v

24542005

SUMMARY

This report documents technical information that supports a business decision to remove cancer hazard labels from latex products containing vinyl chloride monomer. Controlled experiments in a closed, unventilated room relate ambient concentrations of vinyl chloride monomer (AVCM) to residual vinyl chloride monomer (RVCM) in stripped vinyl latexes. Commercial latex consuming operations have also been analyzed to estimate work place AVCM. Measurements were made by personnel monitoring in one of these operations. Our current standard of 25mg/kg maximum RVCM (wet basis) for vinyl latex products is well within the necessary limit for compliance to standards described by the Occupational Safety and Health Administration (OSHA).

Critical latex RVCM concentrations are defined. At the critical RVCM, the air in a closed, unventilated room will reach the OSHA action level, time weighted average (TWA), 95% confidence, in a 4 hour test period. Test results for three vinyl latexes are:

<u>Latex</u>	<u>Latex Temperature, °F</u>	<u>Critical RVCM, mg/kg</u>
Geon 576	110	22
Geon 450X20	110	38
Geon 352	110	>50

These results are translated to other vinyl latex products based on equilibrium partial pressure data. The assumption is made that diffusion of VCM through the latex-air interface is the controlling step. This is a worst case assumption.

<u>Latex</u>	<u>Plasticizer, pphr</u>	<u>Base Resin</u>	<u>Latex Temperature, °F</u>	<u>Calculated Critical RVCM, mg/kg</u>
Geon 351	0	---	110	29
Geon 580X29	22.4	Geon 351	110	29
Geon 580X119	65	Geon 352	110	17

Based on measured and calculated data, the critical RVCM is estimated for other plasticized latexes based on Geon 351 and Geon 352 resin.

580X52	35	Geon 352	110	25
580X158	30	Geon 352	110	27

Obviously, current stripping practices in the plants are sufficient to keep our vinyl latex products below critical RVCM levels. The product specifications for Geon 576 and Geon 580X119 could be changed to 18mg/kg and 15mg/kg maximum RVCM respectively.

BFG32156

24542006

A typical Geon 576 compounding operation was modelled. At up to 40mg/kg RVCN, the OSHA action level is not exceeded where ordinary industrial ventilation is provided, viz., 6 turnovers per hour.

A coating operation at Rhineland Paper Co. was analyzed. A clear coating of Geon 576 at 70mg/kg RVCN will not create non compliance AVCM concentrations even if all the RVCN transfers to the air between the coater and the ovens. This again assumes ordinary industrial ventilation. At 22mg/kg RVCN, the AVCM is about 0.10 ppm using the same assumptions.

Both the BFGoodrich Corporate Environmental Health Laboratory and Wausau Insurance Companies, a private environmental health engineering service laboratory, confirmed AVCM concentrations at Rhineland to be well under the OSHA action level.

Sanitas coats scrim with two different pigmented Geon 580X52 compounds. The base coat and the top coat are applied in a single pass through the coating and drying system. We have estimated that the OSHA AVCM concentration limit is reached with Geon 580X52 at 25mg/kg RVCN only when all of the monomer transfers to the atmosphere between the coaters and the ovens, and when the ventilation system turns over air only one time every three hours. These conditions are highly unlikely.

BFG32157

DISCUSSION

I. Introduction

In October 1974, the Occupational Safety and Health Administration (OSHA) published a safety and health standard concerning exposure of industrial workers to vinyl chloride monomer (VCM). This standard set a permissible exposure limit of 1 ppm by volume in air as a time weighted average (TWA) over an 8 hour period. Excursions up to 5 ppm are permitted over a period not to exceed 15 minutes. The standard is written for, but not limited to, employers who handle VCM. Employers in the fabricating industry are also subject to the standard where exposures approach the permissible limits. Employers handling or using fabricated products are excluded from the standard based on the absence of "adequate evidence of exposure to vinyl chloride in these operations." A fabricated product is defined as a product made wholly or partly from PVC which does not require further processing at temperatures, and at times, sufficient to cause mass melting of the PVC. In many applications latex may be considered a fabricated product and therefore the user can be excluded from the standard. Where latex may be considered as being used in the fabricating industry, exposures are not likely to approach the permissible limits.

OSHA describes an "action level" at 1/2 the permissible exposure limit, viz. 0.5 ppm TWA over an 8 hour period. Initial personnel monitoring is required where vinyl chloride is used and where a product or products containing PVC are fabricated. Monitoring must be repeated monthly where levels are measured to be >1 ppm and quarterly if >0.5 ppm. Monitoring may be discontinued when 2 consecutive readings 5 days apart show <0.5 ppm. But monitoring must be resumed if the employer believes that for some reason the exposure level may have increased. According to OSHA, statistical data must show 95% confidence limits on air concentration measurements as follows:

<u>Range</u>	<u>Limits</u>
0.25-0.50 ppm	±50%
0.50-1.00 ppm	±35%
>1.00 ppm	±25%

There are additional requirements if the action level is exceeded. Among these requirements are:

- 1) show evidence of action to reduce exposures by engineering and by work practice controls, e.g., provide alarms, provide protective clothing, provide training, etc.
- 2) keep records of personnel monitoring

BFG32158

24542007

- 3) provide medical surveillance on workers
- 4) post signs and labels
- 5) limit access to regulated areas

All of these requirements add expense to manufacturing operations. The expense can be avoided only by eliminating vinyl chloride or by showing that the concentration of vinyl chloride in the working environment cannot be greater than 0.5 ppm TWA for 8 hours.

OSHA states in their written standard that exemptions on the basis of residual vinyl chloride in a polymer are "not justified nor necessary". Employers are given the opportunity to "discontinue many duties" upon a showing of no exposures above the action level.

The purpose of this work is to provide objective laboratory data to support what we already know: vinyl latexes stripped to 25mg/kg RVCM (wet basis) can be handled, where ordinary industrial ventilation is in operation, without the likelihood of exposing workers to ambient VCM concentrations above the OSHA defined action level. With such objective laboratory data, the management of the Latex Division can support a business decision to remove cancer hazard labels from vinyl latex products. It is suspected that these labels are unnecessarily inhibiting sales of labeled latex products.

II. Residual Vinyl Chloride Monomer (RVCM)-Shipped Latex Products

Vinyl latex products are polymerized to maximum conversion consistent with good polymer thermal stability and good reactor productivity. About 1-2% of the VCM charged remains at the end of the polymerization process. This RVCM is reduced by flash evaporation into an evacuated receiver. Energy is provided by injection of live steam into the latex prior to flashing. The injected steam also compensates for water loss in the evaporator. By 1975 we were able to strip vinyl latexes to 50-100mg/kg routinely in new production facilities. In compliance with OSHA regulations we began to attach cancer hazard labels to shipping containers. Our customers began to collect personnel monitoring data. We are not aware that any of our customers have had to take any action other than personnel monitoring. We are aware of negative reactions to cancer hazard labels. Some customers have found substitutes for vinyl latex to avoid the nuisance and cost of dealing with the problem.

BFG32159

We have made continuous efforts since 1975 to improve stripping operations in the plants by process studies and by capital improvements. We are now able to routinely produce vinyl latex products at RVCM contents of 25mg/kg (wet basis) maximum. There is one exception, Geon 350X2, is a latex stabilized by a heat sensitive emulsifier system that cannot be stripped in the conventional manner. This product is sold to only one customer. It is acceptable to this customer at a specified RVCM content of 250mg/kg. They are able to handle the latex without OSHA compliance problems.

Plant stripping experience for most of 1980 is summarized in Table I. The average RVCM level is well below the specification level of 25mg/kg for all the major products.

BFG32160

24542008

TABLE I

PLANT DATA - RVCN, MG/KG - MAJOR PRODUCTS

Product	351	352	576	580X119	580X158	460X6 460X9	460X45 460X46	590X4	652
LGCP Jan.-Oct. 1980	8.4	12.0	7.8	6.6	7.0				
Ave.									
Number	63	76	61	40	6				
Range	3-22	3-25	0-17	3-10	4-9				
ALGCP 12/21/79-11/14/80	17.8	13.9	15.0	10.4	10.1	5.5	9.9	3.7	12.3
Ave.									
Number	7	49	54	2	27	32	6	10	30
Range	10-24	0-24	8-21	10-11	4-22	0-14	3-18	0-11	0-22

BFG32161

III. Experimental Plan

A plan was developed which could allow us to relate AVCM concentrations to RVCM concentrations in the latex. Three latex products were chosen for this study: 1) Geon 352, our highest volume vinyl chloride resin latex, 2) Geon 576, our highest volume externally plasticized vinyl chloride resin latex, and 3) Geon 450X20, a high solids, internally plasticized, acrylic modified vinyl chloride latex. The original data set of 12 experiments included the three latexes at two latex temperatures (72°F and 110°F) and at two RVCM levels (as obtained from the plant and after adding a measured quantity of VCM.) The original set was later extended in efforts to improve the quality of the data correlation. A detailed description of the experimental procedure follows in the next section.

IV. Procedure - R. E. Shaffer

A. Latex Spiking

1. 12 gallons of Geon 576, Lot 2006139, were charged to a 15 gallon reactor. The reactor was sealed and the latex stirred at slow speed.
2. An amount of VCM, about equal to 75 ppm, polymer basis, was added to the reactor from a hypodermic syringe.
3. After 2 hours mixing, the latex was transferred to 2-five gallon lined metal pails, to within ≈ 2 inches of the top, and sealed. One pail was used for a 110°F experiment and the other was used for room temperature work. Each pail contained about 42 pounds of latex at about 57% total solids.
4. Geon 352, Lot 190448, and Geon 450X20, Lot 2911010, were similarly spiked. Each of the three latexes was used then at two RVCM levels.

B. Test Area

1. The experiments were done in a closed room of approximately 1000 ft.³ volume (10.5' x 10' x 9.5'). A ceiling vent and the door to the room were sealed with tape. The room was not ventilated. The ceiling material was 2 ft. X 4 ft. porous, rigid panels about 3/4 inch thick.

C. Air Sampling Equipment

1. Bendix, Micronair II Air sampling pumps, Part No. 2417504-001
2. Bendix stainless steel personnel monitoring collection tubes, Part No. 5516675-1, packed with specially activated carbon for VCM analyses. Their tubes are used repeatedly after a reconditioning process.

BFG32162

24542009

D. Pump Calibrations

The pumps were calibrated by personnel from the ALTC environmental group to provide an air flow rate through the charcoal tubes of ≈ 15 cc/min. The flow rate was increased to 50 cc/minute for the 15th through the 20th experimental runs where glass disposable charcoal sampling tubes from the Mine Safety Appliance Corporation were used in place of the s.s. tubes.

E. Air Sampling Pump Locations

1. For four hours preceding a latex run, duplicate "blank" air samples were taken in the closed work area. Two pumps were placed on a lab bench approximately 3.7 inches off the floor and about 1 foot from the wall.
2. During the 4 hours of a latex test, two pumps were placed side by side 37 inches off the floor and within 2 inches of the wall. Two pumps were placed in the center of the room 33 inches off the floor and directly over the latex. Two more pumps (6 total) were placed 89 inches off the floor directly over the latex. Collection tubes were connected within a few inches of the pumps. The s.s. collection tubes were reconditioned before each use by heating for 3 hours at 250°C and purging with nitrogen. This was twice the usual reconditioning time at 250°C . The extra purging time for these experiments assured complete thermal exhaustion of the tubes so that interference from this source could be eliminated.

F. Latex Test

1. Right after air "blank" samples were taken, a pail of latex, preheated to 110°F , was placed on the floor in the center of the test area.
2. Two motor driven impellers were used to provide good surface movement to the latex.
3. Two heating elements were put in the latex preadjusted to control at 110°F .
4. The 5 Bendix pumps were turned on, latex and room temperatures were recorded, and a 4 oz. latex sample was taken from the pail
5. An air circulating fan, placed on the floor about 2 feet from the latex, was turned on at low speed. The fan was directed at a 90° angle away from the pail to avoid cooling the latex but still circulate the air in the room.
6. The door was closed and sealed.

BFG32163

7. After 4 hours the pumps were turned off, temperatures were recorded and another 4 oz. latex sample was taken.
8. The latex samples were analyzed at ALGCP for residual vinyl chloride by gas chromatography. The analyses are routinely done there (BFG Proc. No. 1005-E).
9. The charcoal tubes were analyzed for VCM at ALTC by Pete Dymterko. The thermal exhaustion technique was used for the analysis. The analysis results were converted to ambient vinyl chloride concentration (AVCM) based upon the pumping rate, the time and the VCM adsorbed.
10. The test area was ventilated for ≈16 hours before collecting more "blank" samples. Latex testing conditions were, 1) spiked with VCM, 2) as received, 3) 110°F latex temperature, 4) room temperature. The air was at room temperature for all the experiments.

A schematic diagram of the experimental apparatus is shown in Fig. 1.

G. Special Test--Controlled VCM Release

1. Data from the charcoal tube analyses were not as reproducible as expected, so after run #8, a different experiment was tried. A cylinder of VCM was put in the test area and a small, known amount of VCM was metered continuously at a constant rate into the closed room for 4 hours. Six charcoal collection tubes and pumps were placed in the usual locations. These data are recorded in the tables between tests #8 and #9. This special test was conducted by Pete Dmyterko.

H. Latex Skinning

1. Run #16, 450X20 at 110°F, formed a thick film over the latex starting near the heater. By the end of the 4 hour test there was only about 4 square inches of clean latex surface visible. The latex appeared to be covered with foam and polymer. Later tests with 450X20 were run with latex reduced to 54.0% T.S. at the start. This greatly reduced skinning.
2. During test #15, 450X20 at room temperature, some of the Bendix pumps stopped working. So none of the tubes from test #15 were analyzed. The experiment was later repeated as test #19.

BFG32164

24542010

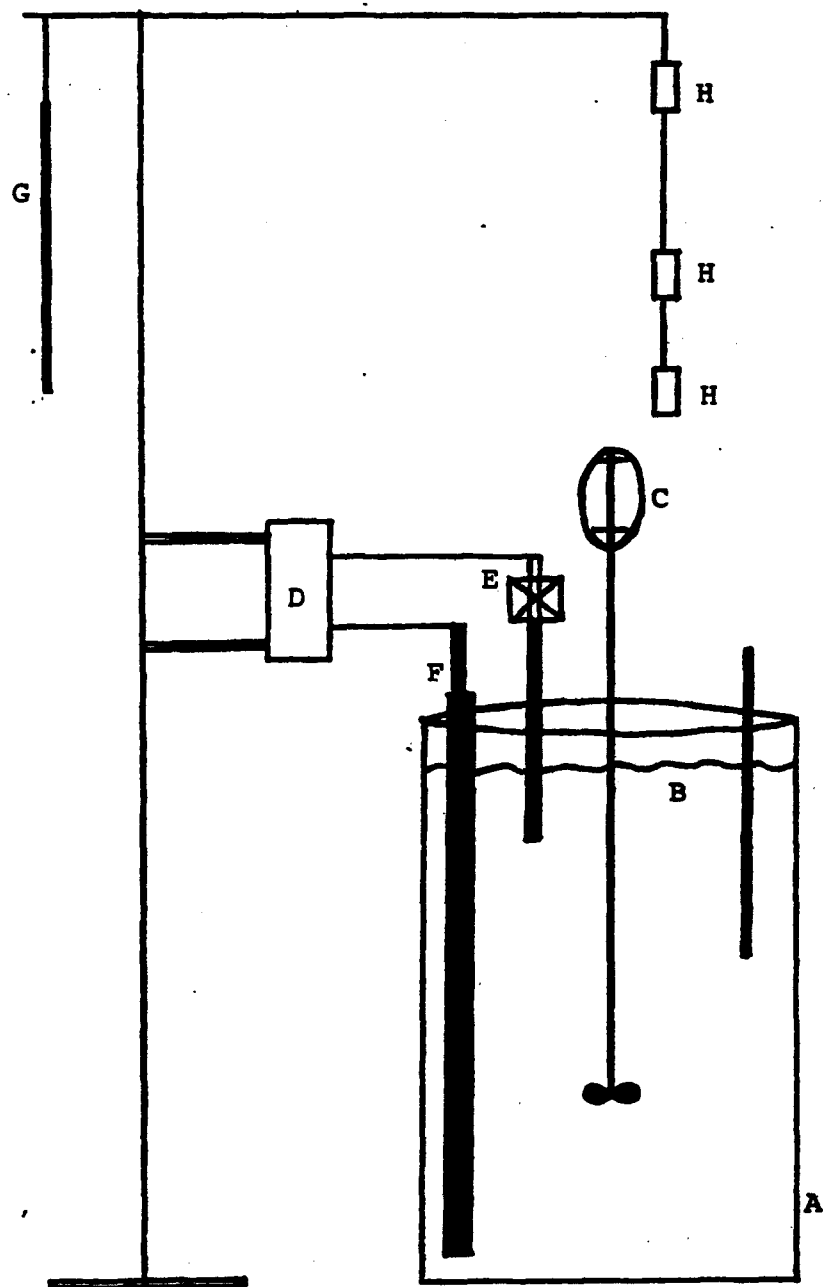


Fig. 1 Schematic Diagram of Experimental Apparatus

- A. Latex container
- B. Latex liquid level
- C. Agitator
- D. Transistor relay
- E. Thermostat
- F. Heater
- G. Thermometer
- H. Air sampling pumps

BFG32165

3. During test #7, 352 at 110°F, one of the heating elements apparently overheated and started to decompose some polymer. The test area filled with smoke. A considerable amount of smoke was detected in adjoining rooms as well. This test was stopped after 195 minutes. The tubes were later analyzed as in other tests.

Glass charcoal sampling tubes from Mine Safety Appliance Corporation were used for tests #15 through #20. These replaced the stainless steel collection tubes used through test #14. Carbon disulfide extraction replaced thermal exhaustion as an analytical technique. The data are recorded in Table II.

Experimental data are in books 911-83 pages 128 - 161 and 911-88 pages 1 - 10.

BFG32166

24542011

V. Testing--Air Sample Tubes - Peter Dmyterko

A. Analysis for Vinyl Chloride

Standard environmental testing techniques were used to measure the concentration of vinyl chloride (VCM) in the air. Air sampling was accomplished by passing the air through charcoal collection tubes for four hours at a known flow rate. The VCM in the air was adsorbed on to the charcoal as the air was drawn through the tubes by a vacuum pump. The VCM level collected on the charcoal was then determined by one of the two following analytical procedures. In the first procedure, the VCM was thermally desorbed from the charcoal using a Bendix Flasher Unit and analyzed by flame ionization chromatography. The second procedure involved desorbing the VCM from the charcoal with carbon disulfide before gas chromatography analysis. The ppm levels of VCM in the air were then calculated from the micrograms of VCM found on a set of tubes and the volume of air sampled.

B. Sampling Procedure

The detailed procedure for sampling the VCM in air using charcoal tubes is presented in BFGoodrich Sampling Procedure No. 2800-A (see Appendix). Both glass and stainless steel charcoal tubes were used in the sampling procedure. The glass tubes were employed when the VCM was to be determined by the carbon disulfide procedure. The glass tubes utilized were MSA Charcoal Sample Collection Tubes (Part No. 45900004 purchased from Mine Safety Appliance Co.). The charcoal in these glass tubes has already been preconditioned by the supplier and the tubes are sealed to prevent contamination. The seals at the ends of the tubes are broken just before the tubes are to be used for sampling.

