U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
WASHINGTON, D.C. 20210

DEC 17 1975

JAN 02 1975
R N WHEELER JR.

Mr. R. N. Wheeler, Jr.
Vinyl Chloride Resins Manager
Union Carbide Corporation
270 Park Avenue
New York, New York 10017

Dear Mr. Wheeler:

This is in response to your joint letter with Mr. John Whittlesey dated June 17, 1975, petitioning for modifications of the Exposure to Vinyl Chloride Standard, 29 CFR 1910.1017 (formerly 1910.93 recodified May 28, 1975).

There are no plans presently to amend the Vinyl Chloride Standard. A revised program directive is contemplated, although we are not certain as to the date it will be available. Please be assured that your comments and suggestions are greatly appreciated and they will be considered fully in the revision of the program directive. In the meantime, the following administrative decisions have been made:

1. 29 CFR 1910.1017(a) and (b)(6) Scope and application (2), (3) and (b) Definitions (6)

The standard defines a fabricated product as being one which is "made wholly or partly from polyvinyl chloride, and which does not require further processing at temperatures, and for times, sufficient to cause mass melting of the polyvinyl chloride resulting in the release of vinyl chloride."

"Release of vinyl chloride" means the release of an amount of vinyl chloride which would likely result in employee exposure at or above the action level without regard to the use of engineering controls. Products which can be classified as fabricated products are exempt from the provisions of the vinyl chloride standard. All other products are subject to the requirements of the standard. If the employer uses or manufactures a product which is not a fabricated product, he must initiate monitoring procedures. If the monitoring reveals that the employees are not exposed to vinyl chloride at or above the action level, the employer's operations will be exempt from the

provisions of the standard. However, if the monitoring reveals exposure at or above the action level, the employer must implement the procedures specified in the standard.

2. 29 CFR 1910.1017(b) Definitions (5).

The petition requests that the definition of "emergency" be revised to include specific examples, such as fire and explosion. We agree that the definition might well be expanded to include examples. Again, this matter will be addressed in a program directive and not as an amendment to the standard.

The definition of a "massive release" as being "greater than 100 parts per million (ppm)" found in the current Program Directive #200-35, will also be addressed in a revised directive. We agree that the 100 ppm should be changed.

3. 29 CFR 1910.1017(d) Monitoring (4)

The intent of paragraph (d)(4) is that the employer shall be 95% confident that his monitoring result is within 25%, 35% or 50% of the actual value depending on the concentration. Therefore, an employer using a method which has proven vinyl chloride detection accuracy of 25% or less need take only one measurement regardless of the actual vinyl chloride monomer concentration. In concentration ranges where accuracies of 35% or 50% are required, the employer need take only one measurement if the method accuracy is less than the specified accuracy. With methods of unknown accuracy or having errors greater than the specified accuracy requirements, repeated measurements are necessary. In these cases, one may use the coefficient of variation (CV) as a parameter to judge whether or not a sampling procedure is adequate to meet the standard. The CV in percentage units is defined as the standard deviation of the method, times 100, divided by permissible exposure limit. The required CV of the procedure is obtained by dividing the required accuracy by 1.96 (Z value for 95% confidence). Thus, for accuracies of 25%, 35% and 50%, method CV values should be less than 12.8%, 17.9%, and 25.5% respectively.

To repeat, there are no plans presently to amend the standard but your comments on monitoring will be considered in the program directive revision and also in future rulemaking where monitoring is a requirement.

4. 29 CFR 1910.1017(j) Training.

The standard does not specify a level of exposure to trigger training activities. Section 6(b)(7) of the Occupational Safety and Health Act of 1970 provides that employees shall be apprised of the nature of the hazardous substances with which they come in contact.

The evidence we have compiled on vinyl chloride has indicated that it is sufficiently hazardous to warrant training for all personnel who have any possibility of coming in contact with vinyl chloride. There is always the opportunity for accidents to occur and employees should be aware of the possible consequences. There has also been some indication that storage containers may yield high concentrations of vinyl chloride when opened after transporting.

Therefore, it is not likely that the training provisions will be amended. For those operations covered by the standard, training is a requirement.

5. 29 CFR 1910.1017(e), Signs and labels (4)

If there are situations where the blended polyvinyl chloride must be labeled yet contains less than 0.5 ppm residual vinyl chloride monomer, the following wording may be used:

BLENDED POLYVINYL CHLORIDE (PVC)

CONTAINS TRACE AMOUNTS (0.5 ppm)

OF VINYL CHLORIDE.

VINYL CHLORIDE IS A CANCER-SUSPECT AGENT.

We hope that the above clarifications will satisfy your petition for modification and amendment of the vinyl chloride standard. As previously stated, there are no plans presently to formally amend the standard. There will be an addendum or modification of the Program Directive #200-15. Should you wish to discuss any matter further do not hesitate to contact me or members of my staff.

Sincerely,

Barry White
Associate Assistant Secretary
for Regional Programs

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
WASHINGTON, D.C. 20210

DEC 17 1975

RECEIVED
DEC 22 1975
APCI CHEM. CORP.
LAW DEPT.

Mr. Raymond E. Schenck
Attorney
Air Products and Chemicals, Inc.
Five Executive Mall
Swedesford Road
Wayne, Pennsylvania 19087

Dear Mr. Schenck:

This is in response to your letter of June 30, 1975 to Assistant Secretary John E. Stender petitioning for the modification of 29 CFR 1910.1017(b)(6), (formerly 29 CFR 1910.93q(b)(6) recodified May 23, 1975), Exposure to Vinyl Chloride, Occupational Safety and Health Standards.

29 CFR 1910.1017(b)(6) defines a fabricated product as being one which is "made wholly or partly from polyvinyl chloride, and which does not require further processing at temperatures, and for times, sufficient to cause mass melting of the polyvinyl chloride resulting in the release of vinyl chloride."

"Release of vinyl chloride" means the release of an amount of vinyl chloride which would likely result in employee exposure at or above the action level without regard to the use of engineering controls. Products which can be classified as fabricated products are exempt from the provisions of the vinyl chloride standard. All other products are subject to the requirements of the standard.

There are no plans presently to formally modify the vinyl chloride standard. Therefore, we hope that the the above clarification of the regulation will satisfy your petition request.

Should you have further questions, please contact me or members of my staff.

Sincerely,

Barry White
Associate Assistant Secretary
for Regional Programs

ENCLOSURE 1

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration
WASHINGTON, D.C. 20210

DEC 17 1975

Mr. R. S. Brookman, Manager
Research, Development and Technical Services
Firestone Plastics Company
Pottstown, Pennsylvania 19464

Dear Mr. Brookman:

In response to your letter of July 14, 1975, petitioning for modification of the Vinyl Chloride Standard, the following determinations have been made:

1. 29 CFR 1910.1017(b)(5) Definitions

In regards to the definiton of "massive release" in Program Directive #200-35, we agree that the definition should be modified. This will be addressed in a future program directive. In all probability the stipulation of 100 ppm will be removed.

2. 29 CFR 1910.1017(b)(6) Definitions

The standard defines a fabricated product as being one which is "made wholly or partly from polyvinyl chloride, and which does not require further processing at temperatures, and for times, sufficient to cause mass melting of the polyvinyl chloride resulting in the release of vinyl chloride."

"Release of vinyl chloride" means the release of an amount of vinyl chloride which would likely result in employee exposure at or above the action level without regard to the use of engineering controls. Products which can be classified as fabricated products are exempt from the provisions of the vinyl chloride standard. All other products are subject to the requirements of the standard. If the employer uses or manufactures a product which is not a fabricated product, he must initiate monitoring procedures. If the monitoring reveals that the employees are not exposed to vinyl chloride at or above the action level, the employers' operations will be exempt from the provisions of the std ard.

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However, if the monitoring reveals exposure at or above the action level, the employer must implement the procedures specified in the standard.

3. 29 CFR 19101.1017(g)(4)(iii) Respiratory protection

Regarding your suggestion to add a Type C, Supplied Air Respirator, Pressure Demand type, with full or half face-piece to this section:

If an employer can show that a respirator provides equal or greater protection than those specified in the standard, he may be granted an interim order or a variance from the standard. Your company received such an interim order, dated May 30, 1975.

4. 29 CFR 1910.1017(k) Medical surveillance

There is no OSHA regulation requiring an employee to submit to a medical examination. If the employee refuses any medical examination required to be provided by the employer, the employer shall inform the employee of the possible health consequences of such refusal and obtain a signed statement from the employee indicating that the employee understands the risk involved by refusal to be examined.

We greatly appreciate your sharing data, experience and knowledge with us. At the present time there are no plans to formally amend or modify the vinyl chloride standard. We hope that the above clarification of the regulation will satisfy the request in your petition. Should you have further questions please do not hesitate to contact us.

Sincerely,

Barry J. White
Associate Assistant Secretary
for Regional Programs

Copy to T. C. Walker 12/26/75

Copies to: Mr. W. B. Connolly, Jr.
Mr. J. J. Cassidy, Jr.
Mr. C. J. Kleinert
Mr. T. P. Hoy
Mr. R. W. Arnold
Mr. W. M. West
Mr. G. D. Lloyd
Mr. R. A. Peck

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202/457-1116

May 11, 1981

Mr. John R. Lawrence
The Society of the Plastics
Industry, Inc.
355 Lexington Avenue
New York, New York 10017

Re: Employee Training Under OSHA Vinyl Chloride Standard

Dear John:

The purpose of this letter is to inform you of the recent completion of a case involving the employee training provisions of the Occupational Safety and Health Administration (OSHA) vinyl chloride standard. As you may recall, in September, 1978, an OSHA inspector issued a citation to Hooker Chemical Corporation. The citation noted Hooker's alleged failure to provide training on vinyl chloride for employees who worked in the calendering, compounding and warehouse areas.

