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**PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS
TRANSPORTATION PART II. PERMEATION**

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16. Abstract <p>Permeation as a mode of failure for plastics packagings is discussed. The materials properties which determine permeation performance are defined. Measurement methods aimed at determining values for the materials properties are surveyed.</p> <p>A "matrix" scheme is introduced for evaluating the risks associated with the permeation failure of a package containing a hazardous materials lading. Permeation factors influencing reuse of plastic containers are described. Laboratory data from an evaluation of a simple method of test for estimating the intrinsic property of a lading to permeate polyethylene is presented.</p>					
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PREFACE

This report is Part II of a series prepared for the Office of Hazardous Materials Operations under research contract no. DOT AS-50074. It is presupposed that the reader is cognizant of the background material presented in Part I. This part will be concerned exclusively with the permeation aspects of the performance of plastic packagings for the transport of hazardous materials. The authors wish to acknowledge the assistance and cooperation of the following organizations: The Office of Hazardous Materials Operations Staff, particularly Mr. Mario Gigliotti for his guidance to the work from the inception; members of the Plastic Drum Institute of the Society of the Plastics Industry; members of the Manufacturing Chemists Association; and Mr. P. E. Campbell of the Phillips Petroleum Co. These organizations contributed valuable results from their technical experience.

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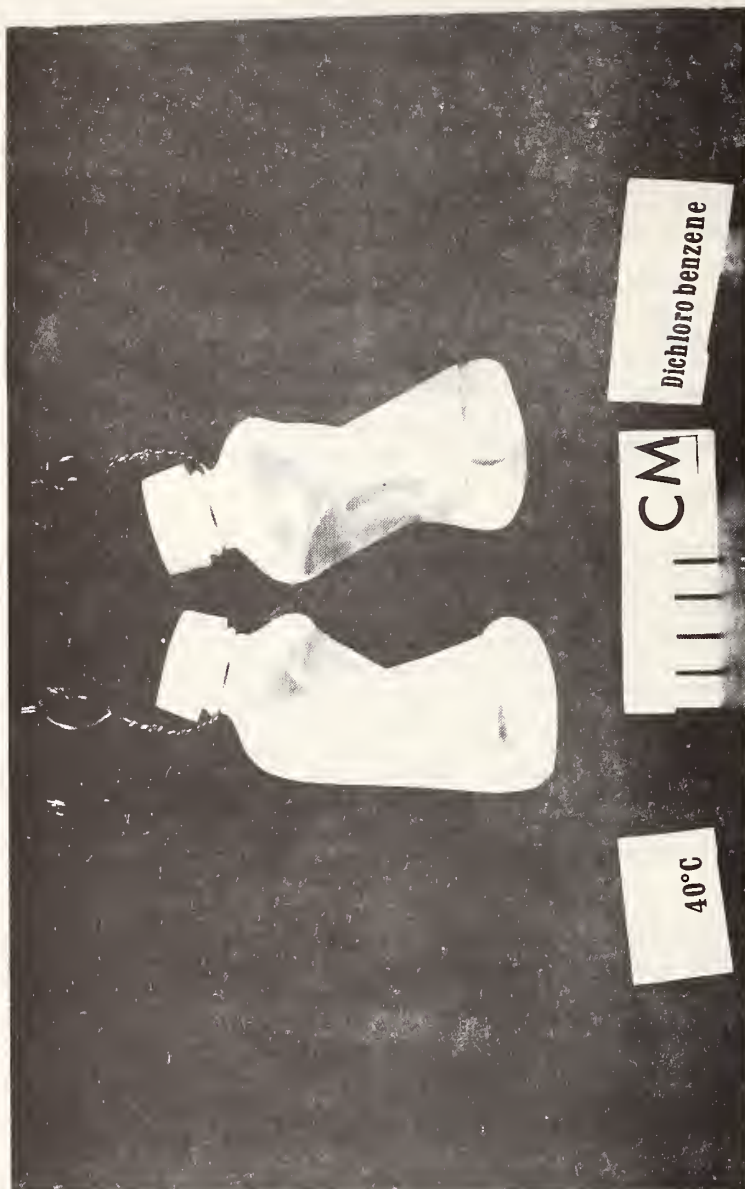


Figure 1 Permeation Failure in a Four-Ounce Polyethylene Bottle. The Bottle is a Type #1 (See Table 8) Boston Round Bottle. Note the essentially complete collapse of the side walls.

Tests such as the one whose result is shown in Fig. 1 offer a good simple route to the identification of materials which tend to permeate polyethylene. The procedure used is described in ASTM Test Method D 2684-73 "Standard Recommended Practice for Determining Permeability of Thermoplastic Containers [2]". The experiments carried out at NBS are described in an Appendix to this report.

Briefly stated, the method consists of filling a blow molded plastic bottle with the substance in question, sealing the bottle tightly, weighing the whole package, and placing it in an oven at a controlled temperature. The weight change of the bottle and its contents is measured periodically and plotted as a function of time. The steady-state rate of weight loss (or gain) can be obtained from the plot.

The results of the experiment clearly depend on:

1. The molecular nature of the lading.
2. The characteristics of the plastic in the bottle.
3. The characteristics of the bottle.
4. The temperature and pressure at which the experiment is carried out.

In a more subtle fashion one might expect the results to depend upon:

1. The amount of lading in the bottle at the start of the experiment.
2. Whether or not the bottle had been previously used.

The packaging industry carries out tests similar to ASTM D 2684-73. Resin or container manufacturers and large-scale shippers are generally the only companies equipped for such tests. In such a testing environment there is little standardization of conditions and results are usually stated in simple pass-fail terms. Each container manufacturer, resin producer, or shipper has tended to develop his own list of loadings and packages which are "incompatible" with each other. There are also recommendations from resin manufacturers which state that certain classes of chemicals may give problems when packaged in containers made from certain resins.

There are useful general guidelines which can be extracted from this body of experience. Table 1 summarizes the guidelines used by a major producer of resins. This table demonstrates the importance of the molecular structure of the lading. Table 7 gives some additional results from the NBS experiments.

It is generally agreed that the density of a given polyethylene has an important effect on permeation rates [3,4]. This effect is due to the semicrystalline nature of polyethylene, an interpretation based on the view that permeation takes place most readily in the disordered matrix in which the crystallites are embedded. The higher the density, the higher the crystallinity, the smaller the "amorphous" content and, therefore the lower the permeation rate. This effect is not one of direct proportionality as can be seen from Fig. 2 [4]. In addition there are a variety of ways of achieving a given density and the curve in Fig. 2 should not be viewed as being a universal one for the system benzene-polyethylene.

In comparing the results of different permeation tests it is important to know something about the molecular properties, especially the density, of the resin used to make the containers.

However, the fact that resin manufacturers characterize their products in terms of density should not, as mentioned earlier, be taken to mean that any product fabricated from that resin will have the specified density. Table 8 shows variations in density from one part of the bottle to another. A density which is higher in the thick part of the container than in the thin part may be attributable to slower cooling in those parts. Similar data from a bottle made from a different resin, also given in Table 8 illustrates that the variations among resins are generally greater than those within a given piece.

TABLE 1

GENERAL GUIDELINES TO COMPATIBILITY OF CHEMICAL REAGENTS WITH POLYETHYLENE

CHEMICAL TYPE	PERMEATION RATE	EXAMPLE #	TENDENCY TO CHEMICALLY ATTACK POLYETHYLENE	NATURE OF HAZARD	REMARKS
1. ALCOHOLS	Low	ETHANOL .0106	Low	FLAMMABLE	
2. WATER-BASED PRODUCTS	Low	NH ₄ OH SOLN 1.57	Low*	POISONOUS, CORROSIVE	WATCH FOR STRESS CRACKING IN SOME CASES
3. ACIDS	Low	ACETIC ACID + .940	Low*	CORROSIVE	NITRIC, FUMING SULFURIC ARE ESPECIALLY DANGEROUS
4. KETONES, ALDEHYDES, ESTERS	Low MODEST	ACETONE .0225	Low to Modest	FLAMMABLE	
5. ETHERS	MODEST	N-BUTYL ETHER .0574	MODEST TO HIGH	FLAMMABLE	
6. SATURATED HYDROCARBONS	HIGH	PENTANE 1.61	MODEST TO HIGH	FLAMMABLE	
7. AROMATIC HYDROCARBONS	HIGH	BENZENE .510	HIGH	FLAMMABLE TOXIC	
8. HALOGENATED HYDROCARBONS	HIGH	BUTYL BROMIDE .215 CCl ₄ .302	MODEST TO HIGH	TOXIC (SOME ARE FLAMMABLE)	

VALUES ARE MOL/M²/24 HR. @ 1 MM THICKNESS

* BE CAREFUL OF EXCEPTIONS

+ MIXTURE WITH UNCERTAIN COMPOSITION. GRAMS ARE USED INSTEAD OF MOLES.