The thermal desorption procedure for VCM analysis utilizes stainless steel collection tubes. Since these tubes are reused, it is necessary to remove any residual organics on the charcoal by preconditioning the tubes just before sampling for the next analysis. The details of this preconditioning step are described in Section VI of Procedure #2800-A. Briefly, the tubes were placed in a Bendix PMCC Conditioning System and nitrogen was passed at a rate of 15 cc/min. through the tubes in a direction opposite to that used during sampling. The tubes were next heated at 250°C for 1-1/2 hours and then cooled to room temperature. For this study, the tubes were again reheated to 250°C and were given an additional hour of purging with nitrogen. After cooling to room temperature, the tubes were ready for sampling.

BFG32168

22542012

Two tubes in series were used at each sample point. Most of the VCM was adsorbed by the charcoal in the first, and the second tube was present to collect any VCM not adsorbed by the first tube. The pump used to draw air through the tubes was a Bendix Micronair II Air Sampling Pump, a low flow rate battery operated pump.

Before sampling was started, it was necessary to calibrate through each tube set and pump used at the various sampling points. The calibration was performed by the long term six hour exposure technique described in Section VII of Procedure 2800-A. First, the charge on the pump was checked and then the pump was turned on for 15 minutes to warm it up. Next, the pump was attached to the flow rate calibration assembly together with the two conditioned collection tubes in series (see figure in Procedure 2800-A). The breathing air was turned on to the calibration assembly. The flow rate through the tubes adjusted to 7.5 to 15 cc/min. by regulating the speed of the pump with the pump flow rate screw. A soap film flowmeter and a stop watch were used to measure the exact flow rate through the tubes. After the calibration was completed, the pump was stopped and the tubes were disconnected from the calibration assembly and attached directly to the pump.

The pumps and tubes were then placed in the area to be sampled and the pumps were started. The starting time was recorded and after 4 hours of sampling, the final flow rate was measured. The pumps were stopped and the final time was recorded. From this data, the average flow rate as well as the total sampling time were calculated. The volume of air sample was obtained by multiplying the average flow rate by the total sampling time.

C. Analysis of Charcoal Tube for VCM

The next step in the testing was to analyze the collection tubes for the micrograms of VCM adsorbed on the charcoal during sampling. One of the two analytical procedures used was BFGoodrich Test Procedure No. 1021-A, "Analysis of Vinyl Chloride Monomer in Air Via Carbon Tube Thermal Desorption." This procedure can be found in the Appendix of this report.

In this procedure, the stainless steel collection tubes were placed in a Bendix Flasher Unit, which was connected directly to a column in a flame ionization chromatograph. The flasher was placed in the "By-Pass" mode during this step of the analysis. The tube was heated at 250°C for

two minutes in order to desorb the VCM from the charcoal. While this step was performed, the tube was isolated from the rest of the system. Next, the flasher was placed in the "Inject" mode of operation permitting carrier gas to pass through the tube. The VCM was flash/desorbed from the charcoal and was carried on to a gas chromatography column in the chromatograph. After this column separated the VCM from other organics in the sample, the VCM was detected by a flame ionization detector. The area of the VCM peak produced was measured by an integrator. The VCM peak area was multiplied by a calibration factor to convert it to micrograms of VCM via the External Calibration Procedure. The micrograms of VCM on both tubes in a series were combined to obtain the total micrograms of VCM. Finally, the ppm levels of VCM in the air was calculated using the micrograms of VCM on the tubes and the volume of air sampled, using a formula found in Section X of Procedure No. 1021-A.

The gas chromatography conditions used in the thermal desorption procedure are listed in Table III.

BFG32170

24542013

Table III

Gas Chromatography Conditions for the
Thermal Desorption VCM Analysis

Gas Chromatograph	=	Hewlett and Packard (H&P) 5720A Gas Chromatography with H&P Model 18788A Electrometer and H&P 18791A oven control, flame ionization detector
Integrator	=	H&P 3380A integrator
Column	=	2 ft x 6 ft x 1/8 inch O.D. stainless steel column packed with Porapak QS 80/100 mesh (Waters Co.)
Carrier Gas	=	nitrogen
Oven Temperature	=	140°C
Flow Rate	=	30 cc/min
Nitrogen Pressure	=	75 psig
Hydrogen Pressure	=	19 psig
Air Pressure	=	30 psig
Detector Temperature	=	200°C
Range	=	10X

Forward Flush Technique: The 2 ft and 6 ft sections of the column were separated by a manual 2 way valve. When the valve was in the analysis mode, the two columns were connected in series permitting the sample to flow through both sections and to the detector. When the valve was in the by-pass mode, high boiling components collected on the 2 ft section were forward flushed to the atmosphere. At the same time, the flow through the 6 ft section was also maintained in a forward mode by an independent source of carrier gas.

Integrator Conditions:

The following conditions were employed on the H&P 3380A Integrator:

Report = Method Mode: External Standard Technique

Start Delay = off

Stop Time = off

Chart Speed = 0.5 cm/min.

Chart = on

Slope Sensitivity = 0.1 mv/min

BFG32171

The VCM retention time under these conditions was about 2.4 minutes. After an analysis, any impurities remaining on the column were forward flushed off the column before the next analysis was start ..

The Procedure for calibrating the analysis is described in Section VIII of Procedure No. 1021-A. The method involves loading conditioned collection tubes with known levels of VCM from calibration gas mixtures. To calibrate a tube, it is connected to the calibration gas mixture, and the gas mixture is allowed to flow through the tube while the VCM in the gas mixture is adsorbed on to the charcoal. The flow rate through the tube and total time the tube is exposed to the gas mixture are measured. Flow rates were typically in the range of 30 to 40 cc/min and total exposure times were in the order of 4 to 10 minutes. The micrograms of VCM adsorbed by the tube is calculated from the flow rate, exposure time and concentration of VCM in the gas mixture. The flow rate through the tubes was measured by means of a soap bubble flow meter and a stopwatch. The calibration was performed with certified gas mixtures (Matheson Co.) containing: 1.09 ppm, 10.2 ppm and 105.9 ppm VCM in air. Duplicate tubes were loaded at the following approximate levels of VCM: 1 µgm, 4 µgm and 40 µgms of VCM. The tubes were analyzed for VCM using the thermal desorption procedure described above and the area for the VCM peak was obtained. A calibration factor for each tube was calculated by dividing the micrograms of VCM on the tube by the VCM peak area. An overall calibration factor was obtained by averaging the factors obtained for all the tubes loaded. The response factors were found to be linear over the calibration range.

In some of the runs, impurity peaks came close enough to VCM peak to prevent full baseline resolution of the VCM peak. In these cases, the H&P Integrator employed a built-in computer program to determine the area under the VCM peak. When this situation occurred for a run, the comment "Interference" was indicated just after the data for the run on the data sheets.

No attempt was made to ascertain whether other components were present along with VCM under the VCM peak. The presence of other components under the VCM peak would cause an error on the high side for the ppm VCM calculated for a sample. There was no indication of other components, however.

Occasionally, abnormally low results were obtained for one set out of the six tube sets which were sampling the same area over the same time period. A thorough check of the analytical system indicated that this problem was not related to chromatography analysis. This type of problem was never observed during the analysis of tubes during the calibration of the analysis. The cause of this problem has not been determined.

BFG32172

24542014

D. Carbon Disulfide Desorption Analysis For VCM

The second procedure used in the analysis of VCM adsorbed on the charcoal tubes was the carbon disulfide desorption technique. The method employed was a modification of NIOSH Method No. P&CAM 178, "Vinyl Chloride in Air" (see Appendix). The modifications in the column used and the calibration procedure were based on recommendations of the Corporate Environmental Lab at BFG Research and Development Center.

The analysis is conducted by first desorbing the VCM on the charcoal in carbon disulfide. The charcoal contents of the glass collection tubes were placed into 2 cc glass vials (Wheaton Co., 223682). Then, 1 cc of carbon disulfide (Fisher Co, #C-182) was pipetted into each vial. The vial contents were next crimp sealed with aluminum caps containing a teflon coated rubber seal. Finally, the sample vials were agitated for 1/2 hour at room temperature on an SKC Charcoal Desorber.

Next, one microliter of the carbon disulfide phase of the vials was analyzed by flame ionization chromatography using the conditions listed in Table IV. An automatic sampler was used to sample the vials. The VCM was resolved from the CS₂ and other organics in the sample by a 10% SP1000 on Supelcoport 80/100 mesh column. The VCM retention time was 3.3 minutes. The area for VCM peak detected by the flame ionization detector was determined by means of a Perkin Elmer Sigma 10 Data System.

The ppm of VCM on a tube was calculated via the External Calibration Technique. The VCM peak for a tube was first multiplied by a calibration factor (micrograms VCM per unit area of response) to obtain the micrograms of VCM. The micrograms of VCM on the front and back up tubes were added together to get the total VCM level for a tube set. Knowing the total micrograms of VCM and the volume of air sampled, the ppm of VCM was calculated using the formula in Section 10 of NIOSH Procedure No. P&CAM 178.

BFG32173

Table IV

Chromatography Conditions for VCM
Analysis by the CS₂ Desorption Technique

Chromatograph	=	H & P 7620A Flame ionization chromatograph
Detector	=	Flame ionization detector
Integrator	=	Perkin Elmer Sigma 10 Data System
Column	=	20 ft x 1/8 inch O.D. x stainless steel x 10% SP1000 on Supelcoport 80/100 mesh
Column Temperature	=	80°C, isothermal
Detector Temperature	=	200°C
Injection Port Temp.	=	250°C
Nitrogen Flow Rate	=	30 cc/min
Hydrogen Pressure	=	12.5 psig
Air Pressure	=	54 psig
Chart Speed	=	1 inch/4 min
Automatic Sampler	=	H & P 7670A
Auto Sampler Conditions	=	operating mode = auto,
Analysis cycle	=	24 min, stop integrate = 22 min
Inj/sple	=	2; syringe stroke = stop 2, 1 µl; wash cycle = min.
VCM Retention Time	=	3.3 min

BFG32174

24542015

The analysis was calibrated by first loading duplicate glass charcoal tubes at the following VCM levels; 1 μ gm, 4 μ gm, and 40 μ gm VCM. The loading procedure used was identical to that described in the calibration procedure for the thermal desorption method. The charcoal in each of these standard tubes was then desorbed in small vials with carbon disulfide as described above. Duplicate analyses were performed on each vial using the above chromatography procedure. The two VCM peak areas obtained for each vial were averaged to obtain the peak area for the standard. A calibration factor for each standard was calculated by dividing the micrograms of VCM loaded on the tube by the average area obtained from the analysis of the standard. An overall calibration factor was determined by averaging the factors for all the individual standards. The calibration was found to be linear over the range of 1 to 40 micrograms of VCM.

At times during the analysis of a series of vials, some drifting of the calibration factor was observed. This problem was found to be related to the use of nickel jets in the flame ionization detector. The carbon disulfide was reacting with the nickel in the jets to form nickel sulfide which tended to coke up the jets. Standards were spaced at intervals throughout the series to compensate for this problem. Eventually, this problem was solved by replacing the nickel jets with stainless steel jets which do not react with carbon disulfide.

VI. Data Analysis

Duplicate air samples, referred to as "blanks" in Table II, were expected to represent background VCM concentrations. Individual tests varied between 0 ppm and 0.19 ppm; 7 data points out of 38 indicated > 0.10 ppm. This is a reflection of the quality of air sample testing rather than a real variation in VCM concentrations in air at the ALTC. Blank test data are summarized in Table V. Note that if the test averages for test #1, the special VCM cylinder test, and Test #16 are excluded, the overall average background VCM concentration is 0.036 ppm and the range is 0.0015 - 0.065 ppm.

Raw data for the 20 latex tests are summarized in Figure 2. One data point is missing; air samples for Test #15 were lost. AVCM concentration was determined by averaging the six air sample test results for a given closed room test. The RVCM concentration was taken as the average between the test result at the beginning and at the end of a closed room test. There is considerable scatter in the data. Results for 450X20 at room temperature in particular seem inconsistent with other results.

BFG32175

Table V

Blanks: Background VCM Concentration in Air, ppm

<u>Test</u>	<u>1</u>	<u>2</u>	<u>Ave.</u>	
1	0.194	0.13	0.16	
2	0.02	0.06	0.04	
3	0.01	0.02	0.015	
4	0.00	0.06	0.03	
5	0.001	0.11	0.056	
6	x	0.05	0.05	
7	0.02	x	0.02	
8	0.04	0.01	0.025	
9	0.06	0.04	0.05	
10	0.02	0.11	0.065	
11	0.08	0.05	0.065	
12	0.08	0.04	0.06	
Cylinder	0.16	0.05	0.105	
13	0.01	0.04	0.025	
14	0.03	0.07	0.05	
15	no data			
16	0.13	0.11	0.12	Excluding #1, #16,
17	0.02	0.01	0.015	cylinder
18	0.01	0.00	0.005	Background Ave. 0.036 ppm
19	0.04	0.03	0.035	Range 0.0015 - 0.065 ppm
20	0.003	0.000	0.0015	

BFG32176

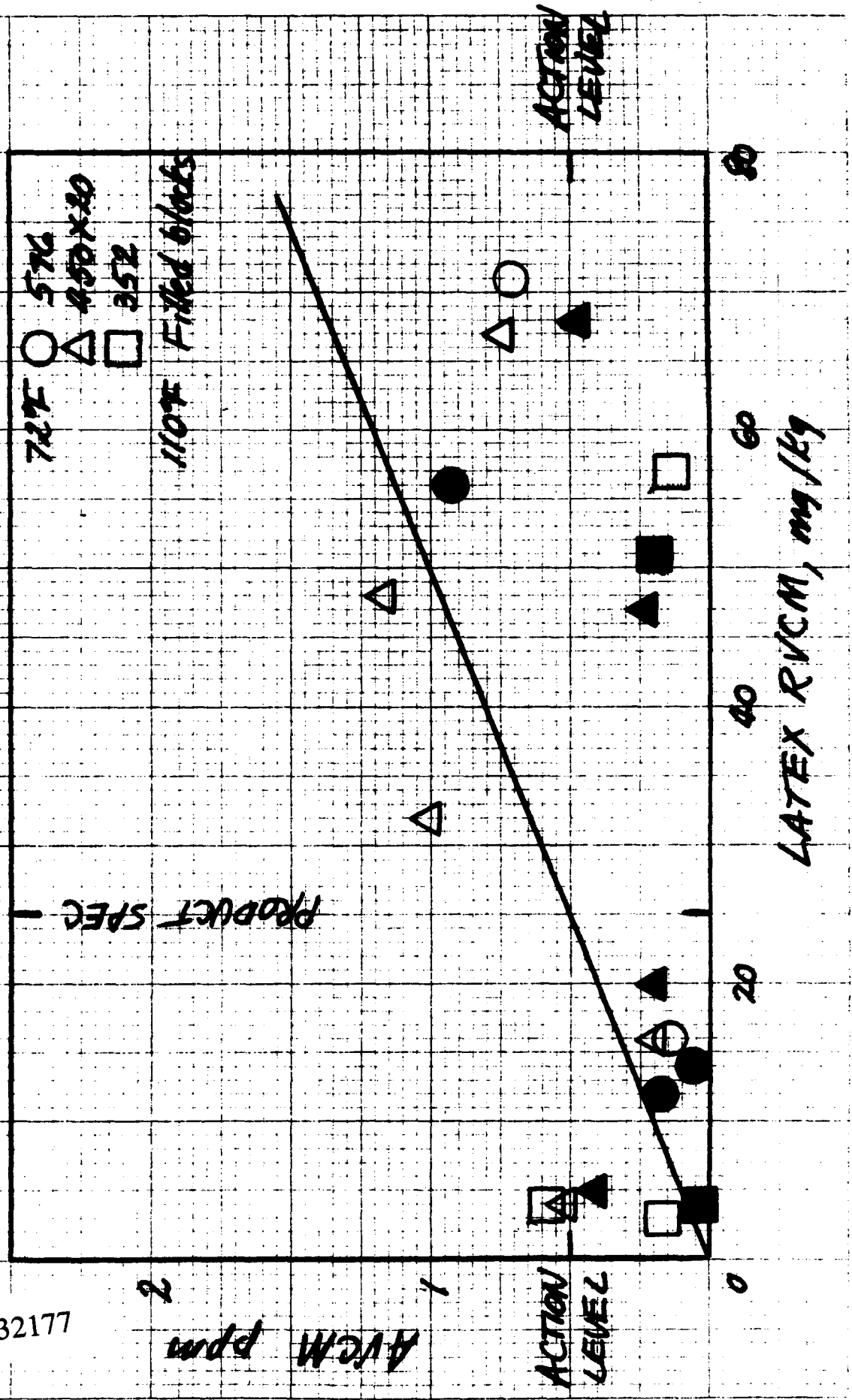
24542016

DIETZEN CORPORATION
MADE IN U.S.A.

Fig.2 AVCM Concentration vs. Latex RVCM Concentration--Raw Data

Note: Straight line connects the origin and the coordinates representing the action level and the current product specification limit

BFG32177



Data were submitted to the Statistics and Computer Group for analysis. Details of this analysis are shown in the Appendix. Critical RVCM levels were determined for the three latexes tested. The action level is assured with 95% confidence at 0.5 ppm AVCM if the VCM concentration in the air is 0.33 ppm. The level of 0.33 ppm, therefore, was used in the correlation to determine the critical RVCM concentration in the latex. Results are summarized in Table VI. As explained in the statistical report only 54 of the air sample test results were used: 14 were rejected because carbon tube loadings were out of the range for good accuracy; 4 were rejected because of interference with VCM in the GC analysis.

BFG32178

24542017

TABLE VI

Critical Levels of RVCM in Vinyl Latexes--
Closed Room with No Ventilation

<u>Latex</u>	<u>Temperature, °F</u>	<u>Critical RVCM, mg/kg (wet basis)</u> (relates to 0.33 ppm AVCM in 4 hours)
Geon 576	72	53
Geon 576	110	22
Geon 450X20	72	27
Geon 450X20	110	38
Geon 352	72	>50
Geon 352	110	>50

It can be concluded from these results that, under worst case conditions, our vinyl latex products as currently manufactured can be used by fabricators without the added manufacturing expense associated with OSHA action requirements. The worst case conditions are:

1) latex at elevated temperature, 2) closed working environment, and 3) no ventilation. In the case of Geon 576 at 110°F, the critical RVCM is 3 mg/kg below the product specification maximum of 25 mg/kg. This is not disturbing, however, since: 1) Geon 576 is made by adding 35 pphr DOP to Geon 351 base resin; the base resin is limited by the product specification to 25 mg/kg, 2) none of the 105 lots of Geon 576 made in 1980 (Table I) was at a RVCM level higher than 21 mg/kg, and 3) these experiments are a worst case situation. Product specifications for externally plasticized products should be changed to reflect the effect of dilution of the resin with plasticizer.

