A Model for the Diffusion of Vinyl Chloride Monomer from PVC Under Various Conditions of Storage

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This example of employee safety activity in the vinyl resin industry is illustrative of the efforts put forth by many to achieve acceptable VCM levels in work areas during all conditions of handling. Since use conditions differ greatly at temperatures above T_g temperatures and are nonstatic, it was deemed necessary to develop a model embracing many variables to allow prediction of atmospheric vinyl chloride monomer levels for any combination of the variables.

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 (T_g). 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 T_g, 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/h
3. Loading (PVC volume/storage volume)—11-34 percent
4. Resin RVCM—0.01-123 ppm
5. Storage time—1-170 h

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: temperature, ventilation rate, and mass/volume ratio. The basic physical model that was chosen to meet these requirements was one based on sealed metal storage bins (55-gal drums) housed in an environmental chamber where the temperature could be varied and controlled. A schematic of the entire experiment is shown in *Fig. 1*. The schematic

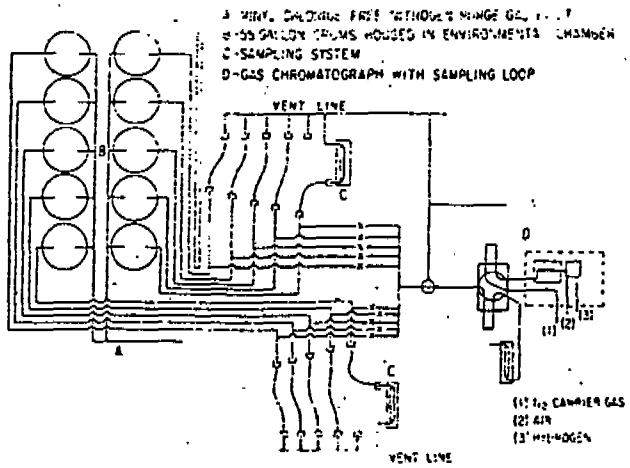

Figure 1.

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 cu ft. 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 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, 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) 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 = min

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, *Eq 1* describes the build-up of VCM in a 55-gal 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/min. The data from this experiment is presented in *Fig.* 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

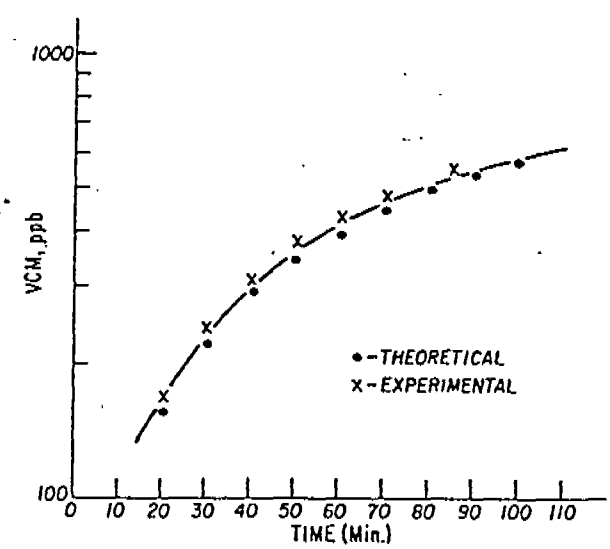

Fig. 2. Theoretical vs experimental build-up of VCM in 55 gal drum after experimental modification.

Method—10 ft × ⅛ in. Porapak Q, mesh 80/100; isothermal at 150°C; nitrogen carrier gas at 30 cc/min; detector—250°C; injection port—150°C

Gas Sampling Valve—10 cc 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:

$$AVCM = Ro^{1.47}L^{0.37}V^{-1.56}[T^{6.0}e^{-(24.1 + .00031\ T)} + .2e^{-.00001167T}]$$

where:

AVCM = atmospheric concentration of VCM in parts per *billion*

Ro = initial RVCM of the resin in parts per *million*

L = percent loading; (resin volume/warehouse volume) × 100

V = ventilation rate in turnovers per hour

T = temperature in °F

t = time in h

As expected, AVCM decreases as:

- RVCM of the resin decreases.
- Volume of resin being stored decreases.
- Ventilation rate increases.
- 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.)
- 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 *Figs.* 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/h, 30 percent 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/h, 80 percent loading of a warehouse volume with VCM containing material), then the resin RVCM must be no higher than 8.5 *ppm*.