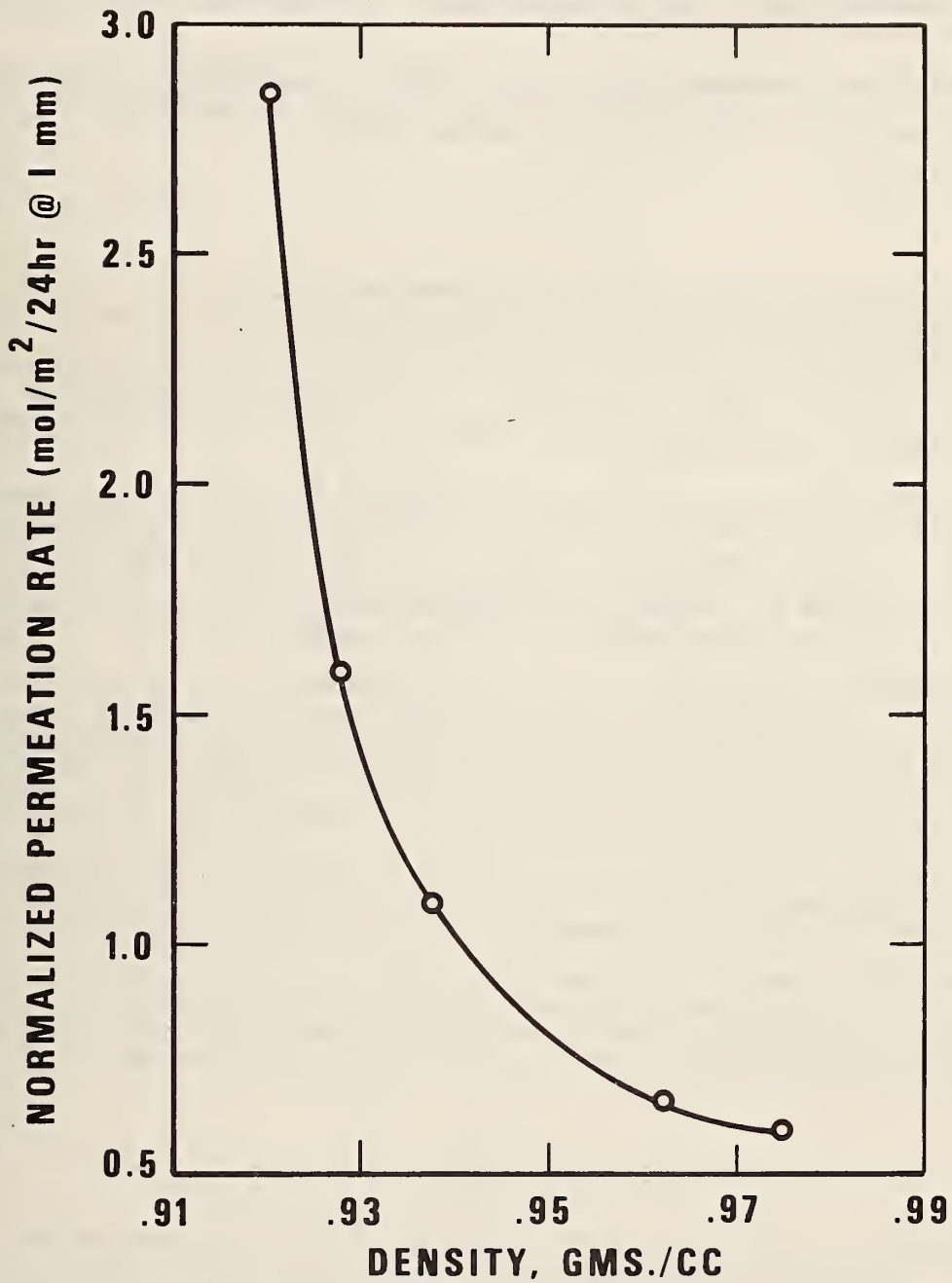


Figure 2 Permeation Rate as a Function of Density: Benzene and Polyethylene [4].

At the beginning of this report the permeation rate was defined as the amount of matter transported across a unit area of a barrier in unit time and it is this form in which the results are given in Table 1 and Table 7. The purpose of doing so was, of course, to minimize the effect of container geometry. There are other ways to express the results of permeation tests. These are summarized in Table 2 and the relationships among them will be examined here briefly.

Define \dot{Q} as the steady-state rate of loss (or gain) of material from a container with a capacity Q_0 . Define F as the permeation flux. If A is the surface area of the container and if the surface is uniform all over the container, then,

$$\dot{Q} = FA; \quad (1)$$

i.e., the rate of loss of product is directly proportional to the area of the container. \dot{Q} is also the rate at which vapors will accumulate in an enclosed space. Naturally, as vapors accumulate on the low concentration side of the barrier the driving force for permeation will be diminished thus F , G , and \dot{Q} will decrease as the vapor concentration approaches equilibrium. However, hazard levels due to flammable or poisonous vapor concentrations are generally well below such equilibrium values and the effect of F and \dot{Q} decreasing with time can be ignored in this context.

It is interesting to note that \dot{Q} generally exhibits no more than a weak dependence on the amount of lading in the container. Experimental verification of this observation is provided by Fig. 5 which shows that the slope of the weight loss curve does not change even though the bottle is only half full at the end of the experiment. In order to reduce the total amount of a product lost through permeation it is, therefore, desirable to keep the surface area of the container as small as possible.

For a container of arbitrary shape with volume V , the Area, A , is given by $A = \phi V^{2/3} F(r)$. ϕ is a geometrical constant depending on the particular shape which is chosen (cube, sphere, cylinder, etc.). The aspect ratio, r , is defined as the ratio between two principal dimensions of the container (for example, the diameter and the height in a cylinder). Table 3 lists ϕ and $F(r)$ for a variety of container shapes. It is easy to see that a spherical container will permeate the least for a given combination of lading and resin.

It is also easy to show that, if it is required to transport a fixed quantity of material which permeates and all other things are equal, maximum protection against permeation failure is gained by packaging the commodity in the minimum number of containers.

Another important determinant of the rate of loss from a container is the wall thickness. If G is now defined as the transmission rate for unit wall thickness and the container has a wall thickness ℓ then, $\dot{Q} = GA/\ell$. The parameter G defined in this way is a characteristic of the container material and the lading taken in combination. G can be solved for by computing

$$G = \frac{\ell \dot{Q}}{A} \quad (2)$$

and can be presumed to have some universal meaning only to the extent that the material is homogeneous. Note that the dimensions of G as defined in this way are: amount of substance per unit area per unit time times unit length. In industrial practice values of G are quoted for a standard unit of length, say 1 mm, and values of G for barriers of different thickness are obtained by dividing G for the standard thickness by ℓ , the desired thickness. The phrase "amount of substance" deserves some comment at this point. For gases the quantity of substances is usually expressed as cubic centimeters of gas at standard temperature and pressure (cc(STP)). For liquids one might use grams as the measure of "amount of substance". The SI system of units provides for amount of substance to be expressed in "moles" and that is how Tables 1 and 7 are expressed.

