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November 12, 1982

Stephen Higgins
Acting Director
Bureau of Alcohol, Tobacco
and Firearms
Department of the Treasury
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20226

Re: Use of Polyvinyl Chloride (PVC) for Manufacturing Plastic Liquor Bottles

Dear Mr. Higgins:

On November 3, 1982, the Department of Treasury released an Environmental Assessment of polyethylene terephthalate (PET) for use in liquor bottles. Page 13 of the Assessment contains a response to Comments that we filed on behalf of our client, The Society of the Plastics Industry, Inc., that polyvinyl chloride (PVC) also be approved for liquor bottle use. The reply states that ATF does not intend to address the use of PVC for manufacturing liquor bottles until there is clear evidence that FDA sanctions the use of PVC for such an application. We are writing at this time to request that you address a new inquiry to the Commissioner of Food and Drugs regarding the status of PVC for packaging distilled spirits.

FDA last commented to ATF regarding this issue in a letter dated January 13, 1981, from Richard J. Ronk, Deputy Director, Bureau of Foods. In that letter FDA indicated that it was reassessing its policies regarding indirect additives largely because of the recent court decision involving acrylonitrile bottles (Monsanto v. Kennedy, 613 F.2d 947 (D.C. Cir.

1979)). On April 2, 1982, FDA announced a significant new policy regarding "constituents" in packaging materials. 47 Fed. Reg. 14464. The notice specifically refers to residual vinyl chloride monomer as the type of "constituent" that would be covered by the policy. The Notice also stated that FDA would implement the policy on a case-by-case basis as administrative needs required.

On August 31, 1982 Gerard L. McCowin, Director, Division of Food and Color Additives, Bureau of Foods, wrote to me stating, "we wish to develop proposals, utilizing the constituents policy, to initiate final action on the food-contact use of ...vinyl chloride polymers." In this connection, Mr. McCowin asked for information on residual vinyl chloride levels and markets for PVC to enable FDA to make calculations from an actual data base rather than by using estimates.

We have now provided FDA with information (a) showing the industry can provide PVC bottles suitable for packaging distilled spirits with a residual vinyl chloride level that does not exceed 10 parts per billion and (b) demonstrating that migration of vinyl chloride to the contents of such bottles will not exceed the upper limit established by the application of the constituents policy. Thus, in our opinion, FDA should now be in a very sound position to make a clear statement that the use of PVC bottles with an appropriately low residual vinyl chloride level is suitable for packaging distilled spirits.

As you may be aware, ATF already has a substantial amount of data in its files regarding the suitability of PVC as a liquor container. A petition requesting that ATF approve polyvinyl chloride (PVC) for liquor bottle use was filed by SPI on January 22, 1980. On June 5, 1981, you requested the submission of new sample bottles for storability testing. The requested samples were hand-delivered to Dr. Charles Midkiff at ATF National Laboratory on August 24, 1981. In light of this background, we would hope that you will have everything necessary to make a suitability determination regarding PVC for use as a liquor bottle once FDA affirms the satisfactory status of this plastic from a health standpoint.

We would greatly appreciate your prompt attention to this matter.

Very truly yours,

Jerome H. Heckman

cc: Dr. Arthur Hull Hayes, Commissioner of Food and Drugs
Dr. Sanford Miller, Director, Bureau of Foods
Mr. Richard Ronk, Deputy Director, Bureau of Foods

INDUSTRY CIRCULAR

DEPARTMENT OF THE TREASURY
Bureau of Alcohol, Tobacco and Firearms
Washington, D.C. 20226

Number: 82- Date:

Polyethylene Terephthalate Liquor Bottles

Proprietors of Distilled Spirits Plants, Importers and Others Concerned:

Purpose: The purpose of this circular is to inform you of a forthcoming ATF Ruling concerning the approval of polyethylene terephthalate containers for bottling distilled spirits. The ATF Ruling will read as follows:

The Bureau of Alcohol, Tobacco and Firearms has been requested to approve the use of polyethylene terephthalate (PET) as a suitable material for the manufacture of liquor bottles.

Section 5301(a) of Title 26, United States Code, provides that the Secretary may regulate the kind of containers designed or intended for use in the sale of distilled spirits. Sections 19.11, 194.11, 250.11 and 251.11 of Title 27, Code of Federal Regulations, provide for liquor bottles to be made of glass or earthenware or of other suitable material approved by the Food and Drug Administration, which has been designed or is intended for use as a container for distilled spirits for sale for beverage purposes and which has been determined by the Director to adequately protect the revenue.

The Bureau is aware of the need to recognize advancing technology which provides materials adaptable or developed for packaging distilled spirits. At the same time, the Bureau is aware of its responsibilities for protecting the Federal excise tax revenues, as prescribed by the Internal Revenue Code (Title 26, U.S.C., Chapter 51); for insuring an orderly marketplace, in accordance with the requirements of the Federal Alcohol Administration Act (Title 27, U.S.C., section 205(e)); and for protecting the environment, pursuant to the National Environmental Policy Act (Title 42, U.S.C., section 4332).

The Bureau recognizes that, in some minor instances, a proof gain of up to two degrees of proof per year (and a corresponding water volume loss) may occur. However, this effect can be minimized by avoiding high storage temperatures, by insuring that the wall thickness of PET containers is uniform, and by insuring market turnover. In any event, ATF has concluded that this characteristic of PET packaging poses no jeopardy to the revenue because the taxable commodity, the alcohol, does not travel through the package wall. The quantity of alcohol does not change between the time of bottling and the point of tax determination. Therefore, it has been determined that the use of PET for liquor bottles provides adequate protection to the excise tax revenue and is a suitable material for this use.

The consumer obtains the same amount of alcohol contained in the product at the time of bottling, since only water is lost. Since the same amount of alcohol is contained in the product with only a very minor, if any, increase in proof, the label on the product provides adequate information to the consumer regarding alcohol content.

In accordance with the requirements imposed by the National Environmental Policy Act, the Bureau prepared an assessment of the projected effect on the environment of PET liquor bottles. The conclusion reached on the pertinent issues was that neither container use nor disposal would have a significant environmental impact.

Held, polyethylene terephthalate (PET) liquor bottles conforming to the following specifications may be used as containers for distilled spirits:

(1) The bottles must be rigid or semi-rigid with molded shape or design which cannot be altered by pressure without damage to the bottle, and the wall thickness of the bottle must be as uniform as possible;

(2) The bottle must be manufactured in an approved standard of fill; and

(3) The material used to construct the PET bottle must meet the Food and Drug Administration's health and safety specifications for the packaging of alcoholic beverages for consumption as promulgated in the Code of Federal Regulations.

Inquiries: Inquiries concerning this circular should refer to its number and be addressed to the Assistant Director, Regulatory Enforcement, Bureau of Alcohol, Tobacco and Firearms, 1200 Pennsylvania Avenue, NW., Washington, DC 20226. Attention: Commodity Classification Branch.

Stephen C. Higgins
Acting Director

PART II-A

27 CFR 19.11: MEANING OF TERMS (Liquor Bottle)
(Also 194.11, 250.11, 251.11)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits when the containers meet the requirements of the Federal Alcohol Administration Act and the materials used to construct the bottles meet Food and Drug Administration specifications for the packaging of distilled spirits.

ATF Rul. 82-12

The Bureau of Alcohol, Tobacco and Firearms has been requested to approve the use of polyethylene terephthalate (PET) as a suitable material for the manufacture of liquor bottles.

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(2) The bottle must be manufactured in an approved standard of fill; and

(3) The material used to construct the PET bottle must meet the Food and Drug Administration's health and safety specifications for the packaging of alcoholic beverages for consumption as promulgated in the Code of Federal Regulations.

PART II-A

27 CFR 194.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .

PART II-A

27 CFR 250.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .

PART II-A

27 CFR 251.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .

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November 12, 1982

Dr. Sanford A. Miller
Director
Bureau of Foods
Food and Drug Administration
200 C. Street, S.W.
Washington, D.C. 20204

Re: Polyvinyl Chloride for Use as a Container for Alcoholic Beverages

Dear Dr. Miller:

In a letter to me dated August 31, 1982, Mr. Gerad McCowin, Director of the Division of Food and Color Additives, requested information available to The Society of the Plastics Industry, Inc. (SPI) bearing on residual monomer levels in polyvinyl chloride (PVC) plastics, and potential markets for such products. We understand that this information would be useful to the Agency as it moves to implement the constituents policy with respect to PVC food-contact applications. We have not yet been able to collect any meaningful information regarding present and potential uses of PVC that would provide the Agency with sound data for calculating a consumption factor, i.e., for determining the percentage of the diet that might be packaged in PVC plastics. However, we have been informed that with respect to PVC bottles, the industry can provide products with residual monomer levels not exceeding 10 parts per billion (ppb) by weight.

We are writing to you at this time solely with respect to PVC bottles because the only application for which PVC is not currently permitted involves bottles, liquor bottles to be

specific. We have received and are enclosing copies of letters from the following resin suppliers and fabricators of bottles stating that they can produce such materials: Aim Packaging, Inc., Brockway Plastics, Continental Group, Ethyl Corporation, Occidental Chemical Corporation; Owens-Illinois, Inc., and The Proctor and Gamble Company.

It should be emphasized again that the data we are providing here relates only to PVC bottles. Film products fabricated from PVC or copolymers thereof utilize different technological processes so that the standards and criteria applicable to bottles may not be relevant. Furthermore, we think it clear and correct, as stated in the Food and Drug Administration's (FDA) September 3, 1975, Notice of Proposed Rule Making, that PVC products such as films and can enamels are of no regulatory concern; nor are we aware of any data reported since 1975 to change this conclusion.

In a letter dated January 23, 1981, addressed to Mr. William T. Drake, at the Bureau of Alcohol, Tobacco, and Firearms (ATF), Mr. Richard J. Ronk responded to an ATF inquiry regarding the regulatory status of PVC for use as a container for alcoholic beverages. Mr. Ronk stated in relevant part that the Agency was "not likely to publish any final regulation or a new proposal regarding polyvinyl chloride" until the Agency had resolved what its policy should be in dealing with trace quantities of carcinogenic residues in food-contact materials. Mr. Ronk also wrote that the Agency was evaluating data which indicated that if current good manufacturing practices are followed, PVC packaging material "with encouragingly low residual VCM levels" can be produced.

Since FDA has now developed its "constituents policy" (47 Fed. Reg. 14,464 (Apr. 2, 1982)) which it is implementing on a case-by-case basis, and because PVC bottles can now be produced with residual vinyl chloride levels sufficiently low as to comply with the safety requirements embodied in the new constituents policy, we are hereby requesting that FDA immediately re-evaluate the status of PVC for use as packaging

material for alcoholic beverages. */ As discussed more fully below and in the technical appendices to this letter, vinyl chloride migration from PVC bottles containing a 10 ppb maximum residual vinyl chloride (RVCM) concentration cannot exceed the "very safe dose" level calculated by FDA's risk assessment procedures. Consequently, the use of these bottle will pose no health or safety problem with respect to the possible migration of vinyl chloride. It is our hope you will concur in our opinion that there is no longer any basis for concern as to the safety of using PVC bottles for packaging distilled spirits provided the residual monomer level does not exceed a concentration of 10 ppb by weight in the bottle walls.

It is our understanding that FDA has determined, utilizing its conservative risk assessment procedures, that a dietary intake of 0.22 µg of vinyl chloride per day will be "very safe." Inasmuch as the Agency considers the average diet to consist of 3 kg of food (both solid and liquid combined), the safe concentration of vinyl chloride in food is 0.073 ppb by weight:

$$\frac{0.22}{3} = 0.073 \text{ µg/kg}$$

In other words, if the entire daily diet, both solid and liquid, were packaged in PVC, a migration level of 0.073 ppb would be permitted and the dietary intake could not exceed 0.22 µg/day.

In dealing with indirect additives, FDA utilizes a "consumption factor" to provide an estimate of how much of an indirect additive might be present in the total diet based upon measured migration data. Thus, if a packaging material is used to package one-third of the diet, migration could be permitted into the packaged portion of the diet at three times the safe level in the total diet. For example, if the safe level of a substance were found from appropriate toxicological studies to be 1 part per million (ppm), migration into the food that actually contacts the packaging material could be as high as 3 ppm. Stated

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*/ In this connection, please take due note of today's release of a new Bureau of Alcohol, Tobacco, and Firearms ruling on other plastic liquor bottles. ATF Rule 82-12 (copy attached).

somewhat differently, if migration into food contacted by a particular packaging material is as high at 3 ppm, the total diet will contain only 1 ppm because only one-third of the diet contacted the packaging material.

Depending upon the actual consumption factor, a number not now known with any precision for vinyl chloride-containing packaging materials, the permitted level of vinyl chloride migration will be higher than 0.073 ppb. If the consumption factor were 0.1 (i.e., if 10% of the diet were packaged in PVC-based materials) migration from such materials could be permitted at a level of 0.73 ppb; if the consumption factor were 20%, migration could be permitted at a level of 0.365 ppb, and so forth. Although we recognize that it is not feasible to set a generally applicable level of vinyl chloride migration until a reliable consumption factor is determined, it is, nevertheless, altogether proper to clear the use of PVC at this time for any application where potential migration does not exceed the safe level (0.073 ppb). If FDA affirms the safety of PVC as a container for distilled spirits at this time, the otherwise permitted level of migration from other vinyl chloride-based products based on consumption factor considerations would not be adversely affected as is shown in detail in Appendix A to this letter.

In other words, the Agency can deal with the liquor bottle question without considering possible inequities that might affect other uses of vinyl chloride-based products. An Agency decision at this time to permit the use of PVC as a container for alcoholic beverages would not adversely affect any future regulatory migration levels that may be applicable to other PVC uses, provided the level of migration from the presently considered uses does not exceed 0.073 ppb.

Appendix B to this letter provides a technical explanation demonstrating that containers with residual monomer levels not exceeding 10 ppb will not leach vinyl chloride into the contents at a level in excess of 0.073 ppb. Stated summarily, the quantity of vinyl chloride available to migrate is so low, and the rate of migration of vinyl chloride from PVC containers made with an RVCM content of 10 ppb or less is so slow that the concentration of vinyl chloride in the contents even after an exaggerated shelf-life exposure at moderately elevated temperatures will not exceed the safe 0.073 ppb level.

One final point needs attention. Mr. Ronk's letter noted that, at the time of writing, FDA could not document the existence of a prior-sanction permitting the use of PVC for packaging alcoholic beverages, despite the statement made by Mr. William F. Randolph, now Deputy Associate Commissioner for Compliance at FDA, at an International Conference in Managua, Nicaragua, in May, 1969, to the effect that FDA recognizes a prior-sanction for PVC for all food-contact uses. Even if this confusion has not yet been clarified, there appears to be no reason why FDA need take any administrative action against the specific use of otherwise satisfactory PVC containers for packaging distilled spirits until it can deal appropriately with the status of PVC containers for all food-contact applications. It appears to be both unreasonable and discriminatory to proscribe the use of such containers for one particular category of foods (i.e., alcoholic beverages) when there is no public health or safety problem involved. Rather, we suggest, that if any further action other than a withdrawal of its 1975 rule making proposal is deemed necessary, the prior-sanctioned status of PVC for all food-contact uses be dealt with in some other regulatory action in due course.

Summarizing, the industry can provide alcoholic beverage containers with a residual monomer content not exceeding 10 ppb and vinyl chloride will not migrate from these containers to the packaged food at a level higher than 0.073 ppb. Consequently, favorable FDA action clearing the use of such products is consistent with the constituents policy. Furthermore, action to clear this limited application will not adversely affect the interests of any other portion of the industry since the permitted vinyl chloride migration levels for other applications will be, if anything, higher as a result of this action than they would be if all packaging materials were subject to the same migration limitation based on an overall consumption factor.

We trust the information we are providing here will permit you to conclude that the use of the PVC alcoholic beverage containers will pose no safety concerns provided the residual monomer level in such containers does not exceed 10 ppb and thus enable you to advise the Bureau of Alcohol, Tobacco, and

Firearms to this effect without further delay. Should you have any questions, however, please let us know so that we can provide answers as promptly as possible.

Very truly yours,

Jerome H. Heckman

Enclosures

cc: Mr. Stephen Higgins
Dr. Arthur Hull Hayes
Mr. Richard J. Ronk

APPENDIX A

ALLOCATION OF PERMITTED MIGRATION LEVELS UNDER THE "CONSTITUENTS POLICY"

Any vinyl chloride-based packaging material will pose no monomer migration problem if the migration level does not exceed the "very safe" concentration of 0.073 parts per billion (ppb). */ Although such uses, per se, will pose no public health or safety concern, it may not be immediately apparent that the early allocation to bottles of a portion of the very safe quantity of vinyl chloride that may be permitted in the diet will not adversely effect the interests of those packaging materials which are not being dealt with at the same time. This, however, is the case.

To demonstrate this mathematically, in general terms:

Let the consumption factor, i.e., the fraction of the total diet contacted as a result of all uses of vinyl chloride-containing packaging materials, be "c."

Let "b" be the fractional portion of the diet contacted by bottles only ("b" must be less than "c").

Let 0.22 μg be the very safe level of vinyl chloride monomer (VCM) in the total diet and

Let 3 kg be the weight of the total diet. (Actual numbers are used here for convenience, but there is no loss in generality. It would be perfectly in order to substitute symbols for these specific values.)

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*/ We understand that the actual FDA document that sets forth the derivation of this figure is not available for public distribution at this time. Nevertheless, we have been informed that the very safe dose has been determined to be 0.22 μg per day. If the entire diet, both liquid and solid, were packaged in PVC, a migration level of 0.073 ppb would assure that the 0.22 μg level would not be exceeded.

Then:

(1) The safe concentration in the total diet is:

$$\frac{0.22\ \mu g}{3\ kg} = 0.073\ ppb$$

(2) The weight of diet contacting vinyl chloride-based products is 3c.

(3) The safe level of migration, taking the consumption factor into consideration is:

$$\frac{0.22}{3c} = \frac{0.073\ ppb}{c}$$

(4) If bottles with migration at or below 0.073 ppb are utilized, the weight of diet packaged in bottles is (3 b) kg, and the weight of vinyl chloride contributed to the diet by this use is:

$$(0.073\ ppb)(3b)\ kg = (0.073)(3b)\ \mu g = 0.22b\ \mu g$$

(5) The remaining weight of vinyl chloride that may be contributed by all other uses is:

$$(0.22 - 0.22b)\ \mu g = (0.22)(1-b)\ \mu g$$

(6) The weight of diet that is packaged in all other vinyl chloride-containing materials is:

$$(3c-3b)\ kg = 3(c-b)\ kg$$

Note: $(c-b)$ is less than $(1-b)$

(7) The permitted concentration of vinyl chloride migrating from all other uses is:

$$\frac{0.22\ (1-b)}{3(c-b)} = \frac{0.073\ (1-b)}{(c-b)} > 0.073\ ppb$$

Thus, regardless of the actual numerical value of the very safe dose, restricting a portion of the total consumption factor to migration at the very safe concentration in the total diet must result in an increase in the permitted level of migration for all other uses.

APPENDIX B

VINYL CHLORIDE LEVELS IN CONTENTS OF BOTTLES

The following considerations demonstrate that the vinyl chloride content of substances packaged in polyvinyl chloride (PVC) bottles cannot exceed 0.073 parts per billion (ppb) provided the bottle walls contain no more than 10 ppb of residual vinyl chloride (RVCM).

Typical wall thicknesses of bottles do not exceed 20 mils (0.020 inches). Consequently, the volume of PVC in 1 square inch of wall surface is 0.020 cubic inches or 0.33 cc. Inasmuch as the density of PVC compounds is somewhat less than 1.4 grams per cc, the weight of PVC in the wall section is somewhat less than 0.46 g (0.33 x 1.4). If the RVCM content is no higher than 10 ppb, the maximum weight of vinyl chloride in that section will be 4.6×10^{-9} g. The Food and Drug Administration (FDA) considers a weight of 10 g of contents to be in contact with each square inch of package surface. Consequently, if all the vinyl chloride were to migrate into the contents, the resulting concentration would be 0.46 nanograms per gram of food or 0.46 ppb.

However, it has been early demonstrated that migration of residual monomer from PVC packaging materials initially proceeds in two directions, part entering the contents of a package, the remainder diffusing to the exterior. Thus, the maximum concentration in the contents could not exceed 0.23 ppb if all of the available vinyl chloride were to migrate into the contents. This cannot occur because, at equilibrium, there will be a partitioning between the concentration of vinyl chloride in the contents and the vinyl chloride in the solid walls of the container so that the 0.23 figure calculated above would be an unapproachable limit. Furthermore, over a very long time period, the direction of migration would reverse because the exterior air would represent an infinite sink; after an initial buildup of vinyl chloride concentration in the contents, the vinyl chloride would then diffuse from the contents through the wall into the exterior air.

Nor is this all. Diffusion experiments conducted by Behrens and co-workers utilizing PVC with relatively high residual monomer contents have demonstrated that over a period of approximately a year at 30°C less than 1/3 of the available vinyl chloride will diffuse. Thus, less than 1/3 of the limiting 0.23 ppb will migrate in one year at 30°C. The time and temperature is quite excessive as simulants for reasonably expected

shelf-life and storage conditions. Thus, even under these conditions, less than 0.073 ppb can be anticipated. Copies of relevant publications are attached.

Studies conducted by Ethyl Corporation and reported to FDA have demonstrated that the diffusion constant for vinyl chloride migration is, in fact, not constant when the residual monomer concentration drops somewhat below 50 ppb. Thus, the calculations based on Behrens' work are high and may be as much as an order of magnitude too high when applied to the containers of interest here which bear not more than 10 ppb of residual monomer. Copies of the Ethyl reports are attached for ready reference.

Although not amenable to calculation, it is known that vinyl chloride tends to accumulate in the headspace over dilute vinyl chloride solutions. Thus, the vinyl chloride content of the solutions as calculated above will be lower by a significant although not readily quantifiable amount because much of the vinyl chloride will be in the headspace and will dissipate when the container is opened. Furthermore, each time the container is used, this same phenomenon will be repeated so that the initial monomer content will decay rapidly.

In summary, bottles made with RVCM levels not exceeding 10 ppb will not yield VCM to the contents at levels exceeding 0.073 ppb.

western union Telegram

WBA273(1729)(4-24259463315)PD 11/11/82 1732

ICS IPMBNGE OSP

4195352144 NL TDBN PORT CLINTON OH 109 11-11 2532P EST

PMS JEROME H. HECKMAN, KELLER AND HECKMAN RPT DLY MGM, DLR

1150 17TH ST NORTHWEST SUITE 1222

WASHINGTON DC 20036

DEAR MR HECKMAN

RESPONSIVE TO THE INQUIRY MADE BY THE (SPI) SOCIETY OF THE PLASTICS INDUSTRY LETTER OF OCTOBER 25 1982, THIS IS TO ADVISE YOU THAT WE ARE CONFIDENT THAT WE CAN MANUFACTURE PVC BOTTLES WHICH WILL CONTAIN NOT MORE THAN 10 PARTS PER BILLION OF RESIDUAL PVC MONOMER.

