



37 Code zero
BFGoodrich General PT-1(4)
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INTERNATIONAL DEPARTMENT

VIA AIR MAIL

October 23, 1974

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Mr. N. Vakili
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Mr. A.M. Vermorken
Mr. D.A. Brooks
Mr. S. Ramaswamy

This transmittal contains information of very recent nature regarding our Code Zero work.

Our Manufacturing Services Laboratory has been trying the Perkin Elmer Head Space Analyzer to measure RVCM content of dry PVC resins, slurry, wet cake and latexes, also to monitor personnel. Progress is summarized in the attached report for September, 1974. Our current status indicates that for greatest accuracy and reproducibility of tests, the Perkin Elmer instrument is superior to the Hewlett-Packard 5711A, although the latter may be preferred for certain OSHA, EPA and FDA tests which are still undefined.

The enigmatic test method situation is of concern to us for obvious reasons, one of which pertains to the high cost of some apparatus. Consequently, Lin Crider has investigated thoroughly and reported in an attachment entitled Analytical and Monitoring Procedures Required for Compliance with the OSHA Permanent Standard for VCM.

See the attached Equilibrium VCM Vapor Concentration over PVC Resin for data which is important in connection with warehousing and shipping of PVC resin.

Excerpts from the Code Zero Task Force - Biweekly Progress Report - 29, dated October 14, 1974

"The Closed Poly experiment in a 4300-gallon glass reactor at ALGCP was discontinued after 61 charges due to excessive buildup on the stainless steel agitator hub..... In the next experiment the agitator hub will be replaced with a new smooth hub to see if a slower buildup in this area will occur."

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"Operation of the 30" steam stripping column at ALGC on unstripped slurry has been successfully demonstrated in connection with the plant monomer recovery system. Four runs have been completed on shortstopped 110X400 slurry which was blown down at 30 psi pressure drop. No carryover was observed at feed rates from 15 to 45 gpm. Rising column pressure drop indicated that column flooding was imminent. Steam consumption was less than 0.2 pounds steam per pound resin and was condensed and returned to the column as reflux. Interface with the isolated, second plant recovery compressor set was trouble free. Initial runs were made with feed to a preliminary cyclone but a later run indicated successful operation without the cyclone."

"Analytical data indicates RVCN levels below 1 ppm after only 10 tray control---performance superior to operation with previously recovered slurry. Diffusion measurements on processed slurry are awaited to see if popcorning via substantial flashing at the elevated temperature (230°F) has improved diffusion characteristics."

"A revised estimate has been received from Girdler for the plant columns and budget estimates have been prepared for interfacing requirements at the plant. These costs were presented at the PVC Plant Managers' meeting October 10, 1974. We are proceeding with estimates and E.A.'s for a total of nine columns."

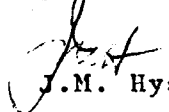
"Efforts to handle Geon 121 in the steam stripping column at Brecksville continue to be unsuccessful. Variation in column operating pressure from 10 psig to 26 Hg vacuum appeared to have no effect on the overwhelming foaming problem. Previous attempts to minimize foam formation with anti-foam were unsuccessful. Means of reducing free soap prior to the use of anti-foam are being investigated as is mechanical defoaming via ultrasonic whistles, but the prospects are not encouraging."

"Extensive work on RVCN removal in dispersion resins has been initiated both in R&D and the plants."

Attached is a copy of a table entitled 1974 PVC Reactor Entry Frequency. That indicates the entries number anywhere from 1-100% of the charges, with an average of 5-10%. Not bad compared with the early days when entry was 100% period.

Last, but far from least, I have attached material from a recent, special Plant Managers' Meeting, dated October 10, 1974. Included are the agenda, summary of important points and decisions, a commentary of labeling practices to be observed, a sketch of VCI stack system and a table of allowable type masks.

Sincerely,


J.M. Hyslop

JMH/lfa

Attachments

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24688002

Inter-Organization Correspondence

TO O.F. Beckmeyer	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO. Cleveland	DATE YOUR LETTER
FROM J.M. Whitney	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO. Avon Lake General Chemical	DATE THIS LETTER 10/7/74
SUBJECT		

Progress Report
Manufacturing Services Laboratory
September, 1974

I. Perkin Elmer Head Space Analyzer & Integrator

1. Head Space Analyzers have been ordered for Henry, Pedricktown, Long Beach and the M.S. Laboratory.
2. Integrators have been ordered for Long Beach, Louisville, Pedricktown and M.S. Laboratory.

The Henry plant is planning to purchase an Autolab IV integrator which will be interfaced with the Head Space Analyzer.

Delivery on above units is now scheduled for January 1, 1975.

II. Head Space Analyzer Projects

1. RVCN Content of Dry PVC Resins - This project has been completed for normal EP resins. Both Louisville and Avon Lake are using the method. Procedure No. 1005-T has been written covering this method.

We have some indications that this method, as written, may not be adequate for special polymers such as 130X17 and copolymers. More development effort is required to verify that these samples reach equilibrium within 1 hour and that no impurities interfere with the VCM peak.

2. RVCN Content of Slurry and Wet Cake Samples - This analysis has been studied by M.Mele at ITC. He will be issuing a procedure for this using the Head Space Analyzer, sometime prior to October 15, 1974. This method will be incorporated into Procedure 1005-T

(continued)

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TO: O.F. Beckmeyer

10/7/74

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Progress Report - Manufacturing Services Laboratory - September, 1974

II. Head Space Analyzer Projects (continued)

3. Personnel Monitoring - Use of the Head Space Analyzer to determine the VCM content of the activated carbon used for personnel monitoring is being evaluated. Initial experimental efforts have shown that this technique can be developed with reasonably good sensitivity.

In this case we are attempting to develop a carbon analysis which will be compatible with our standard Head Space method for PVC resins. Since the standard method operates at 90°C we are forced to use this temperature to thermally elute the VCM from the carbon. To obtain good reproducibility, the samples require long aging periods at 90°C in an oven (17 hours).

To date our best experimental run was made under the following conditions:

Aging Time	--	17+ 1/2 hour
Aging Temp	--	90°C ±1.0
Grams Carbon	--	2.000
Volume Water Added	--	3.0 cc

Equations for the relationship of X (ppm VCM in Perkin Elmer vial) and Y (ppm VCM in air as originally sampled), based on a standard flow of 10 liters air passed through 8.3 grams carbon at a rate of 1 liter per minute, have been developed. These equations are valid for values of Y from 0.1 to 10.0 ppm.

$$X = 26.1592 (Y)^{0.805}$$

$$Y = 0.0174 (X)^{1.2408}$$

Experimental work is in progress to:

1. Determine overall reproducibility.
2. Determine optimum aging period.
3. Evaluate different levels of water.
4. Evaluate use of surface active agents in an attempt to release more VCM to the air.
5. Check regular septums versus teflon septums.
6. Evaluate different lots of carbon black.
7. Develop simple method to accurately prepare calibration carbon tubes for routine instrument standardization.

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TO: O.F. Beckmeyer

10/7/74

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Progress Report - Manufacturing Services Laboratory - September, 1974

II. Head Space Analyzer Projects (continued)

4. Residual Monomers in Latex - This is an important project but no work has been done as yet.

III. Training Program

The M.S. Laboratory is training four ALGC laboratory operators to run the Perkin Elmer head space analyzer. This involves a 3 week period and each man will spend about 3 or 4 full days in individualized training.

- IV. Progress reports of J.P.Cornwell and F.V.Zemanek are attached.