TABLE 2

UNITS FOR THE TRANSPORT OF MATTER THROUGH POLYMER BARRIERS

QUANTITY	SYMBOL	UNITS	FUNCTIONAL	DEPENDS ON
MASS TRANSFER	\dot{Q}	MOLES/TIME		SIZE AND SHAPE OF CONTAINER, VALUE OF F
PERMEATION FLUX	F	MOLES/TIME/AREA	$F = \frac{\dot{Q}}{A}$	THICKNESS OF WALLS, ℓ ; VALUE OF G
TRANSMISSION RATE	G	MOLES/TIME/AREA @ STANDARD THICKNESS	$G = F \ell$	PRESSURE DIFFERENCE, VALUE OF P
PERMEABILITY COEFFICIENT	P	MOLES/TIME/AREA/PRESSURE @ STANDARD THICKNESS	$P = \frac{G}{P_1 - P_2}$	NATURE OF LADING, NATURE OF RESIN, TEMPERATURE

TABLE 3

GEOMETRICAL PARAMETERS FOR VARIOUS CONTAINER SHAPES

$$A = \sqrt[2]{3} \phi F(R)$$

	DIMENSIONS	ASPECT RATIO R	ϕ	F(R)
SPHERE	DIAMETER, D	NOT APPLICABLE	$6 \frac{\pi}{6}$	1
CYLINDER	DIAMETER, D HEIGHT, H	H = DR	$6 \frac{\pi}{4}$	$\frac{R}{3} - \frac{2}{3} + \frac{2R}{3} \frac{1}{3}$
SQUARE PRISM	EDGE OF SQUARE, L HEIGHT, H	H = RL	6	$\frac{1}{3} \frac{1}{3} - \frac{2}{3} + \frac{2R}{3} \frac{1}{3}$

∞

NOTE: F(1) = 1 IN ALL CASES. ALSO THE MINIMUM VALUE OF F(R) IS AT R=1

Thus, the dimensions of G are expressed as moles/unit area/unit time as referred to a barrier of standard thickness.

Certain of the processes used to form polyethylene containers virtually guarantee that homogeneity will not be maintained. For this reason care must be taken in using eq. (2) to reduce results from different containers to a common footing.

As mentioned earlier chemical activity differences across the barrier provide the driving force for permeation. In the case of gases the pressure and in the case of liquids the vapor pressure are appropriate measures of activity.

This leads to the definition of yet another type of coefficient, called the permeability coefficient, and given the symbol P. The definition of P is;

$$P = \frac{G}{p_1 - p_2} \quad (3)$$

where p_1 and p_2 represent the (vapor) pressures on each side of the barrier. To the extent that the material is homogeneous P can be regarded as a parameter which is characteristic of the particular combination of lading and resin under consideration. It is the most desirable way to express the results of permeation measurements.

It is common industrial practice to express the results of permeation tests in terms of the percentage of the original mass which is lost over some period of time (for example, 1 year). This usage measures the economic impact of the permeation loss on the consumer, who is getting less product than he believes he is getting. Permeation results expressed in percentages are, however, irrelevant to assessing the hazards due to the release of hazardous materials through permeation. In this latter instance it must be remembered that, to a first approximation, material permeates out of a plastic container at the same rate whether the container is full or nearly empty.

Those who claim that filling a container half full (or less) is a way to "accelerate" a permeation test are obviously victims of the fallacy of expressing test results in percentage terms.

The discussion up to this point has treated permeation as a steady-state phenomenon. It has been assumed that one is primarily interested in the regime represented by the straight-line portion of responses such as those depicted in Fig. 5. Indeed, such features are of primary importance when one is dealing with relatively thin-walled containers. Fig. 3 depicts the time dependence of permeation flux through the walls of a container which has not been exposed to the lading for $t < 0$. To be noted is the fact that there is an initial period in which there is only a very small flux of material. This is followed by a rapid rise in the flux which is followed, in turn, by a leveling off at the steady-state value. The time to reach a value of 1/2 the steady-state flux, $t_{1/2}$, will be called the "induction time" in what follows. Other authors [6] refer to related times as the "time lag".

The induction time may be on the order of weeks for some combinations of ladings and containers. To a first approximation the induction time varies directly as the square of the wall thickness and inversely as the "diffusion coefficient" D. D is a parameter similar to P in that it depends upon the combination of lading, resin and temperature.

This characteristic induction period is one aspect of the protection which a container affords. Of course, once the container has been exposed to the lading the induction characteristics are altered. For this reason containers which are being reused should be regarded as not having an induction time.

Up to this point the discussion has centered around the transport of matter through the container walls. Another important problem is the uptake of material into the container walls. If C is used to denote the concentration (in moles/unit volume) of permeant in the container material after an infinitely long exposure, S the solubility,

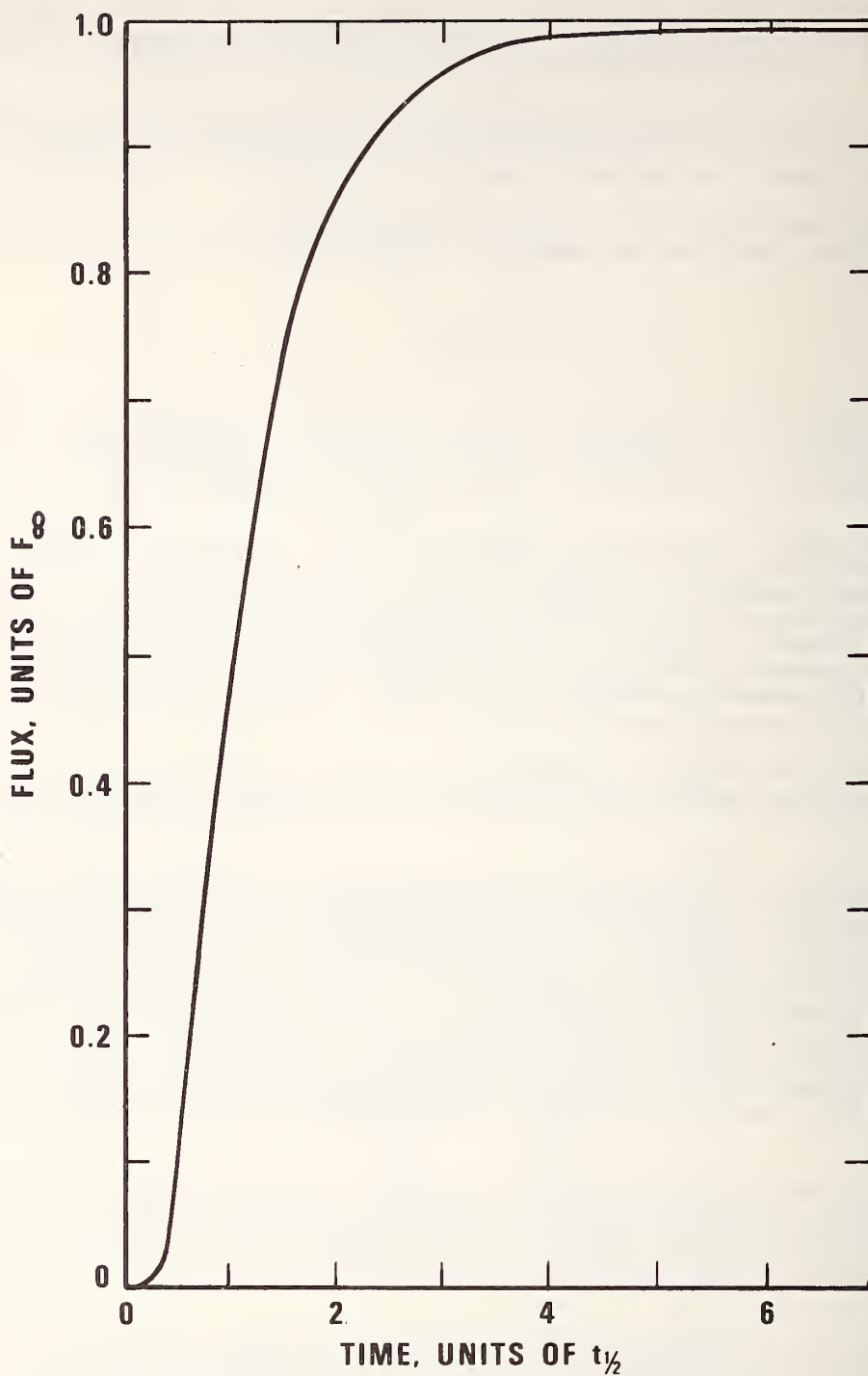


Figure 3 Time Dependence of Permeation Flux. F_{∞} is the Flux Value Obtained After an Infinite Time.

and p is, as before, the (vapor) pressure of the permeant then a relationship $C=Sp$ (known as Henry's Law) is frequently valid. If the concentration is measured as a function of time one finds that the time-scale of the experiment is governed by the induction time discussed earlier. Desorption of material from the container walls is simply the reverse of absorption (or uptake) and is, therefore governed by the same considerations.

