BFG TECHNICAL DOCUMENT

BFGoodrich
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 Rhinelander 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 Rhinelander 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.

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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:

Latex	Latex Temperature, °F	Critical RVCM, mg/kg
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.

Latex	Plasticizer, pphr	Base Resin	Latex Temperature, °F	Calculated Critical RVCM, mg/kg
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.

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:

Range	Limits
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

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.

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.

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.

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.

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.

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.

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.

Table IV

Chromatography Conditions for VCM
Analysis by the CS_2 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

Table V

Blanks: Background VCM Concentration in Air, ppm

Test	1	2	Ave.	
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, cylinder
17	0.02	0.01	0.015	
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	

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.

VII. Translation of Critical RVCM 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

Table VIII

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

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

Corresponds with AVCM = 0.33 ppm in closed, unventilated room

Latex	Plasticizer pphr	Base Resin	Calculated Critical RVCM mg/kg (110°F) (1)		Allowable RVCM Limit for Base Resin mg/kg
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.

Table IX

AVCM Calculated from RVCM Loss Data

Weight of Latex: 42.0 lb.

Test	Latex Tested	Latex % T.S.	Latex Temp., °F	Test Period, min.	RVCM Loss, mg/kg	RVCM Ave., mg/k	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)

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

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. The loss is equivalent to expanding the original volume of 1000 ft^3 to 4350 ft^3 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 ft^2) is taken into account and the diffusion rate becomes: $(1.76)(10^{-4})$ lb/ft^2-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 ft^3/hr. Since the room volume is 1000 ft^3, 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.

IX. AVCM Estimate for a Typical Compounding Operation

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

Work space: volume 20 ft x 40 ft x 25 ft (= 20,000 ft^3)

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

Compound mix tank:

volume 1000 gal.

diameter 60 in.
(liquid-air interface 2830 in^2)

agitated

Latex: Geon 576, 57% T.S., RVCM variable

temperature 110°F

Basis for calculations:

1) The rate of diffusion from the latex to the air space is 1.76×10^{-4} lb/ft^2-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:

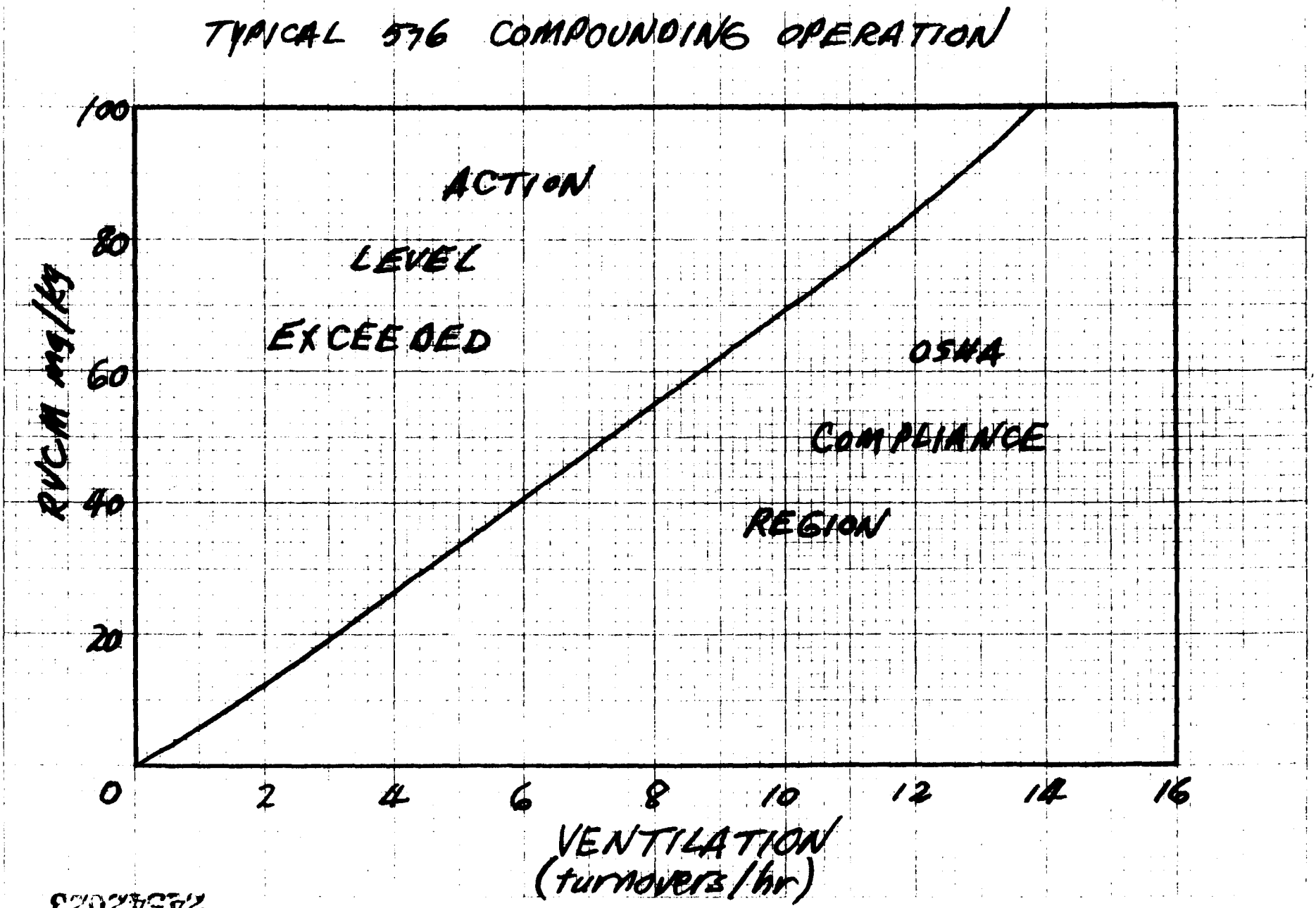
$$p_{vcm} = (0.33)\ (10^{-6})\ \ p_T = (2.475)(10^{-4}) \text{ mm Hg where } p_T = 750 \text{ mm Hg}$$

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, $555.0\ \frac{\text{mm Hg - ft}^3}{\text{lb-mol - °R}}$
T = absolute temperature = 90 + 460 = 550°R

Fig. 5 Ventilation Requirement for OSHA Compliance



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.

A P P E N D I X

BFG TECHNICAL DOCUMENT

APPENDIX NO.

PAGE NO.

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

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

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.

2454426

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.