J.M. Whitney

JMW/bjs

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Inter-organization Correspondence

BFGoodrich

TO	See Distribution	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO.	RECEIVED The B.F. Goodrich Co. Chemical Division	DATE YOUR LETTER
FROM	L. B. Crider	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO.	OCT 10 1974	DATE THIS LETTER October 8, 1974
SUBJECT	Analytical and Monitoring Procedures Required for Compliance With the OSHA Permanent Standard for VCM			

Since the publication of the OSHA Permanent Standard for VCM on Oct. 4, I have been attempting to obtain some clarification as to the specific analytical procedures that will be acceptable to OSHA for compliance with this new regulation. At the present time I can only say that the total picture relating to both the continuous monitoring requirements and personal monitoring procedures are not sufficiently defined to allow an assessment of what these total requirements may be. There are several key bits of information which relate to the cause for this confused situation and of which you should be aware;

- (1) The requirements for monitoring as outlined in 1910.93 g (d) (4) on p. 35869, Vol. 39, No. 194 of the Federal Register (10/4/74) states that the required procedures are available in the "NIOSH Manual of Analytical Methods". This manual does not contain a procedure for VCM. Attached you will find a copy of the Table of Contents from this manual. It is conceivable that the procedure identified as a method for the analysis of "Organic Solvents in Air" (#127) may be the procedure referenced in the Federal Register; however, my contacts at the NIOSH laboratory in Cincinnati do not confirm this.
- (2) The NIOSH laboratory in Cincinnati has a procedure for "Vinyl Chloride in Air" that has not been issued. It is currently classified as an "Operational Procedure" but the precision of the method is unknown. A copy of this procedure is also attached.
- (3) Our contact at SPI on analytical procedures, Dr. Dan Dixler (Keller & Heckman, Washington), also was not able to offer any clarification as to an interpretation of either the continuous monitoring or personal monitoring procedures. To the best of his knowledge no one in the PVC industry has been able to identify the procedures that will be required.
- (4) A letter has been written to Mr. John Stender, Assistant Secretary of Labor, requesting identification of appropriate or acceptable monitoring and analytical procedures.
- (5) A purchase order has been sent to the U. S. Government Printing Office in Washington for 100 copies of the NIOSH manual referenced in the Federal Register. There is a scant possibility that this order will be filled since the only few existing copies are at the NIOSH laboratory in Cincinnati. I was able to obtain only a single copy until additional printings are made.

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Although the specific details of the analytical methods have not been identified our current best judgment is that the personal monitoring procedure will be a charcoal tube sample collection and a gas chromatographic analysis similar to the enclosed NIOSH #178. Personal monitoring will be required for those employees working in areas where VCM can exceed the "Action Level" (0.5 ppm averaged over an 8 hour day). Personal monitoring must be repeated monthly for employees exposed in excess of the "Permissible Limit" (1.0 ppm for 8 hours or 5.0 ppm for 15 minutes). Continuous monitoring is required in areas where VCM levels may exceed the allowable concentration for "the devices in use". Our current inquiry to OSHA has included a request for clarification of this statement.

L. B. Crider
L. B. Crider

LBC/ch

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*Enclosures: (1) Index to NIOSH Manual
(2) NIOSH Procedure #127
(3) NIOSH Procedure #178

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NIOSH

MANUAL OF ANALYTICAL METHODS

Physical and Chemical Analysis Branch
Division of Laboratories and Criteria Development
1014 Broadway, Cincinnati, Ohio 45202

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
1974

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175	1-15	Mercury in Air
Appendix A		Description, Installation, and Operation of Two Stage Thermal Desorption Unit for the Mercury Determination

INDEX OF METHODS ARRANGED ACCORDING TO ANALYTE

<u>Analyte</u>	<u>Matrix</u>	<u>Procedure</u>		<u>P & CAM No.</u>
		<u>Sampling</u>	<u>Analysis</u>	
Acrolein	Air	Impinger	Colorimetric	118
Antimony	Urine		Colorimetric	107
Aromatic Amines	Air	Silica gel Adsorption	GC	168
Arsenic	Air, Urine	Membrane Filter	AA	139
Arsenic	Air, Urine	Membrane Filter	Colorimetric	140
Beryllium	Air, Settled Dust	Membrane Filter	AA	121
	Ore, Swipe Samples			
Beryllium	Air, Settled Dust	Membrane Filter	Emission Spectroscopy	123
	Ore, Swipe Samples			
Cadmium	Air	Membrane Filter	AA	151
Carbon Monoxide	Air	Grab-bag	IR	112
Chromic Acid Mist	Air	Membrane Filter	Colorimetric	169
Chromium (Particulate)	Air	Membrane Filter	AA	152
Cyanide	Air	Impinger	Ion-Specific Electrode	116
Diphenylmethane- diisocyanate	Air	Impinger	Colorimetric	142
Fluoride	Urine		Ion-Specific Electrode	114
Fluorides and Hydrogen Fluoride	Air	Impinger	Ion-Specific Electrode	117
Formaldehyde	Air	Impinger	Colorimetric	125

<u>Analyte</u>	<u>Matrix</u>	<u>Procedure</u>		<u>P & CAM No.</u>
		<u>Sampling</u>	<u>Analysis</u>	
Hydrogen Sulfide	Air	Impinger	Colorimetric	126
Lead	Air	Membrane Filter	AA	155
Lead	Blood, Urine	Vacutainers	AA	101
Lead	Blood, Urine	Vacutainers	Colorimetric	102
Mercury (Particulate, Metallic, Organic Vapor)	Air	Three Section Solid Phase Sampler	Flameless AA	175
Mercury	Blood	Vacutainers	Flameless AA	105
Mercury	Blood	Vacutainers	Flameless AA	167
Mercury	Urine		Flameless AA	103
Mercury	Urine		Flameless AA	165
Metals (General Procedure)	Industrial Hygiene Samples	Membrane Filter	AA	173
Nitrogen Dioxide	Air	Impinger	Colorimetric	108
Oil Mist	Air	Membrane Filter	Fluorescence	159
Organic Solvents	Air	Charcoal Adsorption	GC	127
Ozone	Air	Impinger	Colorimetric	153
Parathion	Air	Impinger	GC	158
Quartz	Coal Dust	Membrane Filter	Infrared	110
Silica (Quartz)	Air, Dust Biological Tissue	Membrane Filter	Colorimetric	106
Silica (Quartz, Cristobalite, Tridymite)	Air	Membrane Filter	X-Ray Diffraction	109
Sulfur Dioxide	Air	Impinger	Titration	146
Sulfur Dioxide	Air	Impinger	Colorimetric	160

<u>Analyte</u>	<u>Matrix</u>	<u>Procedure</u>		<u>P & CAM No.</u>
		<u>Sampling</u>	<u>Analysis</u>	
Sulfur Dioxide	Air	Impinger	Titration	163
2,4-Toluene- diisocyanate	Air	Impinger	Colorimetric	141

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

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. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study 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, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

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 which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply 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 which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, 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 silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. 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 Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.
- 6.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.
- 6.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.
- 6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

- 7.2 Sample of the specific compound under study, preferably chromatography grade.
- 7.3 Bureau of Mines Grade A helium.
- 7.4 Prepurified hydrogen.
- 7.5 Filtered compressed air.
- 8. Procedure
 - 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be vertical during sampling.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.
 - 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.
- 8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50% air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 ml CS₂ should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 85 cc/min. (70 psig) helium carrier gas flow.
 2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
 3. 500 cc/min. (50 psig) air flow to detector.
 4. 200°C injector temperature.

5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 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. Three microliters of solvent are 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 0.2 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, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. 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 should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of 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.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS₂ with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS₂ because samples are desorbed in this amount of CS₂. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS₂. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS₂ in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5ml versus peak area.

NOTE: Since 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 known day-to-day variations and variations during the same day of the FID response.