The data indicate that the critical RVCM for Geon 450X20 at 110°F is higher than at 70°F. This, of course, is not physically possible since the AVCM concentration should relate to the equilibrium vapor pressure of VCM. Since the vapor pressure increases with increasing temperature, the RVCM concentration must be higher at the lower temperature to give the same concentration of AVCM in the room. This anomaly might be explained either by some unknown barrier to diffusion at the higher temperature or by test error. We will not attempt to explain it since more experimental work would be required and we believe this is not necessary to achieve our objective.

VII. Translation of Critical RVCN Data to Other Vinyl Latex Products

When the lid is removed from a container of vinyl latex, VCM concentration gradients are created. This causes diffusion of the monomer to occur. There are several steps in series that the monomer must take in the diffusion process. Picture latex in a closed container. The system is in static equilibrium. The monomer is distributed between the phases: polymer, water, and vapor. The concentration in each of the phases depends upon the solubility of vinyl chloride in the polymer and in the water.

Equilibrium data are available for six vinyl latex products representative of the three types: resin, externally plasticized, and internally plasticized. The data relate vapor concentrations in a closed system with concentrations in the latex over a temperature range. No attempt has been made to determine the distribution of monomer between the water phase and the polymer phase. It has not been important for our purposes to do this. The equilibrium data have been fitted to the mathematical model of this form:

$$P_{vcm} = K_1 W^a e^{-K_2/RT}$$

where: P_{vcm} = partial pressure of VCM, mm Hg
 W = weight percent VCM in the latex at 57% T.S.
 T = absolute temperature, °K
 K_1 , K_2 and a are correlation constants

Values for the correlation constants are shown in Table VII.

Table VII
Correlation Constants: Vapor-Liquid Equilibria

Product	Plasticizer pphr	Base Resin	K_1	K_2	a
352	-	-	$e^{22.26}$	5013	1.08
351	-	-	$e^{21.5}$	4741	1.06
450X20	-	-	$e^{13.1}$	2230	1.03
580X29	22.4	351	$e^{16.0}$	3075	1.02
576	35	351	$e^{11.03}$	1605	0.92
580X119	65	352	$e^{17.3}$	3453	0.95

BFG32180

24542018

The diffusion process starts when the vapor space is suddenly increased to include the air volume surrounding the opened container. The monomer vapor then begins to migrate into the new space as the system tries to establish a new equilibrium. So the monomer begins to move through these steps: 1) diffusion through the air, 2) diffusion through the water-air interface, 3) diffusion through the water, 4) diffusion through the polymer-water interface, and 5) diffusion through the polymer. It is impossible to guess which step controls the rate of increase of AVCM concentration. As a worst case, however, it can be assumed that diffusion through the water-air interface is controlling. The driving force for the diffusion then is the partial pressure of VCM at the liquid-air interface, i.e., the equilibrium partial pressure at the temperature and RVCm concentration of the latex. Equilibrium partial pressures have been calculated for the conditions shown in Table VI. The final result is the average for the six conditions: critical $p_{vcm} = 1.38$ mm Hg. The standard deviation for this result is: $\sigma = 0.65$ mm. This is a large error. The large standard deviation is not surprising considering the large error in the AVCM data. The critical AVCM concentration, 0.33 ppm, thus relates to the critical $p_{vcm} = 1.38$ mm Hg. This pressure is used now to calculate the critical RVCm for the other three products, shown in Table VII, for which equilibrium data are available. Estimates for other plasticized products based on Geon 351 and Geon 352 are then made by interpolation of critical RVCm data as related to plasticizer level. The results of these calculations and estimates are shown in Table VIII. The allowable RVCm limit for the base resin reflects the effect of resin dilution with plasticizer.

BFG32181

Table VIII

Calculated Critical RVCm Levels in Vinyl Latexes
Based on Equilibrium Partial Pressure

Critical $p_{vc_m} = 1.38 \text{ mm Hg}$, $\sigma = \pm 0.65 \text{ mm Hg}$

Corresponds with AVCM = 0.33 ppm in closed, unventilated room

<u>Latex</u>	<u>Plasticizer pphr</u>	<u>Base Resin</u>	<u>Calculated Critical RVCm mg/kg (110°F)</u> (1)	<u>Allowable RVCm Limit for Base Resin mg/kg</u>
352	-	-	35 (>50)	-
351	-	-	29	-
450X20	-	-	38 (38)	-
580X29	22.4	351	29	35
576	35	351	22 (22)	30
580X119	65	352	17	28
580X158	30	352	27 (2)	35
580X52	35	352	25 (2)	34

(1) Value shown in parenthesis is the result from statistical analysis of the data (see Table VI)

(2) Estimated value by interpolation of calculated data

It is significant to note that for every product the critical RVCm, or the allowable RVCm for base resin used to make the plasticized derivative, is higher than the level allowed by the product specification. Two important plastic products have critical RVCm levels below the current product specifications. With the base resin, Geon 351, at 25 mg/kg RVCm, Geon 576 would be at 18.5 mg/kg. With the base resin, Geon 352, at 25 mg/kg RVCm, Geon 580X119 would be at 15.2 mg/kg. The product specification for these two products should be changed to 18 mg/kg maximum and 15 mg/kg maximum respectively.

BFG32182

24542019

VIII. Diffusion Rate Estimate.

It is of interest to know the rate of diffusion of VCM from latex to surrounding air space to which it is exposed. From such information it is possible to estimate possible personnel exposure levels in a working environment under known ventilation conditions. Each of our closed room experiments could provide such information. The amount of VCM transferred during the test can be calculated from latex RVCM data at the beginning and at the end of the experiment. This quantity should be in agreement with the quantity measured as the AVCM concentration during the test.

The calculations have been made based on the following assumptions:

- 1) the rate of transfer from the latex to the surrounding air is constant during the test period,
- 2) the concentration of AVCM changes linearly with time from 0 at the beginning of the test to a maximum at the end of the test,
- 3) the measured AVCM for a given test is the average concentration for the test period.

For the measured AVCM value, the average of the statistically validated air samples taken during a test period was used. Air movement within the room during a test was considered sufficient to eliminate gradients in the air space. Statistical analysis showed no correlation of AVCM concentration with position of the six air sample tubes. Results of the calculations are shown in Table IX. The data are shown graphically in Fig. 3. The graph includes the data point for the special test, described earlier, when a known quantity of VCM was released from a cylinder at a constant rate during a four hour period. During this time six (6) air samples were collected as in all the other tests.

Roughly 23% of the VCM released during a test is detected by air sampling.

Table IX

AVCM Calculated from RVCN Loss Data

Weight of Latex: 42.0 lb.

Test	Latex Tested	Latex % T.S.	Latex Temp., °F	Test Period, min.	RVCN Loss, mg/kg	RVCN Ave., mg/kg	AVCM, ppm (calc.)	AVCM, ppm (test)
1	576	56.9	111.5	240	19.32	55.8	2.56	0.99(4)
2	576	56.9	70.3	240	21.46	71.3	2.84	0.27(3)
3	576	56.9	110.5	240	3.00	14.1	0.40	-
4	576	56.9	72.5	240	0.80	16.1	0.10	1.15(5)
5	352	56.9	112.5	240	16.00	50.8	2.12	0.23(5)
6	352	56.9	74.0	240	4.00	56.8	0.53	0.14(5)
7	352	56.9	109.0	195	-1.10	4.3	-	-
8	352	56.9	74.5	240	0.30	4.2	0.04	-
9	450X20	59.9	110.0	240	11.90	47.3	1.67	-
10	450X20	59.9	73.0	240	15.10	48.4	2.00	-
11	450X20	59.9	110.5	240	1.50	4.7	0.20	-
12	450X20	59.9	75.0	240	1.10	4.0	0.14	-
Cylinder	-	-	-	240	-	-	1.16	0.23(5)
13	352	56.9	74.5	240	0.23	3.2	0.03	0.23(5)
14	450X20	54.0	77.0	240	5.07	31.8	0.67	-
15	450X20	54.0	77.0	240	2.45	19.4	0.32	no data
16	450X20	54.0	110.0	240	3.37	19.7	0.44	0.20(6)
17	450X20	54.0	110.0	240	13.71	67.9	1.81	0.47(5)
18	450X20	54.0	72.0	240	22.35	67.3	2.96	0.74(6)
19	450X20	54.0	72.0	240	5.00	15.8	0.66	0.20(6)
20	576	56.9	112.5	240	3.62	11.5	0.48	0.16(4)

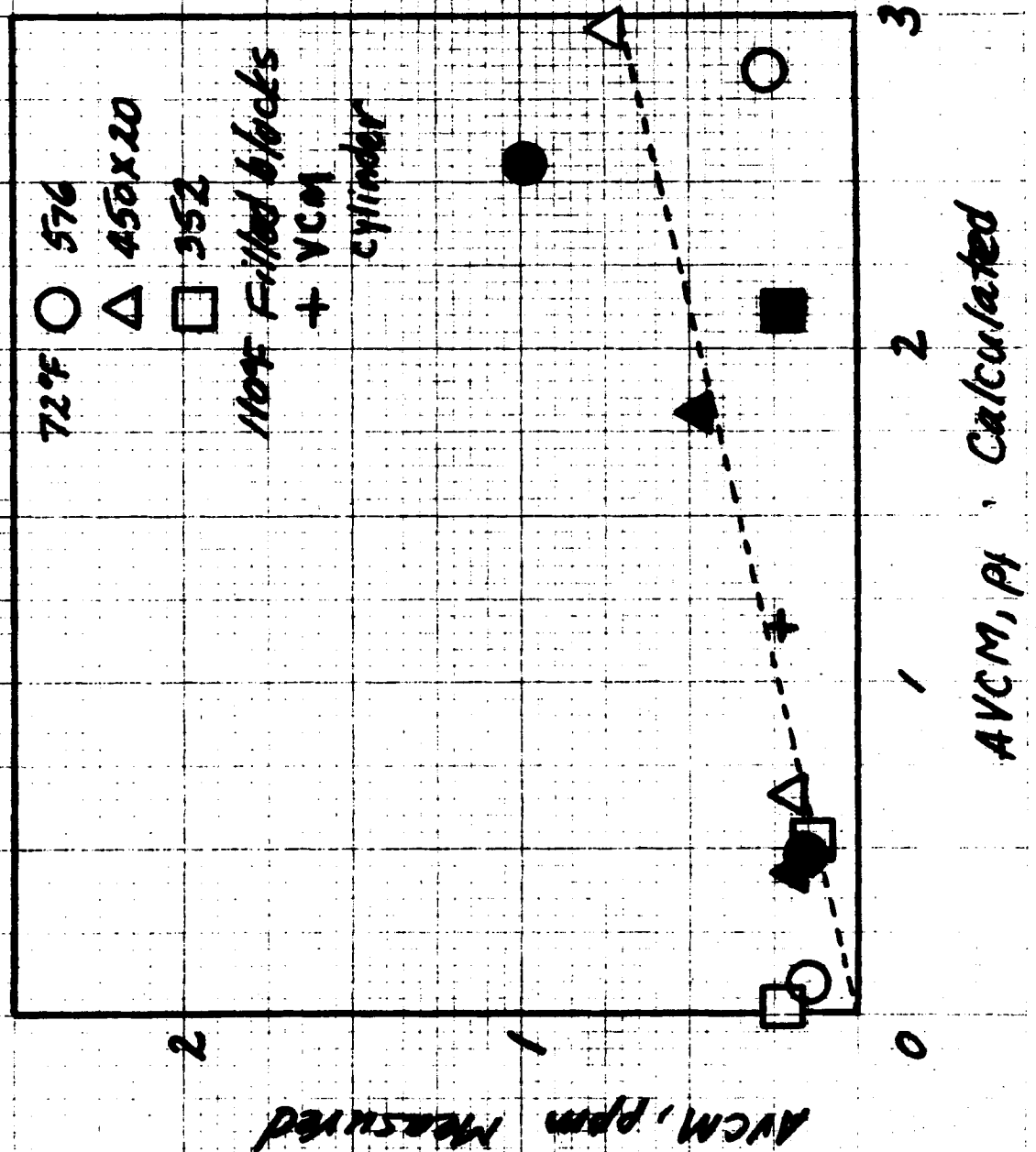
-29-

Note: Invalidated AVCM data are excluded, number in parenthesis indicates the number of valid air samples for the test.

BFG32184

24542020

Fig. 3 Measured AVCM Concentration as Related to AVCM Calculated from Latex RVCM Loss During the Test



BFG32185

This finding is based on the overall average for all the validated tests and is represented by the dotted line in Fig. 3. The failure to detect 77% of the VCM released to the atmosphere is explained by diffusion of monomer through the porous ceiling in the closed room and through joints in wall panels. Adsorption of monomer onto surfaces in the room could also account for some of the loss.³ The loss is equivalent to expanding the original volume of 1000 ft³ to 4350 ft³ with new air during the 4 hour test period.

So, in a case where 0.33 ppm AVCM is the measured concentration as determined by collection of air samples over a 4 hour test period, it can be determined that 42 lb. of latex in the 5 gallon container would have to release 10.57 mg of VCM per kg of latex. And assuming that the rate of release is constant, the diffusion rate is: (11.09) (10⁻⁵) lb/hr. To generalize the result, the latex-air interfacial area (0.6303 ft²) is taken into account and the diffusion rate becomes: (1.76) (10⁻⁴) lb/ft²-hr. This then is the diffusion rate of VCM from latex to air where temperature and concentration conditions are such that the equilibrium partial pressure of VCM is 1.38 mm Hg.

Knowing the rate of evolution of VCM from the latex to the room, an equivalent air flow can be calculated that will maintain 0.33 ppm AVCM. The corresponding air flow is 2117 ft³/hr. Since the room volume is 1000 ft³, this is equivalent to 2.1 turnovers/hr. Sarkar and Mehta reported an equivalent of 0.6 - 1.5 air turnovers/hr. in the same test area under similar test conditions. The system under study by Sarkar was acrylonitrile monomer diffusing from diene and acrylic latexes.

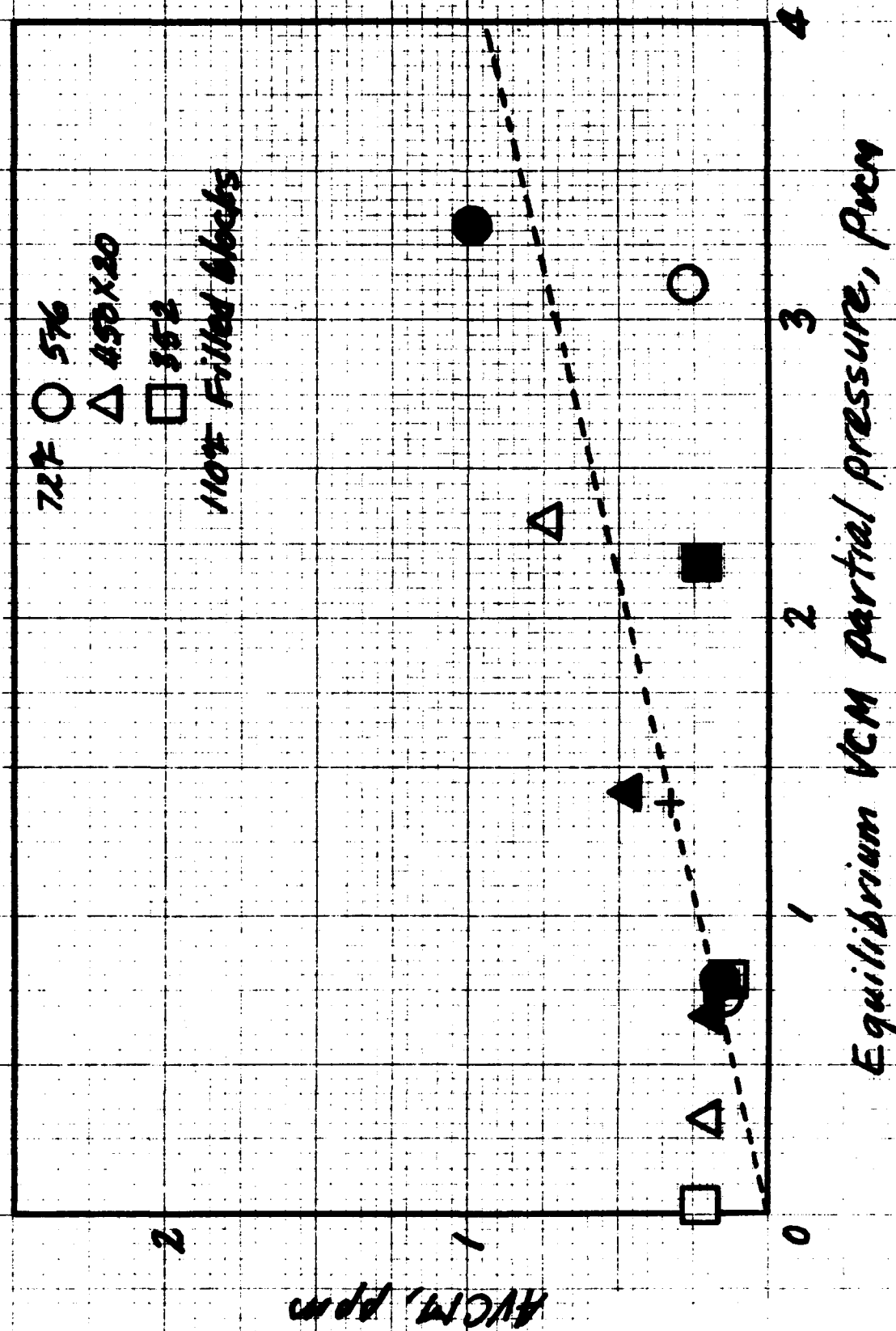
It is safe to assume that the diffusion rate varies linearly with the equilibrium partial pressure of the latex. To check this assumption, equilibrium partial pressures have been calculated for the three latexes tested at the RVCM concentrations and latex temperatures during the tests. Fig. 4 shows how the statistical validated AVCM results relate to the calculated partial pressures. The dotted line connects the origin with the critical coordinates: 0.33 ppm AVCM, 1.38 mm Hg. The fit is good considering the poor quality of AVCM measurements.

BFG32186

24542021

Fig. 4 AVCM vs. Equilibrium VCM Partial Pressure

Note: Dotted line goes through the critical coordinates: 0.33 ppm AVCM, 1.38 mm Hg.



BFG32187

A hypothetical compounding operation has been conceived in order to calculate possible VCM exposure levels in a real work area.

air temperature 90°F
barometric pressure 750 mm Hg
ventilation variable

volume 1000 gal.
diameter 60 in.
(liquid-air interface 2830 in²)
agitated

Latex: Geon 576, 57% T.S., RVCm variable
temperature 110°F

- 1) The rate of diffusion from the latex to the air space is 1.76×10^{-4} lb/ft²-hr at the latex equilibrium VCM pressure of 1.384 mm Hg.
- 2) The rate of diffusion varies linearly with the equilibrium VCM pressure.
- 3) The AVCM concentration is 0.33 ppm, the level at which an air sample indicates the action level is not exceeded with 95% statistical confidence.