THE ABILITY TO MAINTAIN THIS MONOMER LEVEL IS BASED ON ASSURANCES WHICH AIM PACKAGING HAS RECEIVED FROM OUR PVC FOOD GRADE MATERIAL SUPPLIERS WHO HAVE INDICATED THEIR CAPABILITY OF PROVIDING COMPOUND

W.U. 1201-SF (R5-69)

western union Telegram

THAT DOES NOT EXCEED THE 17 PARTS PER BILLION MONOMER LEVEL.

WE DO NOTHING IN THE PROCESSING OF THE MATERIAL THAT WOULD INCREASE THE RESIDUAL MONOMER LEVEL. SINCERELY

MR ARTHUR P MCCAMEY EXECUTIVE VP IN CHARGE OF OPERATIONS AIM PACKAGING INC PORT CLINTON OH

PO BOX 225

PORT CLINTON OH 43452

W.U. 1201-SF (R5-69)

GENC017215

Brockway

plastics

October 27, 1982

Jerome H. Heckman
Keller & Heckman
1150 17th Street, N.W.
Suite 1000
Washington, D.C. 20036

Jerry:

Re: G. R. Munger's letter dated 10/25/82

This is to confirm that given the current status of resin manufacturing, Brockway Plastics is capable of manufacturing rigid and semi-rigid PVC food containers with a RVCM of no more than 10 parts per billion.

From conversations I have had with Dr. Dixler, this should fall within the maximum allowable standards being considered by FDA and further market data as to products, etc. is not necessary.

Should this not be the case, please contact me.

Good luck...

Robert W. Schroeder
Vice President, Sales/Marketing

RWS:rc

BROCKWAY PLASTICS DIVISION
CELLU DRIVE, ROUTE 101A NASHUA, NEW HAMPSHIRE 03063
TELEPHONE 603/ 889-2000

VIA TELECOPIER (202) 296-7682

ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

November 11, 1982

PLEASE ADDRESS REPLY
TO: P. O. BOX 341
BATON ROUGE, LA. 70821

Mr. Jerome H. Heckman
Keller and Heckman
1150 17th Street, N.W.
Suite 1000
Washington, D.C. 20036

Dear Mr. Heckman:

Please be advised that Ethyl Corporation can provide commercially rigid PVC compound with a residual vinyl chloride monomer content of less than 10 parts per billion. Finished products (e.g., bottles) produced from this compound by processors will also contain less than 10 parts per billion vinyl chloride.

Very truly yours,

A. J. Haefner
Director, Plastics Research and Applications

AJH:dsp

cc: Mr. R. M. Marston

Packaging
Forest Products
Insurance
Energy

George K Landon
Vice President

October 27, 1982

Jerome H. Heckman
Keller and Heckman
1150 17th Street, N.W.
Suite 1000
Washington, D.C. 20036

Dear Jerry:

In a letter dated October 25 Monk Munger asked us to advise you whether we can produce bottles of food grade PVC which would have less than 10 parts per billion of vinyl chloride monomer.

We are advised by our resin suppliers that they will deliver resin with a residual monomer level of 5 parts per billion or less. We are reasonably certain that there is no way we can increase the residual monomer level in our bottle making process. It would seem then that we would be safe in stating that we can produce bottles which consistently have residual vinyl chloride monomer present at 10 parts per billion or less.

Very truly yours,

GKL:hoc

cc: G. R. Munger

The Continental Group, Inc.
One Harbor Plaza
Stamford CT 06904

Occidental Chemical Corporation

November 8, 1982

Jerome H. Heckman, Esq.
Keller and Heckman
1150 17th Street, N.W.
Suite 1000
Washington, DC 20036

Dear Mr. Heckman:

Please be advised that Occidental Chemical Corporation can provide rigid PVC film and sheet with a maximum residual vinyl chloride monomer of 10 parts per billion.

We can also provide PVC compounds to manufacturers of film and sheet with a certified RVCM of 10ppb. max. which would in turn enable them to provide film and sheet with the same amount of RVCM.

We trust this is the information you want, and if we can be of further service to you, please let me know.

Sincerely,

Richard L. LaRue

RLR:slc

Richard L. LaRue
Market Development Manager

Occidental Chemical Corporation

November 8, 1982

Jerome H. Heckman, Esq.
Keller and Heckman
1150 17th Street, N.W.
Suite 1000
Washington, DC 20036

Dear Mr. Heckman:

This will serve to confirm our recent conversation that we can supply rigid food-grade PVC compounds for the manufacture of PVC bottles with a residual vinyl chloride monomer content of 10 parts per billion maximum. Therefore, bottles produced from this material would also have a 10ppb. max. RVCM.

The markets which we envision for food-grade PVC bottles would be: vegetable oils, liquor and peanut butter.

It is difficult to predict with any accuracy what percent of a particular food market will convert from glass to plastic or, for that matter, to which plastic, but it is our understanding that assurance of a 10ppb. max. RVCM in the bottle could allow a total diet to be packaged in rigid PVC with an adequate safety margin.

We do know that the liquor packaging industry does want a choice of glass and several plastics, including rigid PVC, and that early experience with food-grade PVC showed economical and safety benefits to the consumer and also overall energy savings for all of the processes involved in the production, shipment, handling and disposal of the containers.

The choice of which plastic the distiller would use is dependent on many factors, but it is clear that they should have a choice. With the imminent approval of PET, for example, and an unpredictable delay in the approval of PVC, we fear that many plastic bottle manufacturers and distillers will be forced to waste a considerable amount of money for investment in bottle design, tooling, production molds, etc., only to have to re-invest the same money, perhaps only months later, to take advantage of PVC's benefits once that material is "approved".

Consequently, if the FDA is going to eventually move favorably on the PVC issue, we think it should be done now to afford the distillers with enough intelligent choices to minimize economic waste.

Please let me know if I can be of further service. I enjoyed talking with you, as always.

Sincerely,

Richard L. LaRue

RLR:slc

Richard L. LaRue
Market Development Manager

TELECOPY [Keller & Heckman off-line telecopy #: (202) 296-7682]

11-11-82

TO: Mr. Jerome H. Heckman
Keller & Heckman
1150 17th St., N.W.
Suite 1000
Washington, D.C. 20036

Dear Jerry:

On October 25 the Society of the Plastics Industry office directed a letter to us to inquire as to whether we can produce bottles made of polyvinylchloride for food grade applications, and whether such bottles could be certified to contain less than ten (10) parts per billion residual vinyl chloride monomer.

We have been in touch with our compound suppliers in this connection and have been assured that they can provide us with compound that contains less than ten parts per billion RVCM. This being the case, it is very clear that we would have no difficulty in producing bottles which contain less than ten parts per billion vinyl chloride monomer.

Sincerely,

W. J. GRAHAM,
Group Vice President, Plastics & Closures
Owens-Illinois, Inc.
One Seagate
Toledo, Ohio 43666

THE PROCTER & GAMBLE COMPANY

IVORYDALE TECHNICAL CENTER

CINCINNATI OHIO 45217

November 4, 1982

Mr. Jerome H. Heckman
Keller and Heckman
1150 17th Street, N.W.
Suite 1000
Washington, D.C. 20036

Dear Jerry:

Confirming our telephone conversation of yesterday, our experience at Procter & Gamble supports the view that SPI advise FDA that manufacturers of rigid and semi-rigid PVC food packaging can meet a RVCM limitation of 10 ppb in their finished articles.

Our recent experience in checking RVCM in five different lots of PVC bottles from three different bottle manufacturers is offered as evidence for our support. Analyses showed results in the range of 3-7 ppb, with an average of 4.2 ppb RVCM. In all cases, Hooker's PVC 2160L was the basic resin used.

If comments from other SPI members do not verify our findings, or if it is decided that the PVC industry will not commit to a 10 ppb RVCM limit for food packaging, I would like to discuss this situation with you promptly.

I look forward to the next meeting of our Food, Drug & Cosmetic Packaging Materials Committee on December 8, when we will undoubtedly be discussing this subject further.

Sincerely,

R. E. Belliveau

jmh

INDUSTRY CIRCULAR

DEPARTMENT OF THE TREASURY
Bureau of Alcohol, Tobacco and Firearms
Washington, D.C. 20226
Number: 82- Date:

Polyethylene Terephthalate Liquor Bottles

Proprietors of Distilled Spirits Plants, Importers and Others Concerned:

Purpose: The purpose of this circular is to inform you of a forthcoming ATF Ruling concerning the approval of polyethylene terephthalate containers for bottling distilled spirits. The ATF Ruling will read as follows:

The Bureau of Alcohol, Tobacco and Firearms has been requested to approve the use of polyethylene terephthalate (PET) as a suitable material for the manufacture of liquor bottles.

Section 5301(a) of Title 26, United States Code, provides that the Secretary may regulate the kind of containers designed or intended for use in the sale of distilled spirits. Sections 19.11, 194.11, 250.11 and 251.11 of Title 27, Code of Federal Regulations, provide for liquor bottles to be made of glass or earthenware or of other suitable material approved by the Food and Drug Administration, which has been designed or is intended for use as a container for distilled spirits for sale for beverage purposes and which has been determined by the Director to adequately protect the revenue.

The Bureau is aware of the need to recognize advancing technology which provides materials adaptable or developed for packaging distilled spirits. At the same time, the Bureau is aware of its responsibilities for protecting the Federal excise tax revenues, as prescribed by the Internal Revenue Code (Title 26, U.S.C., Chapter 51); for insuring an orderly marketplace, in accordance with the requirements of the Federal Alcohol Administration Act (Title 27, U.S.C., section 205(e)); and for protecting the environment, pursuant to the National Environmental Policy Act (Title 42, U.S.C., section 4332).

The Bureau recognizes that, in some minor instances, a proof gain of up to two degrees of proof per year (and a corresponding water volume loss) may occur. However, this effect can be minimized by avoiding high storage temperatures, by insuring that the wall thickness of PET containers is uniform, and by insuring market turnover. In any event, ATF has concluded that this characteristic of PET packaging poses no jeopardy to the revenue because the taxable commodity, the alcohol, does not travel through the package wall. The quantity of alcohol does not change between the time of bottling and the point of tax determination. Therefore, it has been determined that the use of PET for liquor bottles provides adequate protection to the excise tax revenue and is a suitable material for this use.

The consumer obtains the same amount of alcohol contained in the product at the time of bottling, since only water is lost. Since the same amount of alcohol is contained in the product with only a very minor, if any, increase in proof, the label on the product provides adequate information to the consumer regarding alcohol content.

In accordance with the requirements imposed by the National Environmental Policy Act, the Bureau prepared an assessment of the projected effect on the environment of PET liquor bottles. The conclusion reached on the pertinent issues was that neither container use nor disposal would have a significant environmental impact.

Held, polyethylene terephthalate (PET) liquor bottles conforming to the following specifications may be used as containers for distilled spirits:

(1) The bottles must be rigid or semi-rigid with molded shape or design which cannot be altered by pressure without damage to the bottle, and the wall thickness of the bottle must be as uniform as possible;

(2) The bottle must be manufactured in an approved standard of fill; and

(3) The material used to construct the PET bottle must meet the Food and Drug Administration's health and safety specifications for the packaging of alcoholic beverages for consumption as promulgated in the Code of Federal Regulations.

Inquiries: Inquiries concerning this circular should refer to its number and be addressed to the Assistant Director, Regulatory Enforcement, Bureau of Alcohol, Tobacco and Firearms, 1200 Pennsylvania Avenue, NW., Washington, DC 20226. Attention: Commodity Classification Branch.

Stephen E. Higgins
Acting Director

PART II-A

27 CFR 19.11: MEANING OF TERMS (Liquor Bottle)
(Also 194.11, 250.11, 251.11)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits when the containers meet the requirements of the Federal Alcohol Administration Act and the materials used to construct the bottles meet Food and Drug Administration specifications for the packaging of distilled spirits.

ATF Rul. 82-12

The Bureau of Alcohol, Tobacco and Firearms has been requested to approve the use of polyethylene terephthalate (PET) as a suitable material for the manufacture of liquor bottles.

Section 5301(a) of Title 26, United States Code, provides that the Secretary may regulate the kind of containers designed or intended for use in the sale of distilled spirits. Sections 19.11, 194.11, 250.11 and 251.11 of Title 27, Code of Federal Regulations, provide for liquor bottles to be made of glass or earthenware or of other suitable material approved by the Food and Drug Administration, which has been designed or is intended for use as a container for distilled spirits for sale for beverage purposes and which has been determined by the Director to adequately protect the revenue.

The Bureau is aware of the need to recognize advancing technology which provides materials adaptable or developed for packaging distilled spirits. At the same time, the Bureau is aware of its responsibilities for protecting the Federal excise tax revenues, as prescribed by the Internal Revenue Code (Title 26, U.S.C., Chapter 51); for insuring an orderly marketplace, in accordance with the requirements of the Federal Alcohol Administration Act (Title 27, U.S.C., section 205(e)); and for protecting the environment, pursuant to the National Environmental Policy Act (Title 42, U.S.C., section 4332).

The Bureau recognizes that, in some minor instances, a proof gain of up to two degrees of proof per year (and a corresponding water volume loss) may occur. However, this effect can be minimized by avoiding high storage temperatures, by insuring that the wall thickness of PET containers is uniform, and by insuring market turnover. In any event, ATF has concluded that this characteristic of PET packaging poses no jeopardy to the revenue because the taxable commodity, the alcohol, does not travel through the package wall. The quantity of alcohol does not change between the time of bottling and the point of tax determination. Therefore, it has been determined that

the use of PET for liquor bottles provides adequate protection to the excise tax revenue and is a suitable material for this use.

The consumer obtains the same amount of alcohol contained in the product at the time of bottling, since only water is lost. Since the same amount of alcohol is contained in the product with only a very minor, if any, increase in proof, the label on the product provides adequate information to the consumer regarding alcohol content.

In accordance with the requirements imposed by the National Environmental Policy Act, the Bureau prepared an assessment of the projected effect on the environment of PET liquor bottles. The conclusion reached on the pertinent issues was that neither container use nor disposal would have a significant environmental impact.

Held, polyethylene terephthalate (PET) liquor bottles conforming to the following specifications may be used as containers for distilled spirits:

(1) The bottles must be rigid or semi-rigid with molded shape or design which cannot be altered by pressure without damage to the bottle, and the wall thickness of the bottle must be as uniform as possible;

(2) The bottle must be manufactured in an approved standard of fill; and

(3) The material used to construct the PET bottle must meet the Food and Drug Administration's health and safety specifications for the packaging of alcoholic beverages for consumption as promulgated in the Code of Federal Regulations.

PART II-A

27 CFR 194.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .

PART II-A

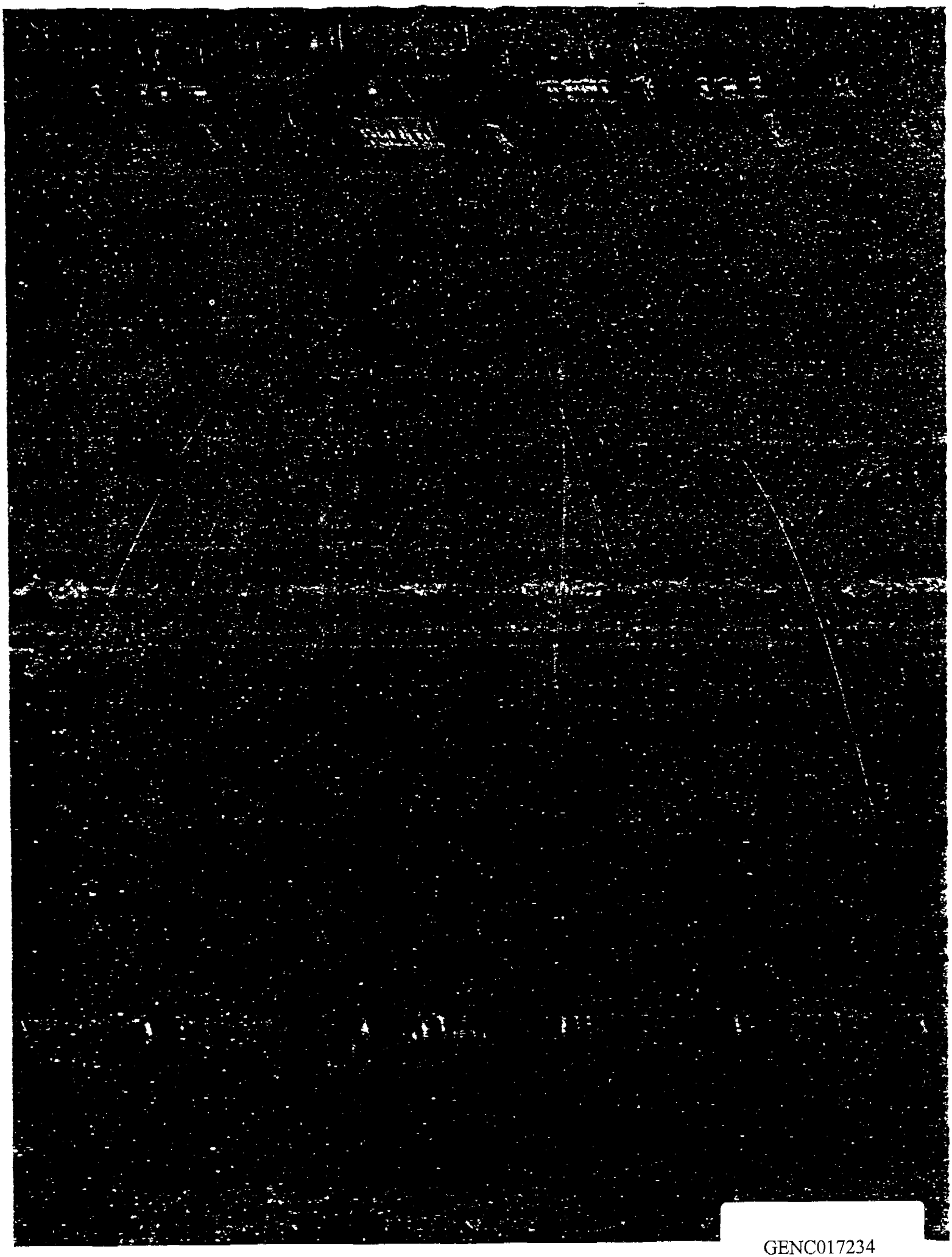
27 CFR 250.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .

PART II-A

27 CFR 251.11: MEANING OF TERMS (Liquor Bottle)

Polyethylene terephthalate (PET) containers are approved for bottling distilled spirits. See ATF Rul. 82-12, page .



GENC017234

THE DIFFUSION OF VINYL CHLORIDE IN POLY(VINYL CHLORIDE)

by

A. R. Berens

Corporate Research, The B. F. Goodrich Co., Brecksville, Ohio 44141

(To be presented at American Chemical Society National Meeting, Atlantic City, September 9-13, 1974, Division of Polymer Chemistry; and to appear in Polymer Preprints, Vol. 15, No. 2, b 203 (1974)

ABSTRACT

The diffusion of vinyl chloride monomer (VCM) in PVC has been studied by electrobalance sorption/desorption techniques on polymers in the as-polymerized powder state over the concentration range 0 - 2000 ppm VCM/PVC and from room temperature to above Tg. The sorption process appears to consist of two stages: 1) Relatively rapid attainment of diffusion equilibrium; 2) Much slower relaxation to swelling-stress equilibrium. First stage sorption/desorption data on uniform-particle emulsion PVC's and porous mass and suspension PVC's fit a uniform-sphere Fickean diffusion model. Diffusion coefficients, D, have been evaluated through this model from sorption half-times using surface average particle sizes determined by nitrogen adsorption. [redacted] with an activation energy of 17 kcal/mol. D appears insensitive to resin type and molecular weight in the commercial range and [redacted] The presence of non-porous, "glassy" particles causes a slowing of the later part of the sorption or desorption process, in accord with a model for spheres of widely varied size. VCM sorption data thus offer a means of evaluating uniformity of PVC resin particle structure.

THE DIFFUSION OF VINYL CHLORIDE IN POLY(VINYL CHLORIDE)

by

A. R. Berens

Corporate Research, The B.F.Goodrich Co., Brecksville, Ohio 44141

INTRODUCTION

In the preceding paper (1) we considered the equilibrium aspects of vinyl chloride monomer (VCM) sorption by poly(vinyl chloride) (PVC). Here we turn our attention to the kinetics of the process, i.e., the measurement and application of the diffusion coefficient (D), which controls the rate of VCM sorption or desorption by PVC. Knowledge of D for VCM in PVC has two important applications related to current concerns about possible health hazards of exposure to VCM: First, in the selection of conditions of time, temperature, and pressure for the effective removal of unreacted VCM in PVC at the end of the polymerization process, and second, in the estimation of the rate at which any residual VCM in finished PVC products will escape into the environment or into other media in contact with the PVC. We present here our results of VCM sorption and desorption rate measurements from room temperature to above T_g in VCM/PVC systems containing the low concentrations of VCM likely to be encountered in practice, less than about 2000 ppm.

Nearly all published studies of diffusion in polymers (2, 3) have dealt with polymer films or sheet samples, presumably for geometric simplicity and ease of data interpretation. Because of our interest in VCM removal from PVC resins, we chose to work with samples in the powder form obtained directly from the polymerization process. While sacrificing some geometric simplicity, the use of powder samples has some compensating advantages; conversely, sorption studies seem capable of yielding useful information about PVC particle structure and geometry.

EXPERIMENTAL

Equipment: All the measurements reported here were made with the recording electrobalance set-up already described (1). To meet the boundary conditions of the diffusion equations used, the pressure of VCM (P_m) in the balance chamber should be changed in sharp steps. By bringing a small vessel to a measured VCM pressure, then quickly opening this vessel to the balance chamber, P_m could be increased to a predetermined new value in a few tenths of a second. Step decreases in pressure, especially to zero, are not so easily achieved. With oil diffusion and mechanical pumps, liquid N_2 traps, and large vacuum lines, we could reduce P_m from 200 mm to ~ 30 microns in one minute. In most experiments, the half-evacuation time was considerably less than the half-desorption time, so no corrections were made for the non-instantaneous pressure change. The response of the electrobalance and recorder provided useful data beginning within 3 to 5 sec. after a pressure change.