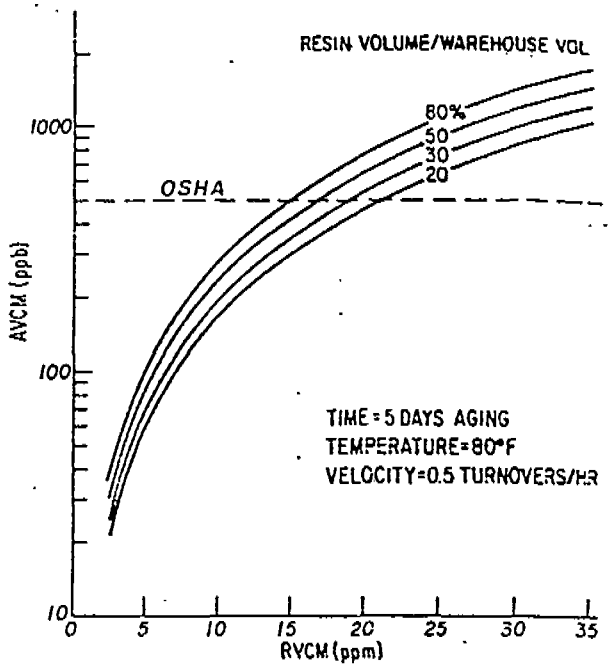

Fig. 3. AVCM vs RVCM and warehouse loading.

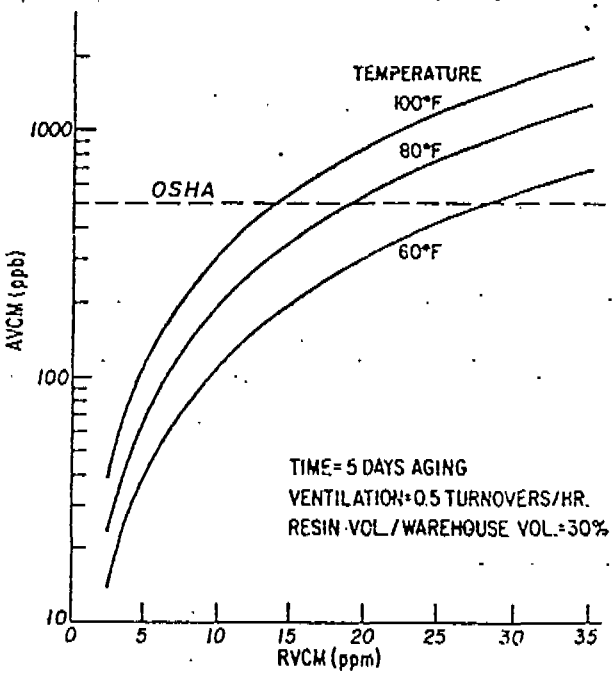

Fig. 4. AVCM vs RVCM and temperature.

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 h), 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

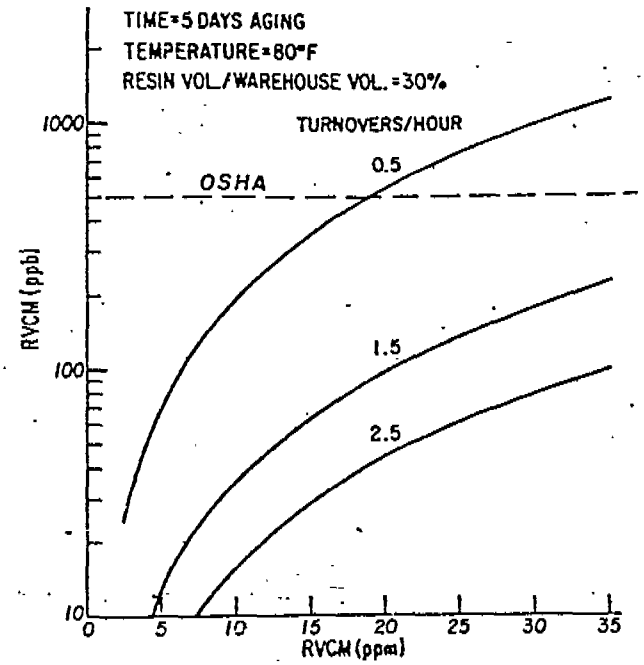

Fig. 5. AVCM vs RVCM and ventilation.