The problem involves calculating the ventilation requirement at various latex RVCm levels to maintain the AVCM concentration at 0.33 ppm by volume. The partial pressure of VCM in the air at 0.33 ppm is:

$$p_{\text{vcm}} = (0.33) (10^{-6}) \quad p_{\text{T}} = (2.475) (10^{-4}) \text{ mm Hg where } p_{\text{T}} = 750 \text{ mm Hg}$$

The air flow required to maintain the AVCM concentration at 0.33 ppm is:

$$V = \frac{W}{M} \frac{RT}{P_{VCM}}$$

where:

- V = air flow, ft^3/hr .
- w = rate of VCM diffusion, lb/hr .
- M = molecular weight of VCM, 62.5 lb/lb - mol .
- R = gas constant, $555.0 \frac{\text{mm Hg} - \text{ft}^3}{\text{lb-mol} - ^\circ\text{R}}$
- T = absolute temperature = $90 + 460 = 550^\circ\text{R}$

The calculations are summarized in Fig. 5. Typical industrial ventilation gives 6 turnovers of air per hour. At this level of ventilation, the Geon 576 used in a typical compounding operation could be at 40 mg/kg RVCM without exceeding the OSHA action level. At the proposed specification limit for Geon 576, 18 mg/kg, only 3 air turnovers per hour are required to stay in the OSHA compliance region.

X. Paper Coating Operation at Rhinelander Paper Company

Geon 576 is used at Rhinelander Paper Company to apply a clear coating to paper.

Work space: volume 20 ft x 150 ft x 100 ft
(= 300,000 ft³)

air temperature 90°F

barometric pressure 750 mm Hg

ventilation 6 turnovers/hr.

Coating operation:

latex applied 40 lb (wet)/ream
(1 ream = 3000 ft²)

coating speed 200 ft/min.

sheet width 96 in.

distance between coater and oven 10 ft.

Latex: Geon 576, 57% T.S., RVCM 22 mg/kg

temperature 110°F

In a worst case situation all of the VCM in the latex would transfer to the surrounding work space. This is highly unlikely because of the linear speed of the sheet and the short distance between the coater and the dryer. The elapsed time is only 3 seconds. The latex is consumed at a rate of 1280 lb/hr. The corresponding rate of VCM evaporation is 0.0282 lb/hr. The air flow rate at 6 turnovers per hour is 1,800,000 ft³/hr. The partial pressure of VCM in the air under these conditions is:

$$P_{vcm} = \frac{WRT}{MV} = \frac{(0.0282) (555) (550)}{(62.4) (1.8) (10^6)} = 7.66 (10^{-5}) \text{ mm Hg}$$

And the AVCM concentration is:

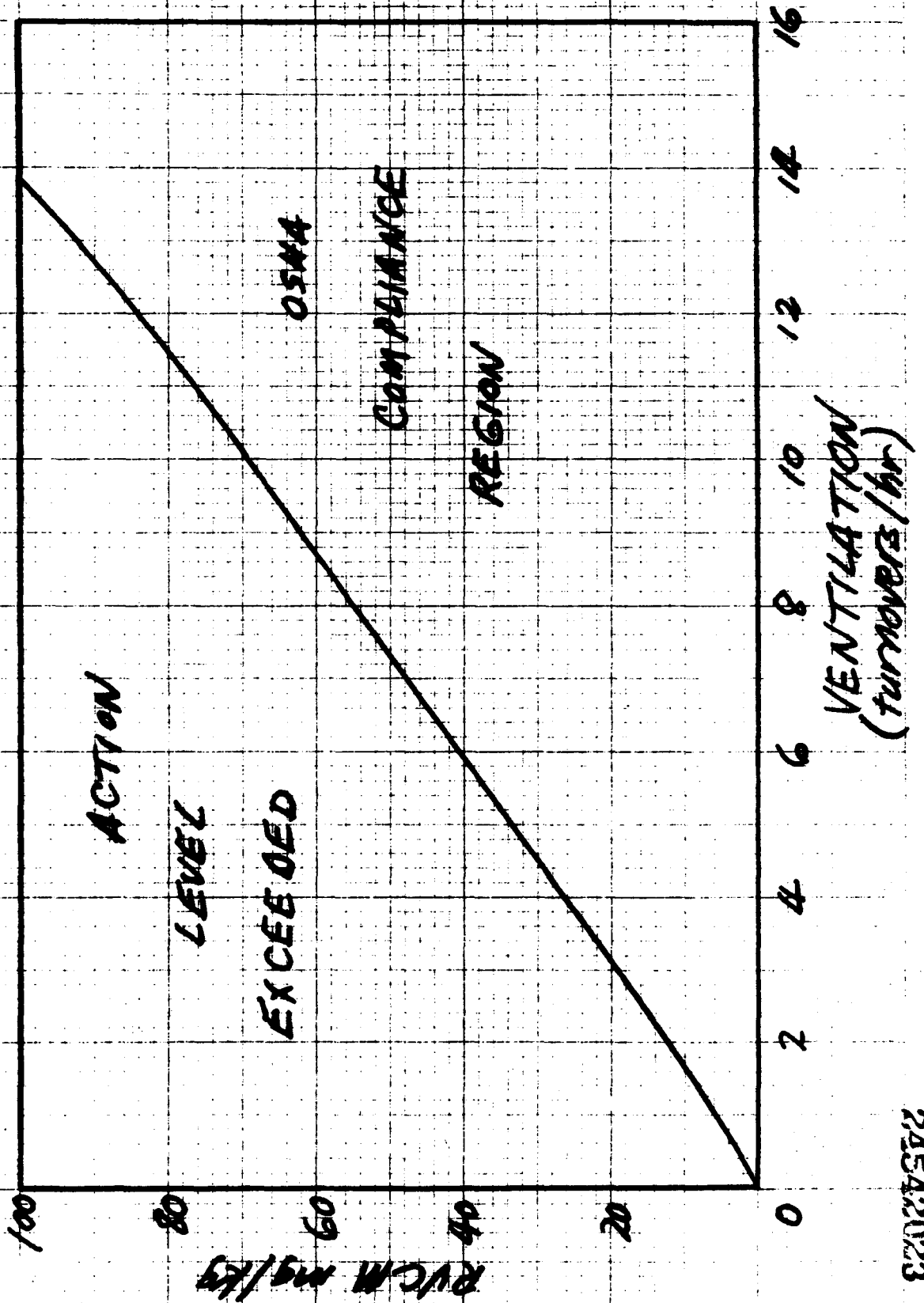
$$AVCM = \frac{(7.66) (10^{-5}) (10^6)}{750} = 0.102 \text{ ppm}$$

This is well below the OSHA action level.

BFG32189

Fig. 5 Ventilation Requirement for OSHA Compliance

TYPICAL 576 COMPOUNDING OPERATION



BFG32190

24542023

The working environment at Rhinelander was monitored during a coating operation using Geon 576. Results were reported by two different laboratories accredited by AIHA:

- 1) the BFGoodrich Corporate Environmental Health Laboratory in Brecksville, Ohio, and
- 2) Wausau Insurance Companies, Wausau, Wisconsin.

These reports are included in the Appendix of this report. Results are consistent with our calculated data.

XI. Scrim Coating Operation at Sanitas

Geon 580X52 is used as a pigment binder at Sanitas in a double coating operation. A base coat compound is applied to the scrim on the first coater. The base coat is dried in an oven. A top coat compound, also based on 580X52, is then applied and the material is again dried in an oven. All these operations take place in one pass through the coating line.

Work space: volume 20 ft x 200 ft x 600 ft
(= 2,400,000 ft³)

air temperature 90°F

barometric pressure 750 mm Hg

ventilation 6 turnovers/hr.

Coating operation:

coating weight

base 5 oz/yd²
top 2 oz/yd²

latex content

base 40.2% wet
top 26.9% wet

line speed 60 yd/min.

sheet width 51 in.

distance between coater and oven

base 4 ft.
top 6 ft.

Latex: Geon 580X52, 57% T.S., RVCM 25 mg/kg

temperature 110°F

Again, the worst case situation is assumed, i.e., the unlikely situation where all of the VCM in the two compounds would transfer to the surrounding work space. The latex is consumed at a rate of 1134 lb/hr in the base coater and at 303 lb/hr in the top coater. The total consumption rate is 1437 lb/hr and the VCM evolved is 0.0359 lb/hr.

$$P_{VCM} = \frac{WRT}{MV} = \frac{(0.0359) (555) (550)}{(62.4) (2.4) (10^6) (6)} = 1.22 (10^{-5}) \text{ mm Hg}$$

And the AVCM concentration is

$$AVCM = \frac{(1.22) (10^{-5}) (10^6)}{750} = 0.016 \text{ ppm}$$

This is well below the OSHA action level. There is no likelihood that the use of Geon 580X52 compounds at Sanitas will create an OSHA compliance problem.

BFG32192

24542024

ACKNOWLEDGMENTS

The authors are grateful for help from the Environmental Control Group: R. D. Hardesty, D. E. Mettler, and L. A. Hilwig who provided the resources for testing air samples; and for data collection skills of technicians in the Latex Group: Paul Clotz, Don Savinsky, Brooks Schmitt, Chuck Shaffer, and Ray Swanson. The professional skills of H. S. Haller and D. E. Farley of the Statistical Services Group are greatly appreciated.

BFG32193

A P P E N D I X

BFG32194

24542025

LIST OF REFERENCES

1. Data book 911-83-128 through 161.
2. Data book 911-88-1 through 10.
3. Satava, R.D., Interorganization Correspondence,
Re: VCM Label Removal, RDS-125-80, 11-18-80.
4. Osborne, E.B., Letter to Customers, Re: Geon Latex-Removal
of Vinyl Chloride Warning Labels, 11-19-80.
5. Farley, D.E. and Haller, H.S., BFG Technical Document,
Subject: Removal of Cancer-Hazard Labels from Geon Latexes,
Statistics and Computer Applications Report, 12-9-80.
6. Weaver, D.E., BFG Technical Document, Subject: Removal of
Vinyl Chloride Monomer from Geon Latex by Flash Evaporation - II.,
Project No. 5025-3681, 7-15-75.
7. Sarkar, C.R. and Mehta, M.M., BFG Technical Document,
Subject: Residual Acrylonitrile (RAN) Levels Permissible
in Hycar Latexes to Comply with OSHA ETS on Acrylonitrile
by Workplace Exposure Simulation Studies, Project Nos. 3654
and 3698, 8-8-78.

BFG32195

BFG TECHNICAL DOCUMENT

THE B F GOODRICH COMPANY CHEMICAL DIVISION **Statistics and Computer Applications** **REPORT**

APPENDIX NO.

PAGE NO.

AUTHOR D.E.Farley-H.S.Haller	LOCATION ALTC	DATE 12/9/80	LOC BOOK REFERENCE
REQUESTED BY: D. E. Weaver	LOCATION ALTC	PROJECT NO. 3696-61	GROUP FILE ACQ. NO.

SUBJECT -

REMOVAL OF "CANCER-HAZARD" LABELS FROM GEON LATEXES

BACKGROUND:

Marketing wants to remove the "cancer-hazard" labels from GEON latexes containing residual vinyl chloride monomer (RVCM). R&D was asked to demonstrate that concentrations of VCM diffusing out of stripped GEON latexes are below the 0.5 ppm action level defined by OSHA.

OBJECTIVE:

Determine the RVCM levels to which GEON latexes must be stripped to ensure, 95% of the time, that VCM in the air will be less than the OSHA action level.

SUMMARY:

1. A computer program was developed which simulates both the OSHA procedure for monitoring worker exposure to airborne VCM and the effects of sampling and testing on compliance with OSHA regulations. Based on this simulation, levels of VCM in the air must be less than 0.33 ppm to ensure compliance 95% of the time.
2. Levels of airborne VCM were correlated to RVCM levels in GEON 576 and 450X20.
3. Airborne levels of VCM (AVCM) do not correlate with RVCM in GEON 352, but the AVCM above GEON 352 does not exceed 0.33 ppm when the RVCM ranges from 3 to 50 ppm. Therefore, the current stripping specification of 25 ppm for GEON is satisfactory.
4. The combined results of simulation and correlation indicate that "cancer-hazard" labels can be removed from GEON 576 and 450X20 if these latexes are stripped to 20 ppm RVCM.

RECOMMENDATION:

Set a maximum RVCM specification at 20 ppm for GEON latexes and remove the "cancer-hazard" labels.

BFG32196

245420226

Removal of "Cancer-Hazard" Labels from GEON Latexes

12/9/80

Page 2

DATA:

The original data set consisted of 12 experiments and 72 samples of airborne vinyl chloride monomer (AVCM). Only 54 AVCM samples were usable. Analytical data for fourteen samples were rejected because the VCM loadings (mg VCM/activated carbon sampling tube) were outside of the 1.0 mg to 10.0 mg range recommended by P. M. Zakriski and J. W. Born (BRDC). Data on four samples were not usable because of interference during the gas chromatographic analysis.

The experimental conditions used are summarized in Table 1, below. A complete set of data used in the correlation analysis can be found in the Appendix (Table 1-A). Rejected data are listed in Table 2-A of the Appendix.

TABLE I

Summary of Experimental Conditions

Latex Type	Average VCM in Latex (ppm by wt.)	Latex Temp. (°F)	Flow Rate for Sampling Pump (cc/min.)	Analytical Method
GEON 352	3.2	72°	15 cc/min.	Bendix Flasher
"	4.3	110°	"	"
"	56.8	72°	"	"
"	50.8	110°	"	"
GEON 576	16.14	72°	"	"
"	11.47	110°	50 cc/min.	CS ₂ Extraction
"	71.25	72°	15 cc/min.	Bendix Flasher
"	55.85	110°	"	"
GEON 450X20	15.8	72°	50 cc/min.	CS ₂ Extraction
"	19.73	110°	"	"
"	67.33	72°	"	"
"	67.86	110°	"	"

Air samples were taken at three different positions inside a closed, unventilated room. Bendix Micronair II personnel monitoring pumps equipped with activated carbon filled sampling tubes were used to sample the air in the room. Two pumps were used at each position.

DISCUSSION:

A. OSHA Regulations

OSHA Regulations define the "action level" for vinyl chloride monomer as 0.5 ppm averaged over an 8-hour work day.¹ OSHA requires an initial monitoring of all areas where employees may be exposed to VCM. If employee exposures exceed the action level, then the employer is required to establish a program for determining exposures for each employee.

BFG32197

Removal of "Cancer-Hazard" Labels from GEON Latexes

12/9/80

Page 3

DISCUSSION: (Cont'd)

A. OSHA Regulations (continued)

If BFG could demonstrate that the RVCM levels in GEON latexes will not produce airborne VCM levels in excess of the 0.5 ppm action level, the "cancer-hazard" labels can be removed from these products. Users of BFG vinyl latexes would not need to establish programs for monitoring employee exposures.

B. Simulating OSHA Test Procedures

The procedure OSHA uses to determine employee exposure to airborne VCM is outlined in Figure 1. A computer program which simulates this procedure (OSHA VCM Compliance) was developed by B. L. Cross. The program calculates an expected % compliance for a given level of airborne VCM and a specific value of the sampling and testing error associated with VCM detection and analysis. The relationship between sampling and testing error, mean AVCM concentrations, and % compliance is illustrated in Figure 2.

According to OSHA regulations the method of monitoring and measuring AVCM levels shall have an accuracy (at 95% confidence) of not less than +50% when AVCM levels range from 0.25 ppm through 0.5 ppm.¹ This required accuracy corresponds to a standard deviation for sampling and testing of +25%.

Using the relationship in Figure 2 and the sampling and testing error specified by OSHA, it is obvious that the maximum level of AVCM which would ensure 95% compliance with OSHA regulations is 0.33 ppm.

C. Do GEON Latexes Comply?

The levels of airborne VCM in a closed room were correlated to RVCM levels in GEON 576 and 450X20. The correlations are illustrated in Figures 3 and 4, respectively. In each plot the level of RVCM in the latex that yields 0.33 ppm of VCM in the air has been identified. These critical levels are listed in Table 2. Proposed stripping specifications for GEON 576 and 450X20 are also listed in Table 2. The proposed specifications are lower because they allow for the error associated with the test for RVCM in the latex.

For GEON 352, the airborne VCM levels do not correlate to the RVCM levels in the latex when the RVCM levels are between 3 and 50 ppm by weight (See Figure 5). However, the airborne VCM levels detected above GEON 352 do not exceed 0.33 ppm by volume. Thus the critical RVCM for GEON 352 is higher than the 50 ppm max. used in these experiments and the specification of 25 ppm need not be changed at the present time.

BFG32198

24542027

Removal of "Cancer-Hazard" Labels from GEON Latexes

12/9/80

Page 4

DISCUSSION: (Cont'd)

C. Do GEON Latexes Comply? (continued)

All three latexes tested will comply at the 95% level to OSHA regulations, if they are stripped to the levels proposed in the following Table 2.