Hooker contested the citation for its Burlington, New Jersey facility on the basis that employees working in these areas were not required to be trained on the hazards of vinyl chloride. Both Hooker and OSHA's monitoring of vinyl chloride in the calender and compound facilities indicated concentrations significantly below the 0.5 parts per million (ppm) action level.

In May, 1979, the administrative law judge issued a decision that adopted Hooker's position and vacated the OSHA citation. The judge held that the training provisions of the standard do not apply to areas where the vinyl chloride level in the ambient air is below the action level of 0.5 ppm.

Although not requested to do so by any party, a commissioner on the Occupational Safety and Health Review Commission directed that the case be reviewed. In responding to the review proceedings, OSHA changed its position and filed a letter stating that the judge's decision should be affirmed. Significantly, OSHA stated that the training requirements were not applicable in this case because Hooker's compounding and calendering operations simply were not processes that could result in hazardous exposure to vinyl chloride.

Because no party sought review by the Commission, and the Commission did not consider the issue one of compelling public interest, it chose not to review the case. Thus, under the Commission's order of March 31, 1981, the judge's decision remains intact.

While the case has limited precedential value, it does clarify what is a regulated area and when training requirements must be met. In addition, the proceedings indicate that OSHA is unlikely to issue citations in circumstances similar to that which existed at Hooker's Burlington facility.

Because the conclusion of this litigation may be of general interest, you may wish to further distribute this letter to the PVC Safety Group. As always, if you have any comments or questions, please feel free to contact me.

Cordially yours,

Peter

Peter L. de la Cruz

cc: Mr. Jerome P. Carroll
Ms. Fran Lichtenberg
Mr. Thomas R. McGrath

EXHIBIT VIII

BFG TECHNICAL DOCUMENT

A PHYSICAL MODEL FOR THE DIFFUSION OF VINYL CHLORIDE MONOMER FROM PVC UNDER VARIOUS CONDITIONS OF STORAGE

by
M. M. O'Mara
L. B. Crider
R. L. Bowles
C. J. Tomanek

B.F.Goodrich Chemical Company
Avon Lake Technical Center
P.O. Box 122
Avon Lake, Ohio 44012

August 25, 1975

Abstract

An empirical model, based on large scale laboratory experimental data, has been developed to show the relationship between the amount of residual vinyl chloride monomer (RVCM) in PVC resin and the concentration of atmospheric vinyl chloride monomer (AVCM) under various conditions of storage. The variables studies in the experimental work leading to the development of this model include temperature, time, ventilation rate, RVCM content of the resin, mass/volume ratio and resin type (varying in porosity).

The results obtained from a statistically designed series of 24 experiments show the interactions of all the variables and permit (1) the effects of the variables to be established and (2) the derivation of a model which permits the AVCM levels to be predicted for any combination of the variables.

The developed model has been used to predict the AVCM level in BFG warehouses at Avon Lake, Louisville and Pedricktown. We have found excellent agreement between predicted and measured AVCM levels at these three locations and under a variety of storage conditions.

Additionally, the model has been used to show that under less than the most severe storage conditions, the OSHA action level will not be exceeded (500 ppb AVCM) when the RVCM content of the stored resin does not exceed 18 ppm. Even under the most extreme storage conditions the OSHA action level is not exceeded when the RVCM content of the resin is 8.5 ppm or less.

Table of Contents

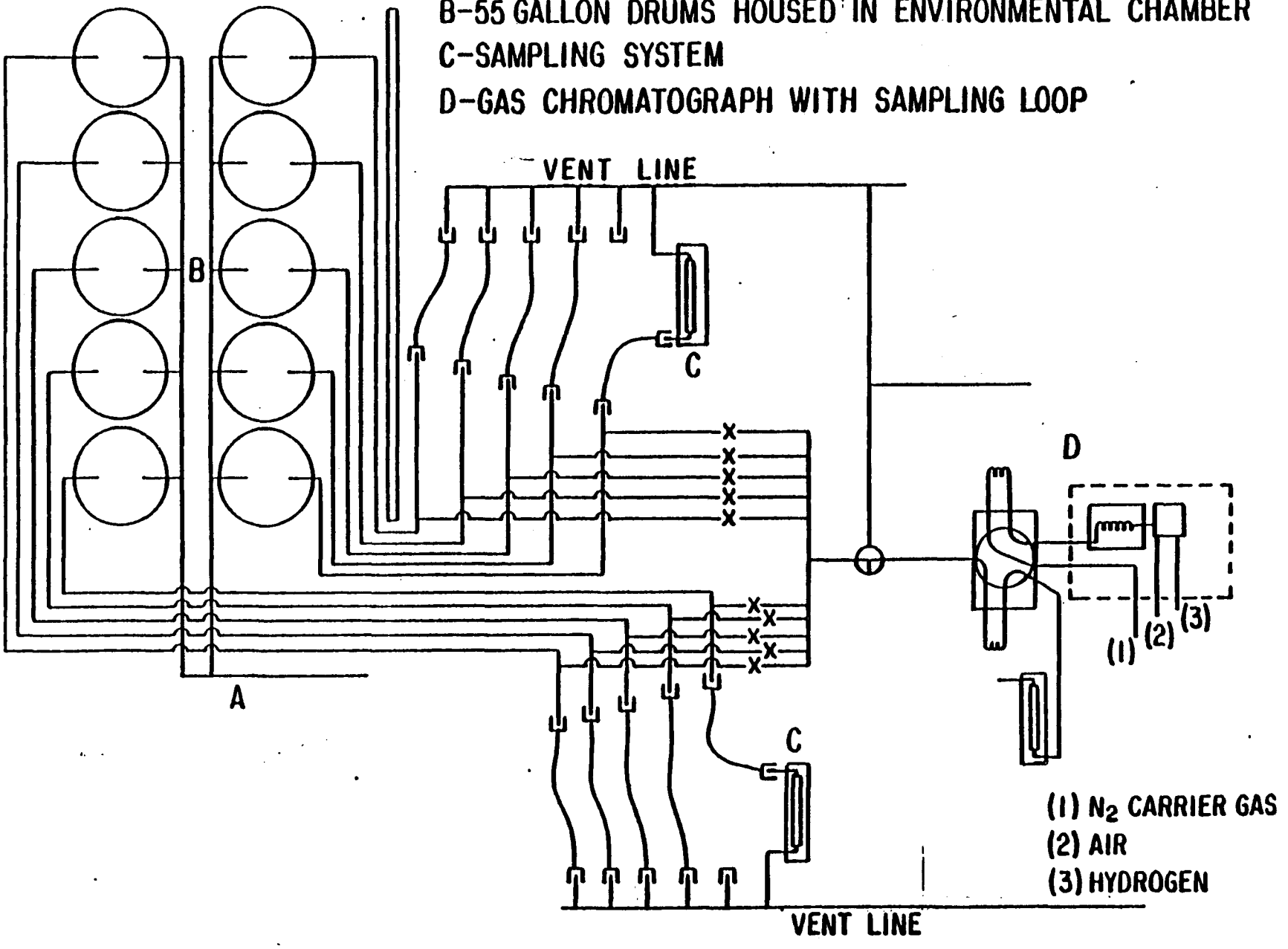


Figure 1

Table II

Basic Description of Physical Model
(Refer to Figure 1)

Section	Description
A	inlet nitrogen purge gas; maximun flow ~ 20 liters/minute
B	environmental chamber containing ten air-tight 55-gallon metal drums
C	55-gallon drum sampling system
D	flame-ionization gas chromatograph/data handling system

