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PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

PART IV. STANDARDIZING PERMEATION MEASUREMENTS

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FINAL REPORT

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NOTICE

PREFACE

This report is Part IV of a series prepared for the Office of Hazardous Materials Operations under Research Contract DOT AS-50074. Part I dealt with performance characteristics of industrial plastic shipping containers which were influenced by mechanical materials properties. Part II surveyed the importance of permeation factors to the performance of containers for hazardous materials transport. Part III addressed the problem of stress-cracking as it relates to plastic containers.

Part IV takes up the problem of standardizing permeation measurements and using the results to ascertain the suitability of ladings or container resins.

Phillips Petroleum Company furnished crucial experimental materials. We also wish to thank Mr. Charles Speas of the Hedwin Corporation for the encouragement and assistance he has given to this work. We are also grateful for the support lent by individual members of the Plastic Drum Institute of the Society of Plastics Industry and members of various committees of the ASTM.

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1. INTRODUCTION

It has long been recognized that permeation is a serious concern to makers and users of plastic shipping containers. There is general agreement about the chemicals which are and are not compatible with polyethylene (the most widely used polymer for shipping containers). A detailed empirical understanding of the problem has been gained through the work of Bent and Pinsky [1][1] which was extended by Salame [2]. The problem has assumed new importance in recent years because of the increasing number of requests to ship an ever-widening variety of hazardous materials in improved plastic shipping containers. In the absence of a systematic practice for making quantitative predictions of permeation performance, it has been necessary to treat each new proposed combination of lading and container as unique. The upshot is laborious, often repetitious, testing accompanied by delays in making packaging decisions.

This report results from a request by the Office of Hazardous Materials Operations of the Department of Transportation to the National Bureau of Standards for assistance in evaluating the question of compatibility in plastic shipping containers. The preliminary findings of this study have already been reported elsewhere [3]. Our earlier work showed that polyethylene was by far the most important resin to be considered in evaluating plastic shipping containers. We also found that permeation failures could be manifested in many ways. All of these failures are, however, the result of transport of substances into and through the walls of the containers by a driving force that arises from the concentration gradient between the inside and the outside of the container. It was recognized that for such transport to occur, the permeant must be soluble in the polymer, as well as being capable of diffusing through the polymer. It is possible to assess these tendencies in various ways. The simplest way we found is to measure the change in mass as a function of time for a container made from the resin in question and filled with the permeant in question.

This approach is used by a number of companies who work with plastic shipping containers but they do not appear to be using practices which would allow all of their data to be put on a common basis for use in making permeation performance predictions. Many manufacturers of shipping containers do not do any permeability testing at all. The necessary testing is done either by their customers, the shippers, or by those who supply the container manufacturers with resin. In the above respects, the measurement situation with respect to permeability measurements may be said to be chaotic.

One way to bring order out of chaos is by the application of standards. We consider the following kinds of standards to have potential benefit in helping to put permeability measurements on a more orderly footing:

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[1] Numbers in square brackets refer to the list of references at the end of this report.

1. Standard methods of test examples include ASTM D 2684[2] and ASTM E-96.
2. Standardized devices - examples include calibrated weights, standard reference materials, and water vapor test cups.
3. Recommended practices - examples include ASTM E-104 and ASTM E-177.

There are other kinds of standards which may be useful in addition to those listed above. The process of developing standards requires the broadest possible participation by those whose interests are at stake. For that reason, we will not present draft standards in this report, but we will concentrate on presenting information which can serve as a base from which standards might be developed by interested parties in the technical community.

One theme of this report will be to highlight the role of standards in making permeability measurements and predictions.

We are confident that suitable standards will find ready acceptance by the user community because they will result in cheaper, yet more reliable, measurements. Performance measurements on full-scale industrial containers are costly and time-consuming. Data can be obtained much more rapidly, cheaply and accurately using laboratory scale devices and it is a straightforward matter to scale the results up to production designs. If all of the data are obtained in a manner which allows easy intercomparison, it becomes possible to make tabulations and formulate models describing interrelationships. We expect that one consequence of a standards-based measurement system would be the production of tabulations of critically analyzed data which would mean that many measurements which are nothing but duplications of ones that have already been made can be eliminated entirely.

There are, as yet, no theories which can be used to correlate the permeabilities of a large number of different ladings. We must, therefore, resort to an empirical approach to making these correlations. Salame undertook such an effort many years ago [2] and the result was his "permachor" scheme. The second theme of this report will be to evaluate Salame's scheme quantitatively and seek ways to adapt it to our needs.

In this report, we will treat permeability as a bulk property of a polymer. Most of our quantitative work will, therefore, apply only to containers in which the polymer (polyethylene in most cases) defines the barrier properties. Various composite container designs will still have to be treated as special cases.

2. THE PERMACHOR - AN EMPIRICAL DEVICE FOR CORRELATING PERMEATION MEASUREMENTS

Using a large data base which had been gathered by Bent and Pinsky for the U. S. Air Force[1], Salame[2] was able to arrive at a simple correlation between measured values of mass loss from standardized bottles, certain properties of the permeant

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[2] Since this report will make frequent reference to various documents produced by ASTM, we have collected the information the reader needs to make reference to these standards in Appendix A. In the text of this report such standards will be referred to only by their number designation.

molecules, and certain (unspecified) properties of the polyethylene resins used in the bottles. This correlation took the form:

$$\dot{Q}(T,r,x) = \dot{Q}(T_0,r,s) \exp [a_r(\frac{1}{T_0} - \frac{1}{T})-b_r(\pi_{xr}-\pi_{sr})] \quad 1$$

$\dot{Q}(T,r,x)$ is the rate at which mass of molecule x is lost from a bottle made from resin r at a temperature T. $\dot{Q}(T_0,r,s)$ is the same quantity evaluated at a reference temperature of T_0 with a standard lading, s. The parameters a_r and b_r are properties of the resin. The quantities π_{xr} are parameters which depend on the choice of permeant molecule and, to a lesser extent, the choice of resin. The π values are called permachors. A natural scale is imposed on the values of the permachors by requiring that π=n for a normal alkane containing n carbon atoms. For molecules other than normal alkanes, the permachors are calculated by means of;

$$\pi_{xr} = \sum_g n_{xg} \pi_{gr} \quad 2$$

where n_{xg} is the number of groups of type g in molecule x while π_{gr} is the group permachor for a type g in the resin r. Permachors can alternatively be defined as effective numbers of carbon atoms which characterize the interaction which gives rise to permeation between a molecular species and a polymer matrix. In this latter definition, the permachor can be treated as a measurable quantity rather than one derived from a calculation. The permachor values for the n-alkanes then appear as fixed points for calibrating the scale of effective carbon atom numbers.

The amount of data which is required in order to extract values for group permachors is very large and acquiring this data involves measurements on substances of limited industrial interest. Group permachors might be of considerable interest to those who wish to study the fundamental mechanisms of molecular transport in polymers.

The parameters a_r and b_r for a given resin can be determined from a relatively small set of measurements on permeants whose permachor values are known, either a priori as in the case of normal alkanes or from previous measurements using a different resin. Once the parameters a_r and b_r are known, it is possible to make a prediction of the permeability at any temperature by making a single permeability measurement at an appropriately chosen standard temperature. If the permachor value of the permeant species has already been established, all that is needed to make a permeability prediction, in addition to a knowledge of a_r and b_r, is a single measurement on a standard molecular species. The preceding two sentences summarize the essence of eq. 1. The utility of the scheme lies in the observation that the permachors are only a very weak function of the differences between resins in a given family and that almost all permeant species posess very similar temperature coefficients of permeability.

The use of permachor values which have been obtained under one set of conditions to make a prediction under a different set of conditions carries with it a certain risk. Incorrect data may have been used, the situation may be an anomalous one, or some precondition for using the method may not be fulfilled. A certain amount of checking of predictions against measured values is necessary to assure the continued integrity of a scheme like the permachor.

The risks due to failed predictions can be minimized by making the measurements at the upper end of the useful temperature range. This serves to protect against anomalously high temperature coefficients. Effects such as solvation of the polymer by the permeant and stress cracking are also accentuated at elevated temperatures. A temperature of 60°C can be safely regarded as meeting the criteria for a suitable test temperature [4].

Measurements made at elevated temperatures are representative of performance at lower temperatures for longer periods of time. In this sense, high temperatures can be said to accelerate the testing. Equation 1 is useful in estimating the amount of acceleration.

3. EXPERIMENTS TO EVALUATE THE PERMACHOR CONCEPT

In this section of the report, we describe a series of carefully controlled experiments which were undertaken in an effort to find characteristics of polyethylene materials which could be used to standardize permeation measurements on industrial plastic shipping containers. The design of the experiments was based on the findings on permachors. The subsequent analysis of the data was such as to allow alternative models to fit the data. The present experiments, like those in our earlier report, were subject to the constraints that they had to be easy to carry out and they had to use equipment which is inexpensive and commonly available.

The factors which we investigated were: the effect of test temperature (3 levels), the effect of alkane chain length (7 levels), and the effect of test bottle design (2 levels). The way these factors related to one another is shown in Table 1. After the experiments had been partially completed, an additional experiment was run in order to check the effect of our procedure for sealing the bottles. Based on the results from this experiment, the step of sealing the bottle threads with a silicone rubber was eliminated in subsequent experiments. Type 3 and type 4 bottles differ from one another only in this matter of sealing.

A proper method of test should include enough information to enable others to obtain precise and accurate values of the quantity that is being measured. The method should describe what measurements to make and what to do with the resulting data. Limitations on the method and precautions to be observed in carrying it out should be stated. Once a method of test has been developed, it should be subjected to interlaboratory evaluation (see ASTM D2188) to ensure that the hoped-for precision and accuracy can actually be attained under field conditions.

In the following paragraphs, we have taken a method of test, ASTM D-2684, which has been subjected to interlaboratory testing. We have made some modifications to the method to make it more suitable to our purposes.

Table 1

Experimental Design for
Mass-Loss Experiments

Lading	40°C		45°C		60°C		50°C	
	Type 2	Type 3	Type 2	Type 3	Type 2	Type 4	Type 3	Type 4
C_7H_{16}	3	3	3	3	3	3	0	0
C_8H_{18}	3	3	3	3	3	3	4	4
$C_{10}H_{22}$	3	3	3	3	3	3	4	4
$C_{12}H_{26}$	3	3	3	3	3	3	4	4
$C_{14}H_{30}$	3	3	3	3	3	3	0	0
$C_{16}H_{34}$	3	3	3	3	3	3	0	0
$C_{18}H_{38}$	0	3	3	3	3	3	0	0

Numbers are degree of replication for each treatment.
Data from shaded blocks were not included in Linear Model Statistical Analysis
+Bottles were not sealed with silicone

3.1 APPARATUS

The apparatus used in our experiments included the following:

1. A forced draft recirculating oven equipped with certain additional safety features for use with flammable liquids. Temperature control was achieved using a proportional controller with a thermistor sensor. Temperatures at several points in the oven were monitored continuously using a multipoint strip chart recorder and chromel-constantan (type E) thermocouples.
2. A top-loading beam balance capable of reading to 10 mg.
3. A set of stainless steel photographic trays for holding groups of bottles filled with permeant.

4. Pipets and pipet-filling bulbs for use in filling the bottles.

3.2 MATERIALS

The materials used to conduct these experiments consisted of:

1. A selection of normal alkanes in liquid form. We used heptane (C_7H_{16}), octane (C_8H_{18}), decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{26}$), tetradecane ($C_{14}H_{30}$), hexadecane ($C_{16}H_{34}$), and octadecane ($C_{18}H_{38}$). The alkanes were obtained as technical grade liquids from a chemical supply house. We did not attempt to further characterize or purify them.
2. A large number of 120 ml bottles of the "Boston Round" shape. The characteristics of the various types of bottles which were used are set forth in Table 2. They were specifically molded for use in these tests by a manufacturer of polyethylene resins. The principal difference between the different types of bottles lies in the resin from which they are molded. This difference is, however, confounded with other small differences, and we have chosen to label the bottles as being simply of different types. The closures were molded phenolic screw-type caps with an inner liner which was an aluminum-foil and paper laminate. The neck finish appeared to be very good.

Table 2

DESCRIPTION OF BOTTLE TYPES

Approximate Volumetric Capacity - 120 ml

Property	Type 2	Type 3	Type 4
Resin	Ethylene-Hexene Copolymer	Linear Polyethylene	
Density (kg/m^3)	942	949	Same as Type 3
Avg. Mass (g)	12.39	11.76	
Total Surface Area (cm^2-estimates)	124.9	125.1	
Thickness (mm) (side wall)	1.08	0.69	
Outside Diameter (cm)	4.51	4.55	
A_{eff}/ℓ_{eff} (m)	17.84	18.23	
Closure	Screw cap with silicone	Screw cap with silicone	Screw cap alone

3.3 PROCEDURE

The procedure used in these experiments can be described as follows:

1. All bottles were individually weighed and identified by number. A random number table was then used to select the order in which the bottles would be used in the experiment.
2. The shelf space in the oven was divided into 42 "plots". A random number generator was used to assign each bottle to its plot for the actual measurement. This randomization procedure served to minimize the bias which might be encountered because of the temperature gradients (amounting to 1°C or so) which were known to be present in the oven.
3. Before each experiment, the oven temperature was adjusted to within 0.2°C of the nominal value. The thermocouple for measuring this temperature was placed close to the thermistor sensing element which was, itself, placed close to the air flow from the heating elements. A final adjustment of the temperature was made after the oven had been operating at its set point for a Saturday and a Sunday.
4. Fresh bottles were filled with 100 ml of permeant at the beginning of the test. This was always on a Monday morning. Hexadecane and octadecane, which are solids at room temperature, had to be heated up to 35°C or so before they could be pipetted into the bottles.
5. Once a bottle had been filled, a bead of room-temperature-vulcanizing silicone rubber compound was placed around the threads of each bottle closure and the closure was screwed on hand-tight. The filled bottles were placed on their respective positions (the "plots") in the carrying trays. When all of the bottles had been filled, they were individually weighed and then allowed to sit at room temperature for an hour or two to give the sealant time to cure. The bottles were weighed in the order given by their "plot" number.
6. The trays filled with bottles were placed in the oven on carefully marked spaces. The time at which this was done was the zero time for the experiment.
7. Subsequent weighings involved removing a tray of bottles from the oven, recording the mass of each bottle on the tray, and replacing the tray in the oven. The top-loading balance permitted rapid enough weighings so that we were not concerned about temperature changes during the weighing process. The process of weighing all 42 bottles consumed about one hour of time. The first set of weights was taken within 2 hours of zero time. The early weighings could not be repeated often enough for us to get good time lag data.
8. The weighings done on a Friday morning eleven days after the start of the experiment were the final ones. The experiment was terminated

at that time and preparations were made for a new experiment.

3.4 PRECAUTIONS

The following pointers have been derived from our experience:

1. While the use of random number tables may seem tedious, they are a useful tool in reducing bias. In our experiments, there is a very large temperature coefficient for the observed effects and bias due to temperature gradients is an ever-present factor.
2. The importance of a proper seal cannot be overestimated. We tested our bottles using a vacuum to ensure a good seal. While the precaution of of using a sealant proved unnecessary in our case, others might need to take positive steps to ensure a good seal. Neck finish is crucial to good sealing.
3. Care must be taken to assure the attainment of steady-state conditions. The way to provide this assurance is to measure the time-lag (see Section 3.5) and carry out the mass-loss measurement for a minimum of 6 to 8 times the time-lag. There is no value in continuing measurements past 6 or 8 time-lags. The amount of time each experiment takes must be tailored to the results. A prescription for the frequency with which data can be collected is as follows: collect data at intervals of 1/16 to 1/8 the estimated time-lag for a total elapsed time equal to one time-lag, then collect data at intervals of one or two time-lags for a total elapsed time equal to at least 6 or 8 time-lags.

3.5 RESULTS AND CALCULATIONS

The results from this experiment are a set of data giving mass as a function of time from the start of the experiment. In order to assess the meaning of the results in more fundamental terms, it is necessary to reduce this large set of values to simpler terms. Figure 1 is a plot of three typical sets of data. After an induction period (which is only barely discernible in Figure 1) the weight loss curves asymptotically approach a straight line of constant slope. This result is as predicted from the theory of permeation [5]. The data should fit an equation of the form:

$$\Delta m = \dot{Q}(t - q(t/\tau)\tau) + \delta \qquad 3.$$

where Δm is the amount of permeant lost after a time t,$\dot{Q}$ is the steady-state rate of mass loss, τ is the time-lag, and q is a function which depends on the nature of the molecular transport process and the initial conditions of the experiment. The random measurement errors are represented by δ. Most procedures for estimating permeation performance fail to take account of the time-lag. Eq. 3 clearly shows that q, the time-lag function, regulates the way in which the rate of mass loss approaches its steadystate value. The quantity τ, which is proportional to ℓ^2/D, is the time-scale on which this approach to a steady state takes place. In order to ensure that one is actually able to estimate the steady-state rate of loss, the experiment should be carried out for at least 6 times the time-lag. We have assumed that the polymer is

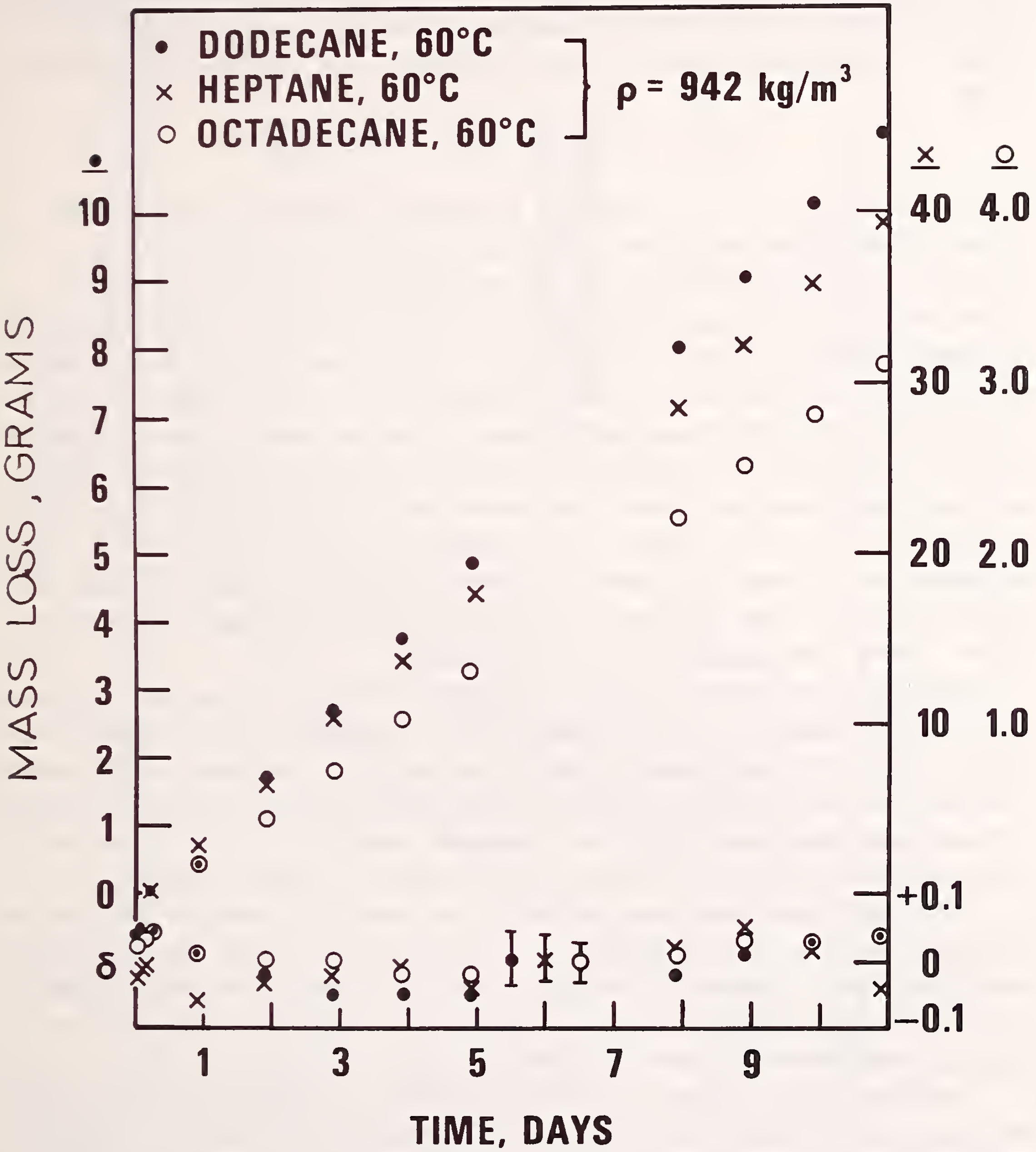

Figure 1: Typical plots of mass loss as a function of time. Note that each plot has its own scale on the ordinate. The three sets of points at the bottom of the figure are the residuals after fitting the observed values to models of the form given by eqn. 3.

initially devoid of permeant and that the transport process is simple Fickian diffusion with a diffusion constant which is independent of permeant concentration in the polymer. The functional form of q which is obtained under the foregoing assumptions is [5]

$$q(x) = 1 + \frac{12}{\pi^2} \sum_{j=1} \frac{(-1)^j}{j^2} \exp \frac{(-\pi^2 j^2 x)}{6} \qquad 4.$$

where, in our case, $x = t/\tau$. Equation 4 is graphed in Figure 2. Equation 3 has properties which allow for an easy iterative procedure to find values of $\dot{Q}$ and τ which best fit the experimental data. It was possible to treat the problem of finding nonlinear least-squares estimates of $\dot{Q}$ and τ by multiple linear regression procedures which used initial guesses of the unknown parameters to calculate vectors of independent variables whose coefficients were $\dot{Q}$ and τ. The estimates derived from a given round of iteration were used as input to the next round of iteration and the process was repeated until there was no significant difference between the values obtained in two succeeding rounds. The process usually converged within 4 iterations. Estimates of the errors in $\dot{Q}$ and τ were also obtained from the regression solutions. The bottom sets of points in Figure 1 are plots of the misfit between the data and the model given by Eq. 3 for the three sets of data plotted in the upper part of the figure. There is no apparent trend in the residuals.

The results obtained for $\dot{Q}$ and τ are plotted in figures 3 through 6. The values plotted are averages of the three values of $\dot{Q}$ and τ obtained for each combination of alkane, bottle, and temperature. As noted previously, the experiment at 50°C revealed that there was no significant difference between bottles which had been sealed with a silicone rubber and those in which no silicone was used. On this basis, the data for type 3 and type 4 bottles were pooled in the subsequent statistical analyses.

The strong trends which were observed in the data will be analyzed quantitatively in the next section. For the present, it is sufficient to say that the steady-state rate of mass loss is observed to increase sharply with temperature and to decrease sharply with alkane number. The rate of mass loss is about 15 percent lower from type 3 bottles than it is from type 2 bottles.

The time-lag data do not tell as tidy a story as do the transmission rate data. This may be partly because the time-lag is confounded with the time that it takes for a stagnant liquid in a bottle to come to temperature equilibrium with its surroundings. It is also reasonable to expect that Eq. 4 is an oversimplification in cases where the permeant acts to plasticize the polymer. It is possible that the lower molecular weight species in our study have a plasticizing effect at higher temperatures. The trend of increasing time-lag with increasing chain length appears to indicate that longer molecules diffuse more slowly in a polymer. This is an expected result. Likewise, the fact that diffusion is slower in the type 3 bottles as opposed to the type 2 bottles indicates that molecules diffuse more slowly in a denser matrix, as was to be expected from previous experience.

More complete discussions of the meanings of these results are to be found in the

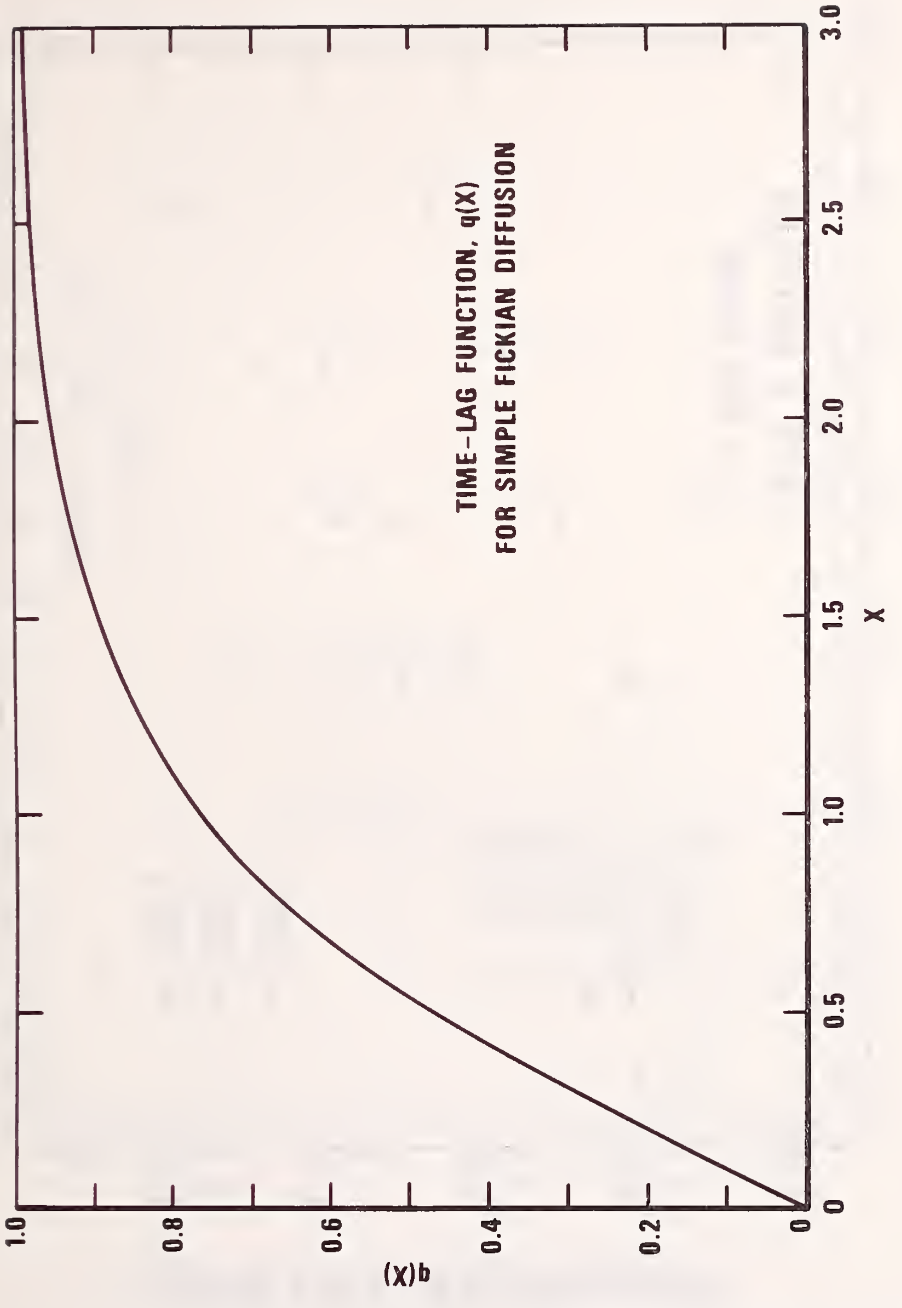

Figure 2: Form of the time-lag function, q(x) for simple Fickian diffusion. The time-lag, τ, determines the response because it is divided into the elapsed time to obtain the dimensionless variable x.

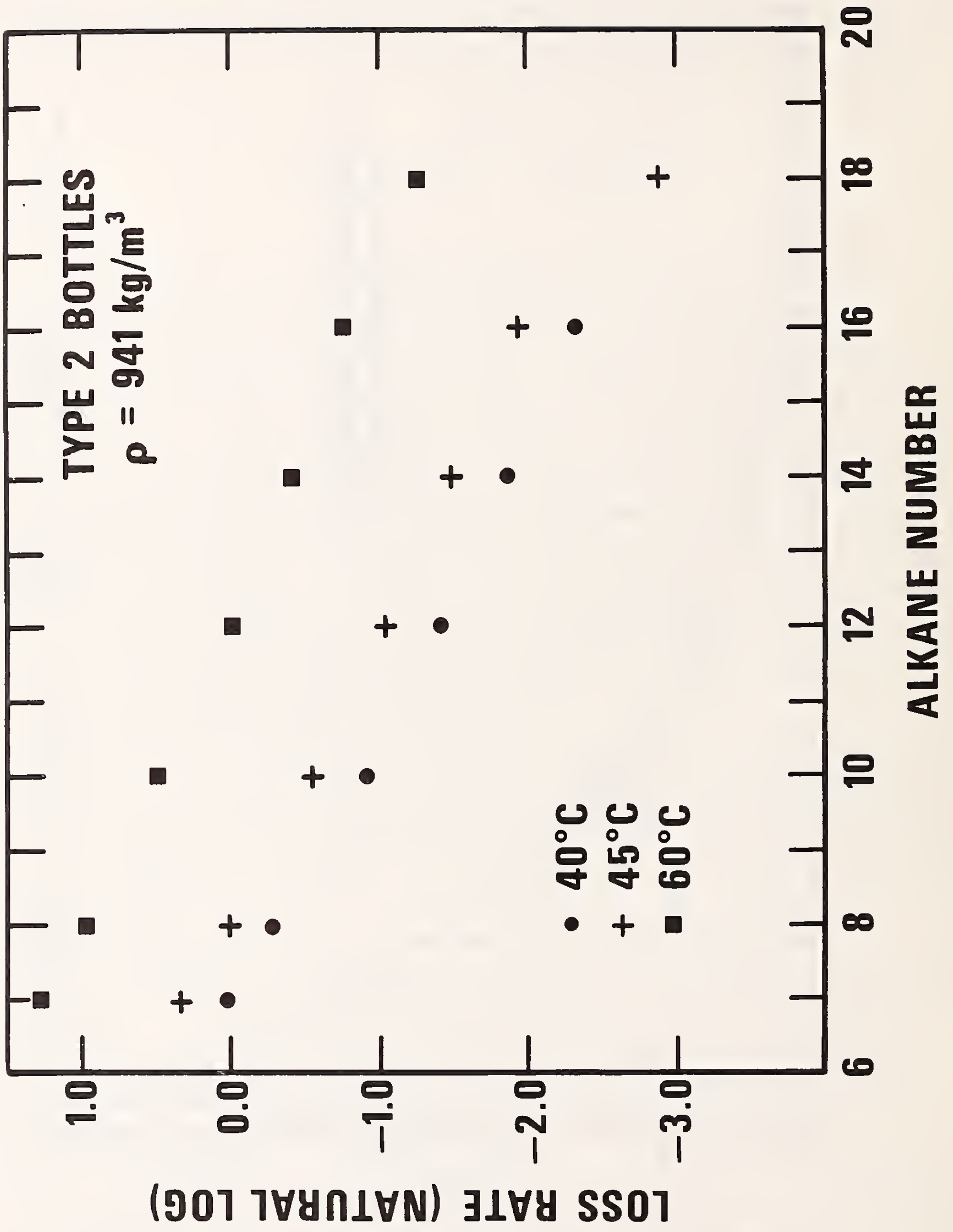

Figure 3: Loss rate as a function of alkane number (semilogarithmic plot). The dimensions of loss rate are grams/day. This plot is for type 2 bottles (P = 941 kg/m^3).

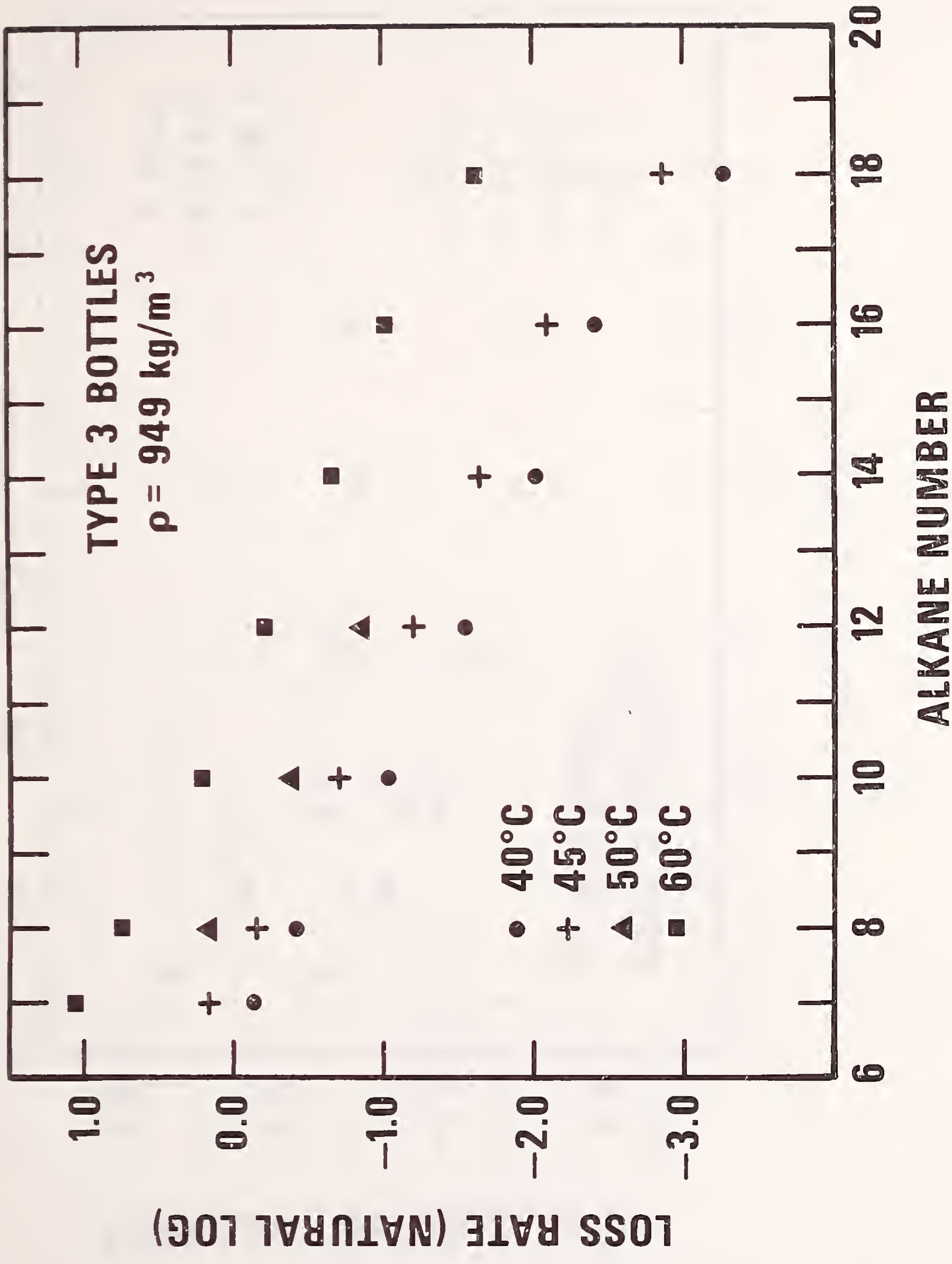

Figure 4: Loss rate as a function of alkane number for type 3 bottles (semilogarithmic plot). The dimensions of loss rate are grams/day.

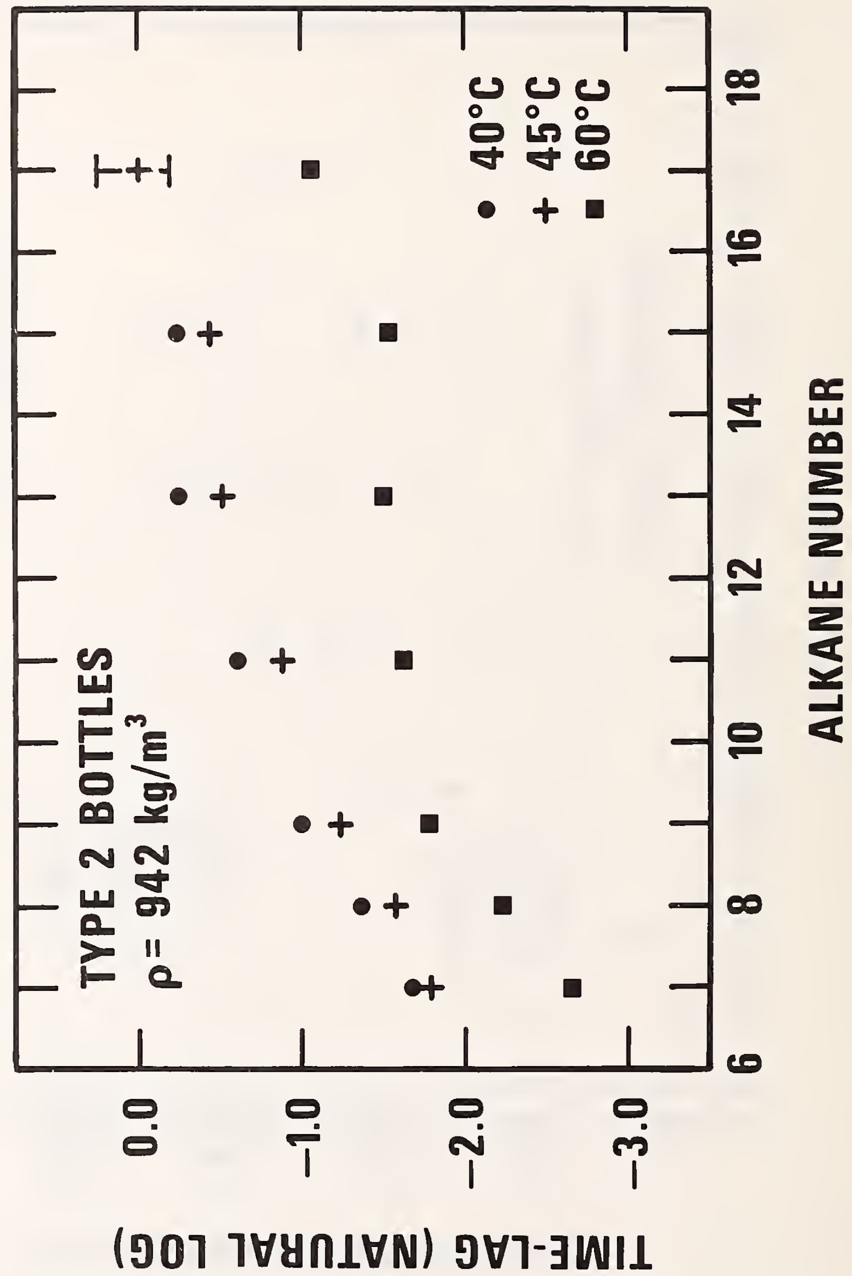

Figure 5: Time-lag as a function of alkane number, type 2 bottles.

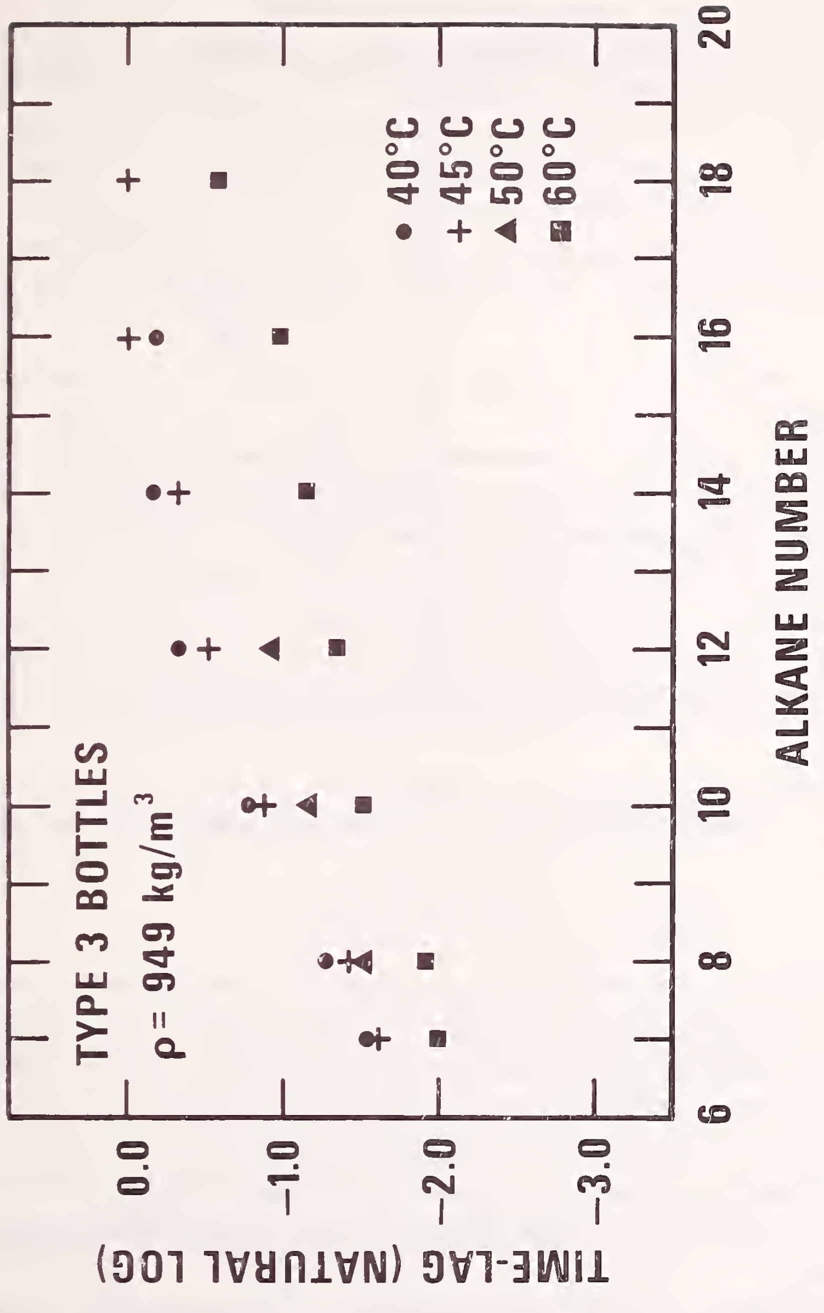

Figure 6: Time-lag as a function of alkane number, type 3 bottles.

later sections of this report.

4. A STATISTICAL MODEL FOR CORRELATING RATES OF MASS LOSS

Each data value obtained from fitting the results to Eq. 3 was labeled by test temperature (T), bottle type (b), and alkane number (n). Because the standard errors in the values of $\dot{Q}(T,b,n)$ were approximately proportional to the measured values of $\dot{Q}(T,b,n)$ we elected to perform statistical analyses on values of $\ln\dot{Q}$ so that we could work with quantities whose standard deviations were uniform. A three-way analysis of variance was performed. The statistical model which was used is given by:

$$\ell n\dot{Q}(T,b,n) = \mu + \alpha_T + \beta_b + \gamma_n + \delta_{nT} + \eta_{Tb} + \xi_{nb} + \text{random errors} \qquad 5.$$

The main effects due to temperature, alkane number, and bottle type were all highly significant. The interaction terms between alkane number and temperature (δ in Eq. 5) and between temperature and bottle type (η in Eq. 5) are highly significant. The interaction term between alkane number and bottle type (ξ in Eq. 5) is not significant. All higher order interactions were treated as contributing to random error. This analysis is not a very useful tool for extending our results to other experiments and another analysis was undertaken using the so-called Linear Model [6].

In this model, the rows and columns of the Analysis of Variance table are expressed in terms of functions. In our case, the appropriate form was:

$$\ln\dot{Q}(T,b,n) = X(T,b) + B(T,b)\ H(n) \qquad 6.$$

The values of the functions X, B, and H are determined only at the points used in the measurements. It is hoped that the functions will have enough meaning that values for other sets of conditions can be derived by appropriate interpolation procedures. Plots of the functions are given in Figure 7. A discussion of how the function values are derived from the data is beyond our present scope. Only those data values which were part of a complete experimental design were used in the analysis. This resulted in the elimination of the shaded entries in table 1 from consideration.

The standard deviation of the residuals to Eq. 5 was .0137. If we constrained the function B to be independent of bottle type as is indicated by the original analysis of variance, we obtain a standard deviation of .0145. This small loss in precision is quite acceptable. We must, however, remember that the two types of bottles used in this experiment were quite similar in the density of the resin used and an assertion that B is independent of bottle type in general is unwarranted. The results of Salame [2] indicate that B depends on resin type when one studies olefin resins.

We will examine some ways to use the model given by Eq. 6 in later section. For the time being, we are content to note that the model reproduces many of the

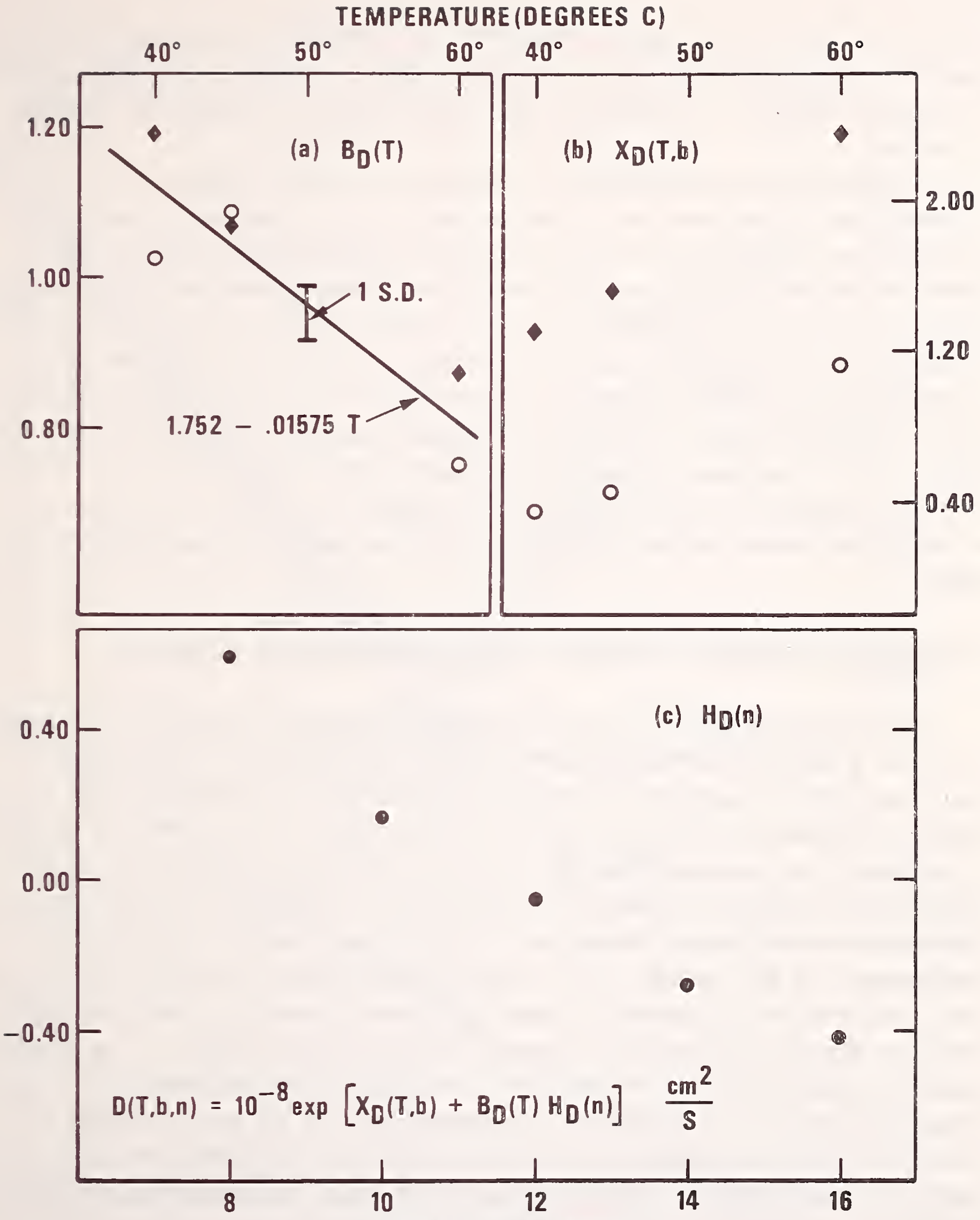

Figure 7: Linear model functions for loss rate data, both bottle types. (a) the function B(T,b), (b) the function X(T,b). The temperature scales apply only to the functions B and X. (c) the function H(n). The units of Q are grams per day.

features of the one developed by Salame [2]. One difference between our work and the result implied by Eq. 1 is that there is a slight curvature in the plot of $\ln\dot{Q}(T,b,n)$ vs. n for n-alkanes. The coefficient b_r is also found to be temperature dependent in our work.

We converted the observed data on time-lags to diffusion constants using $D = \ell^2/6\tau$. A linear model of the same form as that set forth in Eq. 6 was used to analyze the results. The functions $X_D(T,b)$, $B_D(T)$, and $H_D(n)$ are plotted in figure 8. The trends in the functions are much the same as those for the model describing the mass losses. The data are considerably less precise than the mass-loss data. This is reflected in a coefficient of variation of 7 percent or so for fits to the diffusion coefficient data versus a coefficient of variation of 1.5 percent for the mass-loss data. The function $H_D(n)$ falls much more steeply than does the function $H(n)$. $B_D(T)$ is also a much more strongly varying function than is $B(T)$.

If the experiments described above were expanded to cover a much broader range of ladings and resins we might obtain very different results for our statistical models.

5. THE ROLE OF MATERIALS PROPERTIES IN CALCULATING PERMEATION PERFORMANCE

In our previous report, [3], we introduced the materials properties P, D, and S. D and S denote the diffusion coefficient and the solubility respectively. If both D and S are independent of permeant concentration, the permeability, P, is given by the product of D and S. The transmission rate, G, is given by ΔpP where Δp is defined by the saturated vapor pressure of the pure liquid on one side of the barrier and an absence of permeant on the other side. Knowledge of these materials properties provides enough information to calculate most aspects of permeation performance. In this section, we will present a few simple relationships to illustrate how to use the kind of information regarding materials properties that experiments like ours yield. Our purpose is to demonstrate that the knowledge of a few simple materials properties is a sufficient basis for assessing the performance of large shipping containers. We further hope to demonstrate that the great majority of properties measurements can be carried out on small-scale reference containers and that only a small number of tests need be carried out on specimens from production containers. Since tests on small containers are much more rapid and economical than tests on large-scale containers, it follows that a measurement system based on materials properties should prove to be more economical than the trial and error approach now in general use.

We will proceed by developing some general equations relating container performance to materials properties. We will then use these equations to discuss measurement methods for materials properties and the performance of production containers. We will then turn our attention to a modified permachor scheme for predicting the transmission rates of a variety of molecular permeants in various related polymers

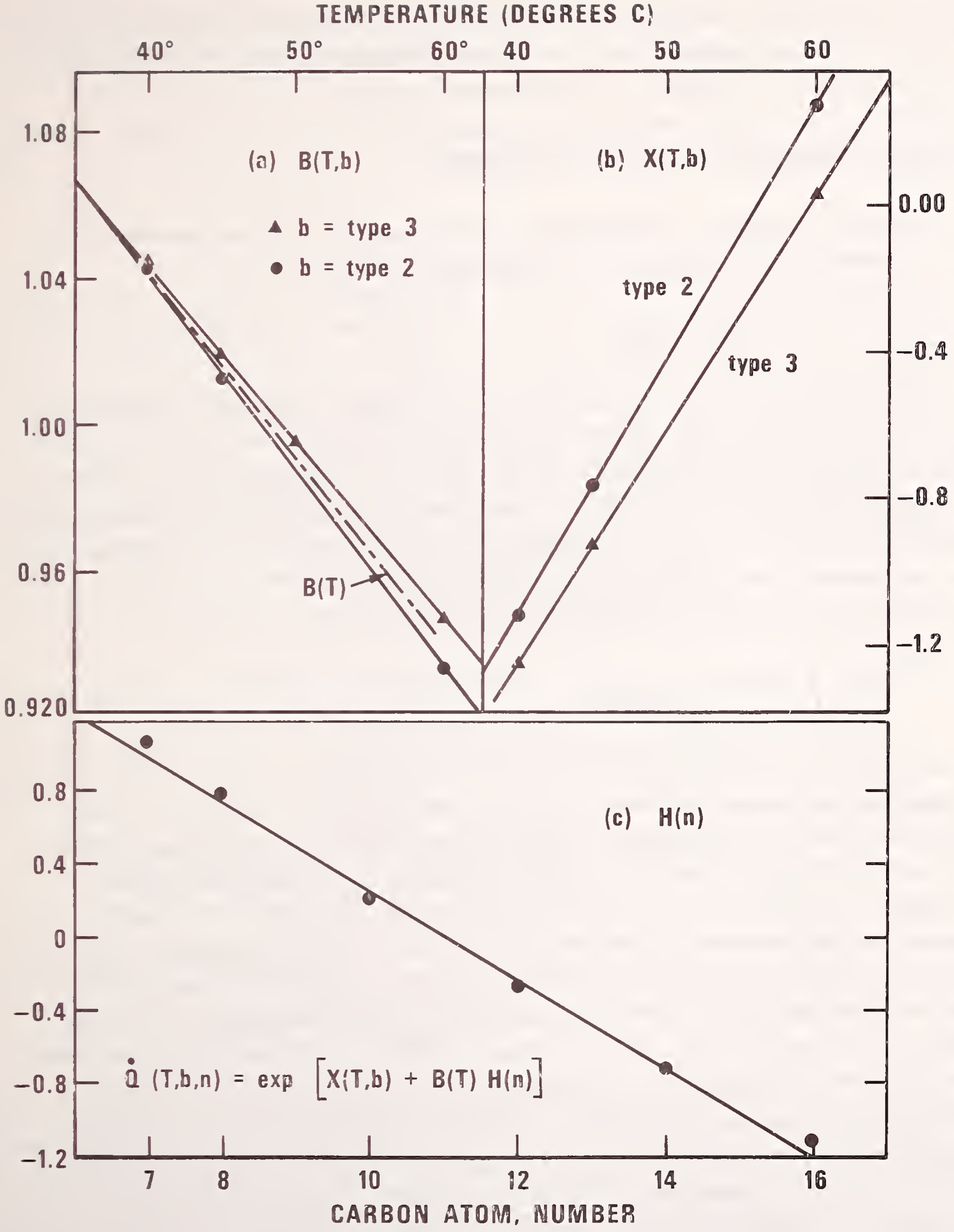

Figure 8: Linear model functions for diffusion coefficient data. The equation that can be used to convert these functions into predicted values of the diffusion coefficient is in the lower part of figure 8c.

based on a knowledge of the state of the polymer (as revealed by a permeation measurement using a standard permeant) and a knowledge of the permeation index (permachor or effective carbon atom number) for the permeant species.

5.1 MATERIALS PROPERTIES AND CONTAINER PERFORMANCE

The amount of permeant passing through a unit area of container surface in unit time at a point u on the surface is approximately given by:

$$F(u) = \frac{G(u)}{\ell(u)}.$$

This approximation is valid to the extent that the radius of curvature of the surface at the point u is much larger than the thickness. The rate of change of thickness between nearby points on the surface must also be low. If these conditions are not fulfilled, we must resort to solutions of the diffusion equation with the appropriate boundary conditions [5]. Enough cases have been solved so that we can estimate the errors introduced by the above approximation when we have to.

The rate of mass loss from a container is given by

$$\dot{Q} = \int_u F(u)du = \int_u \frac{G(u)du}{\ell(u)} \qquad 7.$$

The integral is over the entire surface of the container. In the following discussion we make frequent reference to G as a function of the temperature, the state of the resin, and the permeant. When we need to make this dependence explicit, we will write $G(T,\Lambda(u),x)$ and Λ will be used to denote the state of the polymer. This usage is consistent with our use of u to describe the position of a point on the surface of the container in that the only reason for materials properties to change as a function of position is as the result of a change in the state of the polymer from one position to another. T and x refer to the temperature and to the permeant species respectively. As will be seen presently, the quantities $\dot{Q}$ measured in our experiments and the quantity G being used here differ by only a constant multiplier which should be independent of our choice of permeant. Our experiments up to this point do not yield a good value of this multiplier and we have preferred not to correct for its presence for fear of introducing a bias into our results. It was necessary to bring G under the integral sign in Eq. 7 because of our experience that the state of the resin is not homogeneous throughout the wall of our bottle. A way must be found to express this lack of homogeneity in terms which allow the integral of Eq. 7 to be evaluated. Our experiments demonstrated that the function $X(T,b)$ was sensitive to the state of the polymer. The functions $B(T)$ and $H(n)$ were found to be insensitive within the range of states we examined. On this basis, we can write

$$G(T,\Lambda,x) = G(T,R,x) \exp [\lambda(\chi-\chi_R)] \qquad 8$$

where we have expanded the function $X(T,\Lambda)$ about the reference state R in the following fashion:

$$X(T,\Lambda) = X(T,R) + \lambda(\chi-\chi_R) + \text{terms of order } \gamma^2 \qquad 9$$

The parameter λ is introduced to control the scaling. We have chosen to describe the state of the polymer using the crystallinity, χ. This usage should be interpreted as embracing such morphological parameters as crystallite orientation and crystallite size in addition to density. The sensitivity of the transmission rate to the lading is contained in the function $B(T)H(n)$ which we will examine later. The function X is insensitive to our choice of lading. The relationship expressed by Eq. 9 is consistent with our experimental data. Its validity has not been demonstrated beyond the range of conditions used in those experiments. We are using Eq. 9 simply as an ansatz to see what needs to be done to make good standards.

We can now proceed by expanding the exponential in Eq. 8:

$$G(T,\Lambda,x) = G(T,R,x) [1 + \lambda(\chi-\chi_R) + O(\lambda^2)\ldots] \qquad 10$$

Neglecting terms of order λ^2 and above, this result can be inserted into Eq. 7 to yield

$$\dot{Q} = G(T,R,x)\left\{ \int_u \frac{du}{\ell(u)} + \lambda \int_u (\chi(u)-\chi_R) \frac{du}{\ell(u)} \right\}$$

This result can be shortened to

$$\dot{Q} = G(T,R,x)\ (A/\ell)_{eff}\ [1 + \lambda I_2] \qquad 11$$

The term $(A/\ell)_{eff}$ is of purely geometric origin while I_2 is a function of the resin state. One result of our experiments is that I_2 is not a function of our choice of lading. This result is certainly invalid if the lading swells the polymer appreciably or otherwise alters its state. Eq. 10 expresses all of the problems which are encountered in trying to make measurements of G as a materials property. Eq. 10 also expresses all of the problems the design engineer faces in trying to use materials properties to estimate how his product will perform. We will deal with the question of making good measurements of materials properties first.

In a laboratory environment, it is presumed that we are dealing with a material which is homogeneous over an area that is large enough for us to use in a measurement. The geometry of the test arrangement is well fixed so that the term $(A/\ell)_{eff}$ is adequately known. It would be desirable to have a material which is homogeneous not only in two dimensions (over the surface) but is homogeneous in three dimensions. Measurements made on such a material would then scale properly with thickness and G could truly be regarded as a property of a bulk material. Let us designate this material, which is homogeneous in three dimensions, whose morphology has been carefully controlled, and whose molecules have been intimately characterized, as the primary reference state of the polymer resin we are dealing with. We will label this state by R. It is not clear that we can or should realize such a state of the material. It would have little more than academic interest as a starting point from which to alter the state of the material in a prescribed way.

We can, however, prepare and characterize a less homogeneous state of the material by simple industrial processes. This material is presumed to be homogeneous in two dimensions. The state of the material is independent of position on the surface of the material. In this case, G does not need to be brought under the integral in Eq. 7. Let us label this state as the secondary standard of our material and let us call it σ. $G(T,\sigma,x)$ is then simply the ratio between $Q(T,\sigma,x)$ and $(A/\ell)_{eff}$. Over the narrow range of states we are concerned with $G(T,\sigma,x) = G(T,R,x)\exp[X(T,\sigma)-X(T,R)]$. This equality is a reasonable model for expressing the differences between any two closely related states.

If our secondary reference material is truly homogeneous, the geometrical problem posed by the quantity $(A/\ell)_{eff}$ is the principal obstacle to measuring a transmission rate. It should be remembered that $G(T,\sigma,x)$ is not necessarily representative of a bulk material. This status is reserved for values determined on materials which are known to be homogeneous in three dimensions. If the measurement results do not scale with thickness, there is surely an inhomogeneity in that dimension. In the next section, we will discuss standard reference materials and their role in the standarization process. At that time we will again make use of the notion of states of the polymer.

In using Eq. 11 to understand the design of real shipping containers, we are faced with all possible sources of bais. We are sure to find a difference between the state of the resin in the production container and the secondary reference state. Even if there were no difference in starting resin there would be differences due to the presence of fillers and differences due to processing conditions, to name only the most obvious sources. Let us use C as a label for the average state of the resin in a production container. Deviations from the state C are likely to exist in different parts of the container because of differences in thermal or melt history. The geometry is likely to be very complex because it is difficult to distribute polymer as a homogeneous, uniform coating over the inside of a mold which is, itself, likely to have a complex shape. When the design engineer selects a value for the transmission rate he is likely to select a value which represents a secondary reference state. Putting all of the above factors together yields the following equation for the rate of mass loss:

$$\dot{Q}(T,C,x) = G(T,\sigma,x)\ \exp[X(T,C)-X(T,\sigma)]\ (A/\ell)_{eff}[1 + \gamma I_2(C)/(A/\ell)_{eff}]. \qquad 12$$

All of the terms in Eq. 12 are uncertain by some amount. The extent these uncertainties are removed or minimized is dictated by the precision required of the estimate. Cases where one container is chosen over another on the basis of a minor difference in permeability are unlikely. The term arising out of the difference between the states C and σ is the most important one. Differences between high and low density polyethylenes and the importance of orientation in determining barrier properties [7] are evidence for the importance of state as a variable. The feasibility of accounting for this variability by a term like $X(T,C)X(T,\sigma)$ remains to be investigated. Measurements on sheet specimens cut from production containers using a few selected permeants are the best way to estimate whether this term is important. Because the barrier properties of a plastic are so sensitive to thermal and mechanical history such measurements may be useful for quality control of forming processes.

The geometrical contribution to Eq. 12 is best estimated by dividing the surface of the container up into a number of segments over which the thickness is uniform. The shape factor, $(A/\ell)_{eff}$ is then given by:

$$(A/\ell)_{eff} = \Sigma A_i/\ell_i \qquad 13$$

The accuracy with which this can be done is a measure of our ability to estimate the value of the shape factor. The I_2 term, due to inhomogeneities in the state of the polymer, is difficult to estimate quantitatively. A qualitative estimate can be made by measuring the density of small pieces from various parts of the container. If significant variation is found, it may be wise to investigate the forming process. The uncertainties in the overall permeation performance arising from errors in the shape factor and inhomogeneities in the material are probably negligible.

5.2 THE EFFECTIVE CARBON ATOM NUMBER

Up to now, we considered the state of the material as our principal variable. We have considered equations which can be used to link together values of transmission rate for various states of the resin. These values of transmission rate can, in turn, be used to make predictions of the permeation performance of containers made from the materials.

One of the most interesting results of our work and that of Salame is that there is a systematic way to link materials properties involving different species. We will demonstrate how to determine an effective carbon atom number, $n_e(x)$, for many different permeant species. To the extent that these values behave like the carbon atom numbers of n-alkanes they can be used to derive estimates of how a given permeant species will behave in a polymer which has a given state from a knowledge of how that species behaves in a polymer with a different state. In order to see what the concept of an effective carbon atom number entails, we must examine the following result which can be derived from the statistical model of section 4:

$$G(T,C,n) = G(T,C,n_0)\exp(B(T)H'(n)) \qquad 14$$

The function H'(n) is essentially independent of temperature and largely independent of the state of the polymer. The function which fits our data on the n-alkanes is plotted in figure 9. The abscissa is the number of carbon atoms in the alkane chain. The values derived from our observations are a discrete set. However, since there is a uniform monotonic progression which is correlated with the values of n, it is tempting to write:

$$H'(n) = -h_1(n-n_0)[1-h_2(n-n_0) + O(n-n_0)^2....] \qquad 15$$

The choice of n_0 is somewhat arbitrary. Figure 7 reveals that we can write (approximately)

$$B(T) = -B(T_0)[1 - b(T-T_0)] \qquad 16$$

Combining 15 and 16 gives:

$$B(T)H'(n) = -B(T_0)h_1[1-b(T-T_0)](n-n_0)[1-h_2(n-n_0)] \qquad 17$$

The parameters $B(T_0)h_1$, b, and h_2 must be chosen so as to fit experimental transmission rate data on n-alkanes. The choice of the n-alkanes as a homologous series for making these correlations is once again, somewhat arbitrary. In the temperature range that we studied, the n-alkanes are relatively inert with respect to the polymer matrix. This should probably be the primary determinant in choosing a homologous series. Our choice was also conditioned by the fact that the measured transmission rates were high enough to be interesting. If we make permeation measurements using odd-numbered n-alkanes, we can reasonably expect their H' values to fall on the curve defined by Eq. 15. Members of a different homologous series would be expected to give H' values which fall off of the correlation line. This is illustrated by the hypothetical points in figure 9. If we have a permeant x whose value of n_e is unknown, we can proceed by taking the ratio between the transmission rate of permeant x and that of permeant n_0. The following equation results:

$$B(T)H'(x) = \ln[G(T,C,x)/G(T,C,n_0)]. \qquad 18$$