TABLE II

Critical Levels of RVCM in Vinyl Latexes

<u>Latex</u>	<u>Latex Temp.</u> <u>(°F)</u>	<u>Critical RVCM</u> <u>Level (ppm by wt.)</u>	<u>Proposed RVCM</u> <u>Spc. (ppm by wt.)</u>
GEON 576	72°	53	20
"	110°	22	"
GEON 450X20	72°	27	20
"	110°	38	"
GEON 352	72°	>50	25
"	110°	>50	"

D. References:

1. Federal Register, Vol 39, No. 194, Sect. 1910.39g, p. 35896, Oct. 4, 1974.

DEF:HSB:vmt

D. E. Farley

H. S. Haller

Distribution:

R. L. Bowles
E. J. Leeson

BFG32199

Removal of "Cancer-Hazard" Labels from Gen Latexes

11/3/80

Page 5

FIGURE 1
OSHA
SAMPLING PROGRAM

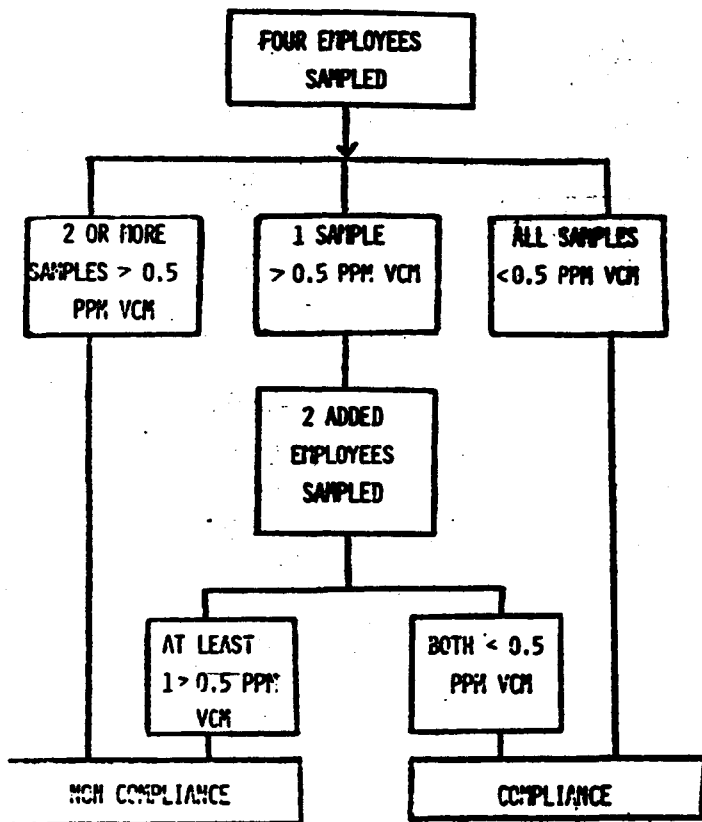
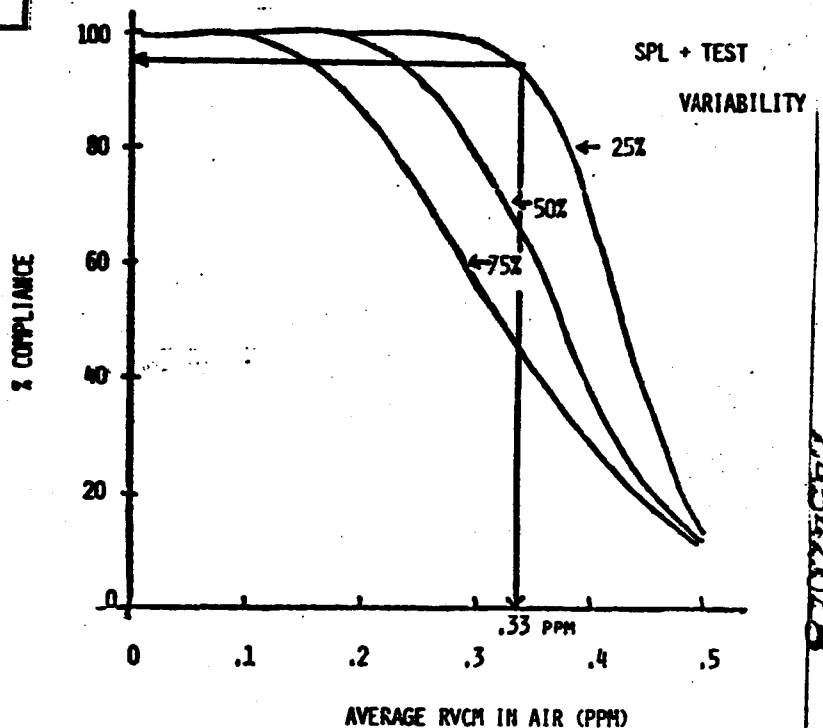


FIGURE 2

EFFECT OF AVERAGE RVCM IN AIR AND
SAMPLING + TESTING VARIABILITY
ON CHANCES OF COMPLIANCE



BFG32200

24542028

Removal of "Cancer-Hazard" Labels from Geon Latexes

12/9/80

Page 6

FIGURE 3

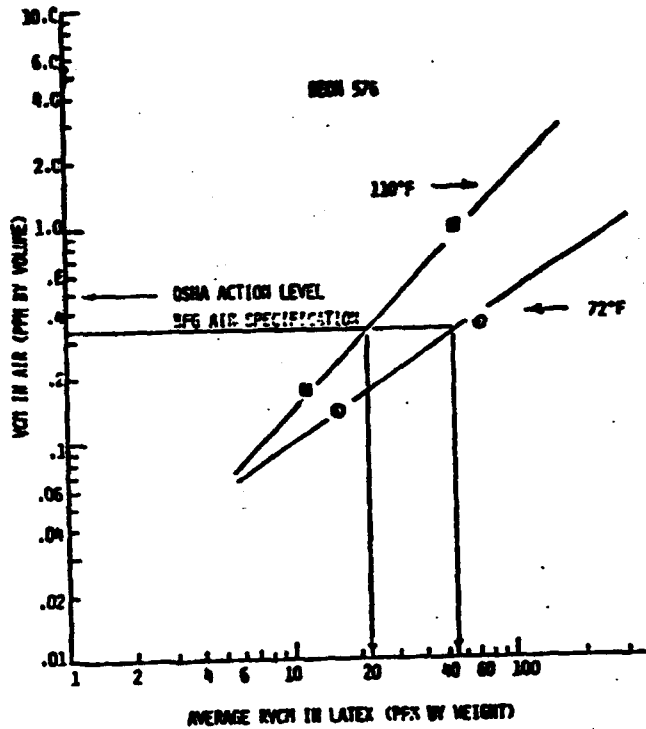


FIGURE 4

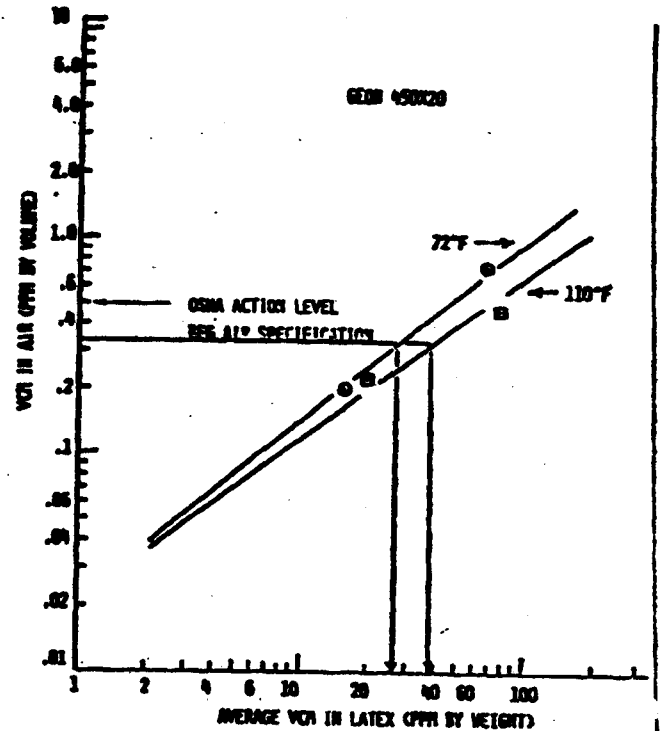
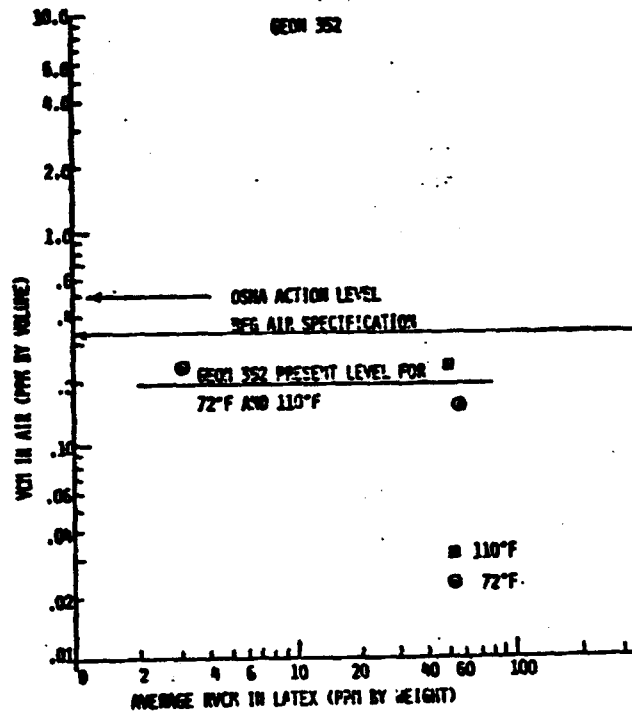


FIGURE 5

GEON 352



BFG32201

APPENDIX

Table 1-A

Summary of Usable AVCM Data

Latex Type	Average RVCM in Latex (ppm by wt.)	Latex Temp. (°F)	Airborne VCM (ppm by vol.)	Analytical Method
GEON 352	3.2	72°	.12	Bendix Flasher
"	"	"	.28	"
"	"	"	.14	"
"	"	"	.16	"
"	"	"	.47	"
"	56.8	72°	.13	"
"	"	"	.16	"
"	"	"	.13	"
"	"	"	.18	"
"	"	"	.09	"
"	50.8	110°	.38	"
"	"	"	.26	"
"	"	"	.19	"
"	"	"	.12	"
"	"	"	.21	"
GEON 576	16.14	72°	.18	"
"	"	"	.14	"
"	"	"	.15	"
"	"	"	.16	"
"	"	"	.12	"
"	11.47	110°	.21	CS ₂ Extraction
"	"	"	.16	"
"	"	"	.12	"
"	"	"	.14	"
"	71.25	72°	.38	Bendix Flasher
"	"	"	.31	"
"	"	"	.12	"
"	55.85	110°	1.31	"
"	"	"	.97	"
"	"	"	.62	"
"	"	"	1.07	"
GEON 450X20	15.8	72°	.16	CS ₂ Extraction
"	"	"	.27	"
"	"	"	.25	"
"	"	"	.16	"
"	"	"	.20	"
"	"	"	.17	"
"	19.73	110°	.21	"
"	"	"	.16	"
"	"	"	.15	"
"	"	"	.33	"
"	"	"	.28	"
"	"	"	.06	"
"	67.33	72°	.90	"
"	"	"	.65	"
"	"	"	.52	"
"	"	"	.62	"
"	"	"	.94	"
"	"	"	.80	"
"	67.86	110°	.52	"
"	"	"	.41	"
"	"	"	.45	"
"	"	"	.44	"
"	"	"	.51	"

BFG32202

24542029

Removal of "Cancer-Hazard" Labels from GEON Latexes

12/9/80

Page 8

APPENDIX (Cont'd)

Table 2-A

Rejected Data

<u>Latex</u>	<u>Average RVCM in Latex (ppm by wt.)</u>	<u>Latex Temp. (°F)</u>	<u>AVCM Level (ppm by vol.)</u>	<u>VCM Loading (mg)</u>
GEON 352	4.3	110°	0.05	0.327
"	"	"	0.02	0.132
"	"	"	0.04	0.252
"	"	"	0.04	0.266
"	"	"	0.05	0.312
GEON 352	56.8	72°	0.09	0.759
"	3.2	72°	0.02	0.207
"	"	"	1.60	13.96
"	50.8	110°	.12	.95
"	"	"	.07	.611
GEON 576	55.85	110°	1.58	13.02
"	"	"	.04	0.377
"	71.25	72°	3.12	17.56
"	"	"	1.27	11.68
GEON 352	56.8	72°	(interference)	
"	" 50.8	110°	"	"
GEON 576	16.14	72°	"	"
GEON 450X20*	67.86	110°	"	"

*The analytical method used for this 450X20 sample was CS₂ Extraction. All other samples were analyzed using the Bendix Flasher Method.

BFG32203

BFGOODRICH CHEMICAL DIVISION

Standard Sampling Procedure No. 2800-A

Page 1 of 8

TITLE: Sampling Procedure for Vinyl Chloride in Air Using the Bendix Personnel Monitoring Collection Columns

TYPE: Carbon Adsorption Tube

PRODUCT: Ambient Breathing Air and Related Air Samples

I. SCOPE

The purpose of this procedure is to identify the equipment required, and to outline the proper method of air sample collection used in monitoring the level of vinyl chloride monomer (VCM) in air via the Bendix Flasher - Personnel Monitoring Collection Column system.

II. PRINCIPLE

The Bendix system of sampling involves concentrating the organic vapors found in industrial air on an adsorbent reusable charcoal tube. Air from the breathing zone of the work is drawn through the adsorption tube with the aid of a small low-flow battery-operated pump. The system enables the Personnel Monitoring Collection Column to be connected directly to the analytical column of a laboratory gas chromatograph after sample collection. The organic vapors are thermally desorbed into the gas chromatograph permitting quantification of the volume of vinyl chloride monomer sorbed during the previous exposure period. The volume of the air sample drawn through the tube is measured, and the corresponding parts per million exposure level to vinyl chloride can be calculated.

(continued)

REASON FOR REISSUE: To include routine replacement of O-rings in the sampling system, and to add control charting of the breakthrough on a monthly basis.

	<u>APPROVALS</u>	<u>DATE</u>
Date Issued <u>8/10/78</u>	1. M.S. Lab <u>J.P. Cornwell</u>	<u>12/9/75</u>
Issued From <u>M.S. Lab</u>	2. Akron <u>A.J. Vielhaber</u>	<u>12/12/75</u>
Written By <u>J.A. Baclawski</u> <u>L.Wallis</u>	3. Avon Lake <u>D.G. Desrosiers</u>	<u>1/5/76</u>
Revised By <u>R.A. Mansfield, Jr.</u>	4. Calvert City <u>E.E. Atkins</u>	<u>1/12/76</u>
	5. Henry <u>C.D. McCrosky</u>	<u>1/12/76</u>
	6. Long Beach <u>C.W. Ball</u>	<u>1/7/76</u>
	7. Louisville <u>R.R. Taylor</u>	<u>1/5/76</u>
	8. Pedricktown _____	_____
	9. Orange <u>--</u>	<u>--</u>
	10. Port Neches <u>--</u>	<u>--</u>
	11. ALTC <u>E.G. DeCapita</u>	<u>12/11/75</u>
	12. Brecksville <u>P.M. Zakriski</u>	<u>1/19/76</u>
	13. BFG International <u>J.M. Hyslop</u>	<u>1/19/76</u>

BFG32204

III. INTERFERENCES

1. Flashing and analysis of each tube does not always remove 100% of the VCM from the previous collection period. It is therefore necessary to "pre-flash" or condition each PMCC in the Bendix Manifold Flasher to remove residual material which may remain from the previous analysis.
2. After conditioning and prior to sample collection, the PMCC's are to be capped and stored in a desiccator. Maximum storage time is 24 hrs. Moisture pick-up will reduce the capacity of the PMCC.
3. After the exposure period and prior to laboratory analysis, the PMCC's are to be stored in a desiccator or freezer. A separate desiccator is required for storage of exposed tubes. It is recommended that the maximum aging time should not exceed 24 hours.
4. High sample air flow rates for extended time periods contribute to premature "breakthrough" (loss of VCM during sampling). Calibrate the flow to the prescribed "safe" flow rates as indicated in this method. Back-up tubes are also used to indicate if breakthrough occurs.
5. Excessive moisture levels or other organic hydrocarbons in the sampling atmosphere may displace VCM on the PMCC and thereby reduce the capacity of the collection column. It is therefore necessary to monitor and note sampling temperature, % relative humidity as well as exposures to other hydrocarbons during the collection period which could interfere with the analysis (see Section IX-2).
6. Report any unusual circumstances occurring during the sample collection period which may be thought to alter VCM results. Examples: Poly entry, high levels in the process area as indicated by leaks or other area monitoring equipment.
7. Any pump failure or loss of battery charge during the exposure period will cause an error in the calculated sample air volume (see Section X-2 on page 8).
8. As the tube holders and back-up conversion kits are used, the O-rings begin to degrade and wear. This causes leaks in the system which can produce false breakthrough readings. All the O-rings in the PMCC holding assemblies must be changed every six months (see Section X-3).

IV. SAFETY

1. Persons doing the sampling work may potentially be exposed to high levels of VCM. All pertinent safety regulations regarding VCM exposure are to be followed by both the sampler and individuals being monitored.

BFG32205

IV. SAFETY (cont'd.)

2. Observe all normally accepted safe operating practices pertaining to the specific area being sampled.
3. Use appropriate safe handling procedures associated with compressed air cylinders.
4. Observe all normally accepted safe practices in handling electrically heated equipment.

V. APPARATUS

A. Sampling Equipment

1. Bendix, Micronair II - Permissible air sampling pump, Part No. 2417504-0001 equipped with battery recharger, Part No. 3900-11 (single unit) or multiple unit recharger - Part #2416418-0001. Sipin or other NIOSH approved pump systems may be substituted.
2. Bendix, stainless steel Personnel Monitoring Collection Columns, Part No. 5516675-1 packed with specially activated carbon for VCM analyses. All new PMCC's should be inspected to insure that screens are properly seated prior to flashing.
3. Bendix, tube holders, PMCC.
4. Bendix, back-up conversion kit (tandem tube adapters), Part No. 551-8164.
5. Bendix, PMCC manifold flasher, to accommodate 20 tubes complete with oven. A nitrogen gas cylinder and appropriate regulator are also required with this apparatus.
6. Bendix, bypass orifice to adjust pump for low flows if required.
7. A supply of O-rings, 1/4" I.D., 3/8" O.D., 1/16" diameter. Use Viton O-rings with manifold flasher service.

B. Calibration Assembly

1. Hewlett Packard - Soap Film Flowmeter 1-10-100 ml, Part No. 0101-0113 or Sargent Soap Bubble Flowmeter 25 cc in 5 cc-divisions, Part No. S-38588-40 or equivalent.
2. Fisher U-tube manometer 90 cm 36 inches, Fisher Cat. No. 11-286C, to be filled with water or equivalent.
3. Scott Sling Pack Cylinder breathing air supply. Equipped with Hudson No. 2000 Oxygen Therapy regulator 193H with output calibration in liters per minute.

V. APPARATUS (cont'd.)

B. Calibration Assembly (cont'd.)

4. EICO, Battery Tester - Model 584. EICO Electronics; Flushing, N.Y. or equivalent.
5. Stainless steel tubing 1/4" and the appropriate fittings to be installed between breathing air source and the PMCC (see attached diagram of the calibration assembly).
6. Tygon tubing 1/4" I.D. and the appropriate tubing connectors.
7. Stopwatch
8. Stainless steel air reservoir with vent holes. Approximately 250 cc volume. Fabricated as per diagram.

C. Miscellaneous Equipment

1. Sling Psychrometer, Bacharach Inst. Co., Pittsburgh, Pa., +20 to 120°F, Part No. 12-7011 or equivalent.
2. Lab desiccators and desiccant. Two are required, one for exposed samples and one for flashed tubes.
3. Appropriate record forms.

VI. CONDITIONING PMCC'S FOR USE

- A.) 1. PMCC's may be reflashed by the laboratory to remove any residual VCM from the previous analysis. This process may be repeated until the tube is free of any residuals as indicated by the laboratory analysis.
- B.) 1. An alternate method of PMCC conditioning incorporates the use of the Bendix Manifold Flasher which facilitates simultaneous conditioning of up to 20 PMCC's.
2. Secure the unscribed end of the PMCC's to be conditioned in the fittings of the manifold block.
3. Bring the oven to the 250°C temperature and initiate the N₂ carrier gas flow at a rate of approx. 10 cc's per minute per tube. Allow to purge for at least one hour. Longer times may be used.
4. Cool, carefully remove PMCC's, cap and store in a desiccator for use.

BFG32207

VI. CONDITIONING PMCC'S FOR USE (cont'd.)

5. It is recommended that PMCC's stored more than 24 hours be reconditioned prior to use. All new PMCC's must be conditioned prior to initial exposure.

VII. BENDIX PUMP CALIBRATION

For the purposes of both short term "task" sampling breathing air analyses as well as long term "time weighted average" breathing air sampling, there are two standardized sampling time periods associated with specific pump flow rates. The following pump calibration procedure covers the long term, 6-hour exposure period. For instructions on short term sampling, refer directly to step 10 of this section.