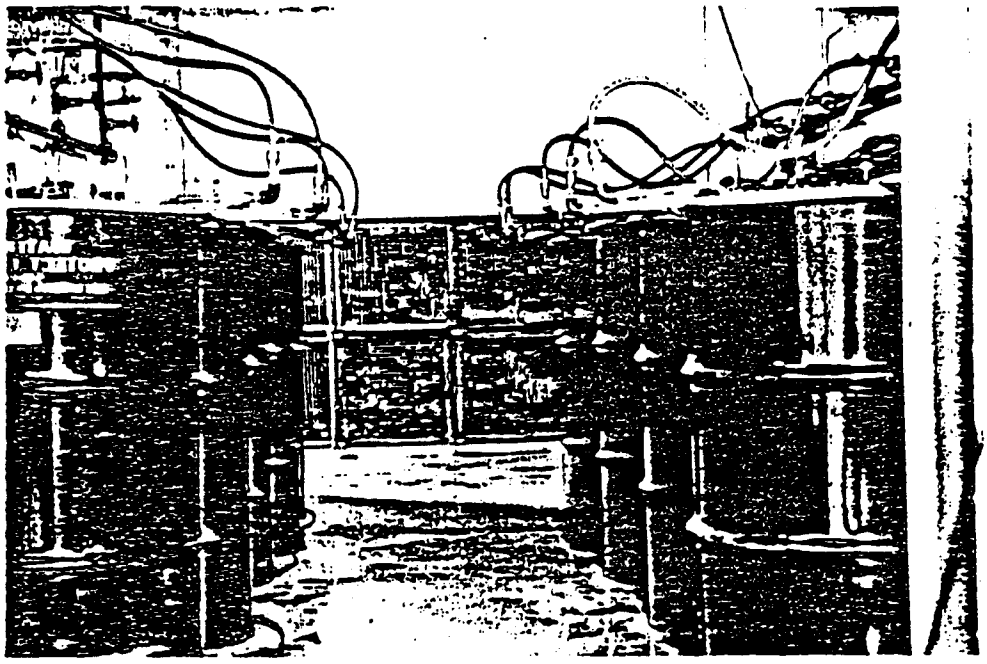


Figure 2

A

B

A - Nitrogen Purge Gas Inlet System
B - 55 Gallon Drums in Environmental Chamber

Figure 3

C Sampling System Manifold

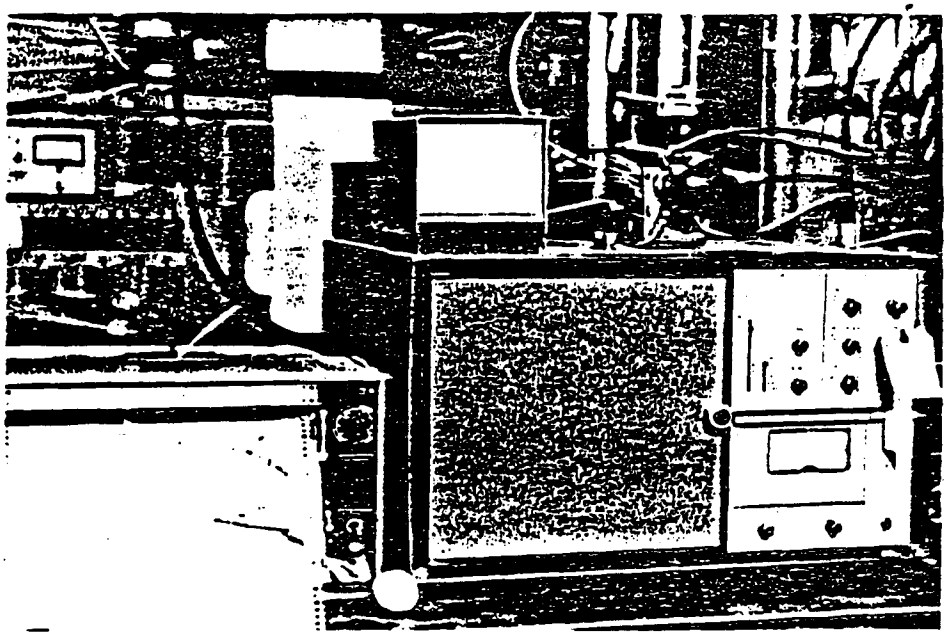


Figure 4

D - Gas Chromatograph with Sampling Loop

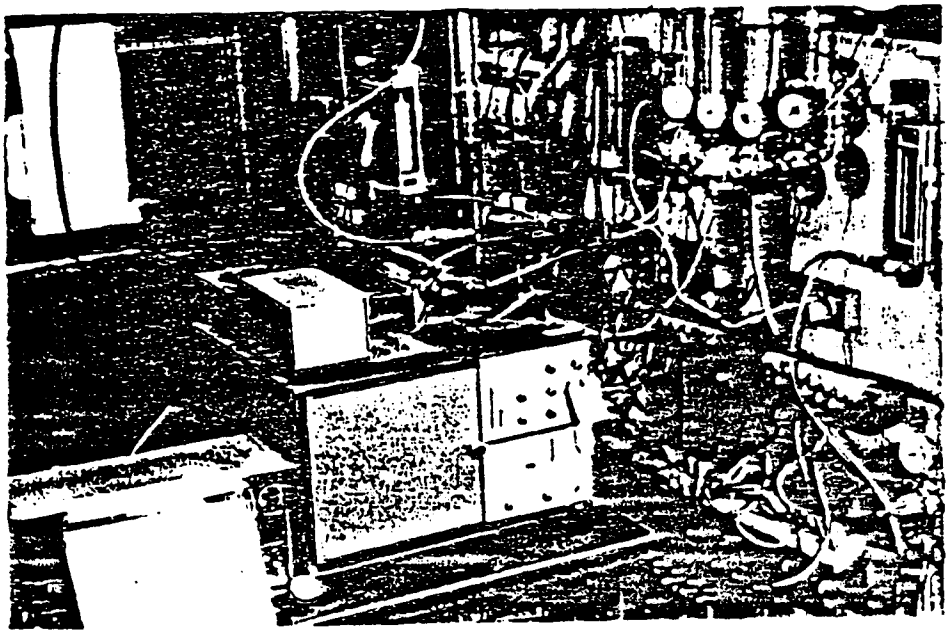


Figure 5

C

D Gas Chromatograph with Sampling System

Table III

Gas Chromatograph and Data Handling System Used to Monitor AVCM Levels

Gas Chromatograph

System - Hewlett-Packard Model 5711 Flame Ionization Gas Chromatograph

Method - 10' X 1/8" Porapak Q, mesh 80/100; isothermal at 150°C; nitrogen carrier gas at 30cc/minute; detector - 250°C; injection port - 150°C

Gas Sampling Valve - 10cc sample loop

Data Handling System

System - Hewlett-Packard Model 3380 Integrator-Calculator

Calibration of the system was accomplished through the use of commercially available standards (Precision Gas Sampling Corporation) and dynamic dilution of those standards. A typical calibration (checked periodically) and a regression analysis of that data is summarized in Table IV. This analysis indicates good linearity over the range from 128 - 2000 ppb of VCM in the atmosphere. The slope from the linear regression analysis was used as input to the integrator/calculator in order to calculate all data. It is important to note that as the sampling proceeded to a range outside of the calibration range shown in Table IV, new calibrations were carried out to reflect these different ranges. At no time was a calibration extrapolated beyond the experimentally determined range and used as a basis for analysis.

(C) Theoretical Diffusion of VCM in the Physical Model

It was necessary to check out the performance of the system in terms of theoretical diffusion. The main reason for doing this was to provide a final and independent check of the model, the sampling system and the analytical system interacting together. It was further felt that this approach would lead to a definition of any VCM system absorption (or leakage) problems. The ab initio derivation of the mathematical model which describes the build-up of a gas in a dynamic system is described below.

if:

C_o = concentration of incoming air stream
C_t = concentration in drum at any time (t)
V = volume of drum
M = flow into and out of drum
t = minutes

Table IV

VCM Calibration of Gas Chromatograph

Calibration Data

VCM Concentration ppb	Integrator/Calculator Response
128	2030, 2024, 2013
423	6819, 6847, 6846
623	9736, 9755, 9880
822	12331, 12278, 12479
1109	16703, 16336, 16800
2292	34740, 34910, 34841

Linear Regression Analysis

ppb = m (response) - 12.36

m = 0.0663 ± .0004

correlation: 0.9997

VCM into drum = VCM out of drum + accumulation

$MC_o d_t = MC_t d_t + V d_c$

$V\, d_c/d_t = MC_o - MC_t$

$d_c/d_t = \frac{M}{V}(C_o - C_t)$

$$\frac{d_c}{C_o - C_t} = M/V\, d_t \qquad (1)$$

integrating this over the limits from $0 - C_t$ and $0 - t$ yields:

$- n (C_o - C_t) = M/V(t) + A$

or

$C_t = C_o - A\, e^{-M/V(t)}$

at $t = o$, $C = o$ $\therefore A = C_o$

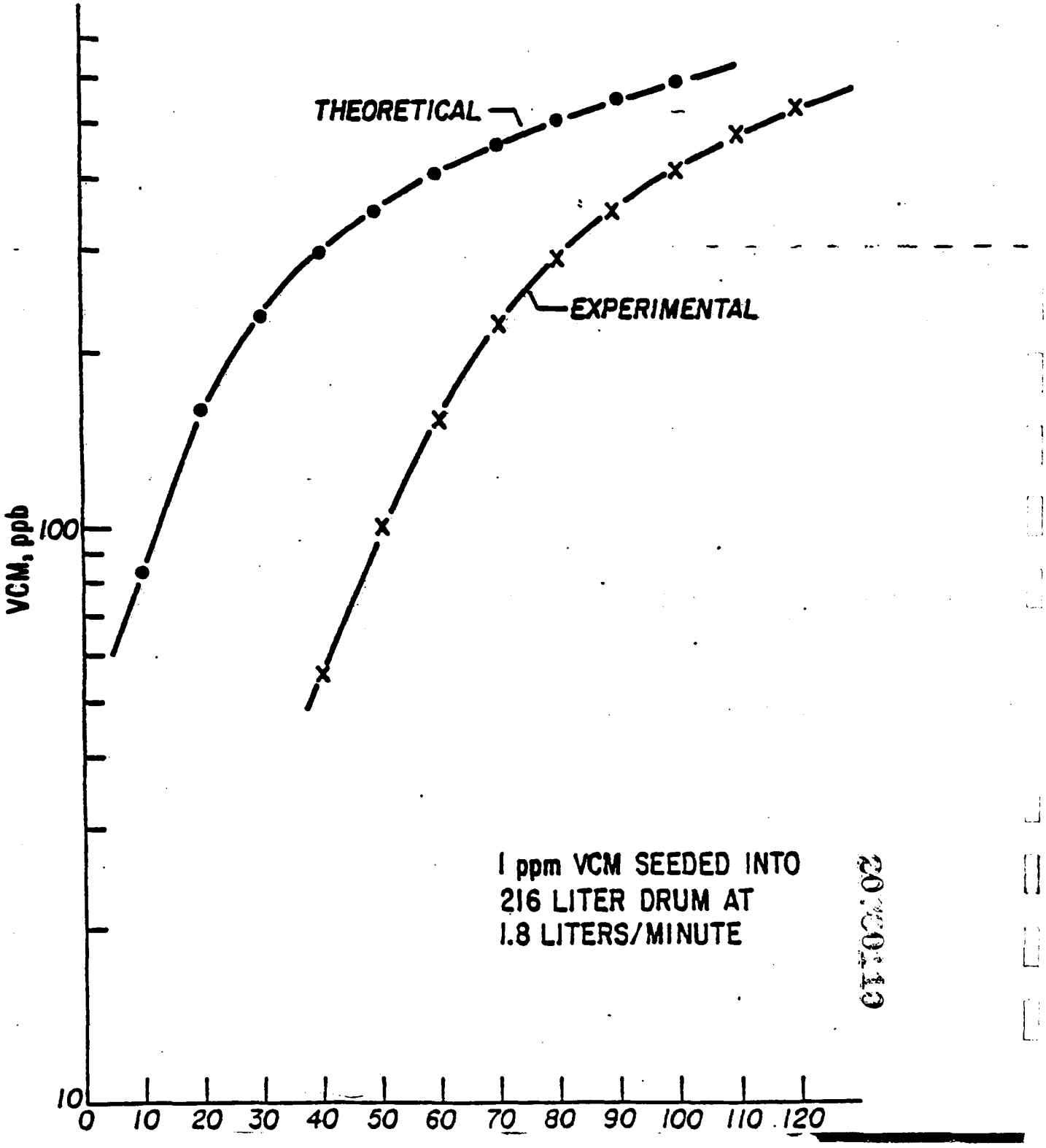
$C_t = C_o [1 - e^{-M/V(t)}]$

In essence, equation (1) describes the build-up of VCM in a 55-gallon drum when VCM at a concentration of C_o is flowed into the drum* at a rate equal to M. At any time = t, the concentration of VCM in the drum is C_t. To test this equation, a 1 ppm VCM standard was flowed into a drum (216 liters) at a rate of 1.82 liters/minute. It can be seen from Figure 6 that there is not a satisfactory agreement between the theoretical and the experimentally determined build-up of VCM in the model. It can be seen from Figure 6 that for any concentration of AVCM, the time increment between the two curves is approximately 40 minutes. This induction period was analyzed to be a diffusion

*Flow into the drum and flow out of the drum is equal.

Figure 6.

THEORETICAL vs. EXPERIMENTAL BUILD-UP of VCM in 55 GALLON DRUM



problem within the large drum. This inherent analytical flow was corrected by installing 3 inch mixing fans in each of the 55-gallon drums. The data presented in Figure 7 was obtained after this experimental modification was made. This treatment unequivocally demonstrated that VCM could be monitored in real time as it diffused from PVC resins under controlled ventilation conditions in a dynamic closed system. It also demonstrates the validity of the entire sampling methodology and VCM standards.

V. Diffusion of VCM From PVC Resins in Model

This section contains a summary of all diffusion experiments carried out in the statistically designed study. More detailed information (concentration/time data, etc.) on all experiments can be found in the Appendix. The purpose of this section is to provide a rapid means for comparing the various experiments carried out in this study. In order to make this comparison so that order of magnitude trends can be seen, the following data is provided:

(1) resin type (A, B, C . . .)

(2) residual VCM in resin (RVCM)

(3) exposure temperature (°C)

(4) total exposure time (hours)

(5) ventilation rate (turnovers/hour)

(6) resin mass/storage volume ratio (lbs./ft.^{3})

(7) maximum AVCM level reached and time of maximum (ppm, hrs.)

These data are summarized in Table V.

Figure 12.

AVCM vs. RVCM and WAREHOUSE LOADING

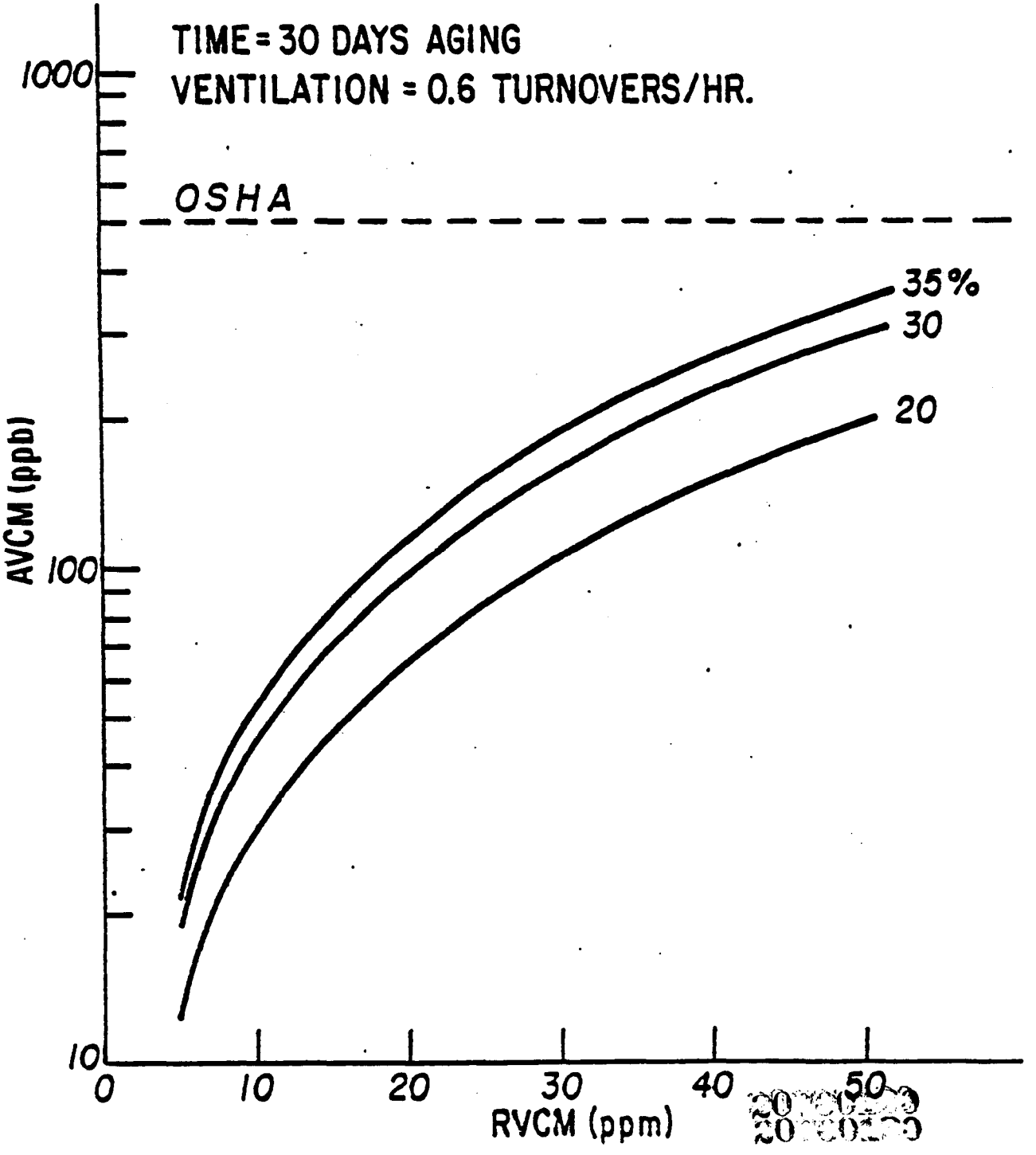
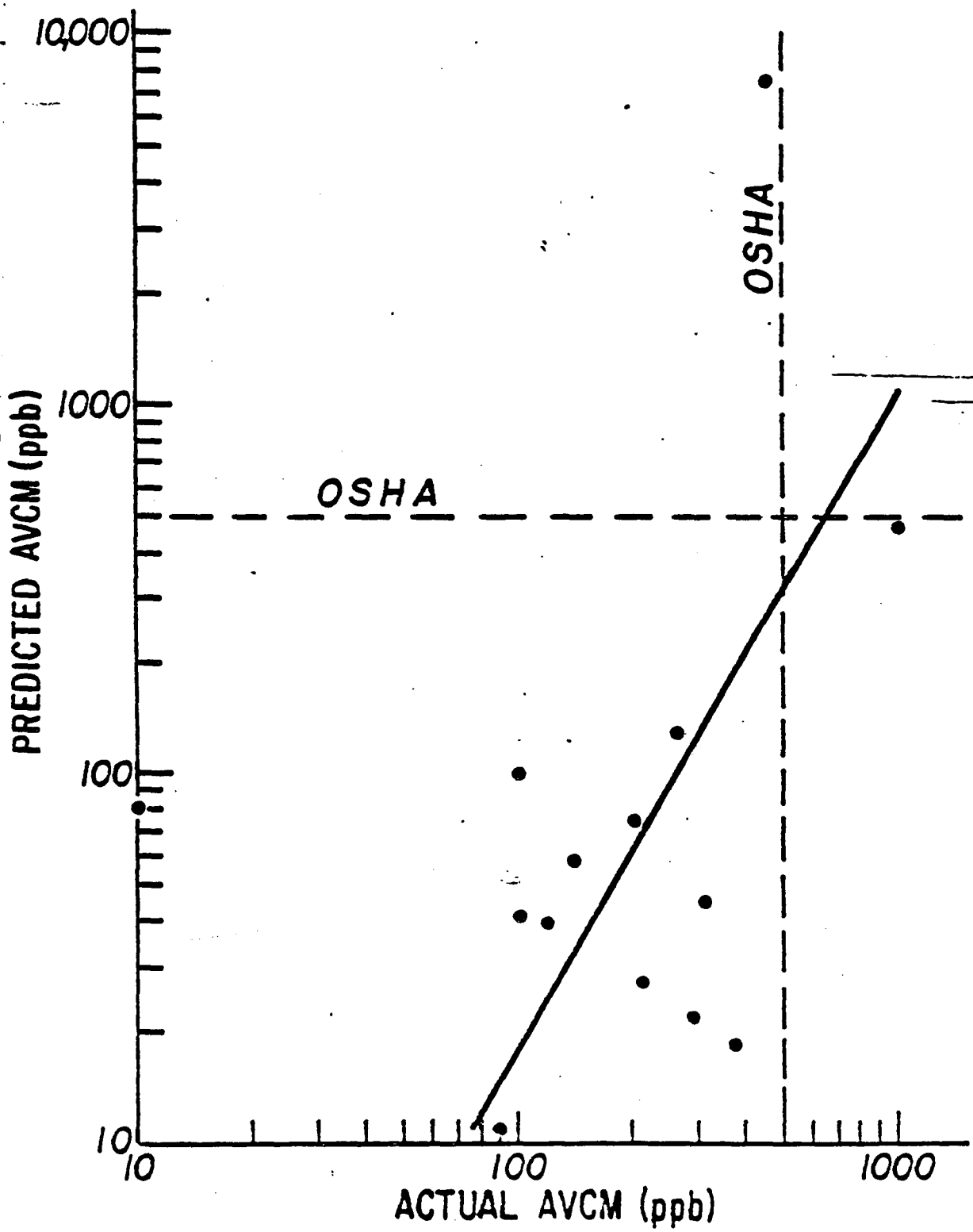


Figure 13.