It is easy to show [6] that the permeability, P , is related to the diffusion coefficient, D , and the solubility, S , by;

$$P = DS \quad (4)$$

This relation emphasizes that, for permeation to take place a lading must both diffuse into and be absorbed by the container material. Measurements of D and S require relatively sophisticated experimental methods. For this reason, eq. (4) does not appear to be a very good route to the estimation of permeability coefficients.

There are a number of calculations related to container performance which can be carried out once values of D and S are known. Persons who wish to estimate permeation performance would, of course, have to be familiar with these ideas. The interested reader will find these topics dealt with in detail in the books by Crank [7] and Crank and Park [6].

The evaluation of permeation performance involves answering two questions: 1) What is the tendency of a given lading to permeate polyethylene? and 2) How well does a container of a particular design resist permeation?

Fortunately, the answer to the first question is largely independent of the answer to the second. In more concrete terms this means that a ranking scheme in which a measured quantity, say P , is used to rank permeants with respect to a given resin is unlikely to be altered by changing resins. If one assumes that the number of ladings of interest is N and that the number of container designs is equal to M then under the "uncoupling" assumption most of the information needed to characterize a $N \times M$ combinations can be obtained from a number of measurements proportional to $N + M$. Neither N nor M have to grow very large before important economic advantages can be realized.

The results obtained in studies leading to the "Permachor" method of estimating permeation in polyethylene [8] demonstrate that such an approach may be feasible.

The outline of permeation phenomena presented above has necessarily been very sketchy. Such topics as non-Fickian behavior and the concentration dependence of D and S have not been discussed although they may be very important for certain hazardous materials. The attempt which has been made has been to provide a basis for a quantitative approach to permeation performance.

MEASUREMENT METHODS FOR PERMEATION PERFORMANCE

The previous discussion has outlined some quantitative features of permeation performance and some parameters which influence such performance have been identified. The question to be addressed in this section is "How can one actually measure permeation phenomena in the laboratory?"

Conceptually, the problem is very simple. One needs 1) a source of permeant 2) a means of supporting the barrier material and 3) a means of measuring the amount of permeant which has passed through the barrier in a given time interval. A certain amount of auxiliary equipment for maintaining temperatures and protecting personnel will also be required.

Actual measurement systems can cost from a few thousand to many tens of thousands of dollars. A simple system could be set up using equipment and procedures similar to those given in the Appendix. NBS experience indicates that values of P accurate to 10% or better can be estimated from such experiments. Further testing is presently being conducted with the goal of establishing standard conditions for such a test. For convenience, this test will be referred to as "the bottle test".

The term "bottle" is here used to indicate any free-standing object fabricated (except possibly for the closure) from the resin of interest. In the event that the specimens of barrier material which are available do not lend themselves to such treatment the "cup" test used for Water Vapor Transmission Rate (ASTM E 96) [2] could be used with suitable modification. This test is also a mass-loss test.

While the bottle test or the cup test yield quite satisfactory values for P they do not, in general, give good values for $t_{1/2}$. This is because the balances which are used to weigh heavy objects lack sensitivity to small mass changes.

To gain the required sensitivity one must go away from mass loss as the quantity to be measured and use a detector which signals the appearance of minute amounts of permeant on the outside of the "bottle".

In discussing detection systems one can divide the available range into two parts: 1) those sensitive to total quantity of material and 2) those sensitive only to selected components. Perhaps the simplest form of the former type of detector is represented by the Dow Cell (ASTM D 1434) [2] used to measure gas transmission rates of film materials.

Modern adaptations of the Dow Cell afford a high degree of sensitivity [9] and further research is underway to determine how useful it can be for organic vapors as permeants.

One example of the more specialized type of detection system is the Modern Controls OXTRAN [10]² system in which permeating gas is passed through a fuel cell and the current resulting from the presence of O_2 is measured. This system is in wide use in the packaging industry.

Other approaches use chromatographic or photometric [11] detection systems which can be "tuned" to the compound of interest. This latter feature is of interest when dealing with mixtures. Such systems have not yet become commercially significant. Up to this point the emphasis has been on the direct measurement of the permeability coefficient P. It should be noted, in passing, that P can also be calculated from measured values of D and S in eq. 4. Measurements of sorption and desorption kinetics provide an alternative route to the estimation of D and S [6]. The sorption and desorption methods may become the methods of choice when only small quantities of polymer are available or it is desired to limit the amount of the lading which one is working with.

Underlying any measurement system is the concept of standards. Data must be obtained and reported in a fashion such that comparisons with other data are meaningful.

In the case of permeation data this means that the quoted values should be obtained using resins (and fabrication procedures) which are carefully standardized and carefully characterized. This would allow for a quick and easy comparison of one permeant as being more of a problem than another.

In order to accomplish this degree of standardization it is desirable for some one party to obtain a large supply of well-characterized resin similar to those used in actual containers and, using carefully controlled processes, fabricate standard specimens, possibly in the form of bottles, from this resin. Careful characterization of a sample of the resulting specimens could be done so that users would be able to check their own test facilities and procedures. The remainder of the supply of specimens would be made available to persons who need to make permeation tests as they need them. The suggestion that the standard specimen be available in the form of bottles is based on the idea that tests such as ASTM D 2684 offer the most readily available route to a widely-used, standards based system of performance measurement for permeation.

²The identification of products of specific manufacturers is intended only in specifying experimental conditions. Such identification does not, in any way imply endorsement by the National Bureau of Standards.

The supply should be large enough to permit measurements using the original batch of bottles over a long period of time. Due to the wide range of resin compositions in industrial use it may be necessary to provide standard specimens made from more than one kind of resin. Tests aimed at establishing specifications for standard bottles are currently in progress.

The above survey of test methodology is intended to indicate that the principles of permeation methods are widely understood. The number of methods in common use is small and instrumental techniques tend to be rather specialized.

A need does exist to develop flexible, accurate instrumental methods for use in an industrial environment. A necessary corollary to the development of such methods is the development of standards for use in calibrating the instruments and characterizing the measurement systems. The ASTM, SPI and other elements of the consensus standards system should be persuaded to adopt a wider variety of standard methods of test for permeation of substances other than gases. These same bodies should also be encouraged to incorporate permeation tests into their specifications for resins.

Another important area of measurement concern is in the non-destructive evaluation of containers for reuse. Here the need is to identify chemical species which are absorbed in the container walls. Such species may, in time, desorb and contaminate a lading with disastrous effect.

From an instrumentation viewpoint the problem is one of spectroscopy or chromatography. Special fittings and vacuum systems could be devised which would sweep vapors from a 55-gallon drum into a trap. The substance in the trap could be vaporized for subsequent analysis by gas chromatography or infrared spectroscopy. The objection to these methods that they require skilled personnel is a very valid one and there may not be sufficient interest to justify the considerable expense.

The question as to whether a particular lading will be absorbed in the container walls and how long it will take to desorb can be answered quantitatively by using values of D and S from permeation experiments and qualitatively by observing that any substance with a reasonable value of P is bound to be absorbed.

In this brief discussion of measurement methods the emphasis has been on the evaluation of P (or G) as materials properties. In principle once P or G is known for a given combination of resin and lading the performance of a container made from the given resin can be calculated by straightforward engineering procedures. The next report in this series will give some examples of how this is done.

More subtle problems arise when one tries to calculate what G would be in a certain resin (say resin Y) when its value in another resin (say resin R) is given. There is a reasonable likelihood that such measurements can be made reliably enough for transportation purposes. There is work in progress which is evaluating literature proposals on the subject [8].