1. Remove the Bendix Micronair II pump from its battery charger and record its identification number along with the identification numbers of the primary and secondary conditioned PMCC's in the appropriate space on the laboratory data form.
2. Check the pump battery with the battery tester. Do not use if not fully charged.
3. Turn the pump on and let it run on the bench for 15 minutes while the battery equilibrates.
4. Attach the pump to the calibration assembly along with the two conditioned PMCC's in series. The scribed end of the PMCC is to be directed toward the breathing air supply source. The Bendix tandem tube adapter is used to connect the PMCC's. See the attached diagram of the flow rate calibration assembly.
5. Turn on the breathing air supply at a flow rate of approximately 1 liter per minute.
6. Turn on the pump and adjust the pump flow rate screw to achieve a difference between the height of the water columns on the U-tube manometer of 2 inches. This represents a pressure of 2 inches water below atmospheric pressure.
7. Using the soap film flowmeter and a stopwatch, accurately time 1.0 cc of flow. Convert to pump flow rate in cc/min. by the following equation: $60 \text{ sec./min} \div \text{sec./cc} = \text{cc/min.}$

Record the measured flow rate in cc/min. in the appropriate space on the laboratory data form. The allowable flow rate range is 6 to 14 cc/min. If outside this range bring to the attention of the supervisor in charge (see Appendix Step 1).

BFG32208

22542032

VII. BENDIX PUMP CALIBRATION (cont'd.)

8. Turn off the pump and disconnect the PMCC's and pump from the flow rate calibration assembly. Connect the tandem PMCC's to the pump using a length of Tygon tubing and an adapter. The primary PMCC is the one farthest from the pump. Again the scribed end of each tube is to be directed away from the pump.
9. Repeat calibration Steps 1 thru 8 for each pump - PMCC sample collector combination. Pump - sample collection combinations as calibrated must be used within 8 hours. If not exposed within this period, pumps are to be put back on charge and PMCC's are to be reconditioned. Recalibration is also necessary prior to use.
10. There are two basic sample collection time intervals, 6 hours, and 15 minutes. The permissible time exposure range for the 6 hour sampling conditions is 4-7 hours, while that of the 15 minute sampling conditions may range from 15 to 30 minutes. The above calibration conditions are for the 6 hour exposure periods. Use the calibration procedure stated above for the 15 minute exposure periods with the following exceptions: Set pressure drop at 7 inches of water, time 10 cc of flow and convert to cc/min. flow rate by the following equation: $600/\text{sec. for } 10 \text{ cc} = \text{cc/min.}$

The acceptable flow rate range for the 15 minute sampling time interval is 40 to 60 cc/min.

VIII. SAMPLING PROCEDURE

1. Locate the person to be monitored. Attach the pump in a comfortable position and clip the PMCC in his/her breathing zone.
2. The pump is turned on. The start time and personal identification are recorded.
3. The employee is to be instructed to wear the sample collection unit AT ALL TIMES during the exposure period, and to perform his daily activities in a normal manner. Arrangements are to be made at this time for the subsequent pump removal at the end of the sampling period. Note should be made of anticipated job duties and locations. This knowledge will facilitate possible "task" sampling of high VCM concentration operations.
4. Note should be made of any unusual circumstances occurring during the collection period which may influence the VCM exposure level, in order that the subsequent reported analysis value can be related to the work activity during the exposure period.

VIII. SAMPLING PROCEDURE (cont'd.)

5. Note should be made of respiratory protection worn by the employee during the sample collection period.
6. At the conclusion of the sample collection period, the pump flow rate is to be measured. The flow rate is to be measured in the field using a portable flow meter and stopwatch. The pump is then turned off and the final flow rate in cc/min. and the time when the pump was turned off are recorded.

IX. REPORTING AND CALCULATIONS

1. Report both the initial and final flow rates (see Appendix #2). Average these to obtain the cc/minute average flow rate over the exposure period. Calculate and record the total volume of air sampled in cc's by multiplying the average cc/minute flow rate by the total minutes of exposure. Record this value on the data sheet.
2. Measure and record the ambient temperature and % relative humidity which corresponds to the 8-hour shift during which the sample was collected. Record these values on laboratory report form.
3. When the analysis is complete make a notation on the report concerning breakthrough. Breakthrough is defined as:

$$\frac{\text{ug on PMCC \#2}}{\text{ug on PMCC \#1}} \times 100 > 20\%$$

At the end of the month, sum all the tubes exhibiting breakthrough and divide by the number of tandem tubes tested to calculate a % breakthrough for the month. Control chart these monthly values and watch for trends. A significant increase must be investigated.

X. APPENDIX

1. PMCC tubes which fall outside the acceptable flow rate ranges can be adjusted by tightening and/or replacing the screens and fiberglass packing. It is recommended that a tube preventive maintenance program be initiated for periodic tube checking, replacement of the fiberglass packing and backpressure adjustment.

BFG32210

24542033

X. APPENDIX (cont'd.)

2. Other than battery replacement, there is little maintenance which can be performed on the pumps themselves. However, it is recommended that pump & fall-off rate records be kept for each pump. As much as 35% fall-off in flow rate from the start to the end of an exposure period can be considered normal. Percent fall-off rates greater than this should be investigated for battery failure or pump problems. (Note: This is considered normal for the Bendix, Micronair II pumps. Sipin or other NIOSH approved pumps may exhibit different fall-off flow rate characteristics.)
3. To prevent sampling errors and false breakthrough, the O-rings in the tube holders and back-up conversion kits (tandem tube adapters) must be replaced every six months. Replace them with 1/4" I.D., 3/8" O.D., 1/16" diameter O-rings. Use Viton O-rings when they are exposed to manifold flasher service.

BFG32211

SHIFT _____

PERSONNEL MONITORING - VINYL CHLORIDE MONOMER, BENDIX FLASHER

Ambient Temperature _____

DATE ____ / ____ / ____
Page ____ of ____

% Relative Humidity _____

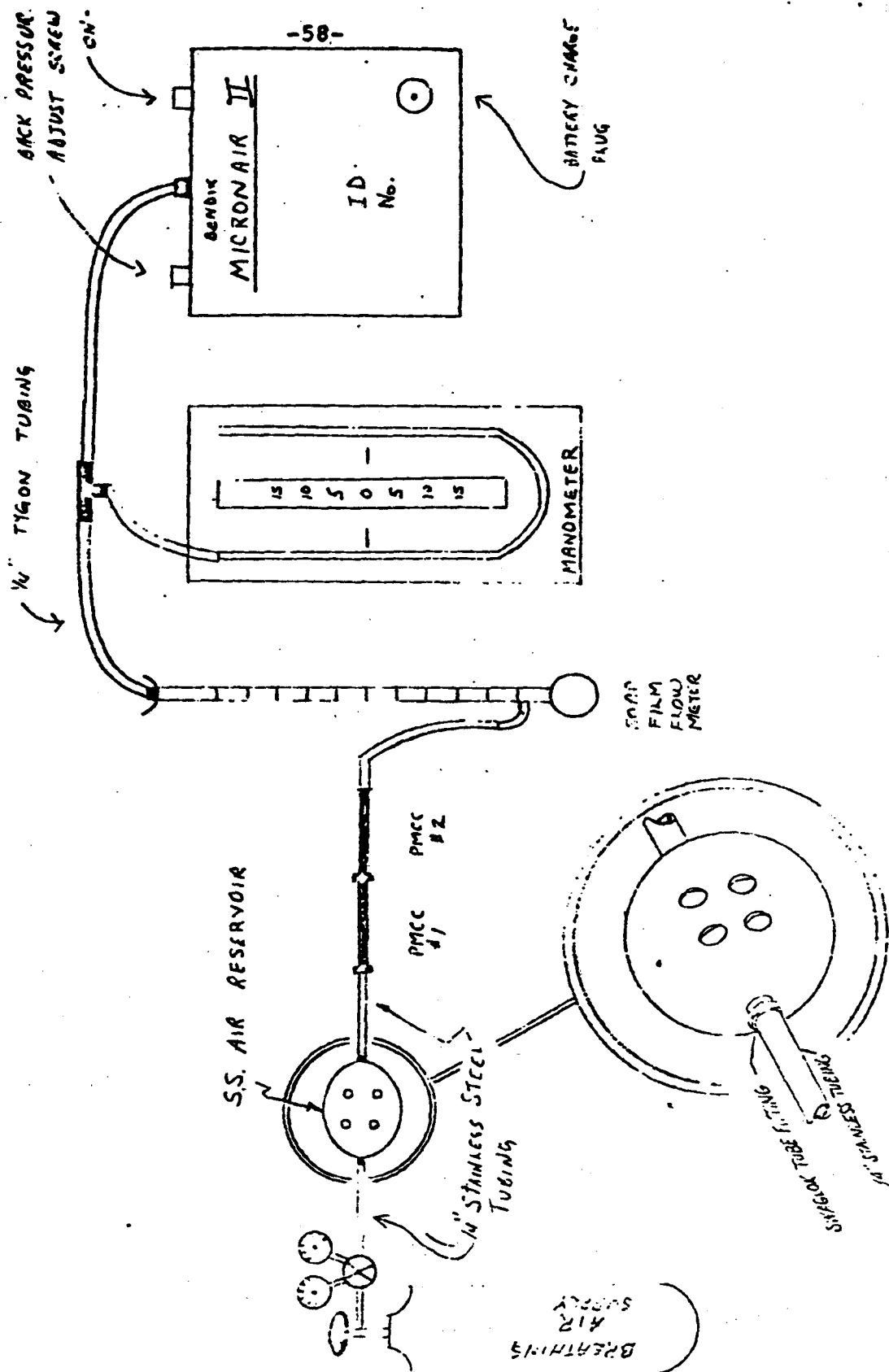
TEST CODE NO.	TUBE NO.	TEST TIME (Min.)	FLOW cc/min. START END	AVG. FLOW cc/min.	SAMPLE VOLUME (cc)	MICRO- GRAMS VCM	% VCM ON Tube 2	TOTAL MICRO- GRAMS VCM	BREAK- THRU YES / NO	REPORT PPM VCM	SPECIAL COMMENTS
1.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
2.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
3.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
4.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
5.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
6.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
7.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
8.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
9.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	
10.	-1	✓	✓	✓	✓	✓	✓	✓	YES	✓	

BFG32212

24542034

Time at START _____ hrs TEMPERATURE _____ °F HUMIDITY _____ %
Time at END _____ hrs TEMPERATURE _____ °F HUMIDITY _____ %
JAN 10/16/77

BENDIX PUMP CALIBRATION ASSEMBLY



BFG32213

B.F.GOODRICH CHEMICAL COMPANY
Standard Test Procedure No. 1021-A

Page 1 of 8

TITLE: Analysis of Vinyl Chloride Monomer in Air Via Carbon Collection Tube Thermal Desorption

TYPE: Gas Chromatograph

PRODUCT: Ambient Breathing Air and Related Air Samples

* Sample collection method to be covered by separate procedure (see Note 3)

I. SCOPE

The use of the thermal desorption technique incorporated in this procedure is suitable for monitoring the level of vinyl chloride vapors in air in relation to personnel exposures. The method, with modifications, can also be utilized for determining exposure to other organic vapors.

II. PRINCIPLE

This system of sampling and measuring industrial vapor enables the collection tubes to be connected directly to the G.C. analytical column after sample collection. The organic vapors are thermally flashed/desorbed from each carbon packed collection tube into a laboratory gas chromatograph, permitting quantification of the amount of vinyl chloride adsorbed during the previous exposure period. A column backflushing technique is utilized to minimize interferences of high boiling components.

III. INTERFERENCES

1. Any material (including moisture) which elutes from the chromatographic column at approximately the same time as vinyl chloride will adversely affect the accuracy of this analysis.
2. Storage of exposed collection tubes, either samples or standards, beyond 24 hours is not recommended. Refrigeration (-10°F) of exposed samples enables collection tube storage of 24 hours without appreciable VCM losses. Calibration tube standards can be frozen along with samples to estimate VCM migration during storage.

REASON FOR REISSUE: General update, and to include use of the Century equipment

	APPROVALS	DATE
Date Issued	3/29/77	1) M.S. Lab J.P. Cornwell 11/29/76
Issued From	M.S. Lab	2) Akron, Plt. 3 Lab
Written By	J.Baclawski	3) Avon Lake
Revised By	J.Baclawski	4) Calvert City E.E. Atkins 11/29/76
Supersedes	1021	5) Henry C.D. McCrosky 3/23/77
		6) Long Beach C.W. Ball 11/29/76
		7) Louisville R.R. Taylor 11/29/76
		8) Pedricktown D.T. Wright 12/6/76
		9) Orange
		10) Port Neches
		11) ALTC
		12) Brecksville P.M. Zakriski 3/1/77

BFG32214

22542035

III. INTERFERENCES (cont'd.)

3. All collection tubes must be pre-flashed prior to their initial use, and must be conditioned prior to each subsequent exposure.

IV. PRECISION

An accurate determination of the total test reproducibility of this method has not as yet been defined. But the standard deviation of the ability to reproduce on calibration standards has been measured at approximately 7% at all three calibration levels of 0.5 μ g, 45.0 μ g and 450 μ g. Data on calibration standards was collected daily over a one month period.

V. SAFETY

1. Vinyl chloride monomer is a suspected carcinogen. Do not release vinyl chloride vapors to the laboratory atmosphere during standard preparation. Standard preparation should be performed in a suitable, properly functioning, lab fume hood and the vapor must be vented to the outside air.
2. Be careful not to come into contact with heated parts of the collection tube oven or chromatograph. Flashed/desorbed tubes are to be removed from the oven unit with needle-nose pliers and should be allowed to sufficiently cool before handling.
3. Handle all electrical connections with care.
4. If for any reason the column is detached from the chromatograph detector, it is first necessary to turn off the hydrogen gas flow to prevent the possibility of explosion.
5. Use the appropriate safe handling procedures associated with compressed air cylinders.

VI. APPARATUS

1. Gas chromatograph, Bendix series 2300 with flame ionization detector (F.I.D.) or suitable equivalent compatible with the thermal desorption unit. Equipped with recorder and/or integrator.
2. Bendix Flasher unit, Model H/S 10 or Century Programmed Thermal Desorber Model PTD-132A.
3. Stainless steel Bendix FMCC (PN-5516677-1) packed with specially activated carbon for the VCM analyses (Bendix Process Inst. Div.). All new FMCC tubes should be inspected to insure that screens are properly seated prior to flashing or Century flared charcoal tubes compatible only with the Century desorber collector FSS-43-CC, backup FSS-41-CC.

VI. APPARATUS (cont'd.)

4. 2 ft. and 4 ft. x 1/8" stainless steel columns packed with Poropak Q 50/80 mesh (Waters Associates, Inc.), or equivalent substitute.
5. Standard cylinders, vinyl chloride in air at 10, 100, and 1000 ppm by volume, Matheson Gas Products; Joliet, Illinois. When ordering, specify zero grade air (vinyl chloride in nitrogen can be used instead of air if desired).
6. Pressure regulators, No. 8L (CGA) Matheson Gas Products (3) required for item 8 above.
7. Rotameter, No. 7221T, 65 mm, aluminum, 1/4" tubing, Matheson Gas Products, Joliet, Illinois. (To be installed downstream of the pressure regulator in each of the calibration gas lines.)
8. Hydrogen cylinder with regulator.
9. Nitrogen cylinder with regulator.
10. Air cylinder with regulator.
11. Instrument air supply and regulator.
12. Filter drier assembly - Perkin Elmer No. 2230117. One for each cylinder (items 8, 9, 10) or equivalent).
13. Flow controllers, Brooks Inst. Div. of Emerson Electric Company, Model 8744 - (3). Installed in hydrogen, air and carrier gas lines if necessary to improve flow control to the F.I.D.
14. Stopwatch (2) and soap film flowmeter (HP 0101-0113).
15. Insulated heating tape - Bristheat Cat. No. B1R-21.
16. Variable transformer - Fisher Cat. No. 9-521-110. } optional
17. 1/8" stainless steel tubing and assorted connectors - Swagelok or equivalent.
18. Monroe Model 1860 statistical programmable calculator or equivalent.
19. Needle-nose pliers.
20. Refer to the apparatus list in the chromatographic backflush accessory procedure - BFG Standard Test Method No. 1053-T.

VII. PREPARATION OF GAS CHROMATOGRAPH

1. Install the column backflush system in the chromatograph oven as is outlined in BFG Standard Test Procedure No. 1053.
2. Connect the output of the thermal desorption unit to the appropriate port of solenoid valve #1 with a short length of 1/8" stainless steel tubing. Install the heat tape and adjust the temperature of the line to approximately 90°C with the variable transformer. (optional)
3. Connect the N₂ supply to the desorption unit inlet and backflush inlet. With the backflush de-energized, the N₂ carrier gas flow to the chromatograph detector is adjusted to approximately 75 cc/min. by utilizing the primary pressure regulator. The carrier gas flow to the detector must be balanced when in the backflush mode, through adjustment of the pressure regulator in the backflush carrier gas supply line.

BFG32216

245A2036

VII. PREPARATION OF GAS CHROMATOGRAPH (cont'd.)

4. Both solenoid valves are to be interfaced with the timer for automatic sequencing of the backflush cycle. The timer cam(s) are to be selected and adjusted so that the VCM has all eluted into the second column immediately before the timer actuates backflushing of the first column. This should take place at about 70% of the VCM retention time in minutes. It can be determined by cutting the cycle progressively shorter until a noticeable response drop is experienced on known VCM standards.
5. Install the filter drier assemblies in each cylinder gas line and adjust the gas flow rates to optimize conditions for the chromatographic system being used. The following are typical flow rates used for the Bendix Series 2300 gas chromatograph:
 - a) Nitrogen Carrier Gas - Set the regulator on the cylinder to 58 psig. Adjust the pressure regulator in the N₂ carrier gas line to obtain a VCM chromatograph peak characterized by clean separation from its neighbors. VCM retention time may vary within 2.5 ± 1.0 min. dependent on the particular column system. See also Step 3 above for adjustment of the backflush N₂ flow.
 - b) Detector Air Supply - Set regulator on the cylinder to 80 psig. A Brooks flow controller is to be installed in this line to provide the optimum constant air flow to the detector between 250 to 350 cc/min.
 - c) Hydrogen Supply - Set the cylinder regulator to 20 psig. A Brooks flow controller is to be installed in this line to provide a constant H₂ flow to the detector between 30 and 40 cc/min.
6. Optimize system temperatures. The following conditions may be used as a starting point:
 - a) Oven (chromatographic columns) ~ 100°C
 - b) Flasher heated block ~ 250°C
 - c) Chromatograph Flame Ionization Detector (FID) ~ 120°C
 - d) Flasher/Desorber oven ~ 250°C
7. The F.I.D. is ignited by pressing the IGNITION button. If flows are properly adjusted, the burner should ignite within five seconds. It may be helpful to raise the H₂ flow by increasing the cylinder pressure to obtain ignition. After ignition return to the desired cylinder pressure.
8. Condition the analytical columns overnight at 230°C. Do not connect the columns to the detector during the conditioning period. Whenever the analytical columns are disconnected from the detector, the hydrogen and air flows should be turned off. NOTE: The maximum temperature limit on the column backflush solenoid valves is 150°C. It may be necessary to remove them or condition the columns in another oven.