PREDICTION of AVCM in WAREHOUSE SAMPLES



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storage conditions varied in temperature, ventilation rate, loading and RVCM (all were approximately at one month's aging = 720 hours), the model predicts the different AVCM results quite well. The somewhat low predictions can probably be explained by the fact that the warehouse samples were bagged (slowing the VCM diffusion slightly) whereas the model was based on material being stored in bulk form.

The accuracy of the model is ±100% in being able to predict the "true" AVCM from a set of storage conditions and resin possessing a certain RVCM.

Acknowledgments

The authors gratefully acknowledge the considerable contributions of H. T. Kim for his assistance in development of the experimental design and the development of a mathematical model evaluating effective diffusivities of VCM in PVC resins; to A. R. Berens for consultation during the course of this work; to M. R. Ritland for assistance in the statistical analysis of the data and to a large number of people in BFG Manufacturing who cooperated in providing large quantities of the specific resins required for this study.

Bibliography

(1) A. R. Berens, L. B. Crider, C. J. Tomanek and J. M. Whitney, "Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography" to be published in J. of App. Poly. Sci.

(2) A. R. Berens, Polymer Preprints 15 (2) 203 (1974).

IX. Appendix

Table V of this report provides a summary of all experiments carried out in order to develop the empirical model. The actual time/concentration data for all experiments is contained in this section; experiment numbers refer to those in Table V. All data is summarized in Table VI. All data is contained in Data Book 001-95 (4/28/75).

Table V2

Experimental (Time/Concentration) Data

Experiment No.	1		2		3		4		5		6		7	8		9	
	t[1]	AVCM[2]	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t AVCM	t	AVCM	t	AVCM
	0.5	.057	.5	<.010	1.0	.012	0.5	.167	0.5	<.01	0.5	.199		0.25	.763		
	1.0	.072	1.0	<.010	1.5	.013	1.0	.162	1.0	<.01	1.25	.324	all less	0.63	.721	all less	
	1.5	.074	1.5	<.010	2.0	.013	1.5	.145	1.5	.046	2.0	.166		1.0	.616		
	2.0	.0755	2.0	<.010	2.5	.015	2.0	.132	2.0	.0456	3.0	.208	than	2.5	.566	than	
	2.5	.0756	2.5	<.010	3.0	.012	2.5	.135	2.5	.0468	5.5	.325		4.0	.417		
	3.0	.072	3.0	.076	3.5	<.01	3.0	.112	3.0	.0467	8.5	.456	.010 ppm	7.0	.254	.010 ppm	
	3.5	.071	3.5	<.010	4.0	<.01	3.5	.119	4.0	.0510	12.5	.472		8.9	.296		
	4.0	.069	4.0	<.010			4.5	.111	5.0	.0501	15.5	.578		11.0	.204		
	4.5	.069	5.5	<.010			5.5	.097	6.0	.0432	16.5	.579		12.9	.093		
	5.0	.068					6.5	.084			17.5	.577		15.0	.065		
	6.0	.069									27.0	.495		17.0	.038		
	7.0	.064												23.0	<.010		
	8.0	.060															

10		11		12		13		14		15		16		17		18	
t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM	t	AVCM
		1.0	.069	.25	.072	.25	.616	.33	.258	.7	209	.8	97.8	1.0	384	1.0	481.6
all less		2.5	.152	.5	.093	.5	.818	.75	.105	18.5	82.3	18.7	17.2, 16.0	19.3	143	2.0	508.6
		4.3	.251	2.0	.187	1.0	.936	1.5	.094	24.0	54.1	24.0	9.2	24.0	119	3.0	527.0
than		6.3	.351	3.0	.109	2.0	.915	2.0	.106	41.0	26.0	40.5	5.8, 5.6	41	77.3	19.1	282.2
		8.3	.445	8.3	.375	3.0	.871	3.0	.112	64.0	12.6	63.6	2.7, 2.9	63.8	33.3	23.5	203.2
.010 ppm		11.3	.535	20.5	.104	8.2	.707	4.5	.125	88.0	5.3, 5.6	87.5	1.06	87.8	15.3, 16.7	54.3	34.8
		12.0	.561	23.5	.056	20.5	.553	11.2	.160	111.5	3.1, 3.1	111.3	0.65	111.3	8.9	95.7	6.2
		16.1	.565	34.7	.324	25.5	.492	26.5	.154	128.0	1.7	128.3	0.27	128.5	4.2	120.0	2.3
		22.0	.525	35.2	.283	35.7	.485	44.5	.174	149.0	0.52	149.3	0.087	149.5	1.5	144.5	1.2
		26.0	.501	44.5	.047	44.5	.396			173.0	0.36	173.0	0.04	173.0	0.76	170.0	0.54

19		20	
t	AVCM	t	AVCM
1.0	272.8	0.5	310.7
2.0	263.4	1.3	406.3
3.0	220.1	2.0	376.2
19.3	108.2	3.1	522.9
54.5	1.8	19.2	417.6
96.3	0.99	21.5	321.1
119.3	0.48	54.3	340.1
144.0	0.32, 0.36, 0.38	54.8	118.5
169.5	0.40	96.0	67.2
		120.0	22.1
		144.3	13.5
		169.8	5.1

[1] All times are in hours

[2] All AVCM is ppm

A MODEL FOR THE DIFFUSION OF VINYL CHLORIDE MONOMER FROM PVC UNDER VARIOUS CONDITIONS OF STORAGE

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INTRODUCTION

Within the past several years significant advancements have been made within the PVC industry to minimize employee exposure to vinyl chloride monomer (VCM). Improvements in PVC manufacturing processes to reduce the residual vinyl chloride monomer (RVCM) content of finished resins has been a key factor in maintaining acceptable VCM levels in work areas during packaging, processing, shipment and storage.

The diffusion of vinyl chloride monomer out of finished PVC resins has been adequately studied [1] at temperatures above the glass transition temperature (Tg). The results of these studies have been particularly useful in reducing RVCM during manufacturing and to predicting RVCM escape to the environment during processing. This new knowledge has also led to a rapid, simple gas chromatographic method [2] for the determination of RVCM in PVC from the analysis of the vapor phase (head space) over PVC powders in a closed container.

This somewhat ideal behavior does not exist at temperatures below Tg, however, and consequently one cannot use existing equilibrium data to predict the concentration of VCM in the air space above PVC resins and in particular under non-static conditions such as exists during the storage and transportation of bagged or bulk resin. In addition to the relative slow diffusion rate at or near ambient temperatures, other factors that affect VCM release include variable ventilation rates, mass-to-volume ratios, RVCM content of the resin and residence time in the storage or shipment compartment.

The primary objective of the research reported in this paper was to develop a physical model for the diffusion of VCM from PVC resin under various conditions of exposure during storage and shipment. The developed model is based on a statistically significant number of large scale diffusion experiments to show the interaction of all the above variables and to allow the prediction of atmospheric vinyl chloride monomer (AVCM) levels for any combination of the variables.

EXPERIMENTAL

It can be postulated that some reasonable understanding of these storage variables and their interactions can be developed from a physical modeling of a storage or shipment compartment. It can also be rationalized that the accuracy of such a model will be much improved if the experimental design is on a large scale that can physically simulate all of the storage variables but under highly controlled conditions. Any experimental design of this type, however, must be thoroughly tested to establish the validity of the test measurements and to assure the absence of any errors as may occur through poor test controls, adsorption of VCM by the system, and possible interfering components that could lead to spurious results.

Using a Computer Optimized Experimental Design (COED), 24 large scale experiments were selected to study the variables listed below to describe their effects and interaction on AVCM in a storage compartment or warehouse. The variables and ranges included:

1.) Temperature - 74-115°F
2.) Ventilation Rate - 0.5-3.0 Turnovers/Hour
3.) Loading (PVC Volume/Storage Volume) - 11-34%
4.) Resin RVCM - .01-121 ppm
5.) Storage Time - 1-170 Hours

In order to meet the demands of the statistically designed (COED) diffusion study, the experimental phase of this program had to be capable of controlling the following experimental parameters:

1.) Temperature
2.) Ventilation Rate
3.) Mass/Volume Ratio

The basic physical model that was chosen to meet these requirements was one based on sealed metal storage bins (55-gallon drums) housed in an environmental chamber where the temperature could be varied and controlled. A schematic of the entire experiment is shown in Figure 1. The schematic is divided into four key areas: (A) the ventilation system, (B) the environmental chamber, (C) the sampling system and (D) the gas chromatograph with data handling system. Clean, dry nitrogen (A) enters the environmental chamber (B) through a split manifold. The ten drums were piped into the two manifolds through ten flow regulators. In this way, ventilation rates could be independently set in each drum. The exhausted atmosphere from the drums was directed to a sampling system (C) that provided a split stream; one for vent and one for sampling. The sampling stream was interfaced to a gas sampling valve/gas chromatograph/data handling system (D). Sequential sampling of each of the drums was possible with this system. The environmental chamber is a Conrad Model WD-624 Temperature Humidity Chamber with an internal volume of 938 cubic feet. Temperature control inside the chamber was ± 2°C; a maximum exposure temperature of 100°C is possible within the chamber.