Materials: The PVC homopolymer resin powders used in this study are listed in Table I.

TABLE I

PVC Samples Used

Sample	Type	Intrinsic Viscosity	Surface Area m^2/g	Glassy-particle content
A	Suspension	1.10	2.3	~ nil
C	"	0.70	< 0.1	very high
D	Emulsion	1.58	9.8	nil
F	Suspension	1.10	0.32	high
G	"	0.65	0.14	moderate
H	"	0.65	0.35	~ nil
J	"	0.75	0.21	high
K	"	0.95	0.69	low
L	"	0.95	0.70	very low
M	"	1.10	1.3	~ nil

RESULTS AND DISCUSSION

General Character of Sorption Curves: In preliminary interval sorption experiments, we found that the nature of sorption vs. time curves depends upon the range of P_m and VCM concentration covered. Figure 1 shows two typical curves for Sample D at room temperature. In the lower P_m range, there is an initial rapid sorption to a VCM content which then remains nearly constant; at a somewhat higher P_m range, a similar rapid initial VCM uptake is followed by a slower further sorption which continues on to very long times. Somewhat similar results were reported by Bagley and Long (4) for the system acetone/cellulose acetate, although two-stage sorption was not observed at such a low penetrant concentration. We believe that the Bagley-Long explanation of two-stage sorption is also applicable to the VCM/PVC system: In the first stage, a uniform concentration of penetrant is reached throughout the polymer; i.e., diffusion equilibrium (or quasi-equilibrium) is attained quite rapidly. The second stage involves a slow relaxation of the swelling stress, permitting further VCM sorption; since diffusion here is much faster than stress relaxation, the second-stage sorption involves a very low concentration gradient from surface to center of the PVC particles.

Our results seem to suggest that one advantage to the use of finely powdered polymer samples is the attainment of diffusion equilibrium before appreciable stress relaxation has occurred. Thus the two stages may be clearly separated. The extent of first-stage sorption then measures the polymer in a state essentially unperturbed by penetrant swelling action, and may be used to assess effects of prior history (Cf. (1)).

In the remainder of this paper, we will deal with experiments at sufficiently low P_m that only the first-stage sorption is evident. Experiments at higher P_m and kinetics of the second stage remain for further study.

Measurement of Diffusion Coefficient, Uniform Particles: Monodisperse emulsion polymers, such as Sample D, represent the simplest possible geometry among polymer powders. Sorption or desorption experiments on such samples may be treated through a solution of Fick's diffusion equation for spherical geometry (5),

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-4Dn^2\pi^2 t/d^2} \qquad (1)$$

where M_t is the weight of penetrant entering or leaving the sphere in time t, M_∞ is the total weight change between initial and final uniform concentrations, and d is the sphere diameter. If $t_{0.5}$ is the time when $M_t/M_\infty = 0.5$, equation (1) gives

$$D = 7.66 \times 10^{-3} \frac{d^2}{t_{0.5}} \qquad (2)$$

Thus, knowing d, D can be obtained experimentally from half-sorption or -desorption times, provided the diffusion is Fickean.

Figure 2 shows the M_t/M_∞ vs. $t^{1/2}$ plot for a typical VCM sorption experiment on a monodisperse emulsion PVC of 0.44u particle diameter. The agreement between the experimental points and equation (1) (fitted to the observed $t_{0.5}$) shows that the sorption closely follows Fickean behavior. Equation (2), using the particle diameter measured by electron microscopy, gives $D = 1.9 \times 10^{-12}$ cm^2/sec.

Diffusion Coefficients, Suspension PVC's: Several studies by electron microscopy (6, 7, 8) have shown that porous particles of suspension PVC are agglomerates of primary or sub-particles of about 1 to 5 microns diameter. Recent scanning electron micrographs in our laboratories indicate that the primary particles in a given sample are fairly uniform in size. This observation suggests the

possibility of applying the uniform-sphere model to diffusion in suspension PVC's.

We also have found that an average size of the primary particles can be obtained from specific surface areas measured by N_2-adsorption. For a sphere, of density ρ, the surface-to-weight ratio is $6/\rho d$. For PVC spheres, $\rho \cong 1.4$, and we obtain

$$\bar{d}_s = 4.29/S_g \qquad (3)$$

where S_g is the specific surface area in m^2/g and $\bar{d}_s$ is the surface-average particle diameter in microns. We find quite reasonable agreement between $\bar{d}_s$ determined in this way and the primary particle diameter estimated by scanning microscopy on sectioned granules of suspension PVC.

Sorption curves on porous suspension PVC's conform quite well to the shape predicted by equation (1), as illustrated in Figure 3. Application of equation (2) to sorption data on Sample A ($\bar{d}_s = 1.85\mu$) at 25° gives $D = 2.0 \times 10^{-12}$ cm^2/sec, in good agreement with our result on monodisperse emulsion PVC. Thus the uniform-sphere model seems applicable to porous suspension PVC, and the dimension controlling sorption rates appears to be the size of the primary particles, not the external diameter of the agglomerate. This means that diffusion of VCM through the pores, and through any pericellular membrane around the gross particle, must be very rapid. Use of the external particle size in calculations of D from sorption data would give values several orders of magnitude higher than ours; this appears to account for the apparent discrepancy between our results and those recently reported by Wolf and Kreter (9).

Concentration Dependence of D: In most of our sorption/desorption experiments, we find that the desorption is somewhat slower than sorption, as illustrated in Figure 3. This is the expected result when D increases with increasing concentration of the penetrant (5). Such an effect seems likely in our system, due to the plasticization of PVC by VCM. Over the limited range of VCM concentrations considered here, the variation of D is small; an average of sorption and desorption values for D is probably a satisfactory figure for most practical applications.

Temperature Dependence of D: We have obtained sorption and desorption curves at temperatures from 25 to 90°C for several suspension PVC resins and calculated D from $t_{0.5}$ and $\bar{d}_s$. Samples of varied $\bar{d}_s$ were needed to bring $t_{0.5}$ into an experimentally accessible or convenient time range. Figure 4 summarizes our results on an Arrhenius plot. The agreement among samples is fairly good; most of the scatter may be attributed to uncertainty in $\bar{d}_s$ or in particle geometry, so there is no clear evidence that D differs significantly from one sample to another. Our samples covered the range of molecular weights (or intrinsic viscosities) of normal commercial PVC's, so it also appears that D is insensitive to molecular weight in this range. D varies with temperature from about 2×10^{-12} cm^2/sec at 30° to 2×10^{-10} at 90°C. The straight line of Figure 4 yields an activation energy of 17 kcal/mol. Limited results at 110°C show no great change in activation energy above T_g.

Results on Rigid PVC Film: A single sorption experiment at 25°C on a specimen of rigid PVC film 0.05 mm thick gave a linear M_t vs. $t^{1/2}$ plot, but the system was still far from diffusion equilibrium after one week. Assuming that the final solubility (M_∞) was similar to that in PVC powders, we estimate $D = 3 \times 10^{-12}$ cm^2/sec. Thus it appears that our values of D may also be applicable to fused (molded or extruded) rigid PVC products, but further experiments are needed to confirm this.

Later Stages of Sorption/Desorption: Plots of M_t/M_∞ vs. $t^{1/2}$ tend to focus attention on the first 90 percent of the sorption or desorption process. Yet, in the removal of unreacted VCM after polymerization, we are concerned with the final

few percent of desorption. For this region, it is instructive to examine plots of $\log(1-M_t/M_\infty)$ vs. t. Figure 5 shows such plots calculated from equation (1) using $D = 2 \times 10^{-10}$ cm^2/sec and various values of $S_g = 4.29/\bar{d}_g$. These curves thus represent the predictions of the uniform-sphere, Fickean model for sorption or desorption of VCM from PVC powders at 90°C; they are essentially linear beyond $M_t/M_\infty = 0.5$.

Experimental $\log (1 - M_t/M_\infty)$ vs. t plots for several representative suspension PVC samples are shown in Figure 6. Deviations from the uniform-sphere model are obvious and quite substantial in some cases. The initial part of the curves, to $M_t/M_\infty \approx 0.8$, show slopes similar to those predicted from the S_g values. But then some of the curves show a pronounced decrease in slope, and others a more gradual curvature. The slope in the later stages does not correlate with S_g.

We attribute these results to non-uniformity of particle structure. Under the optical microscope, samples K and L, for example, appear largely to consist of opaque, porous grains but also contain a number of translucent to clear, "glassy" particles. In such granules the pores between the original primary particles have probably been largely filled in with PVC during polymerization; the effective dimension controlling sorption rate then more nearly approximates the external particle size of perhaps 50 to 150 microns than the few-micron primary particle size. The effect of such particles on the sorption/desorption curves can be estimated through equation (1) simply by adding the curves calculated for various weight fractions of different effective particle size. This procedure is illustrated in Figure 7, where we show the predicted effect of varied weight % of 40 micron ("glassy") particles in a sample otherwise comprising uniform 4 micron particles. Sorption measurements on deliberate mixtures of porous and glassy particles give results closely resembling the calculated curves, as illustrated in Figure 8. For the samples of Figure 6, the extents of sorption at longer times are in good qualitative accord with the relative contents of glassy particles.

The more gradually curved lines of Figure 6 may similarly be interpreted as the result of a narrower, more continuous distribution of effective particle sizes. Thus the shape of sorption curves can provide much useful information about the uniformity of particle structure. In principle, at least, once D is known, it seems possible to obtain a rather complete measure of particle size and size distribution from sorption measurements on polymer powders.

Practical Implications: Our results suggest that removal of residual VCM from PVC resins could be accomplished in feasibly short times and low temperatures, provided the polymer has a relatively high surface area (small primary particle size) and is free from non-porous or glassy particles. The presence of even a small percentage of such non-porous particles will seriously retard the final stages of VCM removal. Similarly, VCM removal will become very slow once PVC particles have become fused into a continuous mass during fabrication. Assuming applicability of our D values to molded or extruded rigid PVC products, it may be shown that escape of any small amounts of residual VCM in such products into the environment will be an extremely slow process. Numerical calculations for products of varied geometry and dimensions can readily be made with available equations (5).

ACKNOWLEDGEMENTS

The author wishes to thank Mr. S. A. Oxenrider for his experimental assistance, and The B. F. Goodrich Company for permission to publish these results.

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Figure 1. VCM SORPTION, SAMPLE D, 23°C

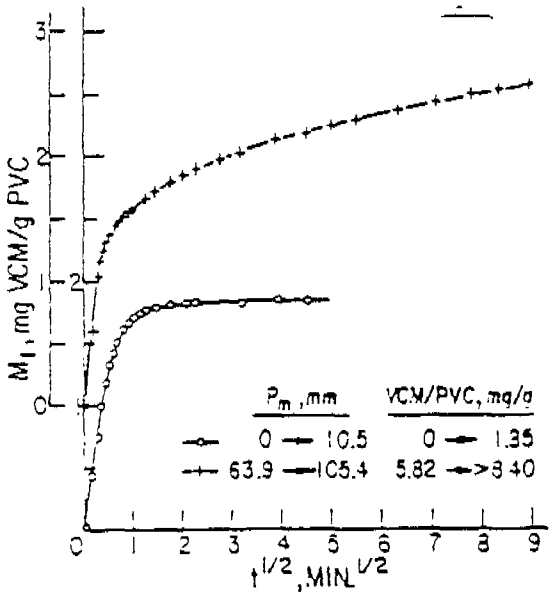


Figure 2. M_t/M_∞ vs. $t^{1/2}$, SAMPLE D, 23°C

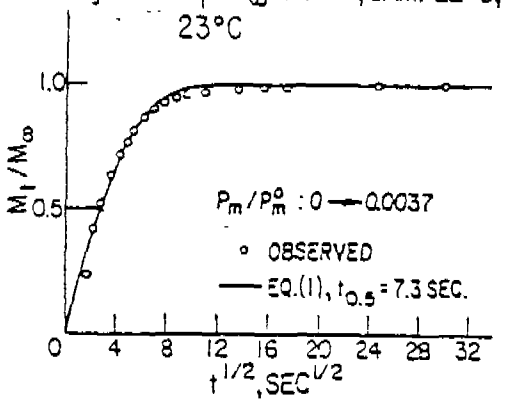


Figure 3. SORPTION/DESORPTION, SAMPLE A, 40°C

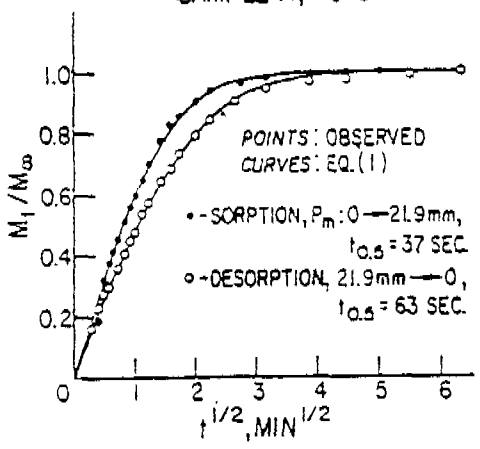


Figure 4. D vs. 1/T

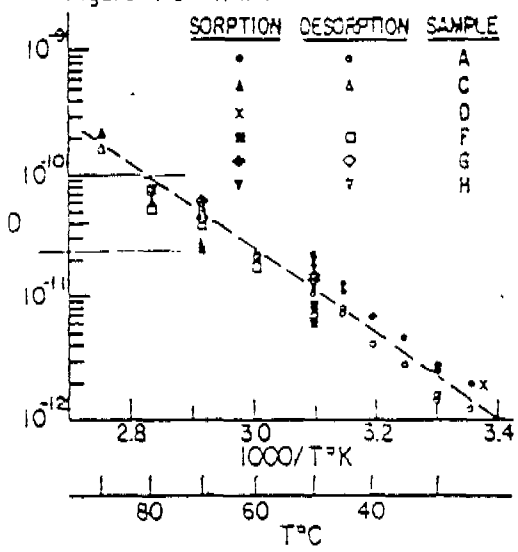


Figure 5. CALCULATED $(1-\frac{M_t}{M_\infty})$ vs. t CURVES for UNIFORM PVC SPHERES, 90°C, $D=2\times10^{-10}$, VARIED S_g

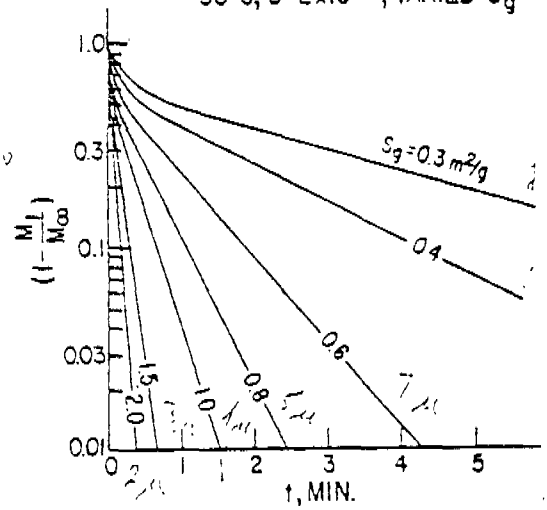


Figure 6. EXPERIMENTAL $(1-\frac{M_t}{M_\infty})$ vs. t CURVES, SUSPENSION PVC's, 90°C

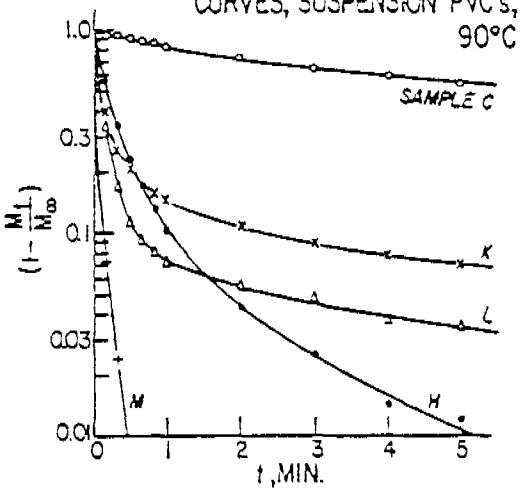


Figure 7. CALCULATED $(1-\frac{M_t}{M_\infty})$ vs. t CURVES for UNIFORM PARTICLES and MIXTURES, $D=2\times10^{-10}$ cm²/sec

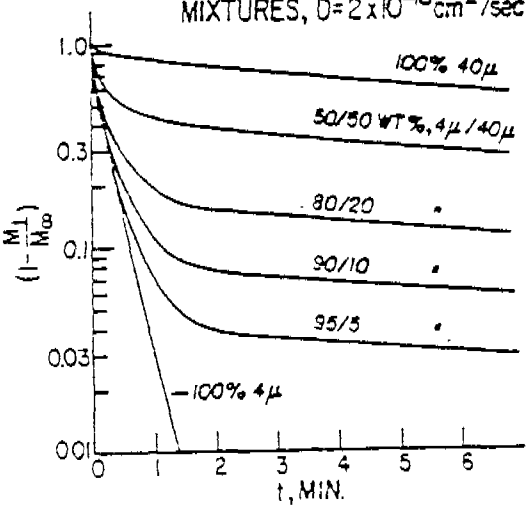
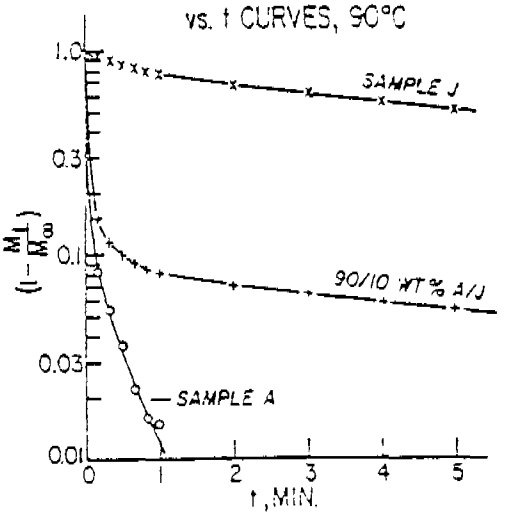


Figure 8. EXPERIMENTAL $(1-\frac{M_t}{M_\infty})$ vs. t CURVES, 90°C



GENC017241

Diffusion and relaxation in glassy polymer powders: 1. Fickian diffusion of vinyl chloride in poly(vinyl choride)

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(Received 10 January 1977)

A model is presented for diffusion-controlled sorption in polymer powders consisting of uniform spherical particles. Gravimetric sorption-rate data for vinyl chloride in PVC powders are found to obey this Fickian model for certain types of samples over limited ranges of vinyl chloride pressure increment or temperature. Superficially similar deviations from the model are caused by particle non-uniformity and by the onset of a relaxation-controlled transport mode. These two causes can be distinguished by appropriate choice of sample type and experimental conditions. A simple modification of the model satisfactorily accounts for the effect of particle non-uniformity upon sorption kinetics for conditions under which transport is diffusion-controlled. The use of powder samples in vapour-sorption experiments seems to afford several advantages over conventional film specimens, including more convenient measurement of the very low diffusivities characteristic of the glassy state, and more definitive separation of the contributions of diffusion and relaxation processes to the overall transport mechanism.

INTRODUCTION

The complex transport behaviour of organic vapours and liquids in glassy polymers has been studied extensively for over twenty years and reviewed by several authors[1-4]. It is now widely agreed that transport involves both a diffusion process, controlled by a concentration gradient, and a relaxation process, controlled by a time-dependent response of the polymer to a swelling stress. As the relative contributions of these two processes change and interact, a wide range of behaviours can be encountered. The observed effects may vary not only with the particular polymer/penetrant system considered, but also with the range of vapour activities or concentrations covered in specific experiments. Rogers[3] has pointed out, for example, that sorption vs. time curves may be pseudo-Fickian, sigmoid, or two-stage as the penetrant concentration is increased. Alfrey *et al.*[5,6] consider simple Fickian diffusion (sorption initially linear with $t^{1/2}$) and Case II sorption (linear with t) as limiting cases representing domination by diffusion and relaxation, respectively. Hopfenberg and Frisch[7] have suggested that virtually the entire range of possible behaviours may be expected in a given system when a sufficient range of temperatures and penetrant activities are investigated. Hopfenberg[3] has also pointed out, however, that at the low temperatures and activities where simple Fickian behaviour in the glassy state might be expected, experimental times become prohibitively long with conventional polymer film samples.

Recently, Vrentas, Jarzebski and Duda[9] have proposed a diffusive Deborah number, $(DEB)_D$, as a criterion for predicting whether transport is diffusion- or relaxation-controlled. This dimensionless number is defined as:

$$(DEB)_D = \frac{\lambda_m}{\theta_D} \tag{1}$$

where λ_m is a mean relaxation time and θ_D a characteristic diffusion time given by L^2/D, with L the sample thickness and D the diffusion coefficient. In this treatment, then, the sample dimension becomes an important factor, in addition to composition and temperature, in determining the transport properties to be anticipated. When λ_m and θ_D are similar in magnitude, anomalous diffusion (involving both Fickian and relaxation processes) is probable. For $(DEB)_D \ll 1$, rubbery-state or viscous Fickian diffusion is expected, while for $(DEB)_D \gg 1$, elastic, or glassy-state Fickian diffusion may occur. Vrentas *et al.* thus suggest adding the Deborah number criterion to the temperature-activity diagrams of Alfrey[5] or Hopfenberg and Frisch[7] for a more general prediction of the type of transport behaviour to be anticipated.

A recent study[10] of transport in the system vinyl chloride/PVC employed powdered polymer samples instead of the film specimens almost universally used in previous vapour-sorption work on polymers. In powder samples, diffusion paths may be reduced by orders of magnitude below the practical limit in films, and it is thus feasible to investigate transport behaviour at high values of $(DEB)_D$. The anticipated, but little studied range of glassy-state Fickian behaviour, and the interesting transition from Fickian to anomalous transport, can thus conveniently be studied.

This paper considers the diffusion of vinyl chloride mono-

mer (VCM) in a variety of PVC resin powders. A model for Fickian diffusion in a system of small, uniform spheres is presented, and it is shown that sorption data obeying this model are obtained within certain limits of sample type and VCM activity. Superficially similar deviations from the model are caused by particle non-uniformity and by a contribution from relaxation-controlled transport. Experimental methods for distinguishing these effects are presented.

Subsequent papers in this series will consider other vapour/polymer powder systems and extend these studies to situations (larger particles and higher vapour activity) where relaxation-controlled transport becomes an increasingly important factor.

EXPERIMENTAL

Materials

Polymer samples used in this study included a number of commercial and experimental PVC homopolymers made by suspension-, mass-, and emulsion-polymerization techniques. All were used in the powder form obtained directly from the polymerization process by normal recovery and drying procedures. Particle structures were characterized by optical and electron microscopy and by nitrogen-adsorption surface area measurements. A few measurements were also made on a sample of rigid PVC film. Specific samples are described where pertinent in the body of the paper.