VIII. CALIBRATION

Calibration checks should be performed during each eight-hour period when the instrument is in use. If left idle for any extended length of time, the system should be conditioned prior to calibration by thermal desorption of several collection tubes containing VCM.

VIII. CALIBRATION (cont'd.)

1. Preparation of Calibration Standards (use fume hood)

Prepare three standard calibration tubes, one each of the 10, 100, and 1000 ppm standard VCM gases, in the following manner:

- a.) Open the standard cylinder and set the outlet regulator at 5 lbs. and open the needle valve at the regulator.
- b.) Set the flow rate, by adjusting the rotameter valve to between 10 and 20 seconds per 10 cc's using the soap film flow meter.
- c.) After the flow rate has been adjusted, connect a pre-conditioned collection tube with the appropriate end toward the cylinder and simultaneously start a stopwatch. NOTE: Do not use tygon connections between the standard gas cylinder and collection tubes. Stainless steel connections are recommended.
- d.) Connect the bubble flow meter to the exit end of the collection tube while it is being exposed to the standard and, using another stopwatch, measure the time in seconds for 10cc volume. Repeat two more times and record the average time to the nearest 0.1 second for 10cc's flow.
- e.) Expose the calibration collection tube to the standard for exactly 4.0 minutes. Remove and cap the tube.
- f.) Repeat for each of the three calibration gas standards.

2. Calculation

To determine the micrograms VCM added to the standard calibration tube, the following calculation is used:

$$\mu\text{gm VCM} = \frac{(60 \text{ sec/min}) (10\text{cc}) (\text{min. of exposure}) (\text{ppm VCM in stand. gas}) (273^\circ\text{K}) (750\text{mm Hg}) (62.5\text{gm/mole VCM})}{(\text{Flow rate in seconds per 10cc}) (296^\circ\text{K}) (760\text{mm Hg}) (22414\text{cc/mole})}$$

See Monroe Program No. 112.1860, which readily performs this calculation.

Repeat for each of the three calibration exposures and record the calculated μgm for each standard (see also Note 2).

3. Preparation of Calibration Curve

- a.) Each of the three calibration tubes is then to be analyzed through the use of the Flasher/Desorber - chromatograph analytical system as is outlined for the normal sample collection tubes in section IX.
- b.) The analysis may be automated for peak area integration or a manual measurement of peak area may be utilized for quantification of the test results. Whichever the case, the measurement of response of each calibration standard is to be plotted versus the calculated $\mu\text{gm VCM}$ for each calibration exposure. Five phase log-log paper is required (see attachment No. 1). A peak height measurement method cannot be used with the Bendix equipment, as PMCC aging has been associated with peak broadening.

BFG32218

24542037

VIII. CALIBRATION (cont'd.)

3. Preparation of Calibration Curve (cont'd.)

- c.) After analyzing and plotting two sets of calibration standards, the best calibration curve can be drawn through the plotted points. It is recommended that the calibration data be analyzed using the two variable linear regression capabilities of a Monroe Model 1860 statistical programmable calculator to obtain the equation of the best fit line for this data, and that this line be plotted as a calibration curve. Monroe program No. 114 can be used to generate the equation for the calibration curve.
- d.) Examine the plot of the calibration data carefully. If there appears to be any non-linearity in the log-log plot, it is recommended the curve be segmented into shorter sections, which approach linearity, and that appropriate sample calculation methods are incorporated which are dependent upon VCM level (see Note 1).
- e.) It is recommended that subsequent calibration checks be control charted. In this manner significant shifts in calibration which may occur will be readily identified. Following control chart rules will also provide a consistent basis for determining if recalibration is necessary. Refer to the B.F. Goodrich Chemical Company "Control Chart Manual" by R.L. Bowles, A.M. Fairlie, W.C. Mayhew and R.S. Morgan, March, 1962. If the daily calibration data violates control chart rules, the analysis system is to be rechecked and troubleshooted until the discrepancy is detected or until it is found that recalibration is necessary.

NOTE 1: A method for segmentation of the calibration curve used in this analysis is outlined in a letter from John Schaap to J.M. Whitney and F.V. Zemanek dated 1/30/75, "Calculation of Personnel Monitoring VCM Exposure from Bendix Flasher Chromatographic Unit". A copy of this report is obtainable from all BFG Chemical PIC Engineers or the M.S. Laboratory.

NOTE 2: An alternate method for preparation of calibration standards which cover a range of concentrations also provides excellent reproducibility. This is achieved by using only one certified calibration gas and varying flow rate and exposure time to obtain different calibration levels. The calculation of μgm on each calibration tube is identical to that outlined in Section VIII - 2. However, if this method is used, a second VCM standard gas is to be available for periodic referencing.

IX. SAMPLE ANALYSIS PROCEDURE

- 1. Turn the power on to the thermal desorption unit and allow its temperature to equilibrate. Refer to the operation manual pertaining to the particular desorption unit being used.
- 2. Exposed collection tubes, as received, are decapped and properly inserted into the thermal oven unit.

IX. SAMPLE ANALYSIS PROCEDURE

3. The collection tube is allowed to desorb for 2 minutes, during which time the recorder baseline, attenuation, and/or integration parameters can be appropriately checked and adjusted.
4. After the desorption step is completed the sample is injected onto the analytical G.C. column and the backflush timer switch is set to "reset". The recorder and/or integrator is also started simultaneously.
5. If using a recorder only, attenuate as necessary to keep the peak height of all peaks in the upper half of the chart. Record the sample identification, analysis start, and attenuation of each peak on the recorder chart. If using an integrator, the logarithmic scale attenuator can be used to keep all peaks on the recorder chart. After 30 seconds have elapsed, switch the timer to "Auto". This will return the backflush timer to the start of the cycle at the completion of the analysis.
6. The recorder will graph the response with time of each low boiling component in the collection tube being analyzed. The backflush of the first analytical column will be automatically actuated by the preset timer immediately after the VCM has eluted from the first column.
If using the Century system, repeat injections may be made on aliquots of single desorbed collection tubes.
7. Record the sample identification, collection tube I.D. number, attenuation, and peak width and height, (or area counts if an integrator is used) and the sample exposure volume (supplied with sample) on the appropriate laboratory data collection form (see Attachment #5).

X. CALCULATION OF RESULTS

1. Manual Calculation

- a) Using the calibration graph of VCM detector response vs micrograms VCM, locate the μg level which corresponds to detector response for the sample.

2. Automated Calculation

- a) Monroe program No. 114.1860 readily performs this task. See attachment 4 for a printout of the program, which includes two-variable linear log-log regression analysis of the calibration standards. See Section VIII, 3, c.

3. Conversion of μg to ppm

- a) Convert the μg result to $\text{ppm}_{(v)}$ of the air volume sampled by the following equation:

$$\text{ppm}_{(v)} = \frac{(\mu\text{g VCM}) (22414\text{cc/mole}) (295^\circ\text{K}) (760\text{mm Hg})}{(62.5\text{g/mole}) (273^\circ\text{K}) (750\text{mm Hg}) (\text{total cc's})}$$

Simplified equation:

$$\text{ppm}_{(v)} = \frac{(\mu\text{g}) (XF)}{\text{total cc's}}$$

XF = 392.69 (see Note #4)

BFG32220

24542038

X. CALCULATION OF RESULTS (cont'd.)

The above equation can be easily calculated using Monroe Program No. 113.1860.

NOTE 3: Although sampling methods are not outlined in this test procedure, it is understood that the capacity of the collection tube has not been exceeded.

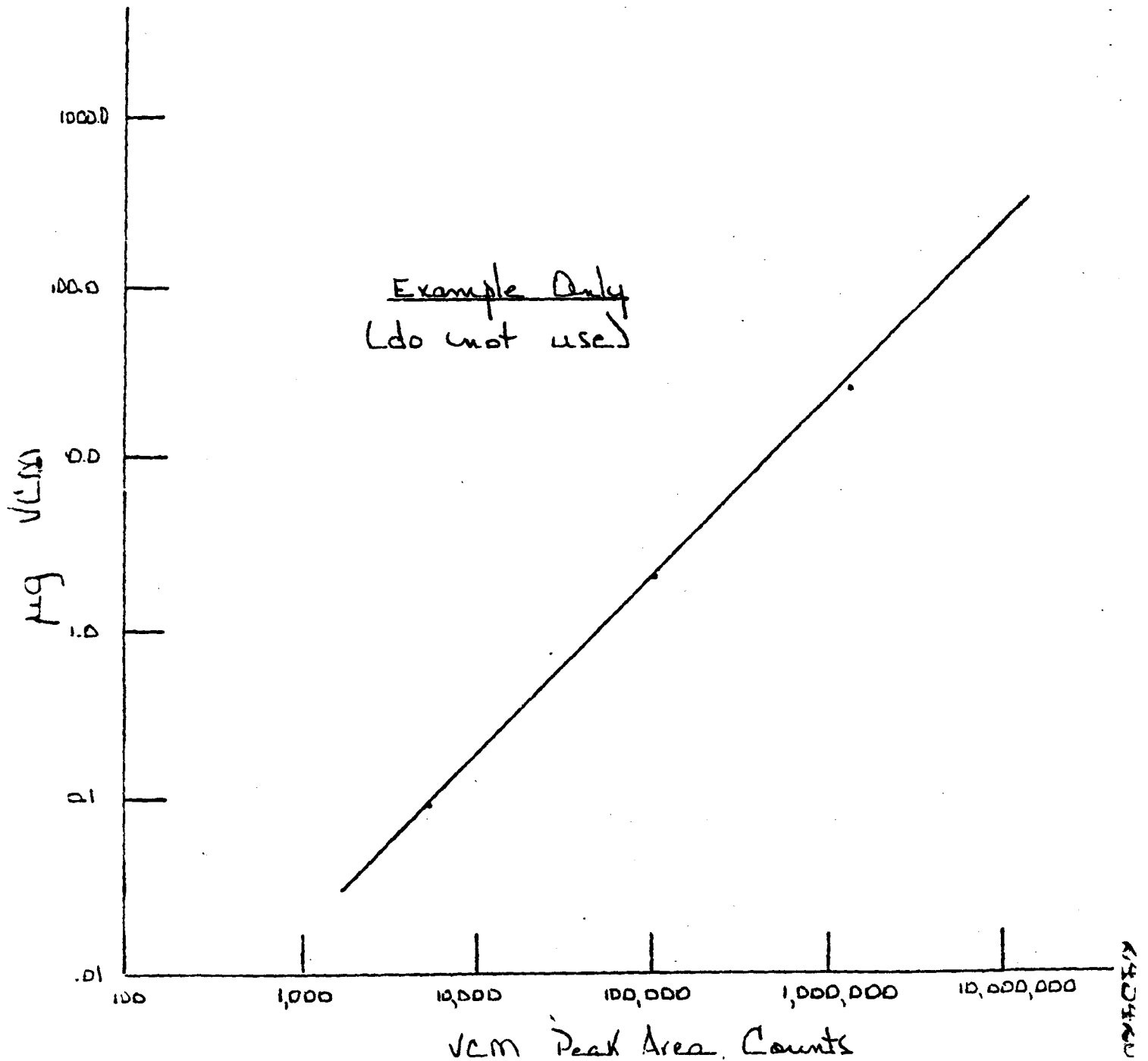
It has been found that collection periods characterized by high air flow rates (50cc/min.), and/or high humidity may lower the capacity of the collection tube dependent upon the length of the collection period and the concentration level being sampled.

NOTE 4: When deemed significant XF should be appropriately adjusted relative to the ambient psychrometric conditions. See also VIII, 2.

BFG32221

-67-
Attachment No. 1
Charcoal Collection Tube Thermal Desorption
Sample Calibration Curve

L5 phase log-log)



BFG32222

Monroe Program No. 112.1860 Printout

BFG32223

Attachment #3
Monroe Program No. 113.1860 Printout

0000	001	
1	001	
2	003	
3	060	
4	175	
5	062	
6	053	
7	116	
8	000	
9	117	
0010	004	
1	056	
2	070	
3	023	
4	002	
5	002	
6	004	
7	001	
8	004	
9	023	
0020	002	
1	011	
2	006	
3	024	
4	007	
5	006	
6	000	
7	024	
8	056	
9	060	
0030	024	
1	002	
2	007	
3	003	
4	024	
5	007	
6	006	
7	000	
8	024	
9	056	
0040	060	
1	020	
2	061	
3	065	
4	127	
5	000	
6	000	

24542040

-ion
Attachment #4
Monroe Program No. 114.1860 Printout

0000	001	/	0050	060	
1	001	/	1	050	F
2	004	/	2	120	
3	060		3	001	/
4	176		4	006	6
5	062	A	5	055	
6	116		6	040	
7	000		7	050	
8	117		8	120	
9	006		9	001	/
0010	055		0060	007	7
1	060		1	055	
2	050		2	056	
3	120		3	060	
4	001	/	4	050	
5	000		5	120	
6	056		6	001	/
7	050		7	010	
8	050	A	8	056	
9	120		9	060	
0020	001	/	0070	050	
1	001	/	1	120	
2	065		2	001	/
3	055		3	011	5
4	060		4	065	
5	050		5	056	
6	120		6	060	
7	001	/	7	050	
8	002		8	120	
9	056		9	002	2
0030	060		0080	000	0
1	050		1	055	
2	120		2	060	
3	001	/	3	050	
4	003		4	120	
5	045		5	000	2
6	056		6	001	/
7	060		7	065	
8	050		8	176	
9	120		9	115	G
0040	001	/	0090	001	/
1	004	/	1	121	
2	056		2	001	/
3	060		3	001	/
4	050		4	036	X
5	120		5	121	
6	001	/	6	001	/
7	005		7	000	0
8	065		8	020	=
9	055		9	121	

BFG32225

Manroe Program -71- No. 114.1860 Printout (cont'd.)

0100	001	/
1	003	3
2	036	X
3	121	*
4	001	/
5	002	2
6	020	=
7	121	*
8	001	/
9	005	5
0110	036	X
1	121	*
2	001	/
3	004	4
4	020	=
5	121	*
6	001	/
7	007	7
8	036	X
9	121	*
0120	001	/
1	006	6
2	020	=
3	121	*
4	001	/
5	011	9
6	036	X
7	121	*
8	001	/
9	010	0
0130	020	=
1	121	*
2	002	2
3	001	/
4	036	X
5	121	*
6	002	2
7	000	0
8	020	=
9	065	

0140	076	6
1	060	
2	052	+
3	060	
4	116	6
5	003	3
6	060	
7	055	
8	176	
9	176	
0150	066	
1	055	+
2	055	
3	060	
4	050	3
5	116	6
6	011	9
7	051	4
8	061	A
9	176	
0160	127	7
1	067	
2	055	+
3	127	7

24542041

BFG32226

BFG32227

-73-
VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte: Vinyl Chloride

Method No.: P&CAM 178

Matrix: Air

Range: 0.008 to 5.2 mg/m³ in
a 5 - liter air sample

Procedure: Adsorption on
activated carbon, desorption
with carbon disulfide, gas
chromatography

Precision (CV_T): 0.08 at
levels of 7 and 71 mg/m³

Date Issued: 9/3/74

Classification: B (accepted)

Date Revised: 1/29/76

1. Principle of the Method

A known volume of air is drawn through two small sorbent tubes in series containing activated carbon (made from coconut shells), which adsorbs the vinyl chloride present in the air sample. The collected vinyl chloride is then desorbed with carbon disulfide, and the resulting solutions are analyzed by gas chromatography with a flame ionization detector. The areas under the resulting peaks are compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 The minimum detectable amount of vinyl chloride was found to be 0.2 ng per injection at a 1 x 1 attenuation on a gas chromatograph. This corresponds to an estimated concentration of 0.008 mg/m³ in a 5-liter air sample analyzed by this method. However, the desorption efficiency from activated carbon of amounts of vinyl chloride as small as 40 ng (0.008 µg/l x 5 liters) has not been determined. Therefore, the detection limit of the overall method may be somewhat higher than 0.008 mg/m³.

2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5 liters. This value is based upon data which indicated that more than 10 liters of air containing 2.6 µg/l (1 ppm) of vinyl chloride could be sampled on activated carbon before 5% breakthrough was observed. This indicates that 5 liters of air containing no more than 5.2 mg/m³ may be sampled without significant breakthrough. (The sorbent tube consists of two sections of activated carbon separated by a section of urethane foam. [See Section 6.2.]) If a particular atmosphere is suspected of containing a high concentration of contaminants or a high humidity is suspected, the sampling volume should be reduced by 50%. A safety factor has been included in the recommended 5-liter volume and the capacity of the first tube should be within these limits except under the most extreme conditions.

178-1

BFG32228

22542042

3. Interferences

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped effectively. Experiments indicate that high humidity severely decreases the capacity of activated carbon for organic vapors.
- 3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.
- 3.3 Any compound that has the same retention time as vinyl chloride at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, may not provide proof of chemical identity. Often, operating conditions can be modified to eliminate interferences. Samples should be analyzed by an independent method when overlapping gas chromatographic peaks cannot be resolved.

4. Precision and Accuracy

- 4.1 The coefficients of variation resulting from the analysis of two sets of sorbent tubes, one set of 27 tubes exposed to a vinyl chloride concentration of 7.2 mg/m^3 in air and another set of 29 tubes exposed to a concentration of 71.3 mg/m^3 , were 0.076 and 0.075, respectively. These values reflect total sampling and analytical error as well as desorption efficiency correction errors.
- 4.2 Experiments were performed to obtain some indication of the accuracy, although accuracy was difficult to evaluate in the absence of a primary standard. These experiments generally involved six sorbent tube samples exposed to a synthetic atmosphere. The calculated value was the concentration expected based on the measured amounts of vinyl chloride and air mixed to prepare the synthetic atmosphere. Therefore the calculated value was not the "true" value, since it was subject to experimental error. The value found from analysis of each sorbent tube, after correction for desorption efficiency, was also compared to that found by the direct injection of gas samples from the same synthetic atmosphere used in loading the tubes. The results of these experiments are shown in the table below. It should be noted that average concentrations determined by analysis of sorbent tubes were within 6% of the average concentrations determined by analysis of gas samples.

Experiment No.		Concentration, calculated, mg/m ³	Concentration, experimental, mg/m ³	Estimated error, % ^a
I	Gas samples	64	71.2 ± 0.7 ^b	
	Sorbent tubes	64	69.8 ± 1.5	-2
II	Gas samples	13	14.5 ± 0.5	
	Sorbent tubes	13	13.6 ± 0.4	-6
III	Gas samples	2.6	2.88 ± 0.07	
	Sorbent tubes	2.6	2.91 ± 0.13	+1
IV	Gas samples	1.3	-	
	Sorbent tubes	1.3	1.27 ± 0.09	-

- a. The estimated error is the average of concentrations determined from sorbent tubes minus the average of concentrations determined from gas samples, divided by the average of concentrations determined from gas samples, multiplied by 100.
- b. The number given is the mean value plus or minus the 95% confidence level. The 95% confidence level is defined as the standard deviation multiplied by Student's *t* at the 0.05 significance level, divided by the square root of the number of samples.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a rapid instrumental method. The method can also be used for the simultaneous determination of two or more components suspected to be present in the same sample by changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the amount of vinyl chloride that the tube will hold before it becomes overloaded. When the sample value obtained for the backup section of the sorbent tube exceeds 20% of that found on the front section, the possibility of sample loss exists. During storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time, 33% of these compounds will be found in the backup section. This may lead to some confusion as to whether sample loss has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20°C. (See Section 8.2.10.)
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop and, therefore, the flow rates across the tubes. Because the pump is usually calibrated for one particular tube, differences in flow rates can occur when sampling through other tubes and can cause sample volumes to vary.