10. Calculations.

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS₂ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = \text{mg}_s - \text{mg}_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m³, which is numerically equal to µg per liter of air

$$\text{mg/m}^3 = \mu\text{g/l} = \frac{\text{total mg (Section 10.4)} \times 1000 (\mu\text{g/mg})}{V_s}$$

10.7 Another method of expressing concentration is ppm; defined as µl of compounds per liter of air

$$\text{ppm} = \mu\text{l of compound}/V_s$$

$$\text{ppm} = \frac{\mu\text{l of compound}}{V_s} \times \frac{24.45}{\text{MW}}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

- 11.1 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. Assoc. J.*, 31:225 (1970).
- 11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.
- 11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).
- 11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ)		GC Column Temperature(°C)	Molecular Weight
			Minimum (a)	Maximum (b)		
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80%
DESORPTION EFFICIENCY BUT HAVE NOT BEEN
THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile	Isobutyl acetate
Allyl glycidyl ether	Isobutyl alcohol
n-Amyl acetate	Isoctane
2-Butoxyethanol	Isophorone
n-Butyl acetate	Isopropyl acetate
n-Butyl alcohol	Isopropyl glycidyl ether
n-Butylglycidyl ether	2,6-Lutidine
Chlorobenzene	Methyl acetate
Cyclohexane	Methyl acrylate
Cyclohexanone	Methyl n-butyl ketone
o-Dichlorobenzene	Methyl ethyl ketone
p-Dichlorobenzene	Methyl isobutyl ketone
Diethyl ether	Methyl methacrylate
N,N-Dimethyl aniline	α -Methyl styrene
Epichlorohydrin	p-Methyl styrene
2-Ethoxyethyl acetate	n-Octane
Ethyl acetate	3-Octanone
Ethylbenzene	Pentane
Ethyl butyl ketone	2-Pentanone
Fufural	α -pinene
Heptane	n-Propyl acetate
Hexane	1,1,2,2-Tetrachloroethane
Isoamyl acetate	Tetrahydrofuran
	Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10%

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Vinyl Chloride (Chloroethene, Chloroethylene)	Method No.:	P&CAM #178
Matrix:	Air	Range:	0.2-1500 ng per injection
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		
Date Issued:	9/3/74	Precision:	Unknown
Date Revised:		Classification:	D (Operational)

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the vinyl chloride present.
- 1.2 The charcoal in the tube is transferred to a small vial containing carbon disulfide where the vinyl chloride is desorbed.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and 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 nanograms per injection at a 1 x 1 attenuation on a gas chromatograph.
- 2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5.0 liters. This value is the volume which the front section of the charcoal tube will hold at 200 ppm before a significant amount of vinyl chloride is found on the backup section. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethan foam. [See Section 6.2.]) If a particular atmosphere

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is suspected of containing a high concentration of contaminants and/or a high humidity is suspected, the sampling volume should be reduced by 50%.

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. Preliminary experiments indicate that high humidity severely decreases the capacity of the charcoal 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 It must be emphasized that any compound which has the same retention time as vinyl chloride at the operation conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk material be submitted at the same time so that identity(ies) can be established by other means.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

The precision and accuracy of the total sampling and analytical method have not been determined.

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 which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more components suspected to be present in the same sample by simply 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 which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time 33% of this compound will be found in the backup section. This may lead to some confusion as to whether breakthrough has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20° .
- 5.3 The precision of the overall method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 An approved and calibrated personal sampling pump for personal and area samples whose flow can be determined accurately at 50 milliliters per minute.
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethan foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing to remove material possibly absorbed on charcoal. The primary absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethan foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 l/min.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (20 ft x 1/8 in) with 10% SE-30 stationary phase on 80/100 mesh, Chromosorb W, acid washed, silanized with dimethyldichlorosilane solid support. 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 Two-ml vials which can be sealed with caps containing teflon-lined silicone rubber septa.
- 6.7 Microliter syringes: 10 μl , and convenient sizes for making standards.

- 6.8 Gas-tight syringes: 1 ml, with open/close valve.
- 6.9 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.
- 6.10 Volumetric flasks: 10-ml or convenient sizes for making standard solutions. It is preferable to have plastic stoppers for the volumetric flasks.
- 7. Reagents
 - 7.1 Spectroquality carbon disulfide.
 - 7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.
 - 7.3 Toluene, chromatographic quality.
 - 7.4 Bureau of Mines Grade A 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 detergent washed and thoroughly rinsed with distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, the ends of the tube are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a backup and is positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube is placed in a vertical position during sampling, open end pointing upward, to prevent "channelling" of the charcoal.
 - 8.3.4 Air being sampled is not to be passed through any hose or tubing before entering the charcoal tube.

- 8.3.5 Bulk air samples are taken along with personal samples, i.e. sample 10-20 liters of the air in the environment using a separate charcoal tube.
- 8.3.6 The flow, time, and/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 5.0 liters (See Section 2.2).
- 8.3.7 The temperature and pressure of the atmosphere being sampled is measured and recorded.
- 8.3.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.
- 8.3.9 One tube is handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.
- 8.3.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. If the samples will spend a day or more in transit, cooling (e.g., with dry ice) is necessary to minimize migration of vinyl chloride to the backup section.
- 8.3.11 Samples received at the laboratory are logged in and immediately stored in a freezer ($\sim -20^{\circ}\text{C}$) 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). It should be pointed out that during long periods of storage (more than 2 weeks), the vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This does not constitute breakthrough.

8.4 Analysis of Samples

- 8.4.1 Preparation and Desorption of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small vial containing 1 ml of carbon disulfide. (Note the addition of the CS_2 is important.) The vial is topped with a

septum cap (See Section 6.6). The separating section of foam is removed and discarded; the second section is transferred to another small vial containing 1 ml of CS₂. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. In any case samples should be analyzed within 60 minutes after addition of CS₂.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 cc/min. (80 psig) helium carrier gas flow
2. 65 cc/min. (20 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 230°C injector temperature
5. 230°C manifold temperature (detector)
6. 60°C isothermal column temperature (oven).

8.4.3 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 are 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.

8.4.4 Measurement of area. The area of 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.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal 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 charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube) particularly at lower values, i.e., 2.5 µg.

8.5.2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A known volume of vinyl chloride gas is injected into a bag containing a known volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated at room temperature and pressure. A known volume is then sampled through a charcoal 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 8.4). Samples taken with a gas tight syringe from the bag are also injected into the GC. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the difference between the average weight of the samples and the weight of the blank divided by the average weight of the vinyl chloride standard gas mixture in the bag or

$$\text{Desorption efficiency} = \frac{\text{Weight on sample} - \text{Weight on blank}}{\text{Weight in standard gas mixture}}$$

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. Specifically, the Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. The regulations currently serve as an emergency standard and 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. 125, Thursday, June 27, 1974.) Note that the above is an emergency standard (temporary) and will be replaced by a permanent standard in October of 1974.

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/1.0 ml versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.

NOTE: Since 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 FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 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 points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS₂. 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 was 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. The volumetric 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 are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in μg , corresponding to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on $\mu\text{g}/1.0\text{ ml CS}_2$ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

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

where:

μg_s = μg found in front section of sample tube

μg_b = μg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.
- 10.4 This total weight is divided by the determined desorption efficiency to obtain the total μg per sample.
- 10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

- 10.6 The concentration of the organic solvent in the air sampled can be expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$ of air

$$\text{mg}/\text{m}^3 = \mu\text{g}/\ell = \frac{\text{total } \mu\text{g (Section 10.4)}}{V_s}$$

- 10.7 Another method of expressing concentration is ppm, defined as $\mu\ell$ of vinyl chloride/liter of air

$$\text{ppm} = \mu\ell \text{ of vinyl chloride}/V_s$$

$$\text{ppm} = \frac{\mu\text{g of vinyl chloride}}{V_s} \times \frac{24.45}{62.5}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

62.5 = molecular weight of vinyl chloride

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," Am. Ind. Hyg. Assn. J. 31, 225 (1970).

Inter-organization Correspondence

BFGoodrich

TO	Distribution List	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO.	RECEIVED U.S. E. 30 Chemical OCT 10 1974 DET 511	DATE YOUR LETTER
FROM	R. L. Toole	FIELD POINT OR AKRON DEPARTMENT & BLDG. NO. Cleveland		DATE THIS LETTER October 8, 1974
SUBJECT	EQUILIBRIUM VCM VAPOR CONCENTRATION OVER PVC RESIN			

Major Objective

Determine concentration of VCM in vapor that might be expected to result from contact with PVC resins having various RVCM levels. Of specific interest was the concentration of VCM to which our customers might be exposed in handling bulk railcars or when breathing the atmosphere which might exist above an enclosed storage hopper or in a confined warehouse.

Minor Objective

Determine the effect of temperature, RVCM concentration and resin type on the equilibrium between VCM in PVC resin and the vapor in contact with that resin.