Equipment and procedures

The measurements reported here were made with a recording Electrobalance (Model RG, Cahn Division, Ventron Instruments Corp., Paramount, California). The balance was mounted in a glass vacuum chamber with connections to a source of VCM vapour and to vacuum pumps. PVC samples were suspended from the balance in a light aluminium pan near the bottom of a 40 cm Kovar hang-down tube, which was surrounded by a circulating liquid jacket for temperature control. Sample weights were from 100 to 500 mg; use of the balance at 1 μg sensitivity thus could detect weight changes as small as 2 ppm. The normal procedure was to evacuate the balance chamber until the sample reached constant weight, then admit VCM vapour to a selected pressure and record weight change with time on a strip-chart recorder (Hewlett–Packard 7100B). Pressures were measured to ±0.1 mmHg with a strain-gauge transducer and digital voltmeter. Because of the large vapour volume and small sample size, sorption caused negligible change in pressure after an addition of VCM vapour.

The diffusion equations used in analysing the data assume that changes of pressure, and consequently of surface concentration, are made instantaneously. This condition can be closely approached for increases of pressure; by bringing a small vessel to a measured VCM pressure, then quickly opening this vessel to the balance chamber, pressure could be increased to a predetermined value in a few tenths of a second. Such sharp decreases in pressure, especially to zero, are not so easily achieved. Using oil diffusion and mechanical pumping, liquid nitrogen traps, and large vacuum lines, pressure could be reduced from, say, 200 mm to ~30 μm in one minute. In most experiments, the half-evacuation time was considerably less than the half-desorption time, so no corrections were made for the non-instantaneous pressure change. The response of the balance and recorder provided useful data beginning within 3 to 5 sec after a pressure change.

MODEL FOR FICKIAN DIFFUSION IN UNIFORM-SPHERE POWDERS

Comparison of experimental data with Fick's Law requires a solution of the diffusion equation appropriate to the sample geometry and experimental boundary conditions. The simplest geometry for powders is a collection of spherical particles of uniform size. This condition can in fact be closely approached in PVC powders prepared by emulsion polymerization. Consequently, as a model to approximate Fickian sorption of VCM by PVC resins, we have used Crank's solution[11] for the non-steady-state diffusion in a sphere in the case of uniform initial concentration through the sphere, a constant concentration at the surface, and constant D. The equation for this case is:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4Dn^2\pi^2 t/d^2) \qquad (2)$$

where M_t is the weight of penetrant entering or leaving the sphere in time t after an instantaneous change in surface concentration, M_∞ is the total weight change after infinite time at the new surface concentration, n is the series of integers, D is the diffusion coefficient, and d is the diameter of the sphere.

The following assumptions are implicit in applying equation (2) to VCM sorption or desorption experiments on PVC powders.

(1) Diffusion obeys Fick's laws.

(2) D is constant over the concentration range covered by the experiment.

(3) The solution for a sphere is applicable to a sample consisting of many spherical particles of uniform size; i.e., diffusion occurs in each particle independently, with no interparticle diffusion.

(4) The PVC powder does, indeed, consist of uniform-sized spherical particles.

(5) At the start and end of the experiment, the VCM concentration is uniform through the particles.

(6) The VCM concentration at the particle surface is always at equilibrium with the surrounding vapour phase.

(7) At time zero, the VCM pressure is instantaneously changed to a new value, thus immediately changing the surface VCM concentration of the particles.

(8) The VCM concentration in the particles is zero initially in the case of sorption starting at zero VCM pressure, and zero finally for desorptions to zero pressure.

(9) There is no concentration gradient in the vapour phase, and no surface layer effect; i.e., transport is limited only by diffusion within the PVC particles.

If all these assumptions are valid, then equation (2) will describe the weight gain (or loss) as a function of time in a VCM sorption (or desorption) experiment. This equation predicts that the time required for a given fraction of the ultimate weight change to occur is independent of the initial or final VCM concentration (or pressure), and is proportional to the ratio d^2/D. This ratio, then, can be determined by fitting equation (2) to the experimental data, but evaluation of D requires independent determination of the particle diameter.

To test the agreement between experimental data and the model, two graphical representations of equation (2) are useful. As shown in *Figure 1*, a plot of M_t/M_∞ (or of M_t) against the square root of time is initially nearly linear, then

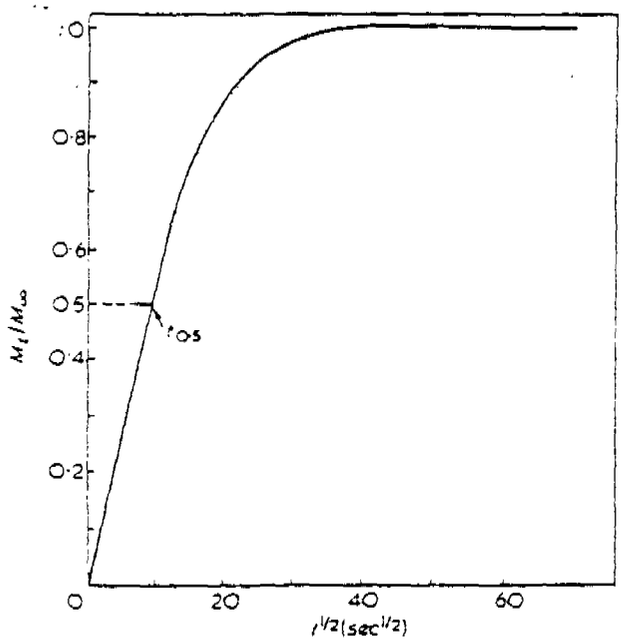


Figure 1 Plot of M_t/M_∞ vs. $t^{1/2}$, calculated from equation (2) with $d^2/D = 10^4$ sec

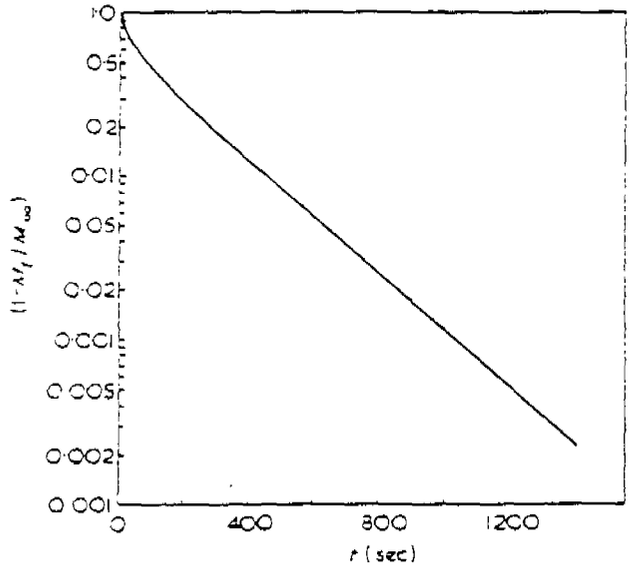


Figure 2 Plot of $\log(1 - M_t/M_\infty)$ vs. t, calculated from equation (2) with $d^2/D = 10^4$ sec

bends over to approach a well-defined limit. A plot of log $(1 - M_t/M_\infty)$ vs. t, as in *Figure 2*, shows initial curvature, then approaches a straight line. Each of these plots also offers a means of evaluating d^2/D from experimental sorption data. From equation (2) it can be shown that $t_{0.5}$, the time at which $M_t/M_\infty = 0.5$, or the 'half-sorption time', is

$$t_{0.5} = 7.66 \times 10^{-3} \frac{d^2}{D} \qquad (3)$$

for t in sec, d in cm, and D in cm^2/sec. Thus $t_{0.5}$ may be interpolated from a plot of M_t/M_∞, or of M_t, vs. $t^{1/2}$ and d^2/D evaluated by equation (3). Alternatively, d^2/D may be obtained from the limiting slope of the $\log_{10}(1 - M_t/M_\infty)$ vs. t plot:

$$\text{Slope} = -\frac{4\pi^2 D}{2.303 d^2} \qquad (4)$$

The determination of d^2/D from half-sorption time depends mainly on the data in the early stages of sorption, while the $\log(1 - M_t/M_\infty)$ method emphasizes the later-stage data.

FICKIAN, UNIFORM-SPHERE BEHAVIOUR IN VCM/PVC SORPTION

Sorption and desorption rate data for VCM in a wide variety of PVC powder samples have been obtained at temperatures from 25° to 110°C and VCM pressures from zero to 700 mm. The experimental data thus extend well below and above the glass transition temperature of PVC ($T_g \cong 85$°C). Relative VCM pressure, $P_{rel} = P/P_0$, where P_0 is the saturated vapour pressure, ranged from zero to a maximum of 0.23 at 25°C (where $P_0 = 3000$ mm) and to a maximum of 0.04 at 110°C ($P_0 = 19\,200$ mm). The form of the M_t vs. $t^{1/2}$ curves was found to depend both upon the type of PVC sample used and upon the pressure range and temperature of the experiment. Curves closely fitting the Fickian, uniform-sphere model, equation (2), are found under limited conditions of VCM pressure or temperature, but only for samples which closely approximate the 'uniform-sphere' requirement.

'Uniform-sphere' PVC samples

By emulsion polymerization, it is possible to prepare PVC powders which consist of spherical particles of diameters from approximately 0.1 to 1 μm, with very narrow size distributions. The M_t vs. $t^{1/2}$ curve from a typical VCM sorption experiment on one such monodisperse sample is shown in *Figure 3*. The experimental data conform very well to the curve calculated from equation (2) using the d^2/D value obtained from the half-sorption time and equation (3).

In the case of PVC resin powders made by suspension or mass polymerization, the gross particles (roughly 100 μm diameter) seen at low optical magnifications are neither spherical nor uniform in size. Electron microscopy has shown, however, that these gross particles are agglomerates of primary particles (~1 to 5 μm diameter) which are approximately spherical and fairly uniform in size within a given resin sample. This observation suggested application of the uniform-sphere model to sorption data on the suspension- and mass-polymerized PVC resins. *Figure 4* shows an illus-

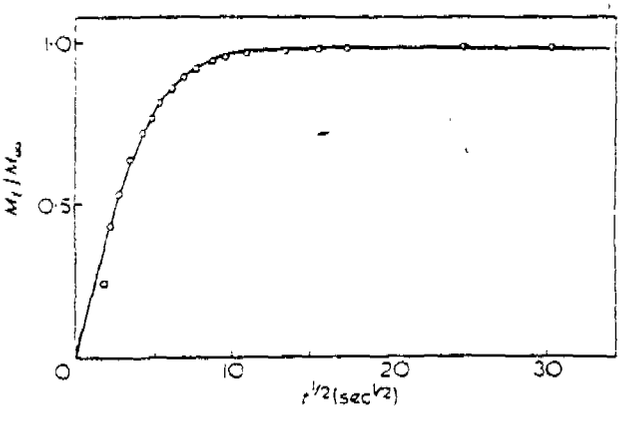


Figure 3 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by 0.44 μm emulsion PVC, 23°C, $P_{rel} = 0 \rightarrow 0.0037$. ○, Experimental; —— equation (2) for $t_{0.5} = 7.3$ sec

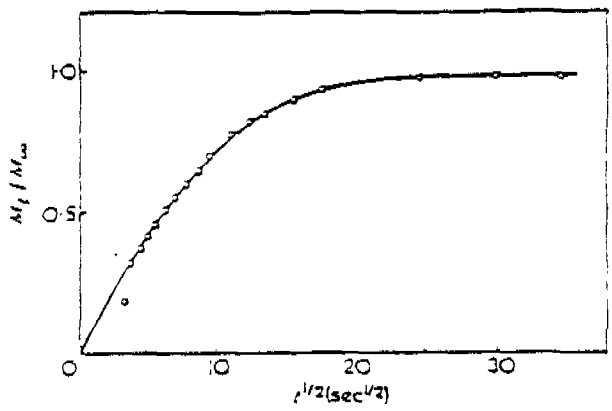


Figure 4 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by suspension-polymerized PVC, 40°C. P_{rel} = 0→0.0048. ○, Experimental; —— equation (2) for $t_{0.5}$ = 38.4 sec

trative M_t vs. $t^{1/2}$ curve from a VCM sorption experiment on a suspension-polymerized PVC; the agreement of the data with equation (2) shows that the uniform-sphere model is an adequate approximation for this particular sample. The degree of agreement with the model, however, varies considerably among different samples of mass and suspension types of PVC. It will be shown below that such variations among samples can be related to the uniformity of their particle structure.

Temperature and VCM pressure conditions for Fickian behaviour

For samples of known uniform-sphere particle structure (monodisperse emulsion PVCs), VCM sorption or desorption data fitting equation (2) are obtained only within certain conditions of VCM pressure and temperature. At temperatures below T_g, such simple Fickian behaviour is observed only for sorption runs covering very small increments of VCM pressure (P_{rel} increments of 0.01 or less), and for desorption runs to zero pressure. Above T_g, equation (2) is obeyed in sorption or desorption runs over the full P_{rel} range covered by the data. Experiments outside these conditions invariably lead to slow changes in sample weight continuing long beyond the time required to reach equilibrium according to equation (2). The sort of deviation from the Fickian uniform-sphere model will also be discussed below.

Determination of diffusion coefficient

When the PVC sample and experimental conditions produce data fitting the Fickian, uniform-sphere model, the ratio d^2/D is most readily determined from the half-sorption time. Sorption or desorption experiments are run to diffusion equilibrium to establish M_∞, then the time, $t_{0.5}$, at which $M_t = 0.5\ M_\infty$ is read from an M_t vs. $t^{1/2}$ plot, or directly from the recorder trace of weight vs. time. D is then calculated via equation (3) from $t_{0.5}$ and d.

The particle diameters used in calculation of D were determined from N_2 adsorption surface area measurements. For spheres of density ρ, the surface-to-weight ratio is $6/\rho d$, thus for PVC (ρ = 1.4):

$$\bar{d}_s = 4.29/S_g \qquad (5)$$

where S_g is the specific surface area in m^2/g and $\bar{d}_s$ is surface-average particle diameter in μm. This measure of particle size agrees reasonably well with electron microscopy for both emulsion PVCs and the primary particles of suspension resins.

Diffusion coefficients determined by this procedure for emulsion, suspension, and mass PVC resins are in good agreement. This result indicates that the rate-controlling factor in VCM diffusion is the dimension of the primary particles in each case, not the agglomerate size in suspension or mass resins. Use of the agglomerate size in calculating D from sorption data would increase D by several orders of magnitude; this factor appears to account for the discrepancy between our results and those reported by Wolf and Kreter[13]

Temperature dependence of D

The diffusion coefficient for VCM in PVC has been determined from half-sorption or -desorption times at temperatures from 25° to 110°C. It was necessary to use samples of differing $\bar{d}_s$ in different temperature ranges, since $t_{0.5}$ becomes inconveniently long at low T when $\bar{d}_s$ is relatively large, while $t_{0.5}$ is too short to measure accurately at the higher Ts when $\bar{d}_s$ is small. For the determination of D, only data closely approximating the Fickian, uniform-sphere model were used; these data therefore covered low VCM pressures and VCM in PVC concentrations up to ~2 mg/g.

Results of these measurements are presented as an Arrhenius plot in *Figure 5*. The agreement among samples is good; most of the scatter may be attributed to uncertainty in $\bar{d}_s$. Since these samples covered the molecular weight range found among commercial PVCs, it does not appear that D varies significantly with molecular weight in this range. The value of D also appears to be insensitive to the type of PVC resin, as emulsion, suspension, and mass resins give very similar results. The straight line of *Figure 5* indicates an activation energy for diffusion of 17 kcal/mol. The equation of this line:

$$D = 3.7\exp(-17\,000/RT) \qquad (6)$$

may be used to estimate D over the temperature range of the data.

[redacted]

In computing results of sorption and desorption runs on the same sample and over a similar VCM pressure increment, it was generally observed that desorption was somewhat slower than sorption. *Figure 6* illustrates this effect for a representative set of sorption and desorption data, plotted as M_t vs. $t^{1/2}$. Consequently, values of D calculated from

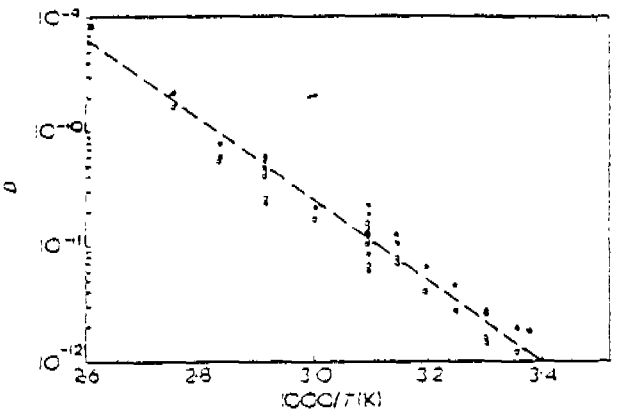


Figure 5 Plot of log D vs. $1/T$ for VCM diffusion in PVC powders: ●, sorption; ○, desorption

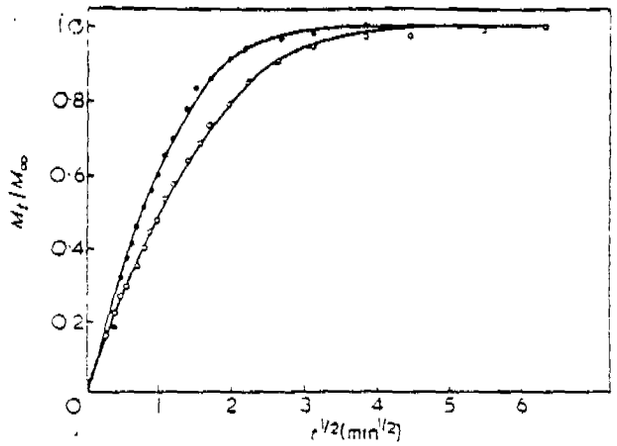
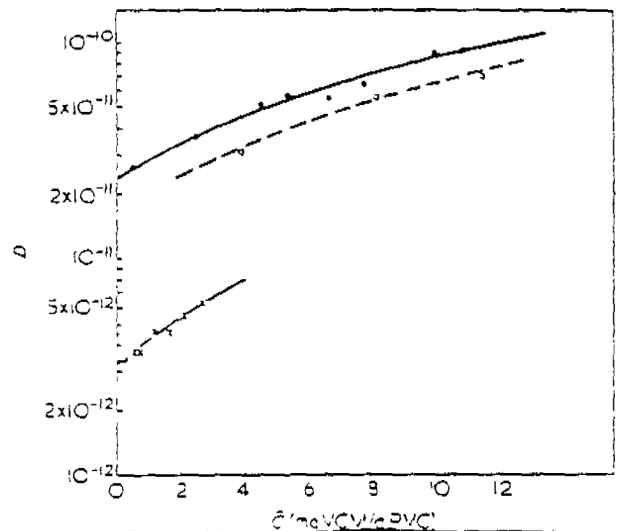


Figure 6 Plot of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption and desorption by suspension PVC, 40°C, $P_{rel} = 0 \rightarrow 0.005 \rightarrow 0$. ●, Sorption; ○, desorption



$t_{0.5}$ for desorption are lower than those from sorption runs; this trend is apparent in the data shown in *Figure 5*. Such an effect is characteristic of systems where D increases with increasing concentration of the penetrant[11] and thus does not seem unreasonable here, since VCM does tend to plasticize PVC. To confirm this effect and estimate its magnitude, we have determined D from several series of sorption experiments in which the VCM pressure was increased in successive steps ("interval sorption" experiments). Results of such runs at 30° and 50°C are shown in *Figure 7* as plots of D vs. $\bar{c}$, where $\bar{c}$ is the average VCM concentration in the PVC during each step.

Results on rigid PVC film

For sorption by a plane sheet or film, the relation analogous to equation (3) for spheres is:

$$t_{0.5} = 0.049\,\frac{l^2}{D} \qquad (7)$$

where l is the film thickness[11]. From the D values obtained on powder samples, equation (7) predicts inconveniently long experimental times for measurements on films of any reasonable thickness. Yet it does seem important to establish whether or not the D values determined in resins would also apply to fused PVC items. For this purpose, VCM sorption measurements were made on a sample of experimental extruded rigid PVC film which contained 2.5 % w/w of a tin stabilizer as the only additive. Sections of thickness 0.005 cm were used in VCM sorption experiments over a pressure interval of 0 to ~100 mm at 25°, 70°, and 90°C. The initially linear M_t vs. $t^{1/2}$ plots, shown in *Figure 8*, indicate Fickian diffusion behaviour. Only at 90°C was equilibrium reached within the time available. For the other temperatures, M_∞ and $t_{0.5}$ were estimated by assuming the equilibrium amount sorbed would be similar to that sorbed by powder samples. The estimated values of D at 25°, 70°, and 90°C were 3.1×10^{-12}, 8.0×10^{-11}, and 5.4×10^{-10} cm^2/sec, respectively. These values are somewhat higher than the average Ds for pure resin powders (see *Figure 5*), suggesting slight plasticization by the stabilizer. Yet the order-of-magnitude agreement indicates that the pure-resin D values should be applicable, to a fair approximation, in estimating VCM migration rates from rigid PVC products. Other support for this approximation has recently been obtained from the good agreement between observed VCM migration rate into water from PVC pipe and the predictions of a model based on pure resin diffusivity values[13].

These few measurements on PVC film demonstrate an important experimental advantage to the use of fine polymer powders instead of sheet or film specimens: the measurement of very low diffusion coefficients can be brought into an experimentally convenient time-scale with powder samples. For example, the half-sorption time for a 0.005 cm film with $D = 10^{-12}$ cm^2/sec is about 14 days; but for a powder of 1 μm particle diameter and the same D, $t_{0.5}$ is only 76 sec.