Calibration of the system was accomplished through the use of commercially available standards (Precision Gas Sampling Corporation) and dynamic dilution of those standards. A regression analysis of the calibration data indicates good linearity over the range from 129-2000 ppb of VCM in the atmosphere. The slope from the linear regression analysis was used as input to the integrator/calculator in order to calculate all data. It is important to note that as the sampling proceeded to a range outside of the calibration range, new calibrations were carried out to reflect these different ranges. At no time was a calibration extrapolated beyond the experimentally determined range and used as a basis for analysis.

It was necessary to check out the performance of the system in terms of theoretical diffusion. The primary reason for doing this was to provide a final and independent check of the model, the sampling system and the analytical system interacting together. It was further felt that this approach would lead to a definition of any VCM system absorption (or leakage) prob-

lems. The ab initio derivation of the mathematical model which describes the build-up of a gas in a dynamic system is described below.

If: C_o = concentration of incoming air stream
C_t = concentration in drum at any time (t)
V = volume of drum
M = flow into and out of drum
t = minutes

then: VCM into drum = VCM out of drum + accumulation

$$MC_o dt = MC_t dt + V dc$$

$$V dc/dt = MC_o - MC_t$$

$$dc/dt = \frac{M}{V}(C_o - C_t)$$

$$\frac{dc}{C_o - C_t} = M/V\, dt \qquad (1)$$

integrating this over the limits from $0 \rightarrow C_t$ and $0 \rightarrow t$ yields: $-n(C_o - C_t) = M/V(t) + A$

or

$$C_t = C_o - Ae^{-M/V(t)}$$

at $t = o$, $C = o$ $\therefore A = C_o$

$$C_t = C_o[1 - e^{-M/V(t)}]$$

In essence, equation (1) describes the build-up of VCM in a 55-gallon drum when VCM at a concentration of C_o is flowed into the drum at a rate equal to M. At any time = t, the concentration of VCM in the drum is C_t. To test this equation, a 1 ppm VCM standard was flowed into a drum (216 liters) at a rate of 1.82 liters/minute. The data from this experiment is presented in Figure 2 and shows a satisfactory agreement between the theoretical and experimentally determined concentration in the modeling system.

The analytical methodology used to determine the VCM in the exit vents from the drum experiments is as follows:

Gas Chromatograph
System - Hewlett-Packard Model 5711 Flame Ionization Gas Chromatograph
Method - 10' X 1/8" Porapak Q, mesh 80/100; isothermal at 150°C; nitrogen carrier gas at 30cc/minute; detector - 250°C; injection port - 150°C
Gas Sampling Valve - 10cc sample loop
Data Handling System
System - Hewlett-Packard Model 3380 Integrator-Calculator

RESULTS AND CONCLUSIONS

The results obtained from the 24 COED designed experiments and a multiple correlation analysis of the results permitted 1) the effects and interactions of the variables on AVCM to be established and 2) the derivations of a model which permits the AVCM levels to be predicted for any combination of the variables studied.

The resulting model for PVC resins with a porosity of 0.2 is:

$$AVCM = Ro^{1.47}L^{0.37}V^{-1.56}\left[T^{6.8}e^{-(24.1 + .00031\,Tt)}t^{.24}e^{-.0000116\,Tt}\right]$$

where: AVCM = atmospheric concentration of VCM in parts per billion
Ro = initial RVCM of the resin in parts per million
L = % loading; (resin volume/warehouse volume) X 100
V = ventilation rate in turnovers per hour
T = temperature in °F
t = time in hours

As expected, AVCM decreases as:
1.) RVCM of the resin decreases.
2.) Volume of resin being stored decreases.
3.) Ventilation rate increases.
4.) Storage temperature decreases (for time periods of 1-9 days); however, if the resin has been stored for longer periods of time (10+ days), then the AVCM is lower at higher storage temperatures. (This is the cumulative result of a higher temperature causing more rapid diffusion at the beginning of aging; therefore, more rapid depletion of RVCM and, thus, lower AVCM at longer agings.)
5.) Storage time increases.

Using the relationships described in the model, maximum RVCM resin levels can be determined which will assure that AVCM levels will be less than 500 ppb OSHA action level for a variety of storage conditions. (See Figures 3-7 which show the effects of temperature, time, ventilation rate, loading and RVCM on AVCM.)

When PVC is stored under the least severe conditions (Temperature = 80°F, Ventilation = 0.5 turnovers/hour, 30% loading of a warehouse volume with VCM containing material, the RVCM of PVC resin must be no greater than 18 ppm to assure that the action level is not exceeded at 5 days.

If the 500 ppb (OSHA action level) must be met even under the most adverse storage conditions (Temperature = 120°F, Ventilation = 0.5 turnovers/hour, 80% loading of a warehouse volume with VCM containing material), then the resin RVCM must be no higher than 8.5 ppm.

Figure 8 shows how well the model predicts the AVCM levels in BFGoodrich warehouse samples obtained in April, 1975 at Avon Lake, Ohio, Louisville, Kentucky and Pedricktown, New Jersey. As the storage conditions varied in temperature, ventilation rate, loading and RVCM (all were approximately at one month's aging = 720 hours), the model predicts the different AVCM results quite well. The somewhat low predictions can probably be explained by the fact that the warehouse samples were bagged (slowing the VCM diffusion slightly) whereas the model was based on material being stored in bulk form.

The accuracy of the model is ± 100% in being able to predict the "true" AVCM from a set of storage conditions and resin possessing a certain RVCM.

ACKNOWLEDGMENTS

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Figure 1.

A-VINYL CHLORIDE FREE NITROGEN PURGE GAS INLET
B-55 GALLON DRUMS HOUSED IN ENVIRONMENTAL CHAMBER
C-SAMPLING SYSTEM
D-GAS CHROMATOGRAPH WITH SAMPLING LOOP

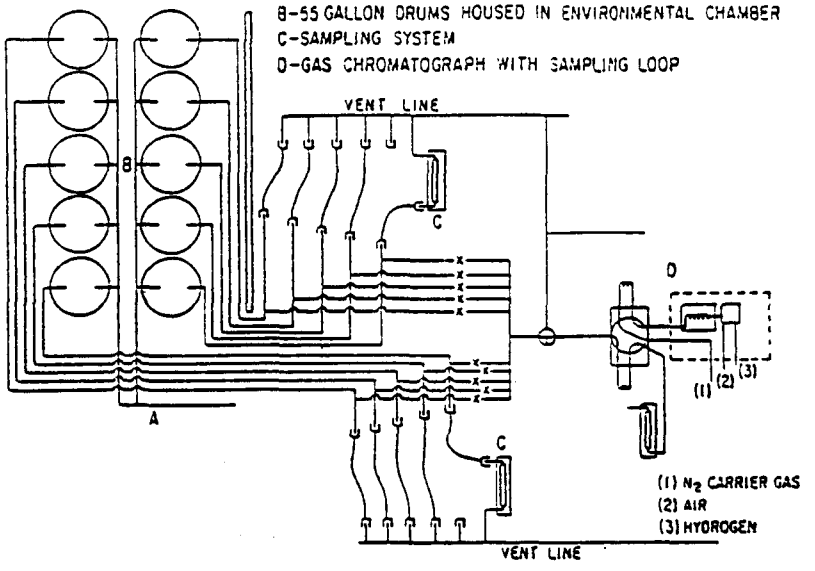


Figure 2.

THEORETICAL vs. EXPERIMENTAL BUILD-UP of VCM in 55 GALLON DRUM AFTER EXPERIMENTAL MODIFICATION

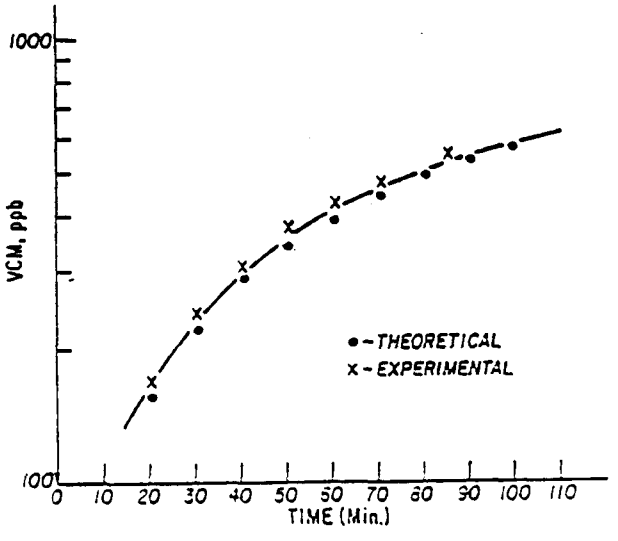


Figure 3.