Results and Recommendation

1. In the normal range of ambient temperature (20°C - 40°C). Concentration in vapor (ppm by volume) would be expected to range from 1-20 times the concentration in the resin (ppm by weight).
2. For any given resin concentration, the value of the equilibrium vapor concentration can be expected to double for every 12 - 15°C increase in temperature.
3. Equilibrium is established rapidly for porous resins at high RVCM levels (approximately one day) but requires as long as two weeks for relatively non-porous resins at 20°C .
4. The effect of RVCM concentration on the equilibrium vapor concentration is unclear.
 - a) for Geon G-92, the equilibrium ratio,

$$\frac{\text{ppm by volume in vapor}}{\text{ppm by wt. in resin}}$$
 appears to increase with increasing RVCM.
 - b) for Geon 102EP-F5, the equilibrium ratio decreases with increasing RVCM.
 - c) in the case of 103EP-F76, the equilibrium ratio seems independent of RVCM.

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Results and Recommendation (continued)

5. The data obtained defines the approximate relationships that can be expected but raises unanswered questions with regard to the effects of monomer concentration, post polymerization history, and particle structure on solubility. These questions can only be answered by a much more basic investigation. Hopefully the significant improvements in analytical procedures that have been developed and these findings will simplify such a study.

Introduction

The early work of Berens had defined the solubility and diffusion relationships of vinyl chloride in PVC. Data for high concentrations of VCM were summarized in the report on Research Project 252-47, dated 9/28/65. New data on diffusion rates and solubility data at low concentrations were developed during the latter part of 1973 and much of this information was summarized in IOC from A. R. Berens to F. E. Krause dated 2/4/74.

In general, the data represented short time, non equilibrium, experiments. Solubility data at the lower (near ambient) temperatures were clearly non equilibrium because of the very slow rate of diffusion of monomer through polymer at these temperatures compared to the time scale of the experiments. In attempting to use these data to help establish a permissible RVCM level in PVC products which would prevent unsafe vapor concentrations above the material, it became clear that further information was needed to better define low temperature ($< 50^{\circ}\text{C}$), low concentration ($\text{RVCM} < 0.1\%$) for typical commercial PVC products. This effort was aimed at obtaining early answers to the present questions regarding expected customer exposure, rather than research data shedding further light on basic physical properties.

Discussion

The program that was established was based upon measurement of the VCM concentration in the vapor space of 60c.c. serum bottles, filled to approximately 70% capacity, with two representative resins, Geon 102EP-F5 and Geon 103EP-F76. Data were to be obtained at two levels of RVCM in each resin, thermostatted at three different temperatures, for periods ranging from one day to three weeks. It was recognized that the experiment depended on closely controlled analytical procedures based on Gas Chromatograph methods. Low RVCM data was especially vulnerable and provision was made for statistical analysis of results.

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Discussion (continued)

The experiments were to be conducted at the Manufacturing Services Laboratory under the direction of J. M. Whitney and analytical work was to be performed by the Avon Lake General Chemical Plant. A single analysis was performed on any one serum bottle with the effect of time determined by periodic analysis of duplicate sample containers.

The following data were obtained:

PVC-Vapor "Equilibrium" Data
102EP-F5

<u>Resin Conc.</u>		<u>Vapor Conc.</u>		
		<u>23°C</u>	<u>30°C</u>	<u>40°C</u>
prelim.	54.2 ppm			
after 20 hrs.	30.4	72.7	115	171
after 44 hrs.	28.8	79.7	108	171
92 hrs.		88.1	116	193
188	28.9	70.1	108	178
332		dupl. (75.8	105.9	200.3
		(72.6	113.2	205.8
Vapor Conc./Resin Conc. after 44 hrs.		2.63	3.74	6.46
prelim.	0.62 ppm			
after 20 hrs.	(0.34?)	8.2	7.1	7.0
after 44 hrs.	0.54	5.0	3.5	3.1
92 hrs.		nil	nil	nil
188	0.124	nil	nil	nil
332		dupl. (nil	nil	nil
		(nil	nil	nil

PVC-Vapor "Equilibrium" Data
103EP-F76

<u>Resin Conc.</u>		<u>Vapor Conc.</u>		
		<u>23°C</u>	<u>30°C</u>	<u>40°C</u>
prelim.	28.5 ppm			
after 20 hrs.	18.6	77.7	124	220
after 44 hrs.	18.2	89.2	148	285
92 hrs.	18.4	124	199	390
188	19.2	131	222	394
332		(152.3	236.6	425.9
) dupl.		(157.7	250.4	436.3

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Vapor Conc./Resin Conc. Avg. after	7.35	11.91	21.78
92 hrs.			

prelim. 0.76 ppm

after 20 hrs.	0.53	10.4	9.9	10.5
after 44 hrs.	0.53	7.4	6.3	8.3
92 hrs.		4.7	1.3	6.1
188	0.33	2.3	3.0	5.8
332)dupl.		(1.87	3.9	6.9
		(2.02	4.8	8.1

Inspection of the data indicate:

1. Equilibrium values for high concentration samples of both resins show the expected effect of increased temperature and this relationship is in good agreement with the data of Berens.
2. Vapor concentrations above 103EP-F76 are almost three times as high as concentrations above 102EP-F5 (solubility of VCM greater in 102EP-F5 than 103EP-F76).
3. Values at low concentrations are very erratic and the results seem illogical.

The inconsistent data obtained at low RVCM levels suggested that there was vapor leakage or that slight solubility of VCM in the rubber septum used to seal the serum bottles was affecting the results. In order to determine the septum effect, three samples were prepared in normal, septum sealed, serum bottles.

- a) One bottle was filled with air, as a blank.
- b) A second bottle was filled with a standard vapor sample containing 18 ppm VCM.
- c) The third bottle was filled with an identical vapor sample but contained an additional rubber septum—cut up into small pieces to provide additional surface area.

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Analysis of the vapor space of these sample bottles after storage at 23°C for three days provided the following results:

a) air blank	analyzed	1.42 ppm	VCM
b) 18 ppm orig.	analyzed	10.75 ppm	VCM
c) 18 ppm plus additional septum	analyzed	6.58 ppm	VCM

It seemed clear that solubility of VCM in the septum was the explanation for the discrepancy in low RVC samples. The limited solubility in the small septum meant that the analysis at higher concentrations was not significantly affected.

In order to eliminate the "septum effect" an experiment was planned in which large (993cc) sample bottles were used. Consecutive samples were taken from the same bottle via a pierced aluminum foil cap—with the needle hole reclosed with a foil and paraffin patch. These data were obtained only at 30°C and the results are shown below.

	102EP-F5		103EP-F76	
	370 gms @ 32 ppm	376 gms @ 0.40 ppm	436 gms @ 103 ppm	432 gms @ 2.5 ppm
after 1 day	128.8	2.64	903.1	8.05
after 2 days	131.1	1.70	983.2	9.9
after 4 days	112.6	1.65	969.9	11.22
after 8 days	125.1	1.72	1140.8	15.8
Avg. ratio (lost three meas.)	3.84	4.23	10.02	4.92

The data for the first two experiments (omitting the erratic low concentration values from the first experiment) are shown in figure 1. Except for the low concentration value for 103EP-F76 (a low value for resin concentration??) the data seem consistent.

The improved method resulting from the elimination of the "septum problem" and the difference that apparently resulted from structure of molecular weight differences between 102EP-F5 and 103EP-F76 led to a third series of measurements.

In run #3 a sample bottle size of 250 c.c. was used and a single sample was obtained after storage for one week at the indicated temperature. The sample bottle was sealed with aluminum foil and two concentration values were studied. In order to gain further insight into the effect of particle structure samples of G-92 resin were included.