FIGURE 1
OSHA
SAMPLING PROGRAM

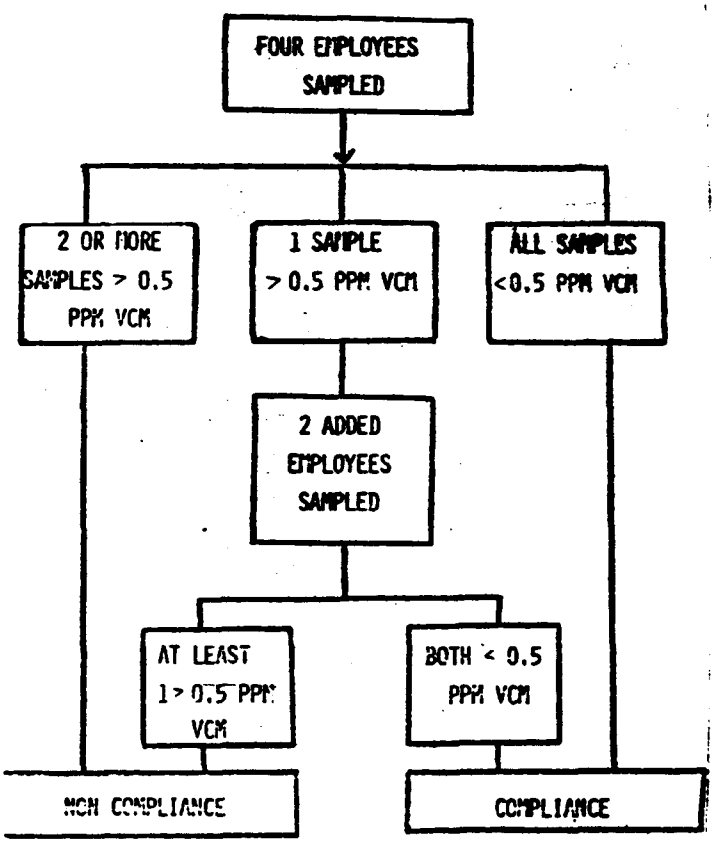
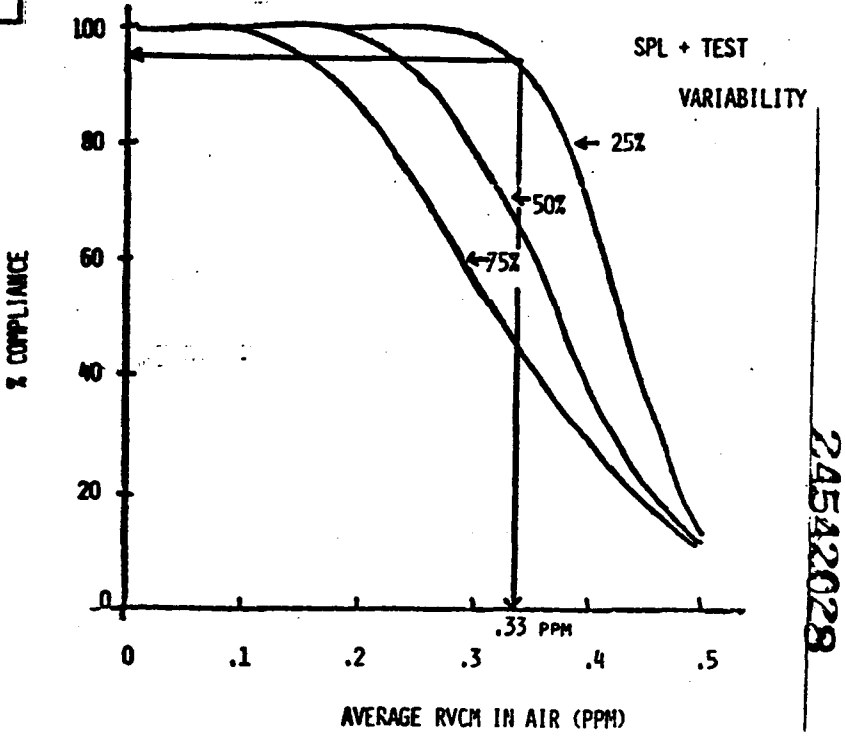


FIGURE 2

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



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	"

BFGOODRICH CHEMICAL DIVISION

Standard Sampling Procedure No. 2800-A

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.

Date Issued 8/10/78

Issued From M.S. Lab

Written By J.A. Baclawski L.Wallis

Revised By R.A. Mansfield, Jr.

	APPROVALS	DATE
1. M.S. Lab	J.P. Cornwell	12/9/75
2. Akron	A.J. Vielhaber	12/12/75
3. Avon Lake	D.G. Desrosiers	1/5/76
4. Calvert City	E.E. Atkins	1/12/76
5. Henry	C.D. McCrosky	1/12/76
6. Long Beach	C.W. Ball	1/7/76
7. Louisville	R.R. Taylor	1/5/76
8. Pedricktown		
9. Orange	--	--
10. Port Neches	--	--
11. ALTC	E.G. DeCapita	12/11/75
12. Brecksville	P.M. Zakriski	1/19/76
13. BFG International	J.M. Hyslop	1/19/76

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.

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 sec./min ÷ sec./cc = 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).

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:

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

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.