DEVIATIONS FROM FICKIAN, UNIFORM-SPHERE MODEL

It was noted above that sorption or desorption vs. time data fitting equation (2) are obtained only when both the

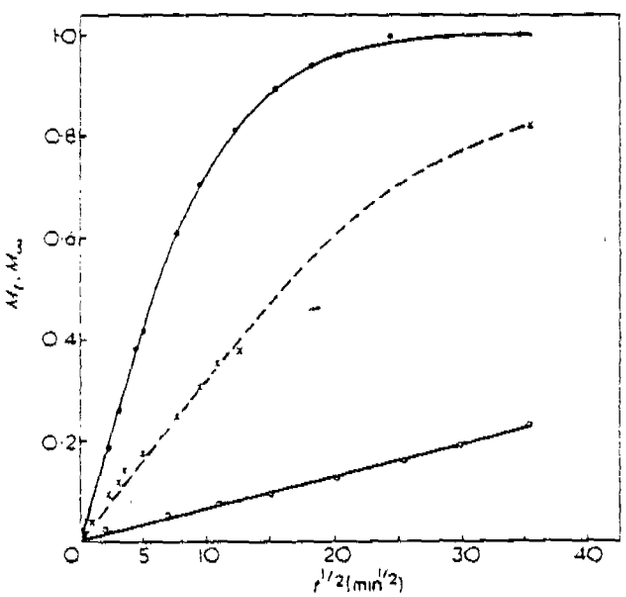


Figure 8 Plots of M_t/M_∞ vs. $t^{1/2}$ for VCM sorption by 0.005 cm rigid PVC film. ○, 23°C, ×, 70°C; ●, 90°C

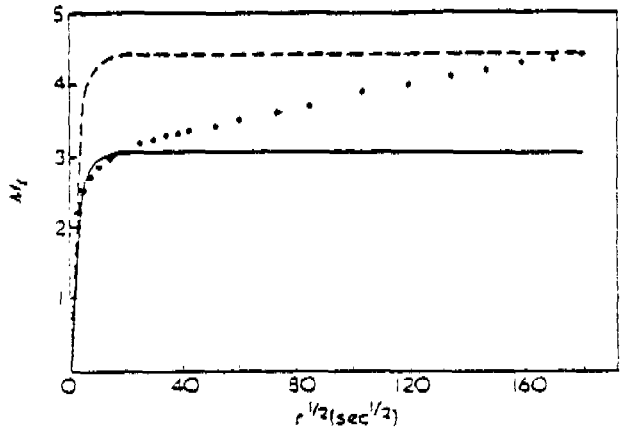


Figure 9 Deviation from equation (2) due to non-Fickian sorption: M_t vs. $t^{1/2}$ for VCM sorption by 0.44 μm monodisperse emulsion PVC, 30°C, P_{rel} = 0.02 → 0.05. ●, Observed: —— and ———, equation (2)

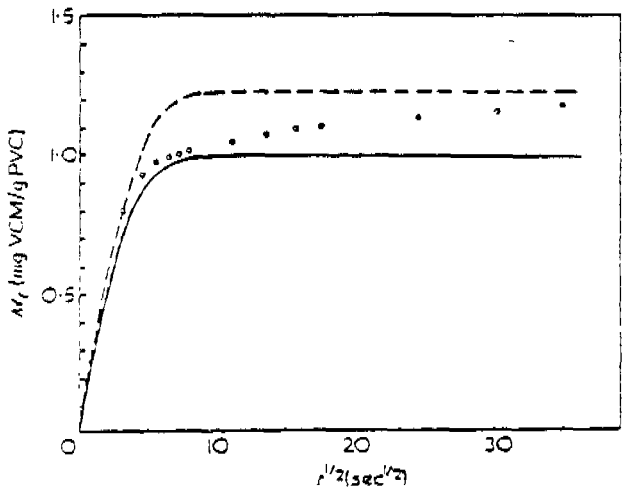


Figure 10 Deviation from equation (2) due to particle non-uniformity: M_t vs. $t^{1/2}$ for VCM sorption by commercial suspension PVC, 30°C, P_{rel} = 0 → 0.015. ○, Observed: —— and ———, equation (2)

PVC sample and the VCM pressure range of the experiment meet certain requirements. Experiments outside either set of requirements lead to weight changes which continue long beyond the equilibration time predicted by the model for the appropriate values of d^2/D. While the results are superficially very similar, it is possible to distinguish clearly two independent causes of this behaviour: particle non-uniformity and non-Fickian diffusion.

Distinction between particle non-uniformity and non-Fickian effects

These two effects can be separated by appropriate choices of sample and experimental conditions. For example, for a monodisperse emulsion PVC (whose sorption–time curve over a small VCM pressure increment fits equation 2), deviations from the model in sorption over a larger pressure increment cannot be attributed to particle non-uniformity; thus a contribution of a non-Fickian diffusion process is indicated. Conversely, when slow equilibration is observed in sorption over a small VCM pressure increment (one which gives data fitting (2) for a monodisperse sample), the deviation from the model can be attributed to particle non-uniformity. Similarly, slow equilibration in sorption or desorption at $T > T_g$ (where the model is obeyed for uniform-particle samples) is also evidence for particle non-uniformity.

Figures 9 and *10* show examples of sorption–time runs in which the deviation from the Fickian, uniform-sphere model can clearly be attributed to particle non-uniformity, in one case, and non-Fickian diffusion in the other. The similarity of the experimental curves shows that these sorption data alone would be insufficient to distinguish the cause of the deviation; the particle structure and pressure increment must also be considered.

By suitable experimental design, then, it is possible to use sorption–time data unambiguously to obtain information about either particle non-uniformity or about the non-Fickian diffusion process. Both sorts of experiment will be discussed further in the following sections.

EFFECT OF PARTICLE NON-UNIFORMITY

Results on commercial resin samples

Sorption or desorption curves on many commercial suspension- and mass-polymerized PVCs, run over small VCM pressure increments, give M_t vs. $t^{1/2}$ plots approximating the uniform-sphere Fickian model. However, when the same data are plotted as $\log(1 - M_t/M_\infty)$ vs. t, emphasizing the later stages of sorption or desorption, substantial deviations from equation (2) are apparent. *Figures 11* and *12* compare the two types of plot for a sorption run at 90°C from vacuum to 200 mm VCM pressure (P_{rel} = 0.015) for a representative mass-polymerized PVC. Since the high temperature and small pressure increment tend to *eliminate* any non-Fickian contribution, the deviation from equation (2) may be attributed to particle non-uniformity.

Previous knowledge of mass- and suspension-PVC particle structure is consistent with a possible effect of non-uniformity on rate of VCM removal. It has long been recognized that certain resins contain a small portion of non-porous particles often identified with 'fish-eye' problems. These particles are detectable by their clear appearance under a low-power, optical microscope, in contrast to the opaque, white appearance of porous particles. They are believed to arise from excessive knitting-together of primary particles during polymerization to form solid PVC regions which may be as large as the gross agglomerated particles of the resin, i.e., up to about 100 μm. Now if this dimension, rather than the few-micron primary particle diameter, is the controlling

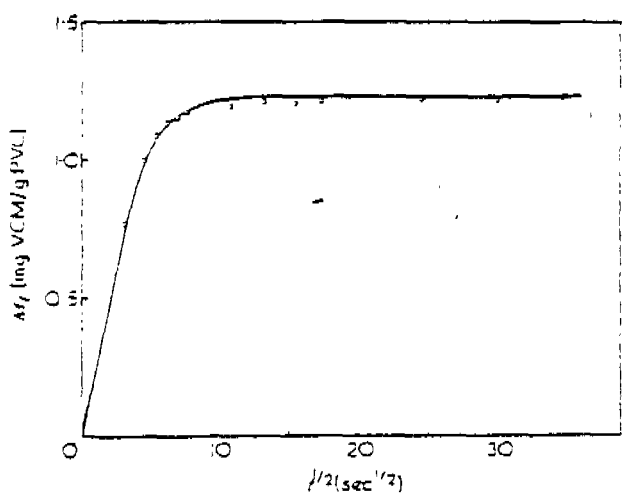


Figure 11 Plot of M_t vs. $t^{1/2}$ for VCM sorption by commercial mass-polymerized PVC, 90°C, P_{rel} = 0 → 0.015. ○, Observed; ——, equation (2) for $t_{0.5}$ = 6.2 sec, M_∞ = 1.23 mg/g

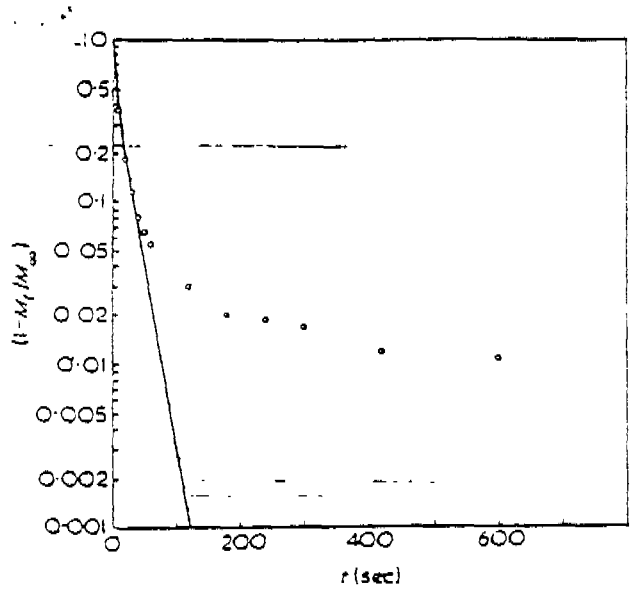


Figure 12 Same data and curve as *Figure 11*, plotted as $\log(1 - M_t/M_\infty)$ vs. t

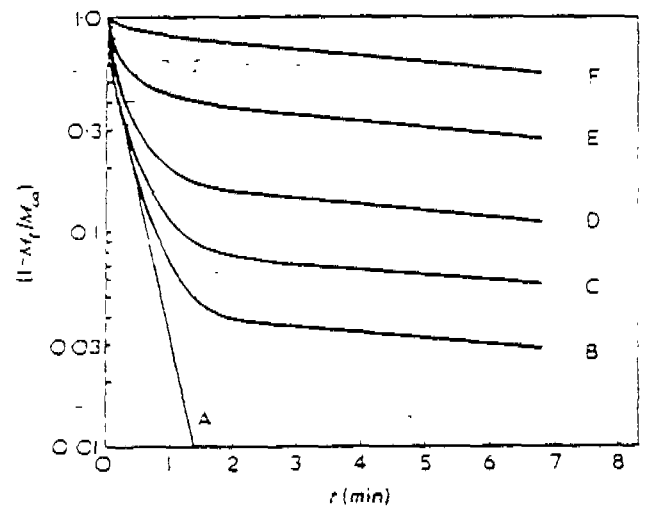


Figure 13 Curves calculated from equation (8) for uniform and mixed particle sizes, with $D = 2 \times 10^{-10}$ cm²/sec. A, 100% 4 μm particles; B, 95/5 % w/w 4 μm/40 μm; C, 90/10; D, 80/20; E, 50/50; F, 100% 40 μm

factor in rate of sorption, then the non-porous particles will sorb VCM much more slowly than the porous ones. The presence of a few such particles in an otherwise porous resin thus could well account for slow sorption or desorption of the last fraction of the total VCM.

Model for non-uniform particles

The effect of a non-uniform particle size can be predicted through equation (2) by simply adding the curves calculated for various particle sizes in proportion to their weight fraction in the sample. Thus we may write:

$$1 - \frac{M_t}{M_\infty} = \frac{6}{\pi^2} \sum_i X_i \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-4Dn^2\pi^2 t/d_i^2) \qquad (8)$$

where X_i is the weight fraction of particles having diameter d_i. To illustrate, the curves shown in *Figure 13* have been calculated by applying equation (8) to hypothetical mixtures of 4 and 40 μm particles for desorption of VCM at 90°C ($D = 2 \times 10^{-10}$ cm²/sec).

Experimental confirmation of the model for non-uniform particles has been obtained through measurements on two resins of different average primary particle size ($\bar{d}_s$ = 1.9 μm, and $\bar{d}_s$ = 20 μm) and on a deliberate 90/10% w/w mixture of the two. The results shown in *Figure 14* agree well with the form of the calculated curves of *Figure 13*. The VCM desorption curves for many commercial suspension and mass PVC resins are also in qualitative agreement with their relative non-porous particle content judged from microscopy.

It thus appears that the effect of non-uniform particle size upon the Fickian sorption of a vapour by a polymer powder can be modelled rather simply through equation (8). The consistency between experimental data and this model suggests, moreover, that vapour sorption measurements may be a useful method for obtaining information about the particle-size distribution of polymer powders. From calculated sorption–time curves for mixtures of two particle sizes (e.g., *Figure 13*) it is seen that the slope and level of the curve at the longer times are dependent on the size and weight fraction, respectively, of the larger particles. Similarly, the curves at short times reflect the size and weight fraction of the smaller particles. It seems clear that the presence of more than two sizes in the population would cause a more gradual change in slope. In principle, an experimental sorption time curve seems to contain the information needed to derive a weight-fraction particle size distribution for a polymer powder. Extraction of the size distribution by fitting equation (8) to the experimental data, however, may be a formidable task. A prerequisite for this technique, of course, would be the demonstration that the chosen experimental conditions produce Fickian behaviour with a sample known to have a uniform particle size; without this evidence, it might be impossible to distinguish particle-size distribution effects from a contribution of non-Fickian sorption.

NON-FICKIAN DIFFUSION EFFECTS

Even with monodisperse, emulsion-PVC samples, sorption experiments below T_g and covering VCM P_{rel} increments greater than about 0.01 show a much slower approach to

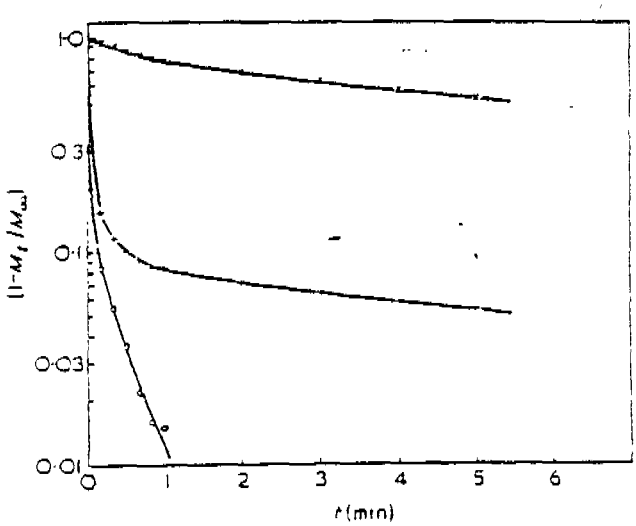


Figure 14 Experimental $\log(1 - M_t/M_\infty)$ vs. t curves for uniform and mixed particle sizes, 90°C. ○, $\bar{d}_s$ = 1.9; ×, $\bar{d}_s$ = 20 μm; +, 90/10 % w/w 1.9 μm/20μm

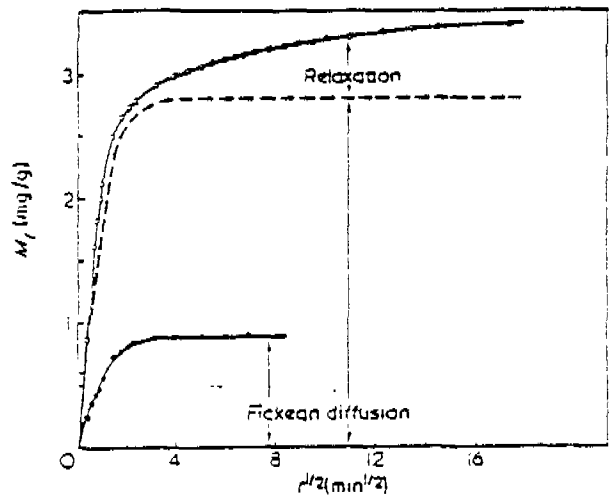


Figure 15 Schematic separation of diffusion and relaxation contributions to VCM sorption by suspension PVC, 50°C. ●, P_{rel} = 0 → 0.002; ○, P_{rel} = 0.002 → 0.019

equilibrium than predicted by the Fickian uniform-sphere model. It is suggested that this behaviour represents the onset of a non-Fickian, relaxation-controlled mode of sorption superimposed on the Fickian diffusion, as indicated in *Figure 15*. A somewhat similar 'two-stage' sorption process has been observed by Bagley and Long[14] for the sorption of acetone by ethyl cellulose and by Fujita[2] for several other systems. Their interpretation also seems applicable to the VCM/PVC system; in the early stage of sorption, the VCM concentration gradient provides the major driving force and the transport process is dominated by Fickian diffusion. When the concentration of VCM resulting from this process is sufficient to develop a significant swelling stress, the slow response of the glassy polymer to this stress produces gradual swelling of the polymer structure and permits additional sorption. This swelling–relaxation process may continue even after the Fickian process has produced a virtually uniform concentration of VCM through the polymer; in this event, the contribution of Fickian diffusion becomes negligible, and the later stage of sorption is dominated by the relaxation-controlled process.

In the fine PVC powders studied here, the short diffusion paths result in equilibration times as short as a few minutes for the Fickian diffusion process. Thus this stage may be essentially complete before appreciable stress-relaxation has occurred. The net result is a first stage which is nearly pure Fickian diffusion and a second stage which is almost entirely relaxation-controlled.

In desorption experiments at a non-zero VCM pressure in VCM/PVC powder systems, a contribution of the relaxation-controlled process also is indicated, as the approach to desorption equilibrium may be very slow[15]. In desorptions to zero VCM pressure, however, the sample weight follows the Fickian curve to a rapid 'equilibrium' of zero VCM content. Resorption experiments[15] have provided evidence that volume relaxation of the PVC continues at a slow process even in the absence of sorbed VCM. It appears that, under vacuum, all of the sorbed VCM escapes by the rapid Fickian process, but volume-relaxation is not necessarily completed during desorption. This behaviour closely parallels the observations of Barrer, Barrie, and Slater[16] in studies on ethyl cellulose.

In contrast to the two-stage sorption behaviour in the glassy state, sorption and desorption experiments conducted above T_g appear to follow simple Fickian diffusion kinetics over the VCM pressure range of the present data (P_{rel} = 0 to ~0.05). Thus, in the rubbery state, the relaxation process seems sufficiently rapid to be complete within the time scale of the Fickian diffusion stage.

This study of the VCM/PVC system indicates that vapour-sorption experiments on polymer powder samples in the glassy state offer a significant advantage over similar experiments with film samples, in that diffusion and relaxation effects may be conveniently separated. The short diffusion times encountered with fine powders permit the attainment of 'diffusion equilibrium' before appreciable relaxation occurs. The extent of first-stage sorption then reflects the state of the polymer essentially unperturbed by penetrant-swelling; this has proved to be a useful technique in assessing the effects of prior polymer history on the properties of glassy PVC[15]. The rate of sorption in the first stage is principally controlled by the Fickian process and, therefore, may be used to estimate a true diffusion coefficient even when the total sorption does not follow the Fickian model. Furthermore, since the second-stage sorption is almost entirely relaxation-controlled, the kinetic and equilibrium parameters describing the slow relaxation processes can be obtained from long-time sorption data. With film specimens, in contrast, diffusion times and relaxation times are often comparable, hence separation of relaxation from purely Fickian diffusion is often impossible.

Further studies on vapour sorption in glassy polymer powders and mathematical treatments of the data to separate diffusion and relaxation rate constants will be reported in the near future.

ACKNOWLEDGEMENTS

The author is grateful to Professor H. B. Hopfenberg for numerous helpful discussions and constructive comments on this work. The permission of The B. F. Goodrich Co. to publish this work is also gratefully acknowledged.

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ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

RESULTS OF EXPERIMENTAL PROGRAM FOR DETERMINATION OF VINYL CHLORIDE MONOMER DIFFUSION IN POLYVINYL CHLORIDE - PHASE II

February 23, 1979

W. E. Burt
G. A. Daniels
G. C. Gaeke

Results of Experimental Program for Determination of Vinyl Chloride Monomer Diffusion in Polyvinyl Chloride - Phase II

The results from the first phase of this experimental program were covered by a report dated June 26, 1978. This report was reviewed with Food and Drug Administration personnel at a meeting in Washington on August 25, 1978. A need for additional experimental work was defined during this meeting. A proposed program to cover this additional work was submitted with a cover letter dated September 5, 1978. A letter of October 19, 1978 from the FDA approved the proposed program and requested spiking and recovery studies using the FDA methodology to demonstrate the precision and accuracy of the method in our hands. The procedures are described in this report. All analyses were obtained with the FDA method with detection by FID.

1. Objective: To determine the replicability of the FDA analytical method for VCM as a function of time at about the 0.001 ppm level in PVC pellets and bottles.

   Procedure: Prepare a well mixed sample of about 40 pounds of PVC compound pellets containing about 0.001 ppm VCM. Prepare a batch of about 500 sixteen-ounce bottles from these pellets. Analyze replicate bottles and samples of compound each month for a period of several months. These data will define replicability among bottles and with compound in which all samples have the same VCM concentration.

   Results: Analysis of the pellets and bottles by month are as follows:

Pellets (as ppm VCM)

October, 1978	November	December	January, 1979
0.0018	0.0007	0.0014	0.0013
0.0011	0.0008	0.0013	0.0012
0.0021	0.0008	0.0018	0.0010
0.0007	0.0009	0.0020	0.0014
0.0007	0.0012		0.0009
0.0015			
Average 0.00131	0.00088	0.00163	0.00116

Bottles (as ppm VCM)

October, 1978	November	December	January, 1979
0.0013	0.0016	0.0014	0.0014
0.0020	0.0017	0.0016	0.0015
0.0020	0.0016	0.0020	0.0012
	0.0012		0.0014
	0.0022		0.0010
	0.0014		
	0.0009		
	0.0006		
Average 0.00176	0.00140	0.00167	0.00130

The October and November analyses were obtained with all pellet analyses in one time period and all bottle analyses in another time period. As analyses appeared to vary with the time period, the December and January data were obtained by analysis of a pellet and bottle sample at the same time.

Conclusion: The standard deviations of the data indicate that replicability of the analytical procedure over a short time period (days) is about 0.0003 ppm and about 0.0004 ppm over a long time period (months) for VCM in PVC at the non-migration level.

2. Objective: To determine if there is a variation in VCM concentration in PVC bottles with time of blowing for bottles blown from a well mixed compound pellet sample.

Procedure: The bottles blown for Part 1 of this program were numerically marked as they were produced. Every tenth bottle was set aside. Bottles for analysis in Part 1 of this program were selected from a numerical distribution represented by the "tenth bottle" samples.

Results: A list of the bottle numbers and the analyses are as follows:

Bottle No.	ppm VCM	Bottle No.	ppm VCM
11	0.0014	321	0.0020
41	0.0012	331	0.0014
51	0.0015	361	0.0016
91	0.0009	401	0.0016
121	0.0020	431	0.0016
141	0.0014	451	0.0020
151	0.0014	471	0.0010
201	0.0022	482	0.0006
221	0.0012		
241	0.0017		
281	0.0013		

Conclusion: There is no apparent variation in VCM concentration in PVC bottles with time of blowing.

3. Objective: To demonstrate that VCM does not diffuse from PVC bottles to the contents with a VCM concentration of about 0.001 ppm in the bottles and at accelerated storage conditions.