6. Apparatus

- 6.1 **Personal Sampling Pump.** The pump should be a properly calibrated personal sampling pump for personal and area samples. It should be calibrated with a representative sorbent tube in the sampling line. A dry or wet test meter or a glass rotameter that will determine the flow rate (50 mL/min) to within $\pm 5\%$ may be used for the calibration.
- 6.2 **Sorbent Tubes.** The glass tubes have both ends flame sealed. Each is 7 cm long, 6-mm o.d., 4-mm i.d., and contains two sections of 20/40-mesh activated carbon separated by a 2-mm portion of urethane foam. The activated carbon is prepared from coconut shells and is fired at 600°C prior to packing to remove adsorbed materials. The primary adsorbing section contains 100 mg of sorbent, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silanized glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 2 in. of water at a flow rate of 0.2 L/min.
- 6.3 **Gas chromatograph** equipped with a flame ionization detector.
- 6.4 **Stainless steel column** (20 ft x 0.125 in.) packed with 10% SE-30 on 80/100-mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). Other columns capable of performing the required separations may be used.
- 6.5 **A mechanical or electronic integrator or a recorder** and some method for determining peak area.
- 6.6 **Vials (2-mL)** that can be sealed with caps containing Teflon-lined silicone rubber septa.
- 6.7 **Microliter syringes** (10- μ L, and convenient sizes for making standards).
- 6.8 **Gas-tight syringe** (1-mL, with a gas-tight valve).
- 6.9 **Pipettes** (0.5-mL delivery pipettes or 1.0-mL type graduated in 0.1-mL increments).
- 6.10 **Volumetric Flasks** (10-mL, or convenient sizes for making solutions). It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

- 7.1 **Carbon disulfide**, spectroquality or better grade.
- 7.2 **Vinyl chloride**, lecture bottle, 99.9% minimum purity.
- 7.3 **Toluene**, chromatographic quality.
- 7.4 **Purified helium**.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be washed with detergent and thoroughly rinsed with distilled water.

8.2 Collection and Shipping of Samples

- 8.2.1** Immediately before sampling, the ends of two tubes are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.2.2** The second sorbent tube is used as a backup and is positioned next to the sampling pump in tandem with the first tube.
- 8.2.3** The sorbent tubes are placed in a vertical position with the larger section of sorbent pointing up during sampling to minimize channelling of the vinyl chloride through the sorbent.
- 8.2.4** Air being sampled is not to be passed through any hose or tubing before entering the sorbent tubes.
- 8.2.5** The flow rate and time, or volume, must be measured as accurately as possible. The sample is taken at a flow rate of 50 mL/min. The maximum volume to be sampled should not exceed 5 liters. (See Section 2.2.)
- 8.2.6** Relatively large volumes (10 to 20 liters) of air also should be sampled through other sorbent tubes at the same time personal samples are taken. These bulk air samples will be used by the analyst to identify possible interferences before the personal samples are analyzed.
- 8.2.7** If the temperature and pressure of the atmosphere being sampled are significantly different from 25°C or 760 mmHg, they should be measured and recorded.
- 8.2.8** The sorbent tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.
- 8.2.9** One tube is handled in the same manner as a sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

- 8.2.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. The use of two tubes in series has eliminated the need for cooling during shipping. However, if two tubes are *not* used, *i.e.*, only one tube is used, and if the samples will spend a day or more in transit, then cooling (*e.g.*, with Dry Ice) is necessary to minimize migration of vinyl chloride to the backup section.
- 8.2.11 Samples received at the laboratory are logged in and immediately stored in a freezer (around - 20°C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20°C, vinyl chloride will equilibrate between the two sections of activated carbon, *i.e.*, it will migrate to the backup section. This phenomenon is observable after 2 weeks and may be confused with sample loss after 1 to 2 months.

8.3 Analysis of Samples

- 8.3.1 Preparation and Desorption of Samples. The two tubes used in the collection of a single sample are analyzed separately. Each tube is scored with a file and broken open at each end. The glass wool is discarded. Both sections of each tube are transferred to a small vial containing 1 ml of carbon disulfide. It is important to add the sorbent to the carbon disulfide and not the carbon disulfide to the sorbent. The vial is topped with a septum cap. The separating section in each tube is discarded. Tests indicate that desorption is complete in 30 min if the sample is agitated occasionally during this period. The samples should be analyzed within 60 min after addition to carbon disulfide. If only one tube is used for sampling, then each section of activated carbon should be analyzed separately.
- 8.3.2 Gas Chromatographic Conditions. The typical operating conditions for the gas chromatograph are:
1. Helium carrier gas flow, 40 ml/min (80 psig).
 2. Hydrogen gas flow to detector, 65 ml/min (20 psig).
 3. Air flow to detector, 500 ml/min (50 psig).
 4. Injector temperature, 230°C.
 5. Detector temperature, 230°C.
 6. Column temperature, 60°C.

8.3.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10- μl syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 μl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5- μl aliquot is withdrawn to the 7.4 μl mark (2 μl solvent + 0.4 μl air + 5 μl sample = 7.4 μl). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected. Automatic sampling devices may also be used.

8.3.4 Measurement of Area. The area under the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The efficiency of desorption of a particular compound can vary from one laboratory to another and also from one batch of sorbent to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the desorption process. Desorption efficiency should be determined on the same batch of sorbent tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube), particularly at lower values, *e.g.*, 2.5 μg .

8.4.2 Procedure for Determining Desorption Efficiency. Sorbent tubes from the same batch as that used in obtaining samples are used in this determination. A measured volume of vinyl chloride gas is injected into a bag containing a measured volume of air. The bag is made of Tedlar (or a material that will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration in the bag may be calculated if room temperature and pressure are known. A measured volume is then sampled through a sorbent tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples. (See Section 8.3.) Samples taken with a gas-tight syringe from the bag are also injected into the gas chromatograph. The concentration in the bag is compared to the concentration obtained from the tubes.

- 00 -

The desorption efficiency equals the amount of vinyl chloride desorbed from the sorbent divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{(\text{amount of vinyl chloride from sorbent})}{(\text{concn of vinyl chloride in bag}) \times (\text{vol of atmosphere sampled})}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 194, Friday, October 4, 1974, pp. 35890-35898).

A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same gas chromatographic conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in $\mu\text{g}/\text{mL}$ versus peak area. There are two methods of preparing standards and, as long as highly purified vinyl chloride is used, both are comparable.

If no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the flame ionization response.

9.1 Standard Preparation

- 9.1.1 **Gravimetric Method.** Vinyl chloride is slowly bubbled into a weighed 10-mL volumetric flask containing approximately 5 mL of toluene. After 3 min, the flask is again weighed. A weight change of 100 to 300 mg is usually observed. The solution is diluted to exactly 10 mL with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of values that are linear from the range of 0.2 ng per injection, the minimum detectable amount of vinyl chloride, to 1.5 μg per injection.

9.1.2 **Volumetric Method.** A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the valve is closed. The tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS₂. The valve is opened and the plunger is withdrawn slightly to allow the CS₂ to enter the syringe. The action of the vinyl chloride dissolving in the CS₂ creates a vacuum and the syringe becomes filled with the solvent. An air bubble (2%) is present and has been found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS₂ and the washings added to the volumetric flask. The volumetric flask is then filled to the mark with CS₂. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and have been found to be stable at this temperature for 3 days. Tight-fitting plastic tops on the volumetric flasks seem to retain the vinyl chloride better than ground-glass stoppers.

10. Calculations

10.1 The weight, in μg , corresponding to the area under each peak is read from the standard curve for vinyl chloride. No liquid volume corrections are needed because the standard curve is based on the number of micrograms in 1.0 ml of CS₂ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank are made for each sample.

$$\mu\text{g} = \mu\text{g}_s - \mu\text{g}_b$$

where: μg_s = μg found on sample tube.

μg_b = μg found on blank tube.

A similar procedure is followed for the backup sections.

10.3 The amounts present in the front and backup sections of the same sample tube are added to determine the total amount of vinyl chloride in the sample.

10.4 The total amount is corrected for the desorption efficiency at the level of vinyl chloride measured.

$$\text{Corrected amount (in } \mu\text{g)} = \frac{\text{amount (in } \mu\text{g)}}{\text{desorption efficiency}}$$

10.5 The concentration of vinyl chloride in air may be expressed in mg/m^3 :

$$\text{mg}/\text{m}^3 = \frac{\text{corrected weight (in } \mu\text{g)}}{\text{volume of air sampled (in } \ell)}$$

10.6 The concentration may also be expressed in terms of parts per million (ppm) by volume:

$$\text{ppm} = \text{mg}/\text{m}^3 \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T+273}{298}$$

where: 24.45 = molar volume (ℓ/mole) at 25°C and 760 mmHg.

M.W. = molecular weight.

P = pressure (mmHg) of air sampled.

T = temperature ($^\circ\text{C}$) of air sampled.

11. References

11.1 Hill, R.H., C.S. McCammon, A.T. Saalwaechter, A.W. Teass, and W.J. Woodfin, "Determination of Vinyl Chloride in Air," in preparation.

11.2 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere." Amer. Ind. Hyg. Ass. J., 31, 225 (1970).

The BFGoodrich Company
Chemical Group
6100 Oak Tree Boulevard
Cleveland, Ohio 44131
216-524-0200

August 28, 1980
RDS-92-80

Mr. Ray Novak - Tech. Dir.
Rhineland Paper Company
Rhineland, WISC. 54501

Dear Mr. Novak:

RE: RESULTS OF AREA MONITORING AT RHINELANDER PAPER COMPANY

On August 7, 1980, Bill Potter and T. S. Bialke visited Rhineland to monitor the Geon 576 papercoating line for VCM emissions.

Sampling Method

The sampling method used in this report was adsorption of VCM onto activated charcoal using SKC charcoal tube at 30-60 cc/min; analysis was by gas chromatography.

Samples were collected from the breathing zone of all employees involved in the coating operation. General area samples were also collected at potential sources of VCM release. Analysis of the samples were performed by the BFGoodrich Corporate Environmental Health Laboratory in Brecksville, Ohio. The laboratory is accredited by AIHA.

OSHA Requirements

The current OSHA requirement as outlined in the Federal Register Vol. 39, No. 194, Part II, Friday, October 4, 1974 is as follows:

- a) Permissible Exposure Limit
1 ppm averaged over any 8 hour period, and a ceiling of 5 ppm averaged over any period not exceeding 15 minutes.
- b) Action Level
The Standard provides for an "action level" of 0.5 ppm TWA.

Results

Results of monitoring coating with Geon 576, lot 2006139, which contained 18.08 mg/kg of residual VCM on a wet basis, are shown on the attached table. The operators of the coating line are exposed to VCM during their workday. However, their exposure according to this data, appears to be within legal limits and significantly less than the OSHA action level of 0.5 ppm.

BFG32238

24542047

Mr. Ray Novak
Rhinelander Paper Company

-2-

August 28, 1980

The results above are based on limited testing and actual continuing factory exposure may be different. The test results are believed to be representative of conditions found under the particular and peculiar operating conditions existing at the time and place where the tests were made and no representations are made concerning other times, conditions or production levels. Submission of the test results is not intended to determine or insure compliance with any standard, specification, governmental regulation or policy, although such results can be useful in establishing the elements necessary for a program of compliance. We hope that the data presented will assist you in continuing to provide a safe workplace for your employees.

The responsibility of maintaining an environment in compliance with OSHA regulations rests with the individual manufacturer.

Sincerely yours,

BFGOODRICH CHEMICAL GROUP
Latex Division

R. D. Satava
Product Manager

/mfk
Attachment

bcc: CF
LF
Bill Potter
OSHA File
Test Data File, D/5410

BFG32239

K. Schneider

Cleveland Chemical

T. S. Bialke

Akron - D/0020, 5-H

8-25-80

RHINELANDER PAPER CO. - VCM

On August 7, 1980 the Rhineland Paper Company, Rhineland, Wisconsin was visited to monitor the workplace for VCM. The visit was made at the request of the customer, since they were using a BFG latex in their operations. Samples were collected on SKC charcoal tubes at 30-60 cc/min.; analysis was by gas chromatography.

Samples were collected from the breathing zone of all employees involved in the coating operation. General area samples were also collected at potential sources of VCM release. Analysis of the samples was performed by the BFGoodrich Corporate Environmental Health Laboratory in Brecksville, Ohio. The laboratory is accredited by AIHA.

The latex used during the coating run contained 18.03 mg/kg of residual VCM, on a wet basis. *lot 2004139*

Results of the monitoring are shown in the attached table. The lower detection limit by the laboratory was approximately 0.1 ppm and, although VCM was detected in all the samples, the quantity present was near this detection limit. Concentrations were significantly less than the OSHA action level of 0.5 ppm.

T.S. Bialke
T. S. Bialke

v

cc: H.W.Dietz/E.B.Katzenmeyer, Jr.

*MA. Ray 7/21/80 - TCC 4.01A
54501*

BFG32240

24542048

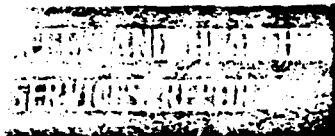
RHINELANDER PAPER COMPANY

VCM MONITORING RESULTS - 8/7/80

<u>Sample/Location/ Operation</u>	<u>Sample Time (min.)</u>	<u>Sample Volume (liters)</u>	<u>Concentration (ppm)</u>
H. Fisher	200	10.2	0.2
Coating/Mixing	223	10.2	0.3
R. Craig, Foreman	426	10.1	0.2
J. Entonuk	190	10.0	0.1
Coater Operator	220	11.3	0.1
J. Haenol, Helper	172	6.0	0.3
	222	8.7	0.2
* G.A. left of deaeration tank, mezzanine	421	19.0	0.1
G.A. south side, 2 ft. above 1st coating station trough	202	10.5	0.1
	213	12.0	0.1
G.A. north side, 2 ft. above 1st coating station	181	11.0	0.2
	215	13.4	0.1
G.A. south side, 2 ft. above 2nd coating station	178	9.9	0.2
	205	11.2	0.1

* G.A. = General Area Sampling

BFG32241



Wausau Insurance Companies

2000 WESTWOOD DRIVE
WAUSAU, WISCONSIN 54401

FOR

W. Thomas Myers, Vice President
and General Manager
Rhineland Paper Company, Incorporated
515 West Davenport Street
Rhineland, Wisconsin 54501

August 18, 1980

CONCERNING

515 West Davenport Street
Rhineland, Wisconsin

REPORTED BY

R. L. Young, senior environmental health engineer; and
M. E. Burkhardt, senior safety consultant; on August 7, 1980

PERSONS CONTACTED

Fran Ratliff, technical director
Ray Novak, technical supervisor for converting

REPORT SUMMARY

ENVIRONMENTAL HEALTH ENGINEERING SERVICE

This survey was made at the request of Mr. Fran Ratliff, technical director, to determine the concentration of vinyl chloride to which employees are exposed while coating paper with polyvinyl chloride.

Fifteen air samples were collected in the employee's breathing zone on activated charcoal tubes utilizing calibrated Mine Safety Appliances Company Model S sampling pumps and a Sipin sampling pump, Model SP-1. The samples were analyzed by means of gas chromatography in our laboratory (AIHA Accreditation Number 34). Results of the air samples are shown in Table I along with the OSHA permissible exposure level and other sampling information.

Reference to Table I shows that no vinyl chloride was detected at the lower limit of detection based on the analytical method and the air volume sampled. The lower limit of detection is well below the OSHA eight-hour

BFG32242

This report covers only conditions and practices observed and considered at the time of this call. It is not intended to indicate that any hazards are adequately controlled or that such conditions or practices meet the requirements

If you have any comments or questions concerning this report, write to G. B. Lemke, Vice-President, Safety & Health Services.

Consultative safety and health services are

CLONING

August 18, 1980

W. Thomas Myers
Rhineland Paper Company
Incorporated

time-weighted average permissible exposure level of one part per million (p.p.m.) and also below the OSHA action level of 0.5 p.p.m.

HO 64

cc: Theodore Asti, Jr.
Richard L. Radt
Larry A. Baker
Richard J. LaCerte
James Berard
Carl Liebert

BFG32243

TABLE I

CONCENTRATIONS OF VINYL CHLORIDE

Rhineland Paper Company
Rhineland, Wisconsin
August 7, 1980

sample number	Sample Location	Concentration of Vinyl Chloride		Lower Limit of Detection (3) P.P.M. (1)	Sample Time
		P.P.M. (1) Found	OSHA PEL (2)		
1	Bob Craig, foreman	None Detected	1	0.2	7:35 a.m.-8:17 a.m.
2	Jerome Fisher, coater mixer	None Detected	1	0.2	7:35 a.m.-8:17 a.m.
3	Jack Antonuk, coater operator	None Detected	1	0.2	7:43 a.m.-8:25 a.m.
4	Bob Craig	None Detected	1	0.3	8:16 a.m.-8:51 a.m.
5	Jerome Fisher	None Detected	1	0.2	8:23 a.m.-9:00 a.m.
6	Jack Antonuk	None Detected	1	0.3	8:33 a.m.-9:07 a.m.
7	Gary Gee, helper	None Detected	1	0.3	8:58 a.m.-12:46 p.m.
8	Jerome Fisher	None Detected	1	0.2	9:17 a.m.-9:55 a.m.
9	Jack Antonuk	None Detected	1	0.2	9:14 a.m.-10:10 a.m.
10	Bob Craig	None Detected	1	0.3	10:01 a.m.-10:34 a.m.

BFG32244

24542050

TABLE 1 - 20 -
(Continued)

-2-

Sample Number	Sample Location	Concentration of Vinyl Chloride		Lower Limit of Detection(3)		Sample Time
		P.P.m.(1)		P.P.m.(1)		
		Found	OSHA PKL(2)			
11	Jack Antonuk	None Detected	1	0.2	10:15 a.m.-10:52 a.m.	
12	Jack Antonuk	None Detected	1	0.3	10:35 a.m.-11:10 a.m.	
13	Jerome Fisher	None Detected	1	0.3	12:39 p.m.-1:15 p.m.	
14	Jerome Fisher	None Detected	1	0.3	2:15 p.m.-2:46 p.m.	
15	Jack Antonuk	None Detected	1	0.4	2:16 p.m.-2:40 p.m.	

BFG32245

- (1) P.P.M. - Parts of contaminant per million parts of air by volume.
- (2) OSHA Permissible Exposure Level - Title 29 Code of Federal Regulations, Part 1910, Subpart Z, Section 1910.1017, Vinyl Chloride.
- (3) Lower limit of detection is based on the analytical method and volume of air sampled.