SHIFT _____

PERSONNEL MONITORING - VINYL CHLORIDE MONOMER, BENDIX FLASHER DATE ___/___/___

Ambient Temperature _____ Page _____ of _____

% Relative Humidity _____

	C	S	S	S	S	S	L	L	L	L	L		
	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 Pump Peak After	
1.	-1							~	~	YES	~		
	-2		~		~	~				NO			
2.	-1							~	~	YES	~		
	-2		~		~	~				NO			
3.	-1							~	~	YES	~		
	-2		~		~	~				NO			
4.	-1							~	~	YES	~		
	-2		~		~	~				NO			
5.	-1							~	~	YES	~		
	-2		~		~	~				NO			
6.	-1							~	~	YES	~		
	-2		~		~	~				NO			
7.	-1							~	~	YES	~		
	-2		~		~	~				NO			
8.	-1							~	~	YES	~		
	-2		~		~	~				NO			
9.	-1							~	~	YES	~		
	-2		~		~	~				NO			
10.	-1							~	~	YES	~		
	-2		~		~	~				NO			

Time at START _____ HRS TEMPERATURE _____ °F HUMIDITY _____ %

Time at END _____ HRS TEMPERATURE _____ °F HUMIDITY _____ %

JNW 10/14/7

2454034

B.F.GOODRICH CHEMICAL COMPANY

Standard Test Procedure No. 1021-A

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

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 - Briskeat Cat. No. B1H-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 N_2 supply to the desorption unit inlet and backflush inlet. With the backflush de-energized, the N_2 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.

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 µgm 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.

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 $ppm_{(v)}$ of the air volume sampled by the following equation:

$$ppm_{(v)} = \frac{(\mu g\ VCM)(22414 cc/mole)(295°K)(760mm\ Hg)}{(62.5 g/mole)(273°K)(750mm\ Hg)(total\ cc's)}$$

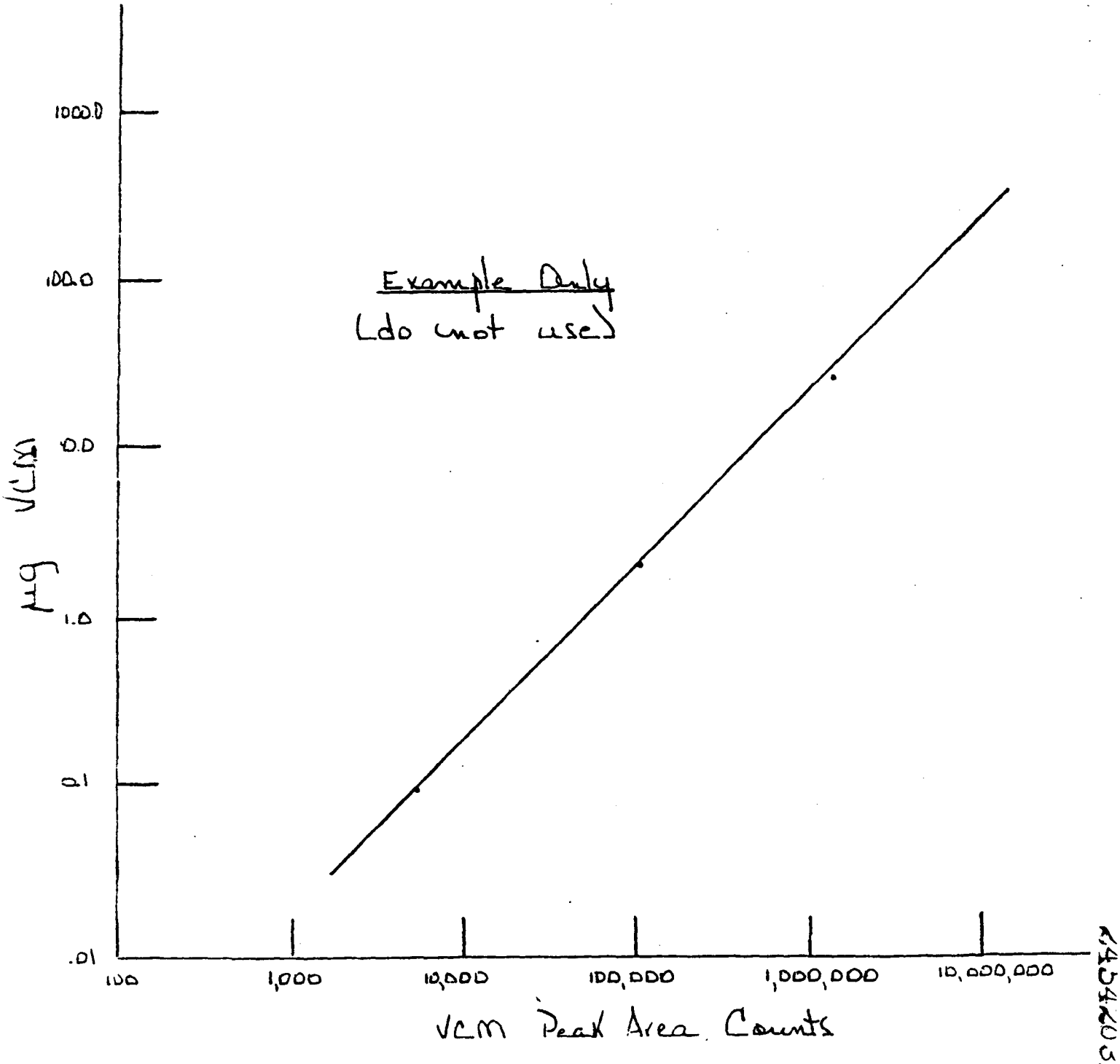
Simplified equation:

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

XF = 392.69 (see Note #4)

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

L5 phase log-log)



4454059

Attachment #3
Monroe Program No. 113.1860 Printout

Monroe Program No. 114.1960 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	8
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	075	K
1	060	
2	052	T
3	060	
4	116	L
5	003	3
6	060	
7	055	
8	176	
9	176	
0150	066	
1	055	I
2	056	
3	060	
4	050	S
5	116	L
6	011	9
7	051	S
8	061	A
9	176	
0160	127	W
1	067	
2	055	I
3	127	W

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.

Experiment No.		Concentration, calculated, mg/m³	Concentration, experimental, mg/m³	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.

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.

8.3.3 **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-$\mu\ell$ 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 $\mu\ell$ 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-$\mu\ell$ aliquot is withdrawn to the 7.4 $\mu\ell$ mark (2 $\mu\ell$ solvent + 0.4 $\mu\ell$ air + 5 $\mu\ell$ sample = 7.4 $\mu\ell$). 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.

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 CS_2. The valve is opened and the plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 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 CS_2 and the washings added to the volumetric flask. The volumetric flask is then filled to the mark with CS_2. 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 CS_2 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.

$$\mu g = \mu g_s - \mu g_b$$

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.

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

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.
Rhinelander Paper Company
Rhinelander, 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 Rhinelander 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.

K. Schneider — Cleveland Chemical

T. S. Bialke — Akron - D/0020, 5-H — 8-25-80

RHINELANDER PAPER CO. - VCM

On August 7, 1980 the Rhinelander Paper Company, Rhinelander, 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.

Mk Rag ~~Ass~~ novak - TCC w.Div.
54521

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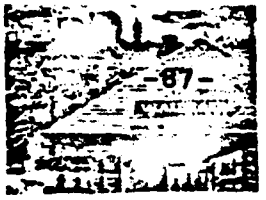

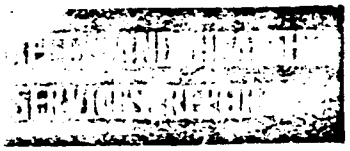

Wausau Insurance Companies

2000 WESTWOOD DRIVE
WAUSAU, WISCONSIN 54401

FOR

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

August 18, 1980

CONCERNING	515 West Davenport Street Rhinelander, 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

2,454,204.9

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

TABLE I

CONCENTRATIONS OF VINYL CHLORIDE

Rhinelander Paper Company
Rhinelander, Wisconsin
August 7, 1980

Sample Number	Sample Location	Concentration of Vinyl Chloride p.p.m.(1) Found	OSHA PEL.(2)	Lower Limit of Detection(3) p.p.m.(1)	Sample Time
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.