Procedure: Store eight bottles as prepared in Part 1 of this program filled and sealed with vegetable oil for six weeks at 120°F. After completion of storage, analyze in triplicate for VCM.

Store twelve bottles as prepared in Part 1 of this program filled and sealed with 50% aqueous ethanol for six weeks at 120°F. After completion of storage, analyze bottles in triplicate for VCM.

Results: Analyses for six bottles with corn oil after accelerated storage are 0.0026, 0.0024, 0.0025, 0.0018, 0.0010, and 0.0039 ppm VCM. Analyses for five bottles with 50% aqueous ethanol after accelerated storsge are 0.0014, 0.0007, 0.0018, 0.0014, 0.0011 ppm VCM.

Conclusions: The average of the analyses of the 19 bottles from Part 1 is 0.00147 ppm VCM. The average for the first five bottles after oil storage is 0.00206 ppm VCM. The average for the five bottles after 50% aqueous ethanol is 0.00128 ppm VCM. With a long term replicability of analysis of about 0.0004 ppm VCM, the three analyses are probably not different. This demonstrates that VCM does not diffuse from PVC bottles to the contents at this VCM concentration in the bottles.

4. Objective: To determine the diffusivity and activation energy of VCM in PVC at low VCM concentrations.

Procedure: Repeat the procedure described in the proposed program Part 3 included with a letter to the Hearing Clerk of March 6, 1978. A different drying procedure was used to remove water from the resin samples which has been demonstrated to remove water without change in the VCM concentration.

Results: Initial VCM concentration in the resin was 0.614 ppm. Experimental data are as follows: (all values as ppm VCM)

ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

February 21, 1979

PLEASE ADDRESS REPLY
TO: P. O. BOX 341
BATON ROUGE, LA. 70821

Dr. Robert Livingston
Food and Drug Administration
Division of Chemistry and Physics
200C Street, S.W.
Washington, D.C. 20204 Mail Code HFF-144

Dear Bob:

We have completed the experimental data in accordance with our proposed program of September 5, 1978. Data complete in December were included in a letter to you of December 12, 1978. This is an informal report of the remainder of the data.

Compound and Bottle Analysis

Continued analyses of compound pellets and bottles blown from compound from the same batch as the pellets are as follows:

		Average
Pellets-(January)	1.3, 1.2, 1.0, 1.4, 0.9 ppb VCM	1.16 ppb
Bottles-(January)	1.4, 1.5, 1.2, 1.4, 1.0 ppb VCM	1.30 ppb

The December and January data were obtained by analysis of a pellet and bottle sample at the same time. This was done because our October and November data were obtained with all pellet analyses in one time period and all bottle analyses in another time period. There was an indication of analytical variation with the time period.

Oil Storage

Bottles stored with corn oil for six weeks at 120°F were analyzed by FID. Individual bottle analyses are 2.6, 2.4, 2.5, 1.8, 1.0 and 3.9 ppb VCM for an average of 2.06 ppb for the first five bottles and 2.37 for the six bottles.

Activation Energy

Initial VCM concentration in the resin was 0.614 ppm. Analyses after the sequential steam stripping periods are: (analyses reported as ppb VCM)

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Stripping Temp. °C	After First Strip	After Second Strip	After Third Strip
50	9.0, 8.5	3.1, 3.4	1.7, 2.3
70	15.4, 10.5	1.9, 1.3	1.4, 1.6
100	3.8, 5.3	3.0, 1.8	1.8, 2.7, 2.1
Composite	7.8, 10.0	3.8, 3.4	---

Temp. Range	First Strip	Second Strip	Third Strip
100-70°C	18.1 K cal	15.3 K cal	9.3 K cal
70-50°C	15.8	25.7	25.5

Feed for the third strip was a composite that analyzed 3.3 ppb VCM.

We are preparing a formal report to cover these data and the data included in the December 12 letter.

Sincerely,

G. A. Hughmark

GAH:mfl
cc: Dr. D. Dixler - Keller and Heckman

Stripping Temp. °C	After First Strip	After Second Strip	After Third Strip
50	0.0038	0.0031	0.0017
	0.0053	0.0034	0.0023
70	0.0154	0.0019	0.0014
	0.0105	0.0013	0.0016
100	0.0090	0.0030	0.0018
	0.0085	0.0018	0.0027
			0.0021
Composite	0.0078	0.0038	--
	0.010	0.0034	--

Feed for the third strip was a composite with duplicate analyses of 0.0033 and 0.0033 ppm VCM.

The Appendix to the report of June 26, 1978 describes the calculation of diffusion coefficients as D/a^2. Calculated values from the above data are:

	D/a^2 (sec^{-1})		
Stripping Temp. °C	First Strip	Second Strip	Third Strip
50	$3.02 \cdot 10^{-5}$	$4.57 \cdot 10^{-6}$	$4.18 \cdot 10^{-5}$
70	$1.26 \cdot 10^{-4}$	$4.69 \cdot 10^{-5}$	$1.39 \cdot 10^{-5}$
100	$1.06 \cdot 10^{-3}$	$2.84 \cdot 10^{-4}$	$1.22 \cdot 10^{-6}$

Calculated activation energies are:

		Activated Energy K cal/g Mole	
Strip	Initial VCM, ppm	100-70°C	70-50°C
1	0.614	18.1	15.8
2	0.0089	15.3	25.7
3	0.0033	9.3	25.5

Conclusions: The activation energy for 50-70°C does appear to increase at very low VCM concentrations. The analytical reproducability is such that lack of precision of the analytical values represents a large error factor for the activation energies at low VCM concentration. Thus, the third strip activation energies are subject to a large error.

ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

February 26, 1979

PLEASE ADDRESS REPLY
TO: P. O. BOX 341
BATON ROUGE, LA. 70821

Dr. Robert Livingston
Food and Drug Administration
Division of Chemistry and Physics
200C Street, S.W.
Washignton, D.C. 20204

Mail Code HFF-144

Dear Bob:

The values for the VCM concentrations after the first strip were interchanged for the 50 and 100°C strips. Please replace page 2 of my February 21, 1979 letter with the attached corrected copy.

Sincerely,

G. A. Hughmark

GAH:mfl
Attachment
cc: Dr. D. Dixler - Keller and Heckman

bcc: W. E. Burt
G. A. Daniels
G. C. Gaeke
A. J. Haefner
J. R. Lees

Stripping Temp. °C	After First Strip	After Second Strip	After Third Strip
50	9.0, 8.5	3.1, 3.4	1.7, 2.3
70	15.4, 10.5	1.9, 1.3	1.4, 1.6
100	3.8, 5.3	3.0, 1.8	1.8, 2.7, 2.1
Composite	7.8, 10.0	3.8, 3.4	---

Temp. Range	First Strip	Second Strip	Third Strip
100-70°C	18.1 K cal	15.3 K cal	9.3 K cal
70-50°C	15.8	25.7	25.5

Feed for the third strip was a composite that analyzed 3.3 ppb VCM.

We are preparing a formal report to cover these data and the data included in the December 12 letter.

Sincerely,

G. A. Hughmark

GAH:mfl
cc: Dr. D. Dixler - Keller and Heckman

Non-Migration Level of Vinyl Chloride Monomer in PVC

A. J. HAEFNER *and* G. A. HUGHMARK

Ethyl Corporation
Baton Rouge, Louisiana

Recent evidence confirms previous findings that VCM in levels of 1 ppb in PVC bottle resins are nonmigratory and that such resins can be produced in commercial quantities.

This is an update on the paper presented at the SPE Meeting in April, 1968. At that time we reported experimental data that indicated a non-migration level of about one ppb VCM in PVC. Our recent work confirms this non-migration level.

EXPERIMENTAL PROGRAM

A three part program was conducted following discussion and review by FDA scientists. All low level VCM analyses in PVC were determined with the FDA analytical method using flame ionization detection.

1. PVC bottle resin was batch steam stripped as a dilute slurry in water at 100°C. Heat up with steam plus strip time at temperature was 1½ h. Intermediate and final samples were filtered and dried at mild conditions prior to duplicate analysis. The experimental data are as follows.

Time (min)	VCM (ppm)
initial	0.0031, 0.0025
15	0.0005, 0.0006
30	0.0006, 0.0005
60	0.0007, 0.0004
final (90)	0.0007, 0.0006

2. PVC bottle resin with an initial VCM concentration of 0.7 ppm was steam stripped as an aqueous slurry at 50, 70, and 100°C to develop diffusion coefficient and activation energy data as a function of temperature and concentration at low VCM levels. Sequential strips for 6 min at 100°C, 45 min at 70°C, and 3.5 h at 50°C were used. Samples were filtered and dried after each strip prior to analysis. Unfortunately, we encountered a problem in the drying procedure with the material from the third strip so that these data are not valid. Similarly, feed analysis for the fourth strip at 50° and 70°C are not available. Experimental data are as follows:

Stripping temp, °C	After first strip	After second strip	After fourth strip	After fifth strip
50	0.025 ppm	0.0074 ppm 0.0113	0.0001 ppm 0.0004	0.0012 ppm 0.0009
70	0.030	0.0040 0.0030	0.0000 0.0008	0.0021, 0.0010
100	0.012	0.0030 0.0019	0.0010 0.0010	
Composite	0.023	0.0120 0.0091		

Feed for the fourth strip at 100°C analyzed 0.0010 and 0.0004 ppm VCM, so a fifth strip was not required at this temperature.

3. Sixteen-ounce PVC bottles with an initial concentration of about 0.0014 ppm VCM were filled with 50 percent aqueous ethanol and stored at 120°F for six weeks and 21.5 weeks prior to analysis of the bottle walls. Bottles from the same batch were filled with vegetable oil and stored at 120°F for six weeks.

Analysis of six bottles from the same batch as was used for storage showed 0.0011, 0.0013, 0.0012, 0.0019, 0.0014, and 0.0013 ppm VCM at the time of filling. Analysis of bottles from this batch six weeks later showed 0.0014 ppm VCM and 0.0018 ppm about twelve weeks later. Also, samples of the ethanol and water for the aqueous ethanol were analyzed to assure that there were no interferences in these on the FID chromatograms. Analysis of six bottles after each of the storage tests showed the following results.

50 Percent aqueous ethanol		*Vegetable oil*
6 Weeks	21.3 Weeks	6 Weeks
0.0004 ppm	0.0009 ppm	0.0030 ppm
0.0007	0.0012	0.0018
0.0007	0.0005	0.0040
0.0007		0.0060
0.0001		0.0032
0.0013		0.0009
Average 0.00065*	0.00087	0.0031

*Average of 0.00076 if the 0.0001 ppm analysis is eliminated because of apparent VCM loss during analysis.

DATA INTERPRETATION

Results from the first part of the experimental program demonstrate that VCM is reduced to a concentration of about 0.0006 ppm in PVC resin at 100°C and that no further reduction in VCM occurs with continued steam stripping at this temperature. Results from the second part of the program indicate that the non-migration VCM concentration is about 0.001 ppm and is independent of temperature between 50 and 100°C.

The results from the third part of the program show that the VCM in the PVC bottles filled with 50 percent aqueous ethanol decreased to slightly less than one ppb after six weeks storage at 120°F and then apparently remained constant for the next 15 weeks. This also indicates a non-migration level at about one ppb VCM in PVC. The VCM level in the PVC bottles filled with vegetable oil show a statistically significant increase in apparent VCM in the bottles after six weeks storage at 120°F. We suspect that non-VCM components were absorbed by the bottles from the oil and that these represent interference with the FID analysis.

Interpretation of the data from the second part of the program is complicated by lack of complete data resulting from the problem in the drying procedure. Diffusion coefficients and activation energies can be estimated from the data. The stripping data are analyzed by assuming that the VCM removal is controlled by diffusion from uniform spheres to a boundary with zero VCM. The relationship between the concentration after a period of stripping and the initial concentration is given by:

$$\frac{C}{C_i} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2 D t/a^2}}{n^2}$$

where C_i = initial concentration, C = concentration at time t, D = diffusivity, and a = particle radius. Generally one or two terms of this equation are adequate for these experiments. The term D/a^2 is useful in calculating the diffusivity from PVC resin data because the particle radius is unknown. This equation is applicable because one week was allowed for equilibration of VCM in the PVC between strips.

	D/a^2, s^{-1}		
Stripping temp., °C	First strip	Second strip	Third strip
50	2.28×10^{-5}	3.74×10^{-6}	No valid data
70	9.96×10^{-5}	5.21×10^{-5}	No valid data
100	1.01×10^{-3}	4.91×10^{-4}	No valid data

Prior data obtained with high VCM levels in this PVC resin show correlated D/a^2 values of 8×10^{-5} and 6.5×10^{-4} s^{-1} at 70 and 100°C, respectively. The values obtained in this work are in good agreement with the prior correlated values.

The VCM contents measured after the fourth strip include the effects of both the third strip and the fourth strip for the 50 and 70°C runs. For the 100°C run the VCM content was not changed by the fourth strip. Likewise, no significant change in VCM content was noted from the fourth to the fifth strip for the 50 and 70°C runs. The results of the fourth and fifth strips at 50 and 70°C and the results of the third and fourth strips at 100°C are taken as measures of the same residual VCM concentration.

A major uncertainty exists in any attempt to estimate diffusion coefficients and the activation energy for diffusion for 50 and 70°C for the lowest levels of VCM. For the 100°C strips it is clear that the minimum residual level is reached at the end of the third strip but this residual level may have been reached after the third strip or required some or all of the fourth strip to reach this residual level. Values of the diffusion coefficient estimated from the average of all VCM determinations and the assumption of 1 or 2 strips are as follows:

	Value of D/a^2, s^{-1}	
Stripping temp., °C	One strip required	Two strips required
50	1.86×10^{-5}	7.58×10^{-6}
70	6.79×10^{-5}	2.64×10^{-5}
100	5.76×10^{-4}	Not required

The values of D/a^2 are shown in *Fig. 1*. The values for the first strip fall very nearly on a straight line and yield a value for the activation energy of 18.2 Kcal. The values for the second strip show a break and yield 19.0 Kcal for the activation energy between 100 and 70°C and 29.0 Kcal for the activation energy between 70 and 50°C. Treatment of the data from the third and fourth strips can yield a range for the activation energy between 70 and 50°C. If it is assumed that one strip is required for both 50 and 70°C then the activation energy between 70 and 50°C is 14.3 Kcal while if it is assumed that one strip is required at 70°C and two are required at 50°C the activation energy is 24.2 Kcal. In both cases the activation energy for the 100-70°C temperature segment is 18.1 Kcal. These values are as follows:

		Activation energy, Kcal/g mole	
Strip	Initial VCM, ppm	100-70°C	70-50°C
1	0.7	18.2	18.2
2	0.023	19.0	29.0
3 and 4	0.0108	18.1	14.3-24.2

CONCLUSIONS FROM EXPERIMENTAL PROGRAM

- A non-migration level of 0.0006 to 0.001 ppm has been demonstrated for PVC resin that is used in bottle compound. This non-migration level appears to be independent of temperature in the range of 50 to 100°C.

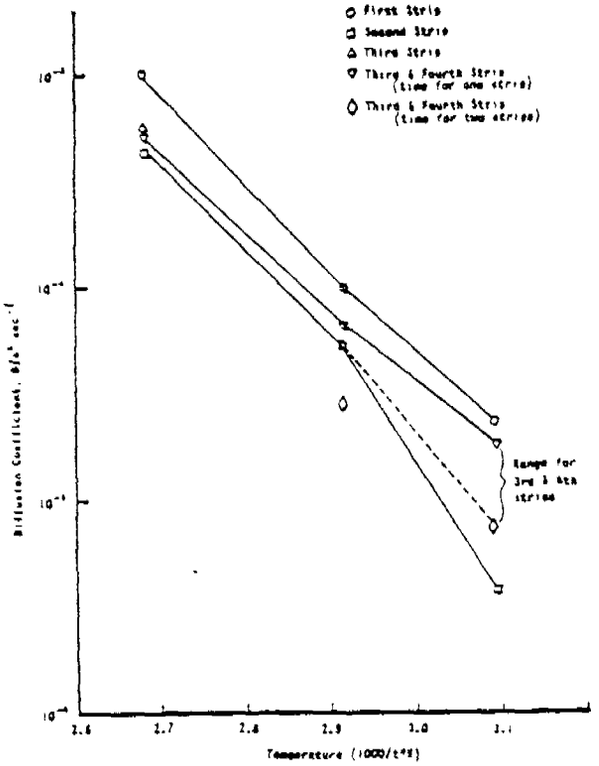

Fig. 1. Diffusion coefficients for VCM in PVC bottle resin.

• PVC bottles stored at 120°F with 50 percent aqueous ethanol as contents show a non-migration level of about 0.0008 ppm.

FUTURE WORK

We plan to repeat the second and third parts of the experimental program including GCMS analysis of the bottles after vegetable oil storage to separate VCM from inteferring components. This is expected to explain the apparent increase in VCM that was shown with vegetable oil. Repetition of the experiments to obtain data for better definition of diffusion coefficients and activation energies can be accomplished by elimination of the drying problem that occurred with the work reported in this paper.

An experimental program shall also be carried out to determine the replicability of the analytical method for PVC bottles. The entire bottle wall from a bottle is required for a single analysis so replication data are not available for what is known to be a large, constant VCM composition sample. Similarly, variability in VCM concentration is not known for bottles in the same batch. This shall also be determined. This work is required because of the small differences in VCM concentration that are required with these experimental programs.

SUMMARY

Experimental data continue to show that there is a non-migration level of about one ppb for VCM in PVC bottle resin and in PVC bottles with food simulating solvents. With the possible requirement for a PVC compound at the non-migration level, we have produced a commercial quantity of compound in the one to two ppb VCM range to demonstrate capability of manufacture of this compound.

Technical / Engineering

*Methods, research, testing**

VCM extraction from PVC bottles

For such vinyl containers, tests show that maximum VCM in contents can be held below 50-ppb level

By G. A. Daniels and D. E. Proctor

Recent problems with vinyl chloride monomer (VCM) extraction by alcoholic contents from polyvinyl chloride (PVC) bottles has caused concern about the use of this material for food packaging. This paper presents the development and results of a model, which provides the relationship between VCM in PVC bottles and the maximum concentration in the contents.

The results predicted from this model show that the maximum VCM concentration in bottle contents can be controlled below the level that is expected to be required by the Food and Drug Administration (FDA) for food-grade PVC containers. These low bottle-content concentrations require a PVC bottle compound with as low as 1 part per million (ppm) VCM. We are able to produce this compound at some increase in cost. While this low VCM level compound may be required for food use, a higher level VCM compound would be appropriate for other regulated but non-food uses. Fig. 1 shows typical regulated and non-regulated PVC bottles.

The authors: Mr. Daniels (right) and Mr. Proctor are associated with the Research and Development Dept. of Ethyl Corp., Baton Rouge, LA. Mr. Daniels joined Ethyl in 1955 and is an expert in the application of the transport processes. Mr. Proctor has 10 years experience in plastics processing and is responsible for technical service for PVC blow-molding compounds.

Statement of problem

Part of residual VCM in PVC bottles at the time of filling is extracted by the bottle contents after time in storage. The VCM concentration in the contents is a function of the VCM concentration in the PVC bottle at the time of filling, the time and temperature of storage, the ratio of the bottle weight to contents and the nature of the contents. One would expect that analysis of samples from PVC bottles with different contents and different storage periods would provide this information. Unfortunately, this direct approach is not applicable because with low VCM concentrations in the bottles, the concentrations in the contents are so low that the analytical error may be greater than the concentrations.

Extraction of VCM from a bottle is an unsteady-state diffusion process. This problem can be solved analytically to provide the relationship between the initial VCM concentration in the bottle and the VCM concentration in the contents as a function of time. Equilibrium data have been obtained experimentally as required by the analytically derived model. Experimental data for VCM in bottles and contents have been obtained at high VCM levels. Contents represent minimum analytical interference to provide data where the analytical error is small in comparison with the VCM concentration. Agreement of the model and experimental data at these high concentrations provides confidence that it is also applicable at low VCM concentrations. The physical nature of the model also provides confidence in the model at these conditions. Experimental data have also been obtained for VCM bottles and contents at low concentrations and, with consideration of analytical error, are useful as an additional confirmation of the model.

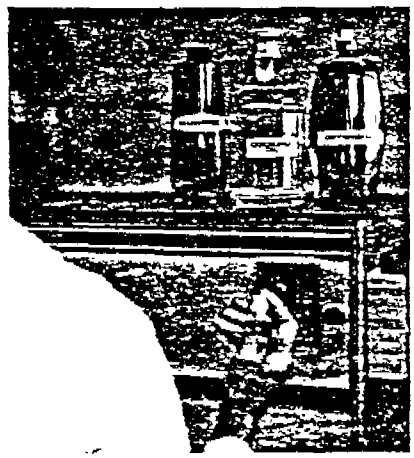

Figure 1. Typical regulated non-food, regulated food and non-regulated PVC bottles

Vinyl chloride in the PVC compound will be distributed uniformly in the compound by the extrusion operation used to process the compound before blowing a bottle. Some VCM will be lost from the compound during the blowing operation. After the bottle is formed and before filling, VCM will diffuse through the bottle wall into the surrounding and interior air. The contents provide a sink of limited capacity for VCM; after the bottle is filled, VCM will diffuse into the contents as well as into the surrounding air, but at some time the concentration of VCM in the contents will increase to a maximum value and diffusion will be from the contents, through the bottle wall and into the surrounding air. Ultimately, the VCM concentrations in the contents and in the bottle wall will decay to zero, but this will require a very long time.

The vinyl-chloride extraction can be stated in mathematical terms, and an expression can be derived which relates the concentration of VCM in the contents and bottle wall to the initial concentration of VCM in the PVC compound, the time, the dimensions of the bottle and the partition coefficient

of VCM between the bottle wall and the contents. Several reasonable and quite defensible assumpuons are embodied in the mathematical statement of the problem:

1. Diffusion of VCM through PVC is the rate-determining step.

2. The VCM concentration is uniform through the bottle wall when the bottle is formed.

3. The VCM is removed from the outer surface of the bottle by the surrounding air as fast as the VCM diffuses to the outer surface.

4. The concentraion of VCM in the bottle contents is completely uniform.

5. The concentraion of VCM at the inside surface of the bottle is in equilibrium with the VCM in the contents. This equilibrium can be described by a partuion coefficient, which is independent of concentration.

6. The diffusion coefficient is independent of time and space.

Differential equations for VCM diffusion in the bottle wall, accumulation in the liquid contents and for equilibrium at the interface between the interior wall and the liquid were then used with the appropriate boundary conditions to obtain solutions for the two cases:

Case I-No VCM is lost from the bottle in the period between bottle formation and filling.