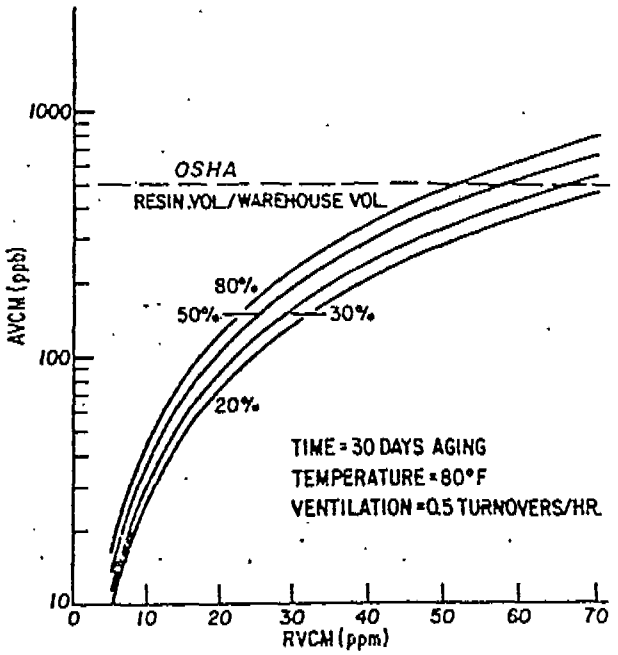

Fig. 7. AVCM vs RVCM and warehouse loading.

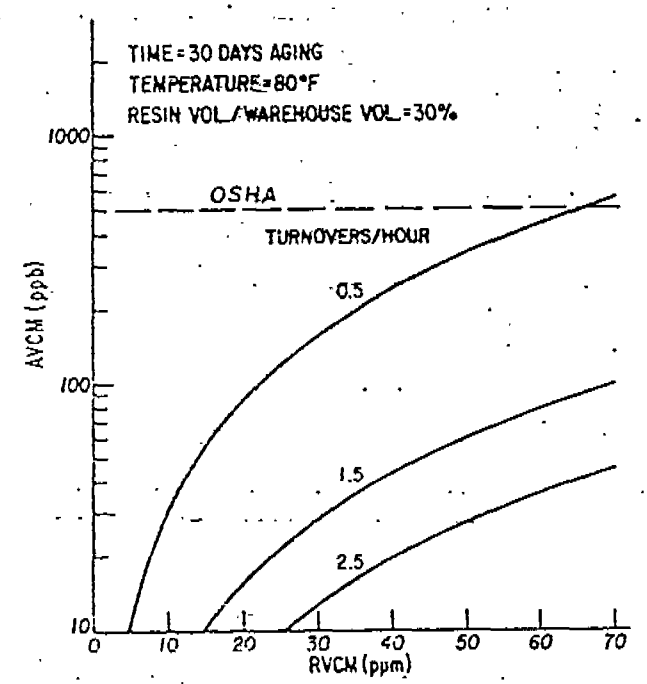

Fig. 6. AVCM vs RVCM and ventilation.

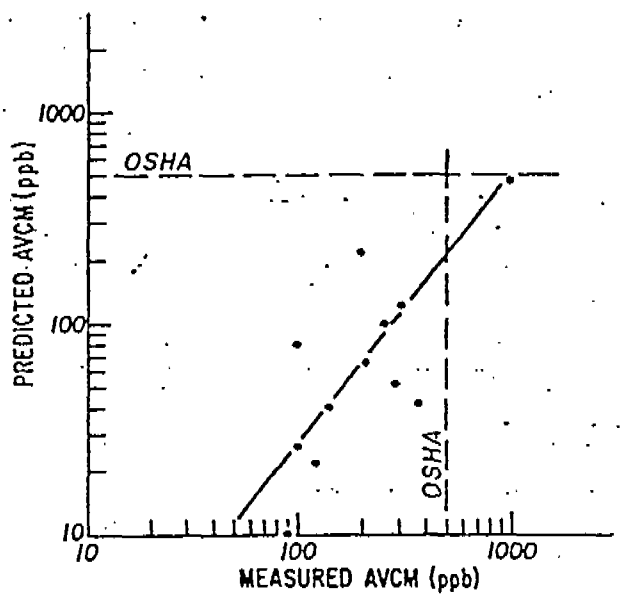

Fig. 8. Prediction of AVCM in warehouse samples.

slightly) whereas the model was based on material being stored in bulk form.

The accuracy of the model is ±100 percent 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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