THE RELATIONSHIP BETWEEN PERFORMANCE DATA AND LEVELS OF HAZARD

In the earlier parts of this chapter a simple method for evaluating the tendency of a lading to permeate polyethylene, the "bottle test", was described. It was further indicated that the relative permeation performance of particular container designs could be evaluated using a relatively small number of tests with standardized loadings on actual shipping containers. In this section the two aspects of the problem will be combined and a demonstration will be made of how such results can be used to establish levels of hazards. Decisions as to whether such hazards are or are not acceptable in transportation and what steps must be taken to regulate them must be of necessity, be left to OHMO.

In assessing levels of hazard the first aspect must be the characteristics of the lading. Table 4 shows how loadings may be grouped into several (in this case 5) classes (categories). This grouping is dependent on two factors: 1) how rapidly the lading permeates polyethylene and 2) how much of it can be tolerated outside the container in an enclosed space. The first aspect is directly related to the G value. The second aspect is established from a knowledge of the toxicity or other hazards of the material. OSHA, FDA, or EPA may well be involved in the setting of such levels.

TABLE 4

LADING CHARACTERISTICS BY CATEGORY

CATEGORY No.	DESCRIPTION
0	PERMEATION THROUGH A STANDARDIZED REFERENCE CONTAINER IS TOO LOW TO BE DETECTABLE. REASONABLE QUANTITIES OF THE MATERIAL CAN BE TOLERATED OUTSIDE THE CONTAINER.
1	PERMEATION RATE IS MEASURABLE. SCALING LAWS INDICATE THAT A SOUNDLY ENGINEERED SHIPPING CONTAINER WILL KEEP RELEASE AT A MINIMUM.
2	PERMEATION RESULTS IN RELEASE WHICH COULD BE ANNOYING. SOME CARE SHOULD BE TAKEN IN SELECTION OF A SPECIFICATION PACKAGE.
3	PERMEATION LEADS TO RELEASES WHICH COULD CAUSE PROBLEMS. EXCEPTIONAL ENGINEERING AND HANDLING REQUIREMENT CAN BE IMPOSED WHICH BRING RISKS WITHIN ACCEPTABLE BOUNDS.
4	A PLASTIC CONTAINER WHICH WOULD KEEP RELEASE OF THIS MATERIAL WITHIN ACCEPTABLE LIMITS IS NOT AVAILABLE.

The following scenario illustrates the measurements and calculations which must be carried out in assigning a lading to a particular category (category 2 is this example). These tests are similar in spirit to those used to classify substances as flammable (e.g., 49 CFR 173.119). Measurements are made using a standardized reference container at 60 °C. The rate of weight loss in the steady-state is obtained. The permeation characteristics of the subject lading are found to be intermediate between two of the standard loadings used to compare actual shipping containers. Based on this data an estimate of the amount of material which will be released into a standard trailer body during a 48 hour period from a legal-limit load comprised of 30 gallon Spec. 34 drums is formed. If the resulting concentration is less than 1/10 of the level set by OSHA for a 20 minute exposure to the vapor but is greater than 1/1000 of the OSHA level then the lading shall be assigned to Category 2.

The above is merely an illustrative scenario and not a specific proposal. A great deal of work must be done before any such proposal can be made. The ranking in Table 4 gives a rough indication of the degree of risk associated with failure because of release through permeation. The higher the ranking, the greater the risk. In this respect the ranking system parallels that established by NFPA for evaluating the flammability, health and reactivity hazards of materials [12].

The reactivity question was omitted from Table 4 in order to keep the table simple. In any final analysis the risk associated with a given lading becoming contaminated as a result of permeation of oxygen or water (to name only two common contaminants) into the package must be made a part of the ranking scheme.

Table 4 is qualitative in nature and is intended only to convey the range of situations which exist with respect to loadings which have been or might be contemplated for transportation in plastic packagings.

The other side of the question, the performance of actual shipping containers is addressed in Table 5. The title of the table uses the word "package" to convey the idea that the container must be tested together with its overpack where appropriate.

The tests which are used to establish which category a design should fall into are carried out using certain standardized loadings. The higher the category that a container is assigned to on the scale of Table 5, the more stringent are the performance requirements imposed on it. Category 4 containers might involve such special engineering treatments as surface sulfonation [13] or layers of material with improved barrier properties [14]. Category 3 might include some of the better containers covered by the present Specification 34.

Table 5, like Table 4, is only intended to give some idea of the range of choices which are available. Taking each aspect by itself there is no way to assess the hazards presented. A substance which presents serious problems in terms of permeation can be shipped safely if a properly designed container is used. On the other hand, a container with low performance should perhaps not be used to ship commodities which pose even minimal hazards.

These ideas are summarized in Table 6. This table is in "matrix" form with the lading categories labeling the columns and the container categories labeling the rows. At the intersection of each row and each column is a number which categorizes the level of risk presented by the particular combination of package and lading. Generally speaking the higher the level of risk derived for a given combination of package and lading using this "matrix" procedure the more drastic are the consequences of the failure of the combination.

TABLE 5

PACKAGE CHARACTERISTICS BY CATEGORY

CATEGORY No.	DESCRIPTION
0	PERMEATION TESTS WITH STANDARD LADINGS INDICATE THAT THIS CONTAINER IS A POOR BARRIER.
1	PERMEATION TESTS INDICATE THAT THIS CONTAINER WILL MAINTAIN RELEASE WITHIN ACCEPTABLE LIMITS FOR A LOW-HAZARD MATERIAL.
2	SUCH PACKAGES REPRESENT GOOD SOUND INDUSTRIAL PRACTICE. PERMEATION TESTS SHOW THAT RELEASE IS WITHIN ACCEPTABLE LIMITS FOR ALL BUT THE MOST TROUBLESOME LADINGS.
3	SUCH PACKAGES REPRESENT THE BEST LEVEL OF NORMAL INDUSTRIAL PRACTICE. RESIN SELECTION, FABRICATION PROCEDURES, QUALITY ASSURANCE PROCEDURES, ARE ALL ABOVE THE NORM.
4	SPECIAL ENGINEERING STEPS HAVE BEEN TAKEN TO LIMIT PERMEATION. SUCH STEPS MAY ONLY HELP FOR ONE CLASS OF LADINGS. CONTAINER IS INTENDED FOR "SPECIAL SITUATIONS", OR "STATE OF THE ART" PROBLEMS.

TABLE 6

RISK LEVEL AS A FUNCTION OF LADING AND PACKAGE

LADING PACKAGE	0	1	2	3	4
0	0	5	5	5	5
1	0	3	3	5	5
2	0	2	2	4	5
3	0	1	2	4	5
4	0	1	2	3	5

CATEGORYDESCRIPTION

- 0 NO PERMEATION HAZARD IS PRESENTED BY SUCH A COMBINATION OF LADING AND PACKAGE.
- 1 ORDINARY CARE IN HANDLING AND STORAGE SHOULD BE SUFFICIENT TO GUARD AGAINST RELEASE BY PERMEATION.
- 2 THE SET OF MEASURES WHICH ARE ORDINARILY TAKEN FOR MATERIALS WHICH ARE KNOWN TO BE HAZARDOUS SHOULD BE EXERCISED.
- 3 THE POTENTIAL EXISTS FOR SERIOUS RISK TO LIFE OR PROPERTY IN A LIMITED NUMBER OF SPECIAL SITUATIONS. CARE SHOULD BE TAKEN TO AVOID THESE.
- 4 THE POTENTIAL FOR RISK TO LIFE AND PROPERTY IS RELATIVELY HIGH. CHOICES WITH REGARD TO TRANSPORTATION OF THE COMMODITY ARE LIMITED. SPECIAL VIGILANCE MUST BE MAINTAINED.
- 5 SUCH SITUATIONS PRESENT UNACCEPTABLE RISKS.

Once again this table is intended only to illustrate a range of available alternatives. It is easy to appreciate that there may be a large number of borderline cases where a particular combination should be moved up or down one notch. This system as outlined does provide for advances in technology which introduce improved products. It also affords a relatively straightforward guide for making the decisions which must sometimes be made when new information about a particular combination of package and lading becomes available as, for example, when a substance is discovered to have a previously unknown toxicity.

PERMEATION AND REUSE

The previous section of this chapter was a demonstration of one possible way to incorporate performance data into a system for assessing hazards. One aspect of the problem which was not considered was reuse.

From the permeation point of view the most obvious difficulties are caused when a substance which has been absorbed in the container walls from one episode of filling, shipping, and storage is desorbed to contaminate a (possibly different) lading in a subsequent episode. It is fair to say that this problem will exist with any substance which permeates polyethylene to any extent at all. Whether the condition poses a hazard or not is a function of the properties of the contaminated lading and the use to which it is to be put. If, for example, the lading is a food product (as some hazardous materials are) then any substance which desorbs into it from the walls of the container may fall within the purview of the Food and Drug Administration.

The entire question of reuse is centered on 49 CFR 178.19 (Specification 34) which provides for an all-plastic container which is reusable but which does not limit the conditions under which the container may be reused. The guidelines for reuse laid down in 49 CFR 173.28 and 49 CFR 173.24, since they are strictly qualitative, are difficult to comply with. It is possible to propose methods for non-destructive evaluation of residual permeants in containers. Such methods could be based on chromatographic or spectroscopic detection. The dairy industry is presently using a system based on a flame-ionization detection principle for examining milk containers which have been returned for refilling [15].

The number of possible combinations of loadings and contaminants is so large that a case-by-case examination of the problem is impossible. Some general guidelines can, however, be offered.

First of all the risk resulting from contamination of the lading must be taken into account when a reusable container is being considered. This could well result in the assignment of a lading to a higher risk category than it would otherwise receive. Secondly, the container performance level may have to be downgraded when a container which may have been exposed to a different lading is to be reused to ship a lading which is sensitive to contamination. The "matrix" procedure outlined in Table 6, should result in a higher level of risk being assigned to such reuse situations.

If shipping containers are placed in dedicated service, i.e., used to ship only one lading and returned to the shipper for refilling, the risk factor arising from contamination of the lading may be reduced. The risk factor is bound to increase even when a given container is reused in dedicated service for the simple reason that no one can be absolutely certain that the container will not be diverted to some other use through ignorance or inadvertence. It should also be remembered that there are cases where the induction time effect provides an appreciable part of the protection against permeation. In such cases a reused container is bound to provide less protection than a fresh one. On this basis the conclusion that reuse of plastic containers for hazardous materials offers significantly increased risks appears to be inescapable. These increases in risk are associated, in large measure, with the permeation properties of polyethylene. Thus, a screening system for evaluating the tendency of loadings to permeate polyethylene would serve to identify loadings which would cause problems in reusable containers. Similarly performance criteria which would evaluate container designs with respect to their qualities as barriers to permeation would also serve to identify designs which would be relatively more satisfactory in a reuse environment.

It should, however, be pointed out that the performance criteria used in setting risk levels in the preceding section are largely based on the materials properties P or G. In the evaluation of absorption and desorption phenomena the diffusion coefficient D is responsible, together with the wall thickness ρ , for regulating the time-scale of the processes. Therefore, cleaning methods which would seek to make contaminated containers available for reuse must be based on somehow increasing the value of D. This can be accomplished by raising the temperature, softening the polyethylene using solvents, or converting the absorbed species to one with a larger value of D. In the latter two approaches steps must be taken to remove the agent used for the purposes mentioned. Any such reconditioning procedures would necessarily include characterization of the amount (and possibly the chemical nature) of the permeant remaining. As pointed out earlier in this report inexpensive equipment usable by unskilled personnel is not currently available.

The number of substances which permeate polyethylene is large enough to render any container which has been in reuse for a significant period of time practically uncharacterizable as to the various permeants which may be absorbed in its walls. Furthermore, there is no evidence that procedures can be developed which can materially aid in the removal of absorbed materials from the walls of a container without compromising the container.

These findings raise serious doubts as to whether indiscriminate reuse of plastic shipping containers such as is encouraged by the existing Specification 34 and the exemptions based thereon is in the public interest.

CONCLUSIONS AND RECOMMENDATIONS

This report has sought to demonstrate that a performance measurement system using very simple ideas and techniques can be devised to evaluate hazards arising from permeation failure of plastic shipping containers.

As a first step in this process, permeation failures, which are somewhat peculiar to plastic containers, must be identified. Some examples of failures produced under laboratory conditions were described. As the next step in the process of constructing a performance measurement system, a simple method of test, the "bottle test", which has already been developed by others for similar purposes was described. This presentation was followed by a brief outline of some other ways to measure permeation. The question of how to estimate the extent of risk arising from permeation was then addressed by introducing a "matrix" scheme which combines the characteristics of the lading and the container, determined separately, into a ranking which represents the level of hazard.

Once a performance measurement system has been constructed it should be incorporated into the regulatory system. CFR 49 does not at present, address itself to the problem of permeation in such a way as to permit the use of measurement results.

The loadings presently being contemplated for shipment in all-plastic containers under existing exemptions include flammable organic solvents whose permeation rate with respect to polyethylene can be shown to create a hazard. This alone is enough to demonstrate that the approach presently being used to evaluate these risks is seriously deficient.

Any system which is devised should call for the reporting of quantitative results obtained under carefully controlled and standardized conditions. Under such a system there would be less need to periodically "rediscover the wheel" and decisions could be taken more quickly and in greater confidence that they reflect field experience.

There is a need for standards at each step of the process. Further work, which is currently in progress, is expected to provide the needed standards. In addition to the work aimed at providing standards studies of the permeation behavior of mixtures and of the effect of permeants which alter the materials properties of polyethylene should be made. The present work which has been concerned with individual reagents addresses only the tip of the iceberg.

APPENDIX

PERMEABILITY OF FOUR-OUNCE POLYETHYLENE BOTTLES TO SELECTED LADINGS

INTRODUCTION

The purpose of these measurements was to assess the suitability of ASTM D 2684-73 (Standard Recommended Practice for Determining Permeability of Thermoplastic Containers) or suitable modifications thereof as a means of screening ladings for their level of activity as permeants in polyethylene. The preliminary measurements reported herein were intended first of all to reveal the range of variation to be expected in the transmission rate, G. A secondary purpose was to determine if suitable results could be obtained with inexpensive equipment.

EXPERIMENTAL PROCEDURE

Four-ounce blow-molded polyethylene bottles with screw-on caps were tested with various ladings. Since explosion proof equipment was not available, no ladings with low flash points were used. A wire loop was attached around the lower neck of each bottle as shown in Fig. 1. The bottles could be weighed empty and also with the wire loop in place. The bottles were filled about three-fourth's full in a fume hood. One hundred to two hundred grams of reagent were required for each bottle. The caps were screwed on with a ring of silicone rubber adhesive inside to form a gas tight seal (except that an epoxy seal was used on the bottles containing hydrofluoric and hydrochloric acid).

After allowing the sealant to cure for an hour or two the total weights were taken and the bottles were placed inside an oven constant temperature chamber with forced air circulation operating at the desired temperature. Two empty bottles were also placed in the oven as a control. A pipe was connected from the vent on the incubator to the laboratory air exhaust system to keep the oven under slightly reduced pressure, so that the permeating vapors would not spread throughout the laboratory. The bottles were set in glass crystallization dishes to protect the heating coil at the bottom of the oven in case of bottle failure.

Tests were run at temperatures of 40, 50 and 60 °C. Each lading was run at two different temperatures depending upon its permeation rate. (See Table 7). The first effect was a buildup of pressure inside the bottle, but as the material permeated a reduced pressure resulted.

The bottles were transferred one at a time to a second smaller oven operated at the test temperature for weighing. A trip balance on top had a wire hook passing through a tube into the chamber (see Fig. 4). Where hazardous materials which permeated at a rapid rate were involved, safety glasses, rubber gloves, and a respirator were worn during the transferring operation. Weights (to the nearest tenth of a gram) and the times were recorded for periods of a week or less up to a month or more depending upon the rate of permeation.

This experimental method did not conform to that set forth in the ASTM procedure in certain details:

- (1) Rather than taking the bottles out and allowing them to cool before weighing, they were weighed at the test temperature in a second oven. In this way, weights could be taken more frequently without influencing the test time.
- (2) A less sensitive balance reading only to tenths of a gram was used. This corresponds to 0.1% for 100 grams of solution and should be sufficiently accurate for this purpose.
- (3) The bottle caps were sealed with a silicone rubber adhesive rather than a plastic to plastic heat seal.

TABLE 7

PERMEATION THROUGH FOUR-OUNCE POLYETHYLENE BOTTLES

BOTTLE	TEMPERATURE °C	NAME OF CHEMICAL	MOLECULAR WEIGHT	AVERAGE WEIGHT LOSS IN TWO WEEKS GRAMS	RANGE IN PERMEATION IN MOL/M ² 24 HR.	
					@	1 MM THICKNESS
TYPE #1	40	TRICHLOROBENZENE	181.45	86.2	2.17	2.20
		O-DICHLOROBENZENE	147.00	96.7	2.94	3.12
TYPE #1	50	EMPTY		00.0		
		HYDROFLUORIC ACID ^A	20.01	0.2	.03	.03
		BUTYL STEARATE	340.59	1.3	.01	.03
		HYDROCHLORIC ACID ^A	36.46	1.4	0.17	0.17
		DIPHENYL METHANE	168.24	14.0	0.35	0.41
		BUTYL BENZOATE	178.23	15.6	0.36	0.44
		TETRADECANE	198.40	25.3	0.54	0.64
		TRICHLOROBENZENE	181.45	169.7	3.93	4.68
		O-DICHLOROBENZENE	147.00	158.0	4.66	5.23
		TYPE #2	50	TRICHLOROBENZENE	181.45	20.6
O-DICHLOROBENZENE	147.00			22.9	0.62	0.62
TYPE #1	60	BUTYL STEARATE	340.59	0.3	.01	.01
		DIPHENYL METHANE	168.24	24.1	0.54	0.79
		BUTYL BENZOATE	178.23	29.8	0.64	0.89
		TETRADECANE	198.40	44.2	0.91	1.14

NOTE A: THE CAPS ON THESE BOTTLES WERE SEALED WITH EPOXY RATHER THAN A SILICONE RUBBER ADHESIVE.

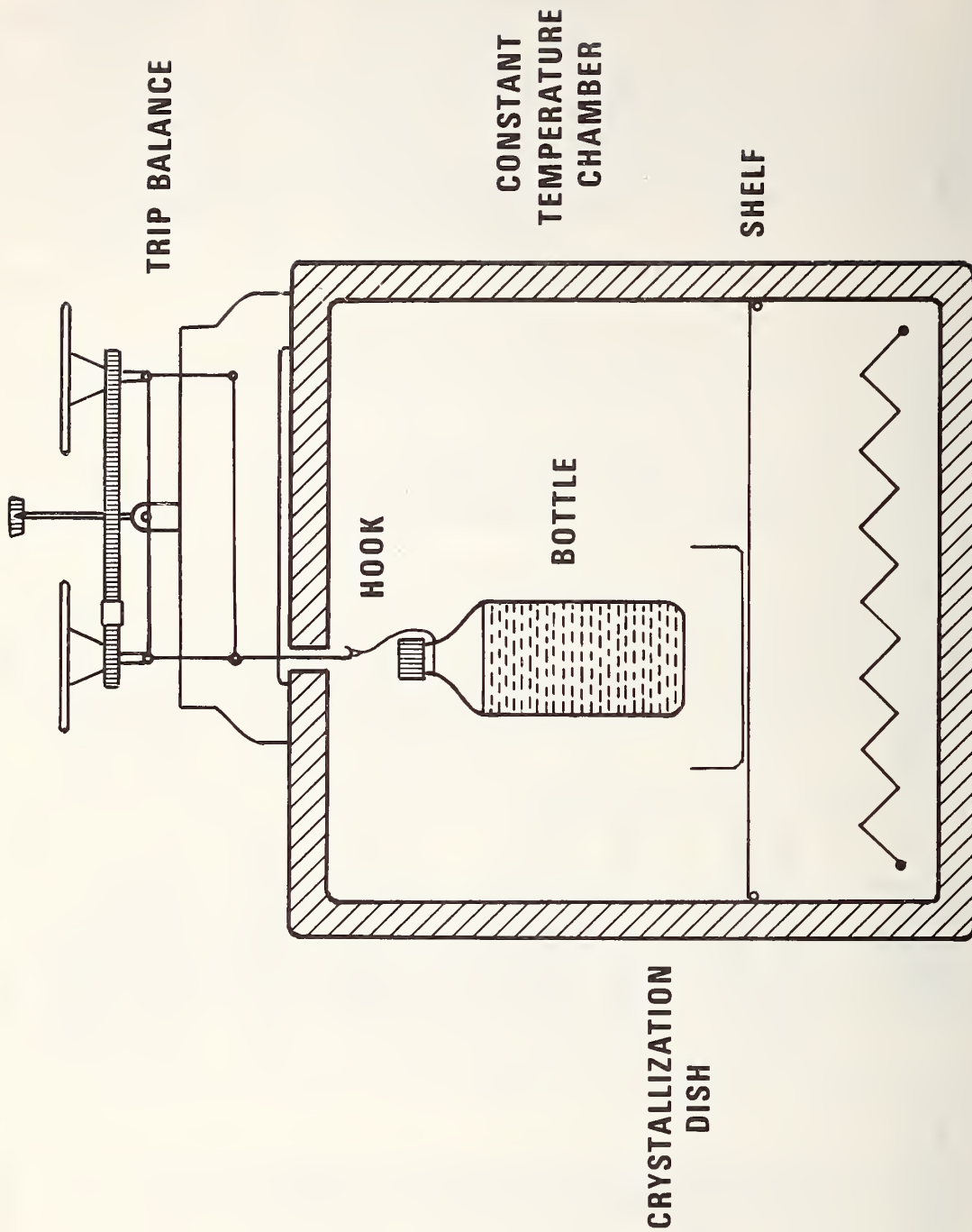


Figure 4 Method of Weighing Bottles (Schematic)

(4) The laboratory temperature was maintained at 22.5 to 0.5 °C, but no provision was made for controlling the relative humidity to $50 \pm 5\%$.

(5) Each bottle was set in a glass crystallization dish rather than having one tray below all the bottles. This is a minor modification.

(6) Two bottles, rather than three, were tested for each condition since it was desired to survey a number of materials.

Two different types of bottles were tested. Dimensional measurements were made on two bottles of each type with a vernier calipers. Then the bottles were cut up and the thickness measured with a micrometer. The densities of pieces cut from different areas were measured by hydrostatic weighing (ASTM D 792, Method A-1). These values are summarized in Table 8.

As discussed in this report and shown in Table 2, the mass transfer rate \dot{Q} is related to the transmission rate G by:

$$\dot{Q} = G \frac{A}{\ell} \quad (A-1)$$

where A is the area and ℓ is the thickness. The bottles used in this experiment did not, however, possess a uniform thickness. Thus A and ℓ in eq. (A-1) must be treated as "effective area" and "effective thickness". The density, while not strictly uniform throughout the walls of the bottle, was sufficiently uniform to permit the assumption that G is everywhere the same. Under this assumption \dot{Q} could be written as:

$$\dot{Q} = G \left(\frac{A_B}{\ell_B} + \frac{A_S}{\ell_S} + \frac{A_T}{\ell_T} + \frac{A_N}{\ell_N} + \frac{A_C}{\ell_C} \right) \quad (A-2)$$

where B, S, T, N, and C stand for bottom, side, taper, neck and closure, respectively. Each of these components could be treated as a simple geometrical shape. The bottom and closure as discs, the side and neck as cylinders and the taper as the frustum of a cone. The individual ratios (A/ℓ) may be added to get an equivalent value for the entire bottle:

$$\frac{A_E}{\ell_E} = \frac{A_B}{\ell_B} + \frac{A_S}{\ell_S} + \frac{A_T}{\ell_T} + \frac{A_N}{\ell_N} + \frac{A_C}{\ell_C} \quad (A-3)$$

For a type #1 bottle $\frac{A_E}{\ell_E} = 155.3 \text{ cm}^2/\text{mm}$ and for a type #2 bottle $\frac{A_E}{\ell_E} = 178.7 \text{ cm}^2/\text{mm}$.

The value of the equivalent area for a bottle depends upon what value is used for the equivalent thickness. Since almost 90% of the mass transfer takes place through the sides, it seems reasonable to use the average thickness of the sides to calculate an equivalent area. For a type #1 bottle with sides 0.876 mm thick this equivalent area is 136 cm^2 . For a type #2 bottle with sides 0.698 mm thick the equivalent area is 125 cm^2 . In ASTM D 2684-73 the area of a standard container is given as 154 cm^2 . The thickness is not specified but is to be calculated from the area and weight of the bottle and the density of the material in it.

TABLE 8

PHYSICAL CHARACTERISTICS OF BOTTLES

	TYPE #1		TYPE #2	
	AVG. WT.	STD. DEV.	AVG. WT.	STD. DEV.
	G	G	G	G
BOTTLE ALONE	16.56	0.14	12.37	.03
BOTTLE & CAP	28.95	0.11	25.78	.06

DIMENSIONS IN CM (SEE NOTE 1)

O.D. NECK "D"	2.1	2.0
O.D. BOTTLE "D"	4.70	4.51
OVERALL HEIGHT "L"	10.9	10.3
HEIGHT TO BASE NECK "H"	9.2	8.9
HEIGHT TO TAPER "H"	8.1	7.7

THICKNESS IN MM (SEE NOTE 2)

	BOTTLE #35	BOTTLE #36	BOTTLE "A"	BOTTLE "B"
BELOW NECK	2.57		1.70	1.73
SIDE	0.89	.86	0.71	0.69
BOTTOM	2.54	2.59	1.61	1.70

DENSITY IN G PER CM³ (SEE NOTE 3)

BELOW NECK	0.9190	0.9190	0.9437	0.9429
SIDE	0.9171	0.9169	0.9406	0.9405
BOTTOM	0.9192	0.9179	0.9434	0.9446

- (1) THESE VALUES ARE ACCURATE TO $\pm .05$ CM.
- (2) ERRORS IN THICKNESS VALUES ARE LESS THAN 0.050 MM.
- (3) DENSITY VALUES ARE CORRECT TO $\pm .0004$.

RESULTS

Type #1 bottles were made of a low density semi-transparent polyethylene. They were slightly larger and had thicker walls than type #2 bottles which were made of a high density polyethylene. In each case the bottle was thicker at the neck and tapering portion below the neck and at the bottom than it was on the sides. For both types of bottles the density of the thicker sections was greater than that of the thinner ones. This is probably due to the fact that the thicker areas cool more slowly after molding and have more time to crystallize than the thinner regions.

After an induction period which was too short to observe in most cases, a plot of the observed weight against time gave a straight line within experimental error (see Fig. 5). From the slope of a straight line fitted to the experimental points by eye, the rate of weight loss could be determined. The results are shown in Table 7. Dividing the rate of weight loss in grams per day by the molecular weight gives the mass transfer rate Q in moles per day. When Q is divided by the equivalent area of the bottle and multiplied by the thickness corresponding to this equivalent area, the transmission rate G , which is also shown in the table, is obtained.

The lowest permeation rates among the chemicals tested were hydrofluoric acid, hydrochloric acid, and butyl stearate, while the highest rates were for dichlorobenzene and trichlorobenzene. The permeation rate increased with the temperature and there is some indication that the variation in rate from bottle to bottle was greater for larger values of G .

CONCLUSIONS

The experiments whose results are summarized in Table 7 were limited, by safety considerations, to a few ladings whose risks, particularly in terms of flammability were judged to be acceptable.

The high permeation rates for trichlorobenzene and o-dichlorobenzene are roughly in agreement with the guidelines in Table 1. The same is true of the values for hydrochloric and hydrofluoric acid.

The fact that tetradecane shows quite an appreciable permeation rate in spite of its great chain length indicated that saturated hydrocarbons such as are found in petroleum products would have quite high permeation rates. More detailed studies, aimed at evaluating the usefulness of the "permachar" [8] correlation are presently underway.

The reagents chosen for these experiments are of rather limited industrial interest when compared with others such as benzene, xylene, toluene, and cyclohexane. These latter substances will have to be tested when a more satisfactory oven becomes available.

Many more measurements will be needed to establish the amount of variability to be expected from the bottles and the best methods for making a satisfactory seal. The temperatures used in this experiment were within those considered to be applicable for brief exposures during transportation. In order to make more realistic calculations which would predict packaging performance over longer time periods it is necessary to extend the measurements to temperatures in the range of 20 °C.

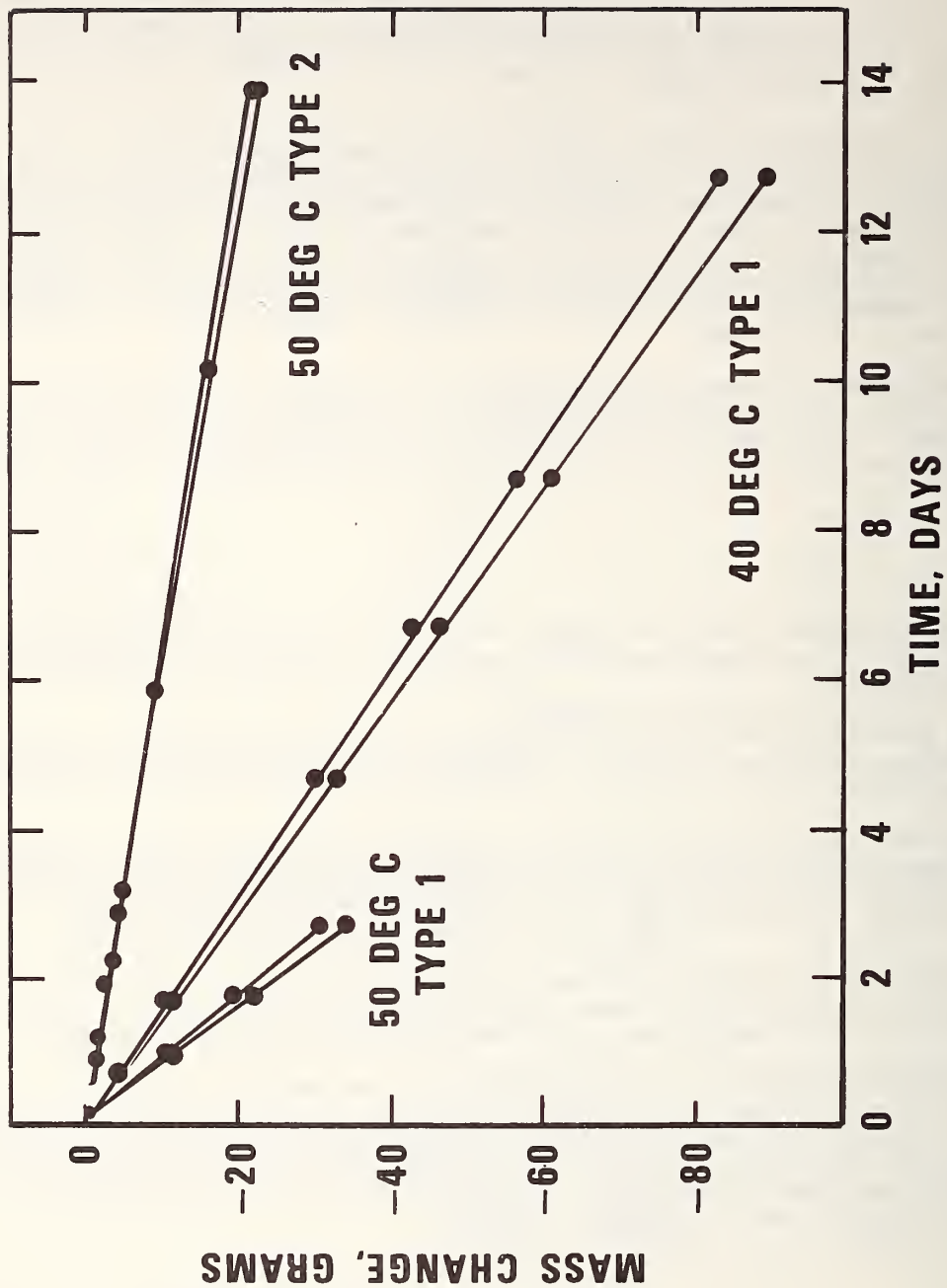


Figure 5 Permeation Loss of o-Dichlorobenzene From Four-Ounce Polyethylene Bottles Under Various Conditions. See Table 8 for descriptions of bottle types.

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