The following data were obtained:

Resin-Vapor Equilibrium Study - Run #3

250 cc sample bottles 70 gms G-92
 85 gms 103EP-F76
 75 gms 102EP-F5

	<u>23°C</u>	<u>30°C</u>	<u>40°C</u>
102EP-F5			
20 ppm	40.55 ppm (2.03)	64.82 ppm (3.24)	77.55 ppm (3.88)
1 ppm	4.88 ppm (4.88)	7.50 ppm (7.50)	10.70 ppm (10.7)
103EP-F76			
33 ppm	249.9 ppm (7.57)	362.9 ppm (11.0)	611.5 ppm (18.53)
0.82 ppm	3.33 ppm (4.06)	7.18 ppm (8.76)	12.52 ppm (15.27)
G-92			
126 ppm	253.5 ppm (2.01)	428.3 ppm (3.4)	642.5 ppm (5.1)
0.91 ppm	0.99 ppm (1.09)	1.19 ppm (1.31)	2.29 ppm (2.52)

Values in () are ppm by volume in vapor
 ppm by weight in resin

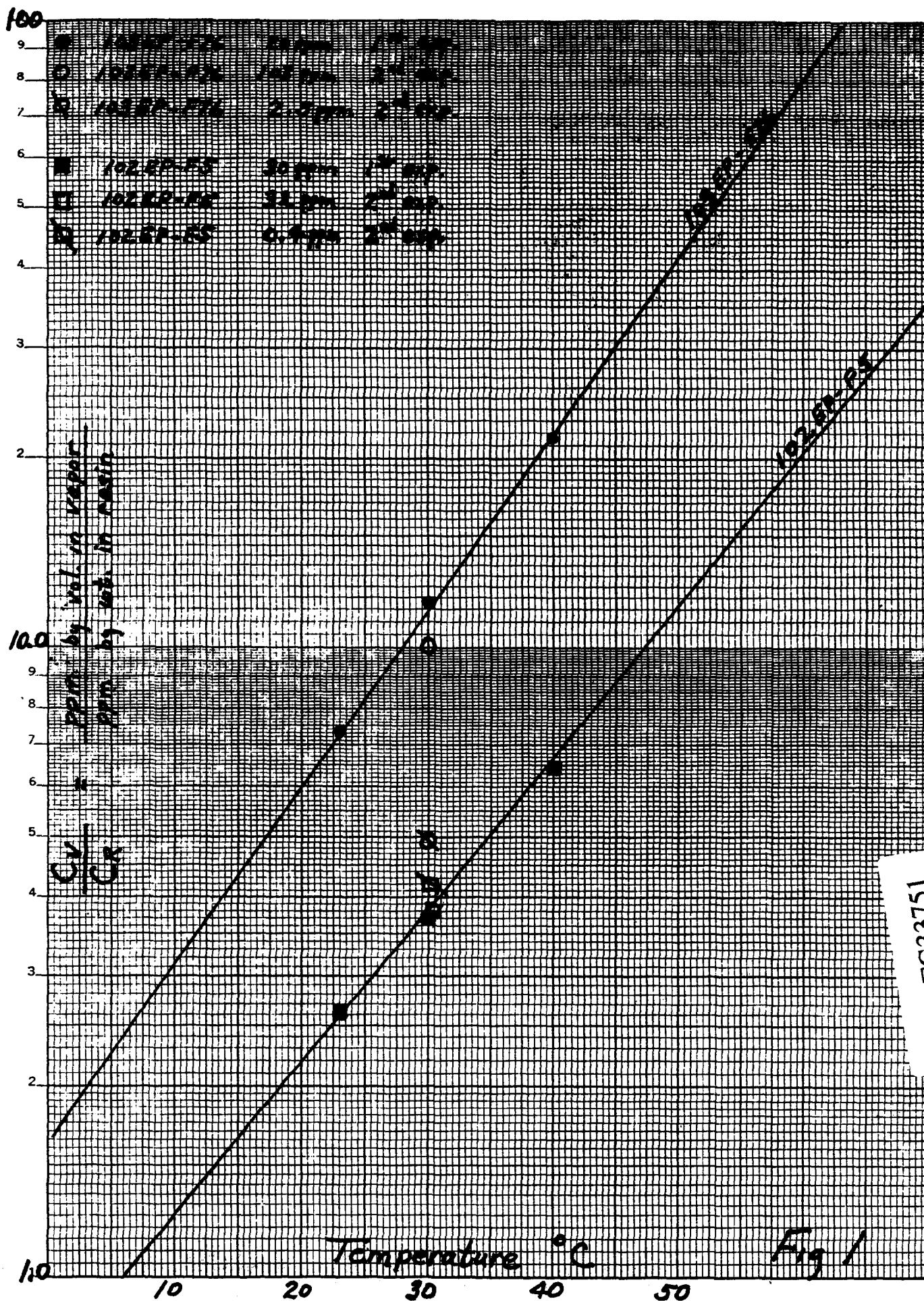
Inspection of these values suggested that solubility was a function of the "fineness" of the ultimate particle structure with G-92 resin having the greatest solubility for monomer and 103EP-F76 having the lowest solubility. In order to pin this down a similar set of measurement were made using Geon 121 and employing the same 250 cc sample size technique.

Sample size 50 gms
 Original RVCM level 9/19/74: 27.5 ppm

	<u>Storage Temperature</u>		
	<u>23°C</u>	<u>30°C</u>	<u>40°C</u>
Vapor Concentration ppm 9/23/74	103.71	172.71	251.86
CV/CR	3.77	6.28	9.16

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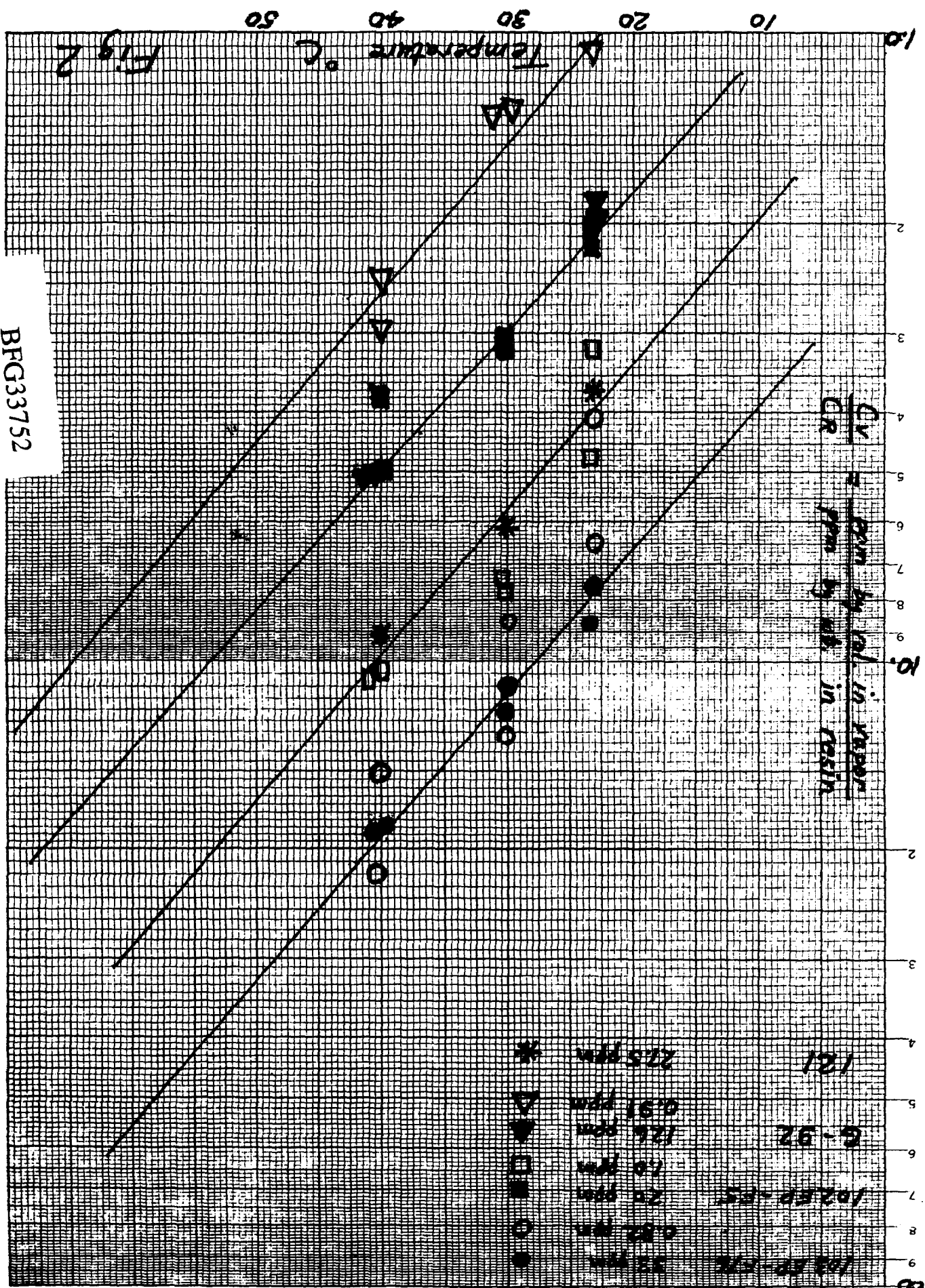


Fig. 2

1408897C

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The equilibrium ratio (CV/CR) for 121 was expected to lie below the values for 102EP-F5 and G-92. As can be seen, this is not the case and there is no obvious explanation for the differences in solubility exhibited by the resins tested.

The data from this set of experiments is summarized in Figure 2.

R. L. Toole
R. L. Toole *pe*

/pk

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DISTRIBUTION

CLEVELAND

W. F. Bixby	E. B. Osborne
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K. Greene	W. M. Smith
E. W. Harrington	R. L. Steller
R. P. Kenney	R. W. Tannehill
T. R. Linak	R. L. Toole
R. W. MacCuspie	A. Vittone
J. F. Malone	H. Waltemate
J. L. Nelson	B. M. G. Zwicker

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HENRY

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A. W. Clements - W. D. Robb

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G. Huddleston
F. Ells
M. Mele

PEDRICKTOWN

A. R. Webber - J. W. Goetsch
W. A. Reed

ALTC

R. L. Bowles
L. Cohen
E. A. Collins
L. B. Crider (2)
J. R. Goots
R. M. Kreager
B. K. Mikofalvy
A. L. Schultz
J. W. Summers
J. A. TePas
G. L. Wheelock

ALTC Group Circulation (4)

D. E. Weaver	C. A. Daniels
G. J. Antlfinger	J. A. Davidson
	L. Chandler
M. G. Morningstar	J. B. Haehn
G. D. Longeway	
R. S. Morgan	H. H. Marty
D. E. Witenhafer	R. A. Jones
	H. H. Yieh
	W. S. Stebbins

BRECKSVILLE

R. J. Fawcett
R. A. Krueger
D. E. Ley
C. H. Lufter - J. B. Pausch

BRECKSVILLE Group Circulation (2)

A. R. Berens	T. W. Boyer
T. R. Paxton	R. J. Davis
R. C. Backderf	C. A. Marshall
	R. V. Kemp
	H. Kehe

ALGC

L. V. Goode
R. N. Rylands - R. S. Mather
J. M. Whitney

ALGC Group Circulation (1)

R. C. Kaminski
B. C. Knoble
J. V. Laughlin

October 14, 1971

TRK 10-8-74

1974 PVC REACTOR ENTRY FREQUENCY
Percent of Vessels Entered

Month	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<u>RESIN/AREA</u>												
<u>EP/GP</u>												
Avon East	4.3	3.4	5.6	4.6	5.1	4.5	2.8	1.8	2.6			
Avon West 1100	22.		8.	12.	5.	10.	7.	3.4	4.			
Avon West 3300	7.		1.	11.3	6.6	3.7	1.	5.	5.			
Henry	4.		4.	4.	3.5	2.	3.	3.	3.			
Long Beach	13		13	13	10	5.	5.	5.	5.			
Louisville B/1	33.		33.	33.	-	2.	3.	1	1.			
Louisville B/111	33.		33.	33.	33.	33.	33.	33.	33.			
Pedricktown	4.		-	-	3.	3.	3.	3.	3.			
<u>G-90</u>												
Avon West	20.		15.	17.	21.	9.	16.	14.	16.			
Louisville	100.		100.	100.	100.	100.	100.	100.	100.			
<u>Dispersion</u>												
Avon West	19.		7.	19.	17.	18.	15.	20.	17.			
Henry 121	6.5		4.	4.	4.	4.	2.	2.	2.			
Henry Lo-Sope	3.		4.	4.	4.	4.	2.	2.	2.			
Louisville	50.		50.	25.	25.	25.	25.	25.	25.			
Pedricktown	10.		10.	10.	10.	10.	4.	4.	4.			
<u>Mass</u>												
Prepo	17	17	17.	17	17	17	17	17	17.			
Autoclave	100.	100.	100.	100.	100.	100.	100.	100.	100.			
<u>Latex</u>												
Louisville	4.		4.	4.	4.	4.	4.	4.	4.			

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PLANT MANAGERS' MEETING
October 10, 1974

8:15 a.m. - Conference Room 1-B

Opening Remarks

A. Vittone

New OSHA Standard

Effect if it Survives Court Attack
Assumptions

E. W. Harrington

✓ Achievable Levels in Work Atmosphere
with Present Programs in Sight

Each Plant

✓ Masks

Type of Masks Allowable

H. Waltemate

Wearing Time Forecasts

Each Plant

✓ Monitoring

PVC Areas

G. D. Schaaf

L. B. Crider

H. Waltemate

Personnel Monitoring

Each Plant

Other Plant Areas

Accuracy

✓ Regulated Areas (What Is Included)

PVC Areas

Signs

Warehouses

Boundries

Public Warehouses

Controls

✓ Lunch Rooms, Showers, Locker Rooms, Clothing
EPA Considerations

E. W. Harrington

✓ Plant Changes Needed to Approach or Meet Standard

Each Plant
Engineering

✓ Effect on Costs, Productivity and People

Group

✓ Medical Surveillance

M. N. Johnson

✓ Labeling

P. J. Weaver

Wrapup Summary on Assignments for Action

EWH/kats
10-7-74

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PVC PLANT MANAGERS' MEETING

Cleveland, Ohio

October 10, 1974

SUMMARY OF IMPORTANT POINTS AND DECISIONS

TO:

N. R. Aquino	P. H. Lawrence
E. M. Begnaud	T. R. Linak
W. E. Brodine	R. S. Mather
D. A. Brooks	J. L. Nelson
A. W. Clements	R. N. Rylands
C. B. Cooper	R. D. Scott
L. B. Crider	R. W. Strassburg
A. M. Fairlie	A. Vittone
R. J. Fawcett	H. Waltemate
C. R. Flynn	P. J. Weaver
L. V. Coode	A. R. Webber
E. W. Harrington	D. J. Wells
W. C. Holbrook	J. M. Whitney
<u>J. M. Hyslop</u>	W. J. Wilcox
M. N. Johnson	C. L. Woods
F. E. Krause	B. M. G. Zwicker
R. M. Kreager	

This meeting was held to discuss the impact of the new OSHA Standards for ambient vinyl chloride in our PVC plants.

1. Mr. Vittone mentioned that SPI and Hooker have taken court action to ask the overturn of the standard. Firestone, Air Products, Tenneco, and Union Carbide have also filed asking relief from the standard. Dow is expected to file late this week and B. F. Goodrich will file early next week. All cases will be consolidated and cleared in the Second District Court, New York City. The earliest possible date for a decision on these court cases will be December 10th. They could drag on for as long as 9 months. The SPI is holding an industry meeting October 11th in Washington to discuss the legal aspect of the new standard and to try to find out who will file briefs and who will support filing a brief opposing this standard.

Robin Tech has indicated via the news media that they can meet the new standard using the Shin-Etsu technology. Jones and Day of Cleveland will represent B. F. Goodrich and Diamond Shamrock in actions concerning the standards.

EPA has not set up any standards yet. Also, the FDA has not indicated what course of action they will take. However, it is expected they may insist on items for single service applications containing less than one ppm, such as film for wrapping meats and items for repeated service like pipe would have to meet a specification of 10 ppm. We have not heard from the Department of Transportation concerning their plans.

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PVC Plant Managers' Meeting
October 10, 1974

2. Bob Webber indicated that he could operate Pedricktown with suitable air masks from plug-in stations if they were arranged so the operator could get from one station to another with the use of a cannister. Therefore, it would be very important to get a cannister plug-in type mask approved by NIOSH. The stairwells and the control rooms could be supplied with fresh, clean air. Pure air cones could be placed over telephones allowing communication without using a mask. The use of a throat mike or a mike installed inside the mask would permit better communication with the computer control center. Bob mentioned that Rohm Haas has an operation in which the operators use air masks all the time. They use plug-in air masks with small egress tanks when required. This plant is located close to the Pedricktown plant and arrangements will be made for a visit to Rohm Haas.
3. Ned Harrington spelled out the basic assumptions for short-term and long-term reduction for vinyl chloride levels.

Short-Term

- a. Push-pull ventilation would be required in all buildings to provide 12 interchanges per hour heated for year-round operation. 20 interchanges per hour unheated will be required for emergencies.
- b. Stacks will be installed to get vinyl chloride up higher in the air for better dispersion.
- c. Local ventilation will be supplied for trouble spots where engineering improvements won't stop leaks.
- d. Purified (activated carbon filtered) air will be supplied for lunch and control rooms.
- e. Cannister masks and air masks will be supplied as necessary.
- f. The waterfill and gas holder system will be evaluated for venting polys prior to opening for cleaning.
- g. The use of a delumper will be tried.

Long-Term

- a. Stripping columns will be installed at all plants and no open slurry tanks will be used until after stripping.
- b. Vent absorbers will be provided for recovery system vent.
- c. Computer control if it can make a substantial decrease in respirator wearing time.
- d. Closed poly operation for pearl resin.

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The use of vent stacks to collect various VCl streams will be used on a temporary basis until such emission sources can be eliminated. W. C. Holbrook said we require permits at Pedricktown and Long Beach for our stacks. Henry will be set up to monitor the dissolving with their new Bendix total hydrocarbon analyzer.

In the future all vents will have to be monitored to measure the emissions from our plant operations for EPA. It is quite possible a gas chromatograph will have to be used in this operation. It was agreed we will go ahead and obtain the materials for these stacks now for installation at all plants. Cleveland Engineering will standardize the design and the plants will handle the installation. Vic Goode will write the overall EA for this job.

Tom Linak will coordinate work with the plants to evaluate the water displacement system of General Tire and Rubber. He will obtain further information concerning their patented delumper used in this system. General Tire vent all miscellaneous vents into their gas holder but the polys are relieved through the standard rupture disc relief valve system.

Tank car unloading lines must be vented into the recovery system or sphere.

4. Herm Waltemate discussed the conversion of our current Scott airpaks to pressure demand systems as required by the standard. Each plant is to submit the number of these units to be converted to Herm. We need NIOSH approval of a combination gas mask and air fed respirator combination. The use of a half-face mask would be preferable since eyes have a tendency to dry out using instrument air. Hoods could be considered since they would apparently be easier to wear than masks. We need further definition from NIOSH on types of masks approved for our use.
5. Stripping columns have been successful in reducing the vinyl chloride level of products to negligible amounts for Geon 102EP F-5 resin. We have not tried UPS-1 type 103EP F-76 at Avon Lake through the column. We have used the column to take unrecovered 102EP F-5 and recover the residual vinyl out of the product and this looks very encouraging. A standardized column has been designed and specified by our Engineering Department. Vic Goode will coordinate a total EA for the procurement of all columns and equipment. A meeting of the plants will be set up in Cleveland to discuss and agree on final design and implementation in their plants. This EA should be prepared in time to go to the November Board meeting.

Engineering will have the package for vent gas recovery ready in about two weeks. This system can be discussed at the meeting in Cleveland.

6. Estimated achievable level by plants:

Avon Lake

East Area: 5 ppm average level, 2 ppm TWA
Old Areas: Under 10 ppm average

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Henry

3 ppm TWA with improved ventilation

Long Beach

4 to 5 TWA but excursions might be high until manhead problem is resolved

Louisville

Building 1: 5 ppm TWA

Other Buildings: Can't get less than 10 ppm TWA

Pedricktown

Short Term: 2 to 3 ppm TWA with 10 to 20 excursions

Long Term: 0.5 ppm TWA with 5 to 10 excursions

To achieve long-term results above requires: spot ventilation systems, stairwell and control room fresh air supply, ventilation for changing recovered vinyl chloride filters. In the mass area: HRC for prepoly, better recovery compressor, more reliable block valves. Also required is the removal of vinyl chloride from HRC water. and filling pots with water for reduced loss of vinyl to the atmosphere.

7. Plants estimated the percent of the time operators would have to wear respiratory equipment under the new standard.

Pedricktown

60-70% of the time for short-term basis, 1975 and 1976
20-25% of the time for 1977

Henry

60-70% of the time

Louisville

Building 1 and other old buildings: 80+%
New Poly: 20% of the time

Long Beach

75% of the time in 1976
50% of the time in 1977

Avon Lake

East Area: 50% of the time by 1976
Old Areas: 75%

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This assumes that the operators will be wearing respiratory equipment at all times when they are out of the control room.

Calvert City

The operators would wear respiratory equipment only for excursions, except for maintenance people who would be required to wear them a great percentage of the time. Their people would prefer hoods instead of face masks.

Avon Lake Technical Center

50% of the time.

Research Center

75% of the time in bays when vinyl chloride is used, and 40-50% of the time in general areas.

Most medical problems in the wearing of respiratory equipment are psychological and not physical. It is expected most people will be able to wear respiratory equipment if it were required.

8. Monitoring -- The new standard appears to place more emphasis on personnel monitoring than on fixed monitoring systems. We need clarification regarding the length of time the personnel monitoring samples are to be taken and the procedure to be used in their analysis. L. Crider has requested procedures for analysis of personnel monitoring samples.

The new standard specifies that personnel monitoring data must be released to the employee. We assume this means that it can be posted on the bulletin board.

The headspace method for analyzing carbon tube personnel monitoring samples is currently being developed by John Whitney and will save a lot of analysis time. If we can get NIOSH to approve this procedure, it would be possible to take many more personnel monitoring samples.

According to the standard, all individuals over the action limit (0.5 ppm VC1) will require quarterly personnel monitoring. People exposed to levels of 1 ppm VC1 will require monthly personnel monitoring. This personnel monitoring must be done on an individual basis and not on a job classification basis. It is inconceivable that we will ever be able to correlate personnel monitoring data with fixed monitoring data at these low levels to meet the new standard. Therefore, it was suggested that the Bendix fixed instrument be used for alarm purposes only and personnel monitoring data would then constitute the major data to meet the compliance to our new standard.

A regulated area is when VC1 or PVC is manufactured, reacted, heated, repackaged, stored, or used and the VC1 level is above the permissible exposure limit of 1.0 ppm TWA. Plants should establish at the earliest possible date all areas such as offices where the VC1 content is less than 0.5 ppm (action level) since regular personnel monitoring is not required. This initial survey will be made to deter-

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PVC Plant Managers' Meeting
October 10, 1974

mine the number of buildings, offices, shops, etc. that can be classified as non-regulated areas.

Contractors working in areas with vinyl chloride concentrations of greater than 0.5 ppm would have to be monitored according to the strict interpretation of the new standard. We will try to establish a variance for contractors since their people are not exposed to vinyl chloride over a lengthy period of time.

It is quite important that we get the instructions OSHA issues to its compliance officers in the field at the earliest possible date. This will help in better defining the standards.

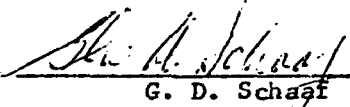
9. It appears that our warehouses will have to be monitored where PVC products are stored. This will be handled under the end products committee in cooperation with Ed Begnaud and his people. All finished products will have to be labeled after the first of January, 1975 according to the new standards. Ed is working with our marketing people to provide the proper markings on the bags..
10. It was agreed to proceed with all the current projects in progress on lunch rooms and shower rooms. The new standard may allow us to eat in control rooms, and this will be reconsidered at plants where this can be advantageous.
11. A daily change of clothing is not specified in the standard: Our present policy can reduce the frequency of clothing changes if it can be done so without personnel problems.
12. Mandatory showers will be eliminated, but employees will be urged to take showers on their own time. This mandatory program will be cut off as soon as it can be without undue personnel problems.
13. Coveralls will be used for poly cleaning by entry. Polys should not be entered until after HRC has been used. Solid charges and other hazardous operations will require the use of a impervious suit and this can be equipped with cooling if required to prevent heat prostration problems.
14. Doctor Johnson outlined the medical surveillance required by the new standard. A copy of this information is attached.
15. Plants estimated productivity loss under the new standard. Long Beach and Pedricktown estimated 20-30% loss in productivity if wearing of air line masks and respirators is required. Henry and Avon Lake could not estimate at this time. Louisville estimates up to 30% productivity loss.

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PVC Plant Managers' Meeting
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16. Discussion on how to present this information to the employees suggested the use of a TV tape so that the same information could be heard at all plants. Mr. Harrington will investigate this with our training department.
17. Mr. Nelson summarized some of the main points at this meeting. The plants are to reduce ambient vinyl chloride levels to the lowest possible levels. Employees are still going to have to wear respiratory protection. The company plans to spend the necessary dollars to solve this serious problem. However, we may lose capacity and productivity in the meantime. Our large polymerization units will present fewer problems; however, it is expected we will obtain lower levels in all of our work areas as we continue to improve operations. We cannot expect the published permanent standard to be changed much, so we should be prepared to meet it. We should stress the challenges and the opportunities that these goals represent to our employees and their continued employment with B. F. Goodrich.


G. D. Schaaf

GDS/clg
10-22-74

Atts.

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COMMENTS ON THE MEDICAL SURVEILLANCE PROGRAM UNDER THE
NEW VINYL CHLORIDE STANDARD

A. Who must be examined and how often?

1. The standards require that all employees exposed above the action level, that is to say, 0.5 parts per million, be examined. Those who have worked for ten years or more must be examined every six months. Those who have worked less than ten years must be examined annually. I think this means that in practice, all employees in our PVC operations must be examined because, even though someone might spend a relatively short time in the area, he nonetheless could easily have a small excursion. It doesn't take much of an excursion to bring his exposure above the allowable 0.5 ppm TWA for an 8-hour day.
2. One very confusing thing in the regulation is that the action level which determines the need for physical examinations is 0.5, whereas the limit which determines a regulated area is 1.0. Therefore, it is conceivable that we could have a number of people who work outside the regulated PVC areas and nonetheless would be required to have examinations on the above schedule if the standard is adhered to rigorously.

B. What does the examination consist of?

1. A general physical examination by a physician.
2. A series of biochemical examinations which is not quite so extensive as the SMA 12 plus GGTP that we are now doing. Since there would be no economy in doing the lesser number of examinations, I would recommend that we continue with our current blood testing program.

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3. The body of the standard indicates that we must test for dysfunction of the kidney and for abnormality in the pulmonary system. It then refers the reader to Appendix A which is headed "Supplementary Medical Information". This appendix refers to additional tests which may be useful and then describes what can be done in the way of testing for kidney and lung problems. I find this very confusing in that it would seem to make examination of the kidney and lungs mandatory and then indicate that any studies of kidney or lung functions are only suggestions rather than requirements of the standard. In practice, I think that we should do our kidney testing by doing a simple urinalysis, checking for albumin and red blood cells and omit the exfoliative cytology which they suggest but which I think would be of very little value and which is quite expensive. As far as pulmonary testing is concerned, I think we might as well plan to do the basic pulmonary function which they recommend, which is a forced one second and total vital capacity with a chest X-ray.

C. What will be required in order to come into compliance?

1. Sufficient physician time to do the required examinations.
2. Access to a laboratory which can do the required blood testing. (I think we already have this pretty well in hand).
3. A pulmonary function testing machine where we do not already have one and someone who is trained to operate it. Any nurse can be readily trained to do this, so this should pose little problem.

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4. Either on-site X-ray facilities or access to X-ray facilities. I think the choice here should be dictated solely by economics. When one considers that the cost of an X-ray on the outside is approximately \$15.00, plus the time the employee loses going to and from the facility, it wouldn't take a very large number of employees to justify installing our own equipment.

D. Suggested plan of action for bringing our examination program into compliance with the new standard.

	<u>Suggested Responsibility</u>
1. Determine the number of physical examinations which would be required at each location annually.	Plant
2. Arrange for sufficient physician time to perform these examinations.	Plant and Environmental Health Department
3. Design the required forms for recording the examination and reporting the results to the employee.	Environmental Health Department
4. Acquire adequate pulmonary function testing facilities at each location if we do not already have it.	Environmental Health Department to provide plants with recommendations on specific equipment
5. Investigate the economics of installing in-house X-ray facilities vs. sending employees outside.	Plant and local physicians
6. Examine the overall dispensary facilities at each location to see whether any physical expansion will be required in order to accommodate the new program.	Plant and local physicians plus Environmental Health Department

M. N. Johnson, M.D.

10/7/74

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W. C. Becker

A. Vittone, Jr.

J. L. Nelson

Plant Managers (12)

E. W. Harrington

T. H. Smith

October 9, 1974

VC1 - LABELING

The October 4, 1974 VCM regulation by OSHA states:

(1) Signs and labels

(1) Areas

Entrances to regulated areas shall be posted with legible signs bearing the legend

CANCER SUSPECT AGENT AREA
AUTHORIZED PERSONNEL ONLY

Further,

- (2) Areas containing hazardous operations, or where an emergency currently exists, shall be posted with legible signs bearing the legend

CANCER-SUSPECT AGENT IN THIS AREA
PROTECTIVE EQUIPMENT REQUIRED
AUTHORIZED PERSONNEL ONLY

Although the October 4, 1974 OSHA Regulation did not address itself to the details of this subject for vinyl chloride, it is recommended that the wording used in the regulations issued early in 1973 on the "14 carcinogens" be followed in the case of vinyl chloride regulated areas. This states that letters on such signs be at least 2" high.

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Labeling VCl and PVC Containers

The specified wordings in the VCM regulation of October 4, 1974 are:

- (3) Containers of polyvinyl chloride resin waste from reactors or other waste contaminated with vinyl chloride should be legibly labeled

CONTAMINATED WITH
VINYL CHLORIDE CANCER-SUSPECT AGENT

- (4) Containers of polyvinyl chloride shall be legibly labeled

POLYVINYL CHLORIDE (or trade name)
CONTAINS
VINYL CHLORIDE
VINYL CHLORIDE IS A CANCER-SUSPECT AGENT

Again, there are no details as to location and size, but the regulations on other carcinogens generally include the language

- (a) under or beside the primary label
- (b) lettering to be not less than 1/2 the size of the primary label, but not less than 8 point type nor more than 1 inch height.

The Transportation and Warehousing Department is in the process of redesigning our "universal" Geon vinyl bags, Gaylords and latex drums, and these will be placed on order in due course, so that you may begin using them for production starting January 1, 1975 for all Geon vinyl products. They will also provide labels which can be attached to shipping containers not so imprinted (off grade, scrap, etc.)

Our Corporate Legal Counsel has also suggested other additions to our labels, product literature and sales documents, to increase the level of customer notification and provide some guidance as to what should be done, e.g.

NOTICE
OPEN, HANDLE AND USE UNDER WELL VENTILATED
CONDITIONS. FOR DETAILS REFER TO OCCUPATIONAL
SAFETY AND HEALTH STANDARDS CHAPTER XVII Part 9010-1910
OF THE DEPT. OF LABOR, U.S. GOV'T DATED OCT. 4, 1974

A letter will be sent to you and our customer list summarizing these changes in package labeling and business materials.

Special consideration of the appropriate labeling of hopper cars and trucks is in progress. Special stickers or placards will be required. Tom Smith will see that you are provided with appropriate material before January 1, 1975.

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Finally, the labeling of vinyl chloride tank cars has been prescribed:

- (i) **V I N Y L C H L O R I D E**
EXTREMELY FLAMMABLE GAS UNDER PRESSURE
CANCER-SUSPECT AGENT

or,

- (ii) in accordance with CFR Part 173, Subpart II, with the additional legends

CANCER-SUSPECT AGENT

applied near the label or placard

Our Transportation Department will have appropriate labels and recommendations in the hands of Calvert City before January 1, 1975 in accordance OSHA and ICC regulations.

/ksc
10/9/14

P. J. Weaver
B. M. G. Zwicker

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