Case II - VCM loss occurs between formation and filling. This can include loss during blowing as well as loss during storage prior to filling.

Experimental procedure, program

The analytical methods for VCM are an essential part of the experimental program. Flame-ionization-detector gas chromotography was used for bottles and contents. The method for VCM in liquid involves the use of a long, small-diameter column to obtain good resolution of the liquid's components. The penalties for using this type of column are long elution and bake-out times between sample injections. The method for VCM in PVC is an adaptation of the prior method and involves injection of a THF solution of the PVC sample. However, variable baseline interferences at about the 1 ppm level adversely affect the accuracy.

Initial experiments were conducted with standard FDA-recognized food-simulating solvents and VCM levels of 100 to 400 ppm in the bottle compound to minimize analytical error. Table I shows the solvents that were used. This experiment, which includes two brands of vegetable oil, began in January, 1974, to obtain room-temperature VCM-extraction data, and the study continues. In April, 1974, 2-oz. capacity bottles made from 1-ppm-VCM PVC were added to the series; 2-oz. bottles were used (1) to maximize VCM level potential in the product for detection, (2) to reduce quantities of solvent used in migration testing, and (3) to allow filling of several bottles with each solvent so any particular bottle need not be resampled.

Another series of extraction experiments was started in April, 1974, using weak solvents (water and 8% ethanol in water) with 2-oz. and 16-oz. bottles. Erratic results were obtained as a result of VCM loss during sampling, because of the very low solubility of VCM in these solvents. Subsequent experiments were conducted with 50% volume ethanol in water to avoid this problem.

The experimental procedure that evolved from the succession of experiments is as follows: A small batch of PVC molding compound is thoroughly mixed prior to bottle blowing. Triplicate bottles from each batch are then analyzed at the time that the bottles are filled with solvent. An average of these analyses is used as the initial VCM concentraion. Immediately after each bottle is filled with solvent to its rated capacity, a foil disc is heat-sealed over the mouth of the bottle, which is then capped to protect the seal. (Experiments indicate that commercial closure losses are negligible with 50% ethanol as the solvent.) The filled and sealed samples are then maintained at the appropriate temperature for the desired time interval. Triplicate samples are analyzed for VCM and the sample bottles are emptied and analyzed for VCM content.

Four sets of experiments were conducted to provide data for comparison with the model. Two-ounce bottles with 50% ethanol were used.

Run 4562 - The bottles were filled 78 78 days after blowing. VCM concentration in the bottles at filling was 82 ppm. Data obtained over five months at 120 deg. F.

Run 4564 - Bottles filled 118 days after blowing, with VCM concentraion in bottles of 101 ppm. Data obtained over four months at room temperature.

Run 4566 - Bottles filled one day after blowing with VCM concentration

Table 1. Experimental data for 72 deg. F storage

Solvent	Bottle	PPM VCM in compound	PPM VCM in contents			
			3 mos.	6 mos.	9 mos.	12 mos.
Water	16-oz. oval	10	0.03	0.09	0.07	0.11
Water	2-oz. cylinder	< 1	nd	nd	nd	
8% ethanol	16-oz. oval	392	2.90	3.00	3.20	5.28
8% ethanol	16-oz. oval	10	0.08	0.05	nd	0.15
8% ethanol	2-oz. cylinder	< 1	nd	nd	nd	
50% ethanol	16-oz. oval	392	4.90	4.70	6.02	8.18
50% ethanol	16-oz. oval	10	0.11	0.16	0.20	0.20
50% ethanol	2-oz. cylinder	< 1	nd	—	nd	
3% acetic acid	16-oz. oval	392	2.40	1.90	3.20	4.83
3% acetic acid	16-oz. oval	10	0.06	0.06	0.06	0.10
3% acetic acid	2-oz. cylinder	< 1	nd	nd	nd	
n-Heptane	16-oz. oval	392	3.90	4.90	4 40	7 63
n-Heptane	16-oz. oval	10	0.07	—	0.19	0.28
n-Heptane	2-oz. cylinder	< 1	nd	nd	nd	
Soya oil	16-oz. oval	392	2.70	4.80	6.45	7.53
Soya oil	16-oz. oval	10	0 065	0.115	0.15	0.26
Soya oil	2-oz. cylinder	< 1	nd	nd	nd	
Cottonseed/ soya	16-oz. oval	392	2.10	4.25	6.60	8.04
Cottonseed/ soya	16-oz. oval	10	.03	.095	.107	0.27
Cottonseed/ soya	2-oz. cylinder	< 1	nd	nd	nd	

*nd — nondetectable

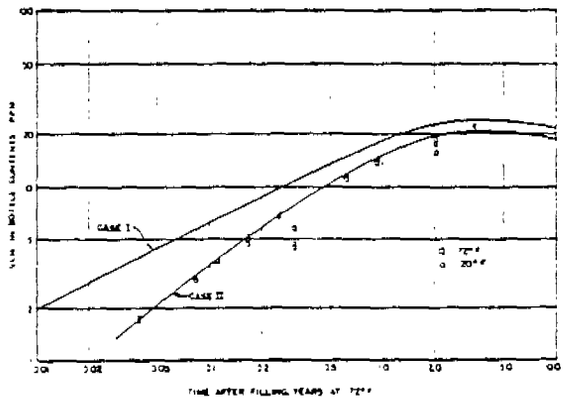

Figure 2. Comparison of experimental data from Runs 4566 and 4567 with model.

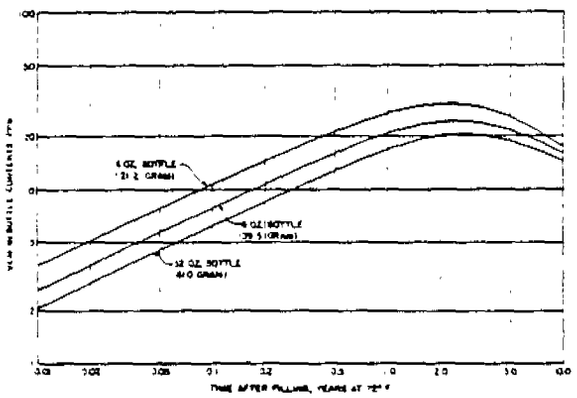

Figure 3. Water

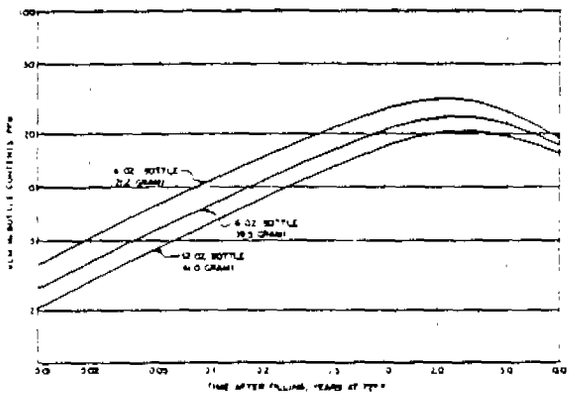

Figure 4. 3% acetic acid.

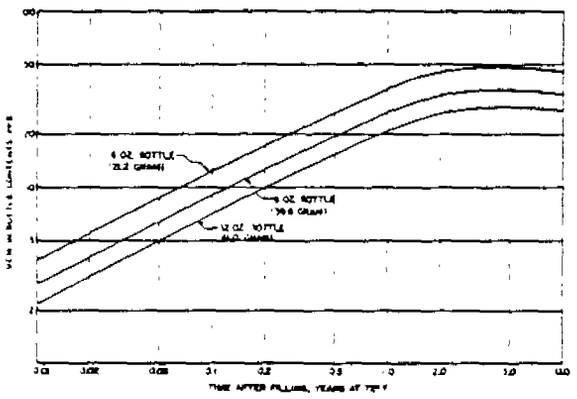

Figure 5. 50% ethanol.

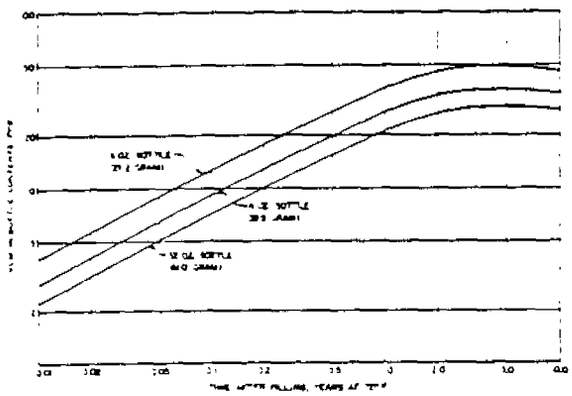

Figure 6. Cooking oil

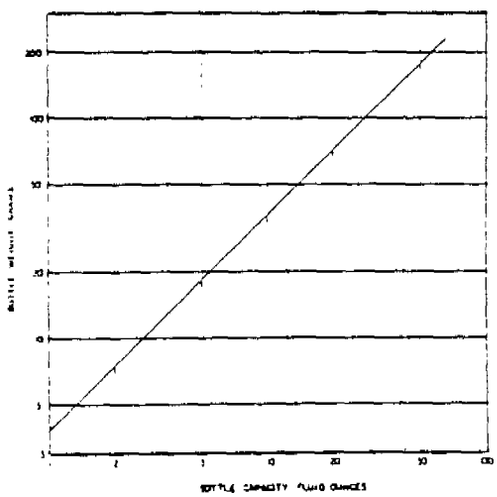

Figure 7. Allowable bottle weight not to exceed 50 ppb VCM in 50% ethanol for bottles made of PVC compound containing 1 ppm VCM

in bottles of 302 ppm. Data obtained over three months at 120 deg. F.

Run 4567 - Bottles filled one day after blowing with VCM concentration in bottles of 304 ppm. Data obtained in same period at room temperature.

Data analysis

The four sets of data provide a range of variables to determine the diffusivity of VCM in the bottle compound and to check the consistency of the models and the data. The 120-deg.-F condition provides an accelerated test as one week at 120 deg. F. is equivalent to about eight weeks at 72 deg.

The difference in time between blowing and filling provides a basis for comparing Cases I and II. Comparison of the data from Runs 4566 and 4567 shows that the rate of increase of VCM concentration in the contents is inconsistent with the Case I model, but is consistent with the Case II model. VCM loss prior to filling was also demonstrated with another experiment, which showed that about 15% of the VCM is lost during the bottle blowing. Therefore, the Case II model was used to analyze the data.

A regression analysis was used to obtain the parameter D/l^2 and the initial VCM concentration from the data for Runs 4566 and 4567. In the parameter D/l^2, D is the diffusivity of VCM in the bottle wall and l is the bottle-wall thickness. The effective bottle-wall thickness represents a combination of the thicknesses for the bottom, side wall and neck.

An excellent fit of the data is obtained to the curve representing the Case II model. Fig. 2 shows a comparison of the data from Runs 4566 and 4567 with the two models. The time scale for the 120-deg.-F-data has been calculated to correspond to the equivalent time at 72 deg. F. A reasonable comparison of the experimental data for Runs 4566 and 4567 can be made with the no-VCM-loss curve (Case I) if half of the VCM lost during blowing is added to the observed values (the other half of the VCM diffuses to the exterior surface and does not appear in the contents) and if the time corresponding to the blowing operation is added to the actual time after filling.

A similar regression analysis was made with the no-VCM-loss curve 4564. The delay between blowing and filling was included. For Run 4564, the 118 days of storage at room temperature plus about 12 days, which corresponds to the VCM loss during blowing, was used as the delay time. For Run 4562, the delay time at 120 deg. F was estimated by dividing the sum of 78 days of room-temperature storage plus 12 days for blowing losses by the ratio of the 120-deg.-F diffusivity to the room temperature (diffusivity determined from the data for Runs 4566 and 4567). Reasonable agreement was obtained between the experimental data and values predicted from the Case II model.

Conclusions

Experimental extraction data, both the VCM concentration in the 50% ethanol contents and the VCM concentration in the bottle wall, determined when using 2-oz. bottles, are consistent with the diffusion-controlled extraction model. This extraction model can be used to predict the effect of different bottle sizes and bottle contents on the VCM level in the bottle contents. Examples are shown by Figs. 3 to 6 for four different bottle contents and three bottle sizes. The calculated data presented by the figures are based upon an initial value of 1 ppm VCM in the PVC compound and are obtained with the Case I model. As this does not allow for the VCM loss during blowing and prior to filling, actual VCM concentrations would be less than is shown by these figures. Thus, these figures represent the maximum VCM that could be expected at these conditions. The maximum VCM concentration shown by the figures is always less than 50 parts per billion (ppb) and would actually be even lower because of VCM loss prior to filling. This maximum VCM concentration is estimated to occur after 2 to 5 years of storage at room temperature, depending upon the contents and the bottle size. Analysis of VCM in weak solvents always shows substantially less VCM than is predicted by Figs. 3 and 4 because of losses with closures and sampling.

It is apparent that VCM concentration in the bottle contents is a function of the ratio of the bottle weight to the volume of the contents. Thus a bottle weight can be calculated for even very small sizes in which a 50-ppb limit will not be exceeded. A 50-ppb maximum VCM concentration (no loss prior to filling) corresponds to about 3.65 g PVC per fluid ounce for 50% ethanol. For average bottle weights, this corresponds to about 5.5 fl. oz. If 15% of the VCM is lost during blowing (typical loss), a maximum level of 50 ppb can be reached at a size of 3.2 fl. oz. for the average bottle. It is apparent that decreased bottle weight for a specific volume will result in a lower maximum VCM concentration in the bottle contents. Fig. 7 shows the bottle weight that corresponds to a maximum VCM concentration of 50 ppb in 50% ethanol contents for 1 ppm in the bottle compound at filling. □

Prediction of Vinyl Chloride Monomer Migration from Rigid PVC Pipe

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Data on the solubility and diffusion of vinyl chloride monomer (VCM) in PVC resin powders have been combined with published solutions of Fick's diffusion equation to yield predictions of the amount and rate of loss of residual VCM (RVCM) from rigid PVC pipe under storage and service conditions. The principal factors controlling VCM migration are the initial VCM content, thickness of the PVC section, temperature, and the age of the PVC product. Analytic solutions are presented for RVCM loss from freshly extruded pipe (uniform VCM concentration) into either the storage environment or the pipe contents. From these solutions, estimates are made for the real-world situation of closed-system service following variable storage periods. The validity of this approach for rigid PVC pipe in water-service is supported by reasonable agreement between its predictions and experimental laboratory data on the VCM content of water stored in PVC pipes. Both the predictive model and experimental data indicate that PVC pipe containing ≤1 mg/kg (1 part per million) residual VCM will result in VCM concentrations in water of less than 0.002 mg/kg under any expected service conditions.

INTRODUCTION

A subject of continuing concern since the discovery of the potential toxic hazard of vinyl chloride monomer (VCM) has been the migration of residual VCM from finished PVC products into the environment or into liquids transported in PVC vessels. Many efforts have been made to investigate this problem by direct analysis for VCM in media in contact with PVC vessels. Early efforts in 1973 were questionable because of the imprecise analytical methods then available. As analytical procedures have been improved, the residual VCM levels in commercial PVC products have been sharply reduced, so the direct analysis for VCM migrating from today's PVC products remains a very difficult problem. Recent data [1] show that sensitivity in the thousandths of a milligram per kilogram range is needed to analyze for VCM in water contained in PVC pipe even at the residual VCM level of 20 mg per kilogram. A reliable model for predicting the amount and rate of VCM migration from available basic transport data and theory thus would be very useful.

Our approach to the development of a predictive model has been to combine the solubility and diffusion data we have obtained for VCM in uncompounded PVC resin powders [2, 3] with the solutions of the Fickean diffusion equations given by Crank [4]. This report summarizes the assumptions and approximations involved in applying these diffusion equations to the VCM migration problem and illustrates the possible calculations with some numerical examples. The predictions of our model are compared with experimental data on VCM contents of water stored in PVC pipe.

CALCULATIONS OF VCM MIGRATION

Background and Assumptions

On the basic assumption that migration of VCM thru PVC is controlled by the diffusion of VCM in the PVC phase, this process may be treated by well-known theory. The basis of classical diffusion theory is the simple differential equation known as Fick's First law,

$$F = -D \frac{\partial c}{\partial x} \qquad (1)$$

which states that the amount of diffusing substance crossing a unit plane area in unit time, F, is proportional to

Reprinted from: Polymer Engineering and Science, vol. 16, no. 8, August 1976

the concentration gradient across the plane, $\frac{\partial c}{\partial x}$. The proportionality constant, D, is called the diffusion coefficient. The minus sign indicates that diffusion always occurs toward the region of lower concentration, i.e., "downhill". Net diffusive transport ceases when the concentration gradient becomes zero, i.e., when the concentration becomes uniform.

The use of Fick's law to calculate useful quantities, such as the rate at which a diffusing substance escapes from a solid object, or the concentration profile within the object, involves some very complicated mathematics. Exact mathematical solutions are generally possible only for geometrically simple shapes and for certain specified initial and boundary conditions. Many of the useful solutions are presented in Crank's text (4), and fortunately it seems that some of the most important problems in VCM migration from PVC can be handled with a few of these equations.

Our application of these equations and our diffusion data to VCM migration from PVC products involves several assumptions:

(1) The diffusion of VCM in PVC obeys Fick's law.

(2) The diffusion coefficient is independent of VCM concentration.

(3) The value of the diffusion coefficient in rigid PVC products is the same as we have determined for pure PVC resins.

(4) The diffusion coefficient is independent of the medium surrounding the PVC; i.e., values we have determined by vapor sorption/desorption also apply to migration into a liquid phase.

Assumptions (1) and (2) have been demonstrated to be very satisfactory approximations at quite low RVCM concentrations by our work on PVC powders (3). More limited experiments on thin, rigid PVC films also support assumption (3), although some variation of D might be expected for varying amounts and types of compounding additives. The use of assumption (4) should be considered a tentatively useful approximation; we shall see that it does seem justified by experimental data on VCM migration into water from PVC pipe.

To describe the diffusion of RVCM from PVC products through Crank's equations, three situations have been considered.

Case I	RVCM loss during storage of a freshly-manufactured PVC product.
Case II	RVCM loss from freshly formed PVC products into a closed medium.
Case III.	RVCM loss into a closed medium from previously aged PVC products.

In both Cases I and II, the initial RVCM concentration is assumed to be uniform through the thickness of the PVC product. this is probably a valid assumption only at the time of extrusion, as the surface concentration of RVCM will quickly decrease upon exposure to a low-VCM environment. Cases I and II differ in the time-dependence of the surface concentration: In Case I the surface concentration of VCM remains essentially zero, as any RVCM escaping is carried away in the environment. this case may represent storage or service in a continuously renewed environment, such as flowing water. In Case II, the VCM concentration in the medium builds up with time, and consequently so does the VCM concentration in the surface of the PVC. Case III is the general situation in a real-world application: VCM loss into a closed medium follows a variable storage period and thus proceeds from a product in which the surface VCM concentration is already depleted. We will see that the aging period between manufacture and closed-system service is quite important in determining the rate of VCM migration into the contents of a PVC pipe.

Now let us consider the details and some numerical examples of each of these three cases.

Case I—VCM Loss During Storage

Consider a freshly extruded PVC product, quickly cooled to ambient temperature and stored in an atmosphere of essentially zero VCM content. The initial RVCM concentration in the product is C_o and may be assumed to be uniform through the product. At the surface, equilibrium is quickly established with the environment and the RVCM concentration is zero. We assume that VCM leaving the PVC is carried away (e.g., good air circulation) so that the surface concentration remains zero. We want to calculate (a) the amount of VCM which leaves the PVC and (b) the concentration profile within the PVC, both as functions of time, temperature, and sample thickness.

Crank gives solutions to this problem for several simple geometries—plane sheets, solid and hollow cylinders and solid spheres. The predictions for hollow cylinders are virtually identical to those for plane sheets, provided the wall thickness is less than the inside diameter. Thus for all practical PVC products (pipes, bottles, sheets, films), we need consider only the mathematical solutions for plane sheets. Equations for the amount of VCM escaping from the sheet may be written in terms of M, the fraction of the original VCM which escapes in time t. The general expression, valid at all times, is

$$M = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-(2n+1)^2 \pi^2 Dt/L^2} \qquad (2)$$

where n is the series of integers (0, 1, 2---), D the diffusion coefficient, and L the sheet thickness. For the late stages of the process ($M > \sim 0.6$), terms beyond $n = 0$ become insignificant, and Eq. 2 becomes

$$M = 1 - \frac{8}{\pi^2} e^{-D\pi^2 t/L^2} \qquad (3)$$

For $M < \sim 0.6$, a very good approximation is given by

$$M = 4 \left(\frac{D}{\pi L^2} \right)^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (4)$$

Thus the initial loss of VCM is proportional to the square root of the storage time after extrusion. For numerical calculations, we need only the sheet thickness and the diffusion coefficient values. From our measurements on PVC resins (3), the value of D at various temperatures is given by

$$D = 3.7 \exp \frac{-17{,}000}{RT} \qquad (5)$$

for D in cm²/sec, T in °K, and $R = 1.987$ cal/mol°K.

Equations 3, 4 and 5 permit prediction of the fractional loss of RVCM from rigid PVC products for different sheet thicknesses, times and storage temperatures. Examples of numerical results are given in *Figs. 1* and *2* as plots of M vs $t^{\frac{1}{2}}$. *Figure 1* shows such RVCM-loss curves for several sheet thicknesses at 30°C, where $D = 2 \times 10^{-12}$ cm²/sec $= 1.73 \times 10^{-7}$ cm²/day, and *Fig. 2*, for a 1 mm sheet thickness at several temperatures.

The concentration of RVCM remaining at time t at various distances from the sheet surface (i.e., the concentration profiles) can also be calculated from the same parameters. Crank gives the general solution as

$$\frac{C - C_o}{C_1 - C_o} = \sum_{n=0}^{\infty} (-1)^n \, erfc\left[\frac{(2n+1)\,l - x}{2(Dt)^{\frac{1}{2}}}\right] - \sum_{n=0}^{\infty} (-1)^n erfc\left[\frac{(2n+1)\,l - x}{2(Dt)^{\frac{1}{2}}}\right] \qquad (6)$$

where C is the concentration at time t at distance x from the center of the sheet, C_o is the initial (uniform) concentration, C_1 is the constant concentration at the surface (zero in our case), and l is the half-thickness of the sheet. "*erfc*" stands for error function complement defined as

$$erfc\, z = 1 - erf\, z \qquad (7)$$

The error function, "*erf*", also called the probability integral, is tabulated in standard mathematical tables. For times short enough that the concentration at the center of the sheet does not decrease significantly below C_o, only the first term of *Eq 6* is necessary; then, using *Eq 7*, we have simply

$$\frac{C}{C_o} = erf\left[\frac{l - x}{2(Dt)^{\frac{1}{2}}}\right] \qquad (8)$$

Using *Eq 8*, or *Eq 6* where necessary, we have calculated concentration profiles at 30°C ($D = 1.73 \times 10^{-7}$ cm²/day) for a PVC sheet 1/8 in. thick (or pipe with 1/8 in. wall). The results at various times are plotted in *Fig. 3*. Note that the VCM lost in the first month comes only from the 100 microns of PVC near the surface. It takes over 20 years in this case for the VCM concentration near the center of the sheet to decrease appreciably.