AVCM vs. RVCM and WAREHOUSE LOADING

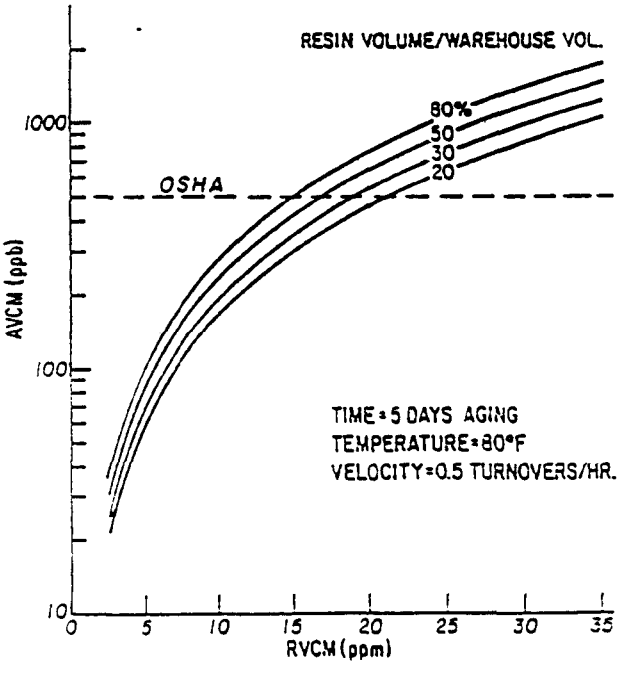


Figure 4.

AVCM vs. RVCM and TEMPERATURE

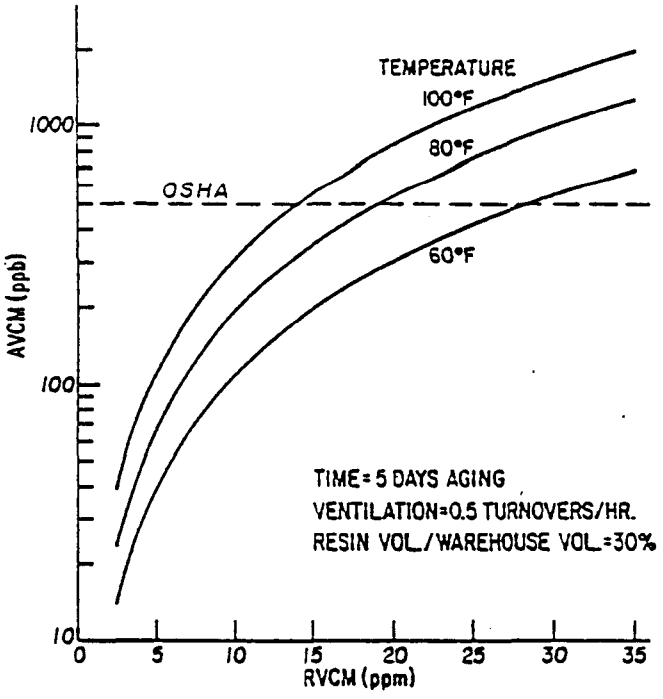


Figure 5.

AVCM vs. RVCM and VENTILATION

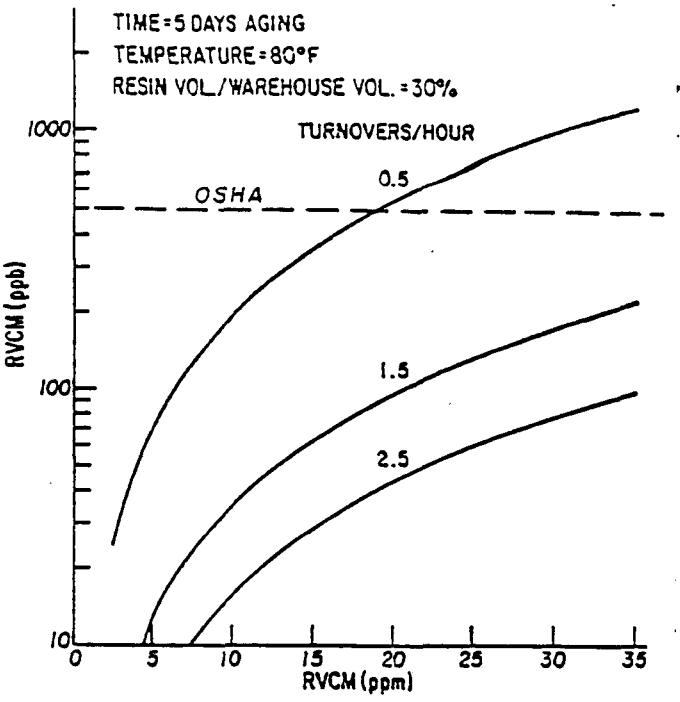


Figure 6.

AVCM vs. RVCM and VENTILATION

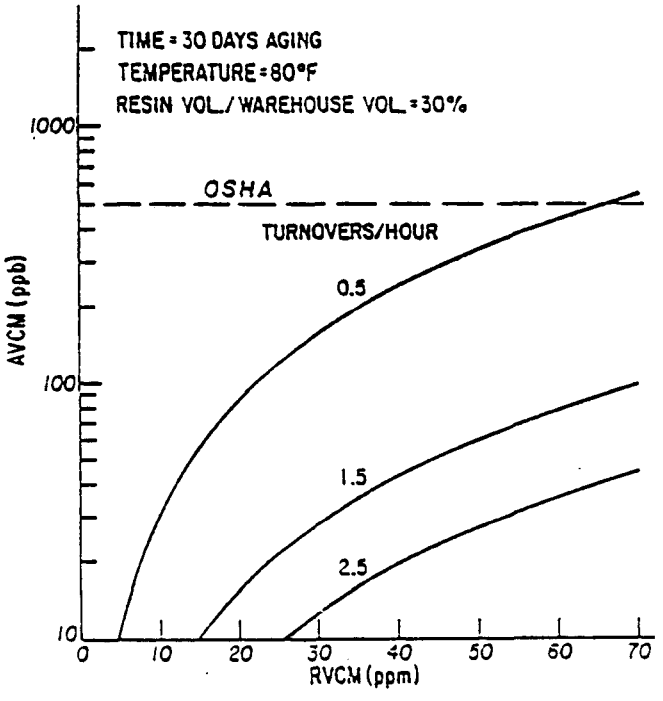


Figure 7.

AVCM vs. RVCM and WAREHOUSE LOADING

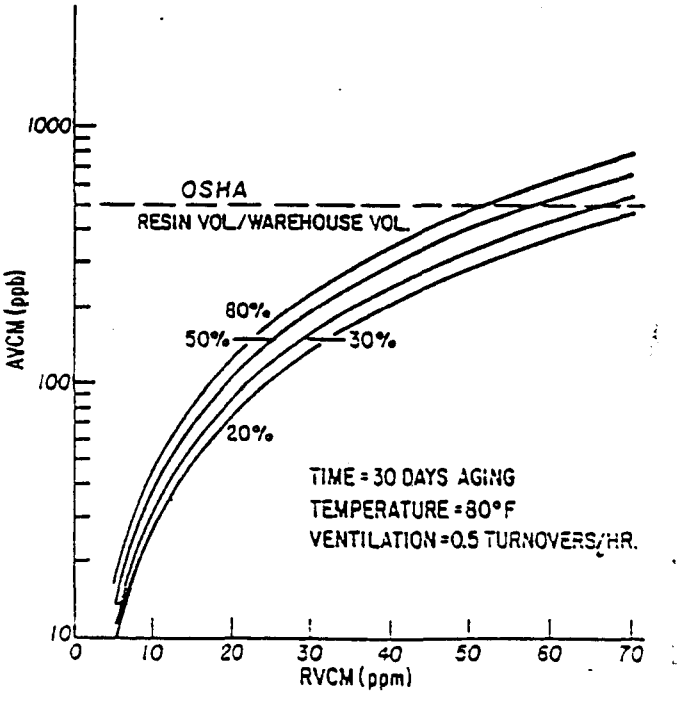
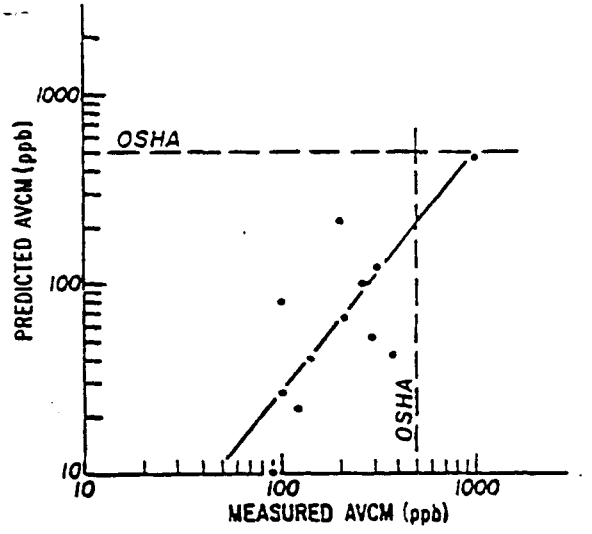


Figure 8.

PREDICTION of AVCM in WAREHOUSE SAMPLES



2. Analysis of Model Variables (Cont'd)

2.3 Truck loading (L)

Equation (1) shows that, as might be expected, increased truck loading produces higher concentrations of AVCM. In discussions with transportation experts the assumption was made that 80% loading is the maximum that could be expected. In this study, therefore, the truck loading was set at 80%.