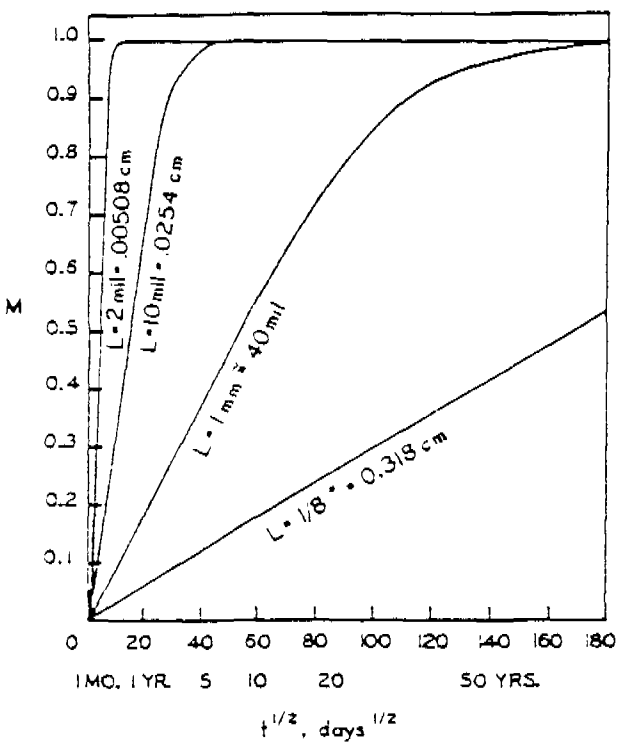

Fig. 1. Fraction of initial VCM content lost (M) vs square root of time (t) for PVC sheets of various thicknesses (L), calculated for 30°C ($D = 1.73 \times 10^{-7}$ cm²/day). Case I.

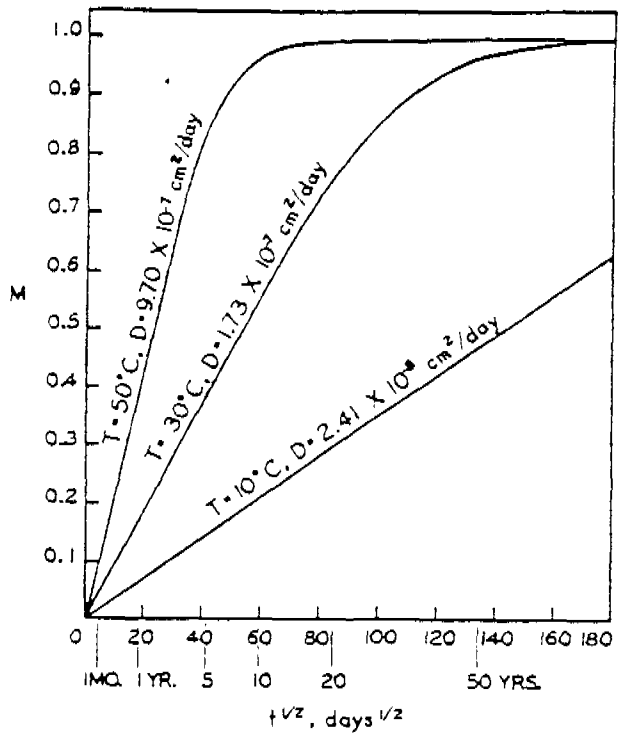

Fig. 2. Fraction of initial VCM content lost (M) vs square root of time ($t^{\frac{1}{2}}$) for PVC sheet 1 mm thick, calculated for various temperatures, Case I.

CASE II—VCM MIGRATION FROM FRESHLY-FORMED PVC PIPE INTO CONTENTS

The Case I calculations may be applied whenever VCM leaving the PVC product is carried away by the environment: storage in circulating air, water-pipe service with flowing water, etc.; so that the surface concentration of RVCM remains essentially zero. For PVC pipes in ordinary service, the outer surface is generally exposed to a low-VCM environment, i.e., a Case I situation. On the inside of pipes with stagnant contents, on the other hand, VCM leaving the PVC builds up in concentration in the contents. Consequently, the inside surface concentration of RVCM in the PVC, assumed to remain in equilibrium with the contents, also increases with time. At very long times, RVCM in the inner half of the

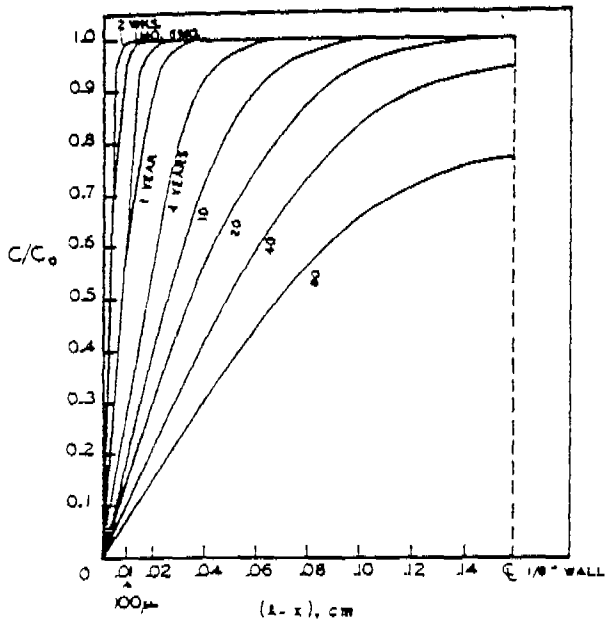

Fig 3 Relative VCM concentration (C/C_o) vs depth below sheet surface ($\ell - x$) at various times, calculated for ⅛ in. thick PVC sheet at 30°C ($D = 1.73 \times 10^{-1}$ cm²/sec). Case I

PVC wall and in the contents will diffuse outward to the environment. This net outward diffusion of VCM will only occur after the VCM concentration at the midline of the wall falls below its initial value; the time at which this occurs can be estimated from concentration profiles such as those in *Fig 3*. Since this effect occurs at such long times for pipes of normal wall thickness, we have not considered it in our model, but instead have applied Case I and Case II calculations independently to the outer and inner halves of the PVC walls, respectively.

The rate and amount of VCM entering the pipe contents may be calculated through equations given by Crank. The maximum amount of VCM which will enter the contents is that required to establish equilibrium between PVC and contents, and is governed by the partition coefficient and the ratio of volumes of PVC and contents. The partition coefficient, K, is defined as the ratio of RVCM concentration in the PVC to that in the contents at equilibrium (both expressed in the same units, e.g., g/liter). The volume of PVC supplying VCM to the container contents, V_{PVC}, is one-half the total PVC volume, as RVCM in the outer half diffuses outward in the situation we are considering. It can be shown that the maximum VCM concentration, $C_{m,max}$ (ppm by weight in the liquid contents of a PVC pipe originally containing C_o ppm VCM, is

$$C_{m\,max} = \frac{C_o d_{PVC}}{K - \frac{V_m}{V_{PVC}} d_m} \qquad (9)$$

where d_{PVC} and d_m are densities of the PVC and contents, and V_m is the volume of the contents.

From our data (2) on VCM solubility as a function of VCM pressure over PVC and water, we have estimated a value of $K = 49$ for the distribution coefficient of VCM between PVC and water at 30°C. It should be noted that this estimate of K assumes that the solubility of VCM in PVC is not affected by contact with water. It also involves a somewhat arbitrary selection of a value for VCM solubility in PVC, since we have shown (2) that this system shows non-ideal and history-dependent solubility. Using this value of K, *Eq 9* predicts that the maximum VCM concentration in water in a 1 in. I.D., ⅛ in. wall, PVC pipe containing 1 mg/kg residual VCM will be 0.027 mg/kg.

The rate of VCM desorption into the pipe contents may be obtained from another of Crank's equations:

$$M = \alpha[1 - e^{T\alpha^2} erfc(T/\alpha^2)t] \qquad (10)$$

where $T = Dt/\ell^2$, M is the fraction of the original RVCM desorbed at time t, and $\alpha = V_m K V_{PVC}$. To illustrate, we have applied *Eq 10* to the 1 in. I.D., ⅛ in. wall PVC pipe filled with standing water. *Figure 4* shows the results, with scales showing both M, the fraction of original RVCM desorbed, and the VCM concentration in the water per original ppm RVCM. Also shown in *Fig 4* is the M vs $t^{\frac{1}{2}}$ plot for Case I. Note that the initial rate of VCM desorption is the same for both Cases I and II, but the buildup of VCM in the water in Case II causes the desorption to slow down as equilibrium is approached.

Case III—VCM Migration in Closed-System Service from Previously Aged PVC Products

When a PVC product is put into closed-system service some time after manufacture, the RVCM distribution through the PVC at the time of filling and closing the container will not be uniform, as was assumed in the Case II calculations. Rather, RVCM will already be depleted near the surface, and VCM migration into the pipe contents will start from a VCM distribution as calculated in Case I (e.g., Figure 3). An analytical solution for this situation has been obtained by Daniels and Proctor (5), but a useful and simpler estimate of the rate

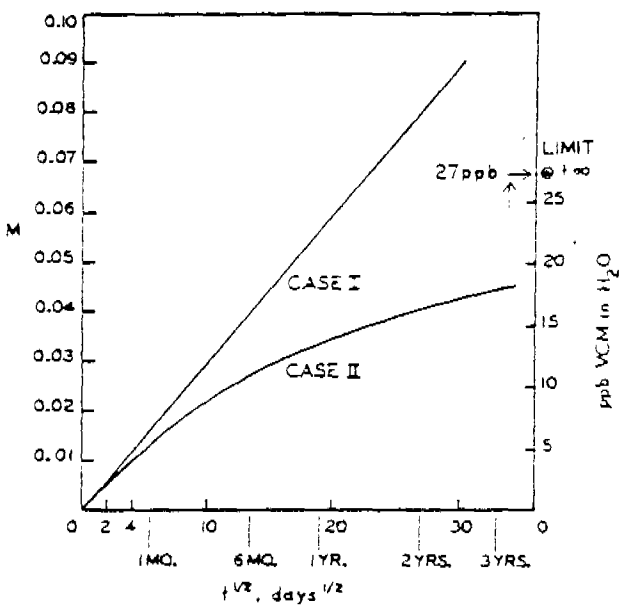

Fig 4 Fraction of original VCM content lost (M) vs square root of time ($t^{\frac{1}{2}}$) for 1 in. I.D., ⅛ in. wall PVC pipe, calculated for 30°C ($D = 1.73 \times 10^{-1}$ cm²/day), Case I and Case II with water in pipe. Right-hand scale gives ppb VCM in water per ppm initial VCM in pipe

of VCM migration can be made by combining results of our Case I and Case II equations. For Case I during desorption of the first 60% of the VCM, *Eq 4* shows that the amount of VCM desorbed is proportional to the square root of storage time. Differentiating *Eq 4* gives

$$\frac{dM}{dt} = 2\left(\frac{D}{\pi L^2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (11)$$

Thus the *rate* of VCM loss is inversely proportional to the square root of storage time. For Case II, we saw that the *initial* rate of VCM migration into the medium in a closed system is the same as in Case I. Thus *Eq 11* also gives the initial rate of VCM migration into the closed system when t is the storage age of the PVC product at the start of closed-system service. Applying *Eq 11* to a PVC product with ⅛ in. wall thickness at 30°C ($D = 1.73 \times 10^{-7}$ cm²/day) gives the curve shown in *Fig 5*. We see that the rate of RVCM desorption drops very sharply in the first few weeks of storage after manufacture.

It is also possible to estimate the amount of VCM which will migrate from a PVC product during a given period of a closed-system service following various Case I storage periods. This estimation may be explained with reference to *Fig 6*, which illustrates the VCM-loss (M) vs $t^{\frac{1}{2}}$ curves for the three cases. Case III is approximated by shifting the origin of the Case II curve to point t_1 along the Case I line, where t_1 is the age of the PVC product at the start of closed-system service. Then the VCM lost from the PVC in the time interval a during continued open-system storage would be, from *Eq 4*

$$\Delta M = 4\left(\frac{D}{\pi L^2}\right)^{\frac{1}{2}} [(t_1 + a)^{\frac{1}{2}} - t_1^{\frac{1}{2}}] \qquad (12)$$

The VCM lost, and entering the contents of a PVC container, in Case III service, will be approximately equal to ΔM for relatively short service periods, and always less than ΔM. *Equation 12* thus is useful for calculating the maximum fraction of the original RVCM which will migrate into the contents of a PVC container during closed-system service for any time period as a function of the age of the container at the time of filling and closing. *Figure 7* illustrates results calculated from *Eq 12* for 7 and 30 day service periods for a ⅛ in. wall thickness at 30°C as functions of t_1. Again we see the important effect of a few weeks prior aging in reducing the amount of VCM migration into the contents.

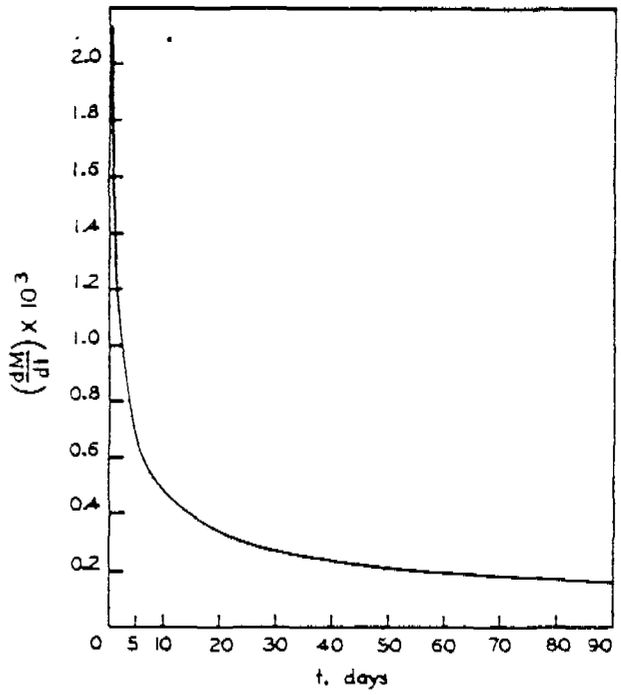

Fig. 5. Rate of VCM loss (dM/dt) vs time for ⅛ in. thick PVC sheet, calculated for 30°C, Case I.

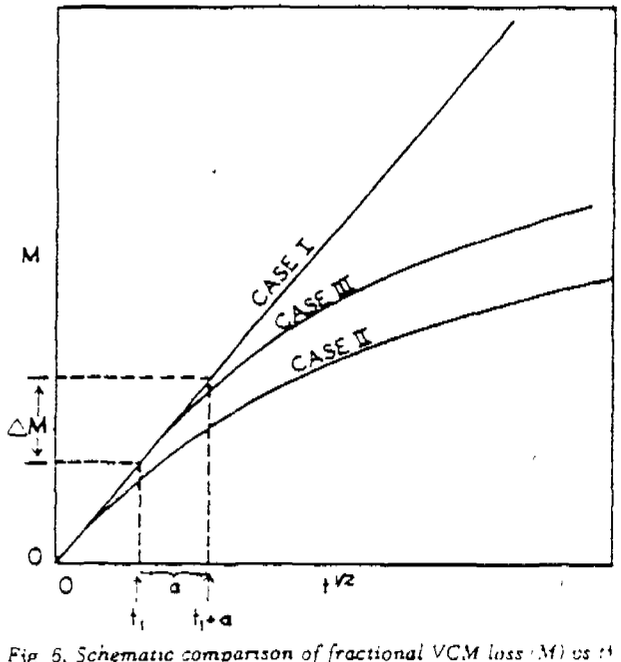

Fig 6. Schematic comparison of fractional VCM loss (M) vs $t^{\frac{1}{2}}$ curves for Cases I, II, and III.

Comparison of Predictions with Experimental Data

The foregoing analysis clearly shows that the age of a PVC product at the start of an extraction test is an important factor in determining the amount of VCM extracted. Since this information is seldom available in reported extraction data, direct comparisons between our predictions and experimental data are possible for only a few cases.

For the data recently obtained by O'Mara and DeCapita (1) on the VCM content of water stored in 1 in. I.D. ⅛ in. wall PVC pipes at 23°C, the *approximate* age of the pipe samples, between extrusion and start of the extraction test, was known. A "headspace" GC analytical method was used to provide sensitivity to low VCM levels in the water (on the order of 1 or 2 thousandths of a milligram per kilogram). We have calculated the VCM content expected in the water, using *Eq 12* with the parameters appropriate to the experimental conditions. D was obtained from *Eq 5*. *Table 1* compares the calculated and experimental results. The agreement must be considered quite satisfactory, especially in view of a) our application of D values obtained from resin powders to pipe compounds, b) the somewhat uncertain age and

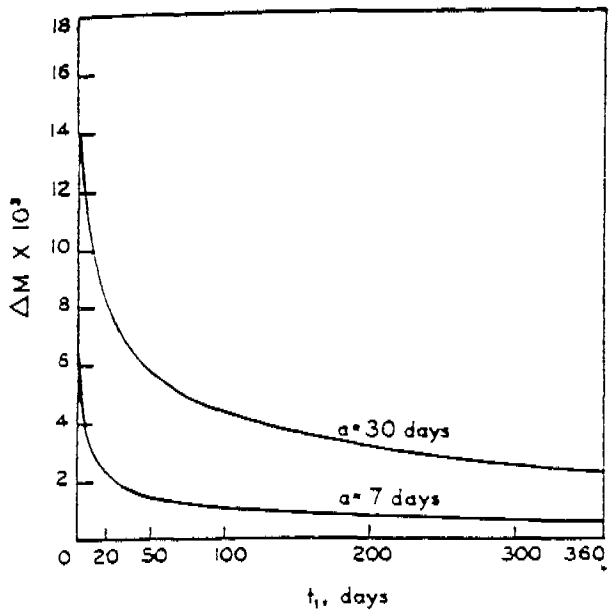

Fig 7. Fraction of original VCM content entering pipe contents (ΔM) for 7 and 30-day extraction periods vs pipe age at start of extraction (t_1), calculated for ⅛ in. wall thickness and 30°C, Case III

storage conditions of the pipe samples, and c) the difficulty of analysis of water for extremely low levels of VCM.

DISCUSSION

While further experimental verification would be desirable, it appears that the simple approach discussed above is quite adequate for describing and predicting the migration of RVCM from PVC pipe into water. The reasonable agreement between predicted and observed migration data for this application of rigid PVC supports the premises that, a) the diffusion coefficient determined for pure PVC resins is applicable to rigid PVC pipe compounds, and b) contact of PVC with water produces little change in the diffusivity of VCM compared to that measured by vapor sorption/desorption techniques. Further, for such relatively thick walled products as pipes, the diffusion into the environment from the outer half of the wall and into the contents from the inner half may be treated as independent processes over normal service lifetimes.

Our simple predictive model may thus be used with some confidence for estimating the concentrations of VCM in water which might arise during actual service of PVC water pipe systems. To illustrate, *Eq 12* has been used to calculate the VCM concentrations resulting from various stagnant exposure times of water in PVC pipes of 1 mg/kg original VCM content and varied diameter, warehouse age before installation and service age. Some results of such calculations are given in *Table 2* for 2, 6 and 8 in. SDR21 pipes in service at room temperature (~23°C). While these data are presented as though they represent stagnant water situations, from known use conditions (flow rates, pipe dimensions and resultant residence time), these calculations can be shown to model dynamic flowing systems.

The figures in *Table 2* clearly show that the highest VCM concentrations would be found in new installations of recently manufactured small diameter PVC pipe after long stagnation periods. Yet even for these most extreme conditions, the predicted VCM-in-water concentrations are well below the level of 0.002 mg VCM/kg H_2O when the original residual VCM content of the pipe is 1 mg/kg or less. In actual installations, stagnation times of more than a few days are rarely encountered. A typical residence time for water in PVC pipes is believed to be about 2 days (6-8) and in this situation, the predicted VCM-in-water concentration falls in the parts-per-trillion range. Thus we may conclude that PVC pipe containing ≤1 mg/kg residual VCM will result in VCM concentrations of less than 0.002 mg VCM/kg H_2O under any expected service conditions, and, therefore, non-detectable by present analytical methods.

Table 1. Comparison of Predicted and Experimental Extraction Results, Water-Filled 1 in. I.D. ⅛ in. Wall PVC Pipe Samples, 23°C

RVCM in pipe, mg/kg	Pipe age, t	Extraction Time, a.days	VCM in water, (mg/kg) Experimental	Calculated
292	~6 mo.	3	0.021	0.0257
292	~6 mo.	7	0.0414	0.0598
292	~6 mo.	14	0.113	0.118
177	~6 mo.	3	0.0173	0.0156
177	~6 mo.	7	0.0335	0.0362
177	~6 mo.	14	0.056	0.0717
22	~6 mo.	3	0.0006	0.0019
22	~6 mo.	7	0.0022	0.0045
22	~6 mo.	14	0.0046	0.0089
29	~1 yr.	14	0.0105	0.0084

Table 2. Calculated VCM in H_2O Concentrations for Stagnant Storage of Water in PVC Pipes of Varied Size and Age and Original 1 mg/kg Residual VCM Content

Pipe size (SDR21)	Warehouse age, days	Service age, years	VCM in water after given storage times, mg/kg 2 days	2 weeks	1 month
2 in.	30	0(new)	.00007	.00044	.00087
	60	0	.00005	.00033	.00067
	90	0	.00004	.00027	.00056
	90	1	.0000180	.000125	.000265
	90	2	.00001	.00009	.000199
	90	5	.00001	.00006	.00013
6 in.	30	0	.00002	.00015	.00029
	60	0	.00002	.00011	.00022
	90	0	.00001	.00009	.00019
	90	1	.000006	.000042	.000088
	90	2	.000004	.00003	.000066
	90	5	.000003	.00002	.00004
8 in.	30	0	.00002	.00011	.00022
	60	0	.00001	.00008	.00016
	90	0	.00001	.00007	.00014
	90	1	.0000045	.000031	.000066
	90	2	.000003	.00002	.000050
	90	5	.000002	.00001	.00003

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