2.4 Ventilation rate (V)

Ventilation rate as measured by air turn-over/hour cannot be readily ascertained for a truck since it is dependent on numerous factors e.g. truck's material of construction, design of truck, speed at which truck is traveling, and climatic conditions. However, an effective air turn-over rate can be calculated from Equation (1) if actual AVCM data measured inside the truck were available. Kruszynski[2,3] and Smith[4] have reported the AVCM concentrations inside the nose of a trailer immediately upon opening the doors, as well as immediately after a trailer has been unloaded. As can be seen from Table 1 AVCM concentrations did not exceed the action level limit for those cases where the samples were taken upon opening the doors. However, data where bag was broken and resin exposed did exceed the limit. Since this is the highest AVCM concentration reported, it was used in calculating the effective air turn-over rate. As shown in Appendix 1 the minimum effective air turn-over rate is approximately 6/hour. However, to ensure greater safety margin simulations were carried out using 3 air turnovers/hour.

3. Discussion of Results

With the variables fixed at levels given in Section 2 , Equation (1) can be solved to predict the resin residual VCM (RVCM) which would produce AVCM concentration below the action level limit of .5 ppm. However, one of the variables, the transportation time, cannot be ascribed a definitive value, and a range of values (4-72 hours) were assumed. Fig. 1 shows the relationship between the resin RVCM and the AVCM concentration inside a truck at 4, 24 and 72 hours. As can be seen from Fig. 1 the AVCM concentrations do not exceed the action limit of .5 ppm provided the resin RVCM content is below 10 ppm. It should be emphasized that Fig. 1 has been predicted using conditions which deliberately maximize the AVCM concentrations inside a trailer transporting PVC resins.

Material	RVCM (PPM)	Sample Type	Sample Point or Operation Monitored	Sampling Time (Minutes)	AVCM (PPM)	Location of AVCM Monitoring
Geon® 83741-132 Lot 00073 (Louisville, KY)	< 1.0	Static	Inside nose of the trailer immediately upon opening doors	29	0.22(2)	Tay Tech, Col. Ohio 4/21/75
Geon® 83741-021 Lot 00111 (Louisville, KY)	1.0	Static	Inside nose of the trailer immediately upon opening doors	55	< 0.01(2)	Pierce and Die Elkhart, Ind. 4/29/75
Geon® 92 Resin Lot 22393	< 1.0	Static	Inside nose of the trailer immediately upon opening doors	51	0.12(2)	Standard Products Cleveland, Ohio
Geon® 83714-004 Lot 41 (Louisville, KY)	< 1.0	Static	Inside nose of the trailer immediately upon opening doors	33	0.13(2)	Jurex, Elk Grove Illinois 5/12/75
Geon® 83789-021 Lot 00216	< 1.0	Static	Inside nose of the trailer immediately upon opening doors	48	0.15(2)	Cooley Inc. (RI) 5/7/75
Geon® 83700-290 Lot 263	< 1.0	Static	Inside nose of the trailer immediately upon opening doors	36	< 0.02(2)	Sackner Products MI 5/19/75
Geon® 222 Lot 02177	Not Recorded	Static	Sample taken inside a 45 ft. van that was just unloaded. Powder on the floor from a broken bag of resin.		1.4(3)	California Warehouse Vernon, CA 12/12/74
			Duplicate		.99(3)	
Geon® 121	Not Recorded	Static	Sample taken as right hand door was opened	N/A	.156(4)	OK Trucking Cleveland, Ohio 12/12/74
Geon®			Duplicate		.109(4)	"
Geon® 83794	Not Recorded	Static	Sample taken in front of bags in the trailer		.035(4)	"
			Duplicate		.082(4)	"

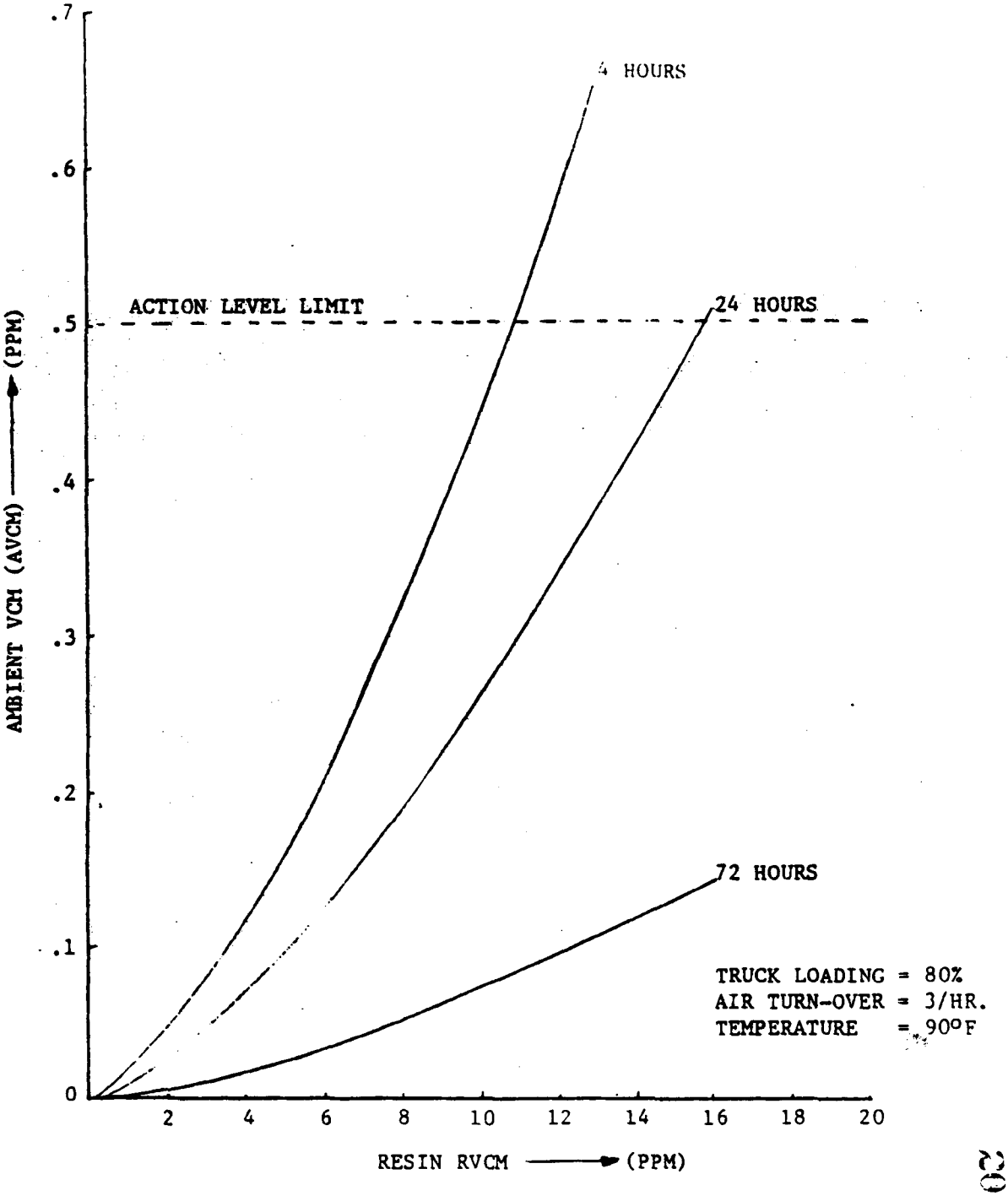


FIG. 1: RELATIONSHIP BETWEEN RESIN RVCM AND THE AVCM CONCENTRATIONS INSIDE A TRUCK AS PREDICTED BY O'MARA ET AL MODEL[1].

APPENDIX 1

Calculation of Effective Air Turn-over/Hr.

Equation 1 (see page 2) can be rearranged to allow the calculation of air turn-over rate (V), viz,

$$V^{1.56} = (R_o^{1.47} L^{.3}/AVCM)\{|T^6 ex(-24.1 = .0031Tt)| + .2\ exp(-.000116Tt)\} \text{ --- } 2$$

As mentioned in Section 2 temperature (T) and truck loading (L) were deliberately set at high values so as to maximize the AVCM concentration and, hence, ensure greater safety margin. Thus T is assumed to be 90°F and loading L is set at 80%. The selection of AVCM data to be used in the above equation is made from Table 1, page 4. The criteria for selecting AVCM data are,

(1) whether conditions under which AVCM data given in Table 1 were measured were similar to the conditions used in the development of the model,

and, (2) ensure that chosen data would minimize the calculated air turn-over rate and, thereby, increase margin of safety.

Based on this criteria, AVCM value selected was 1.4 ppm. However, in order to use this value corresponding resin RVCM (R_o) is also required. Since this was not recorded at the time AVCM data was taken, an estimated value of R_o had to be used. Based on statistical analysis of historical resin RVCM data Haller and Ahmed[5] have shown that in 1974 BFG PVC resins contained 160 ppm of VCM (95% confidence) and 260 ppm (99% confidence). Table 1.1 summarizes the calculated effective air turn-over rates using these values.

Table 1.1

Calculated Effective Turn-over Rate Using 1974 AVCM Data

Resin RVCM in 1974 (PPM)	Transportation Time (Hours)	Calc. Effective Turn-over Rate/Hr
160	4	20
160	24	14
160	72	6
260	4	30
260	24	21
260	72	9

As can be seen from Table 1.1 the minimum air turn-over is calculated to be 6. Since the lower value maximizes AVCM concentration, it is preferable to use air turn-over rate of 6/Hr. However, to build an even greater safety margin it is desirable to reduce this value even further. Accordingly, the number used in subsequent calculation is 3/Hr. (= 6/2).

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(4) Smith, T. H., BFG Customer Service Report, 1/3/75.

(5) Ahmed, M. J., Haller, H. S., BFG Technical Document, 3/31/83.

MJA:HSH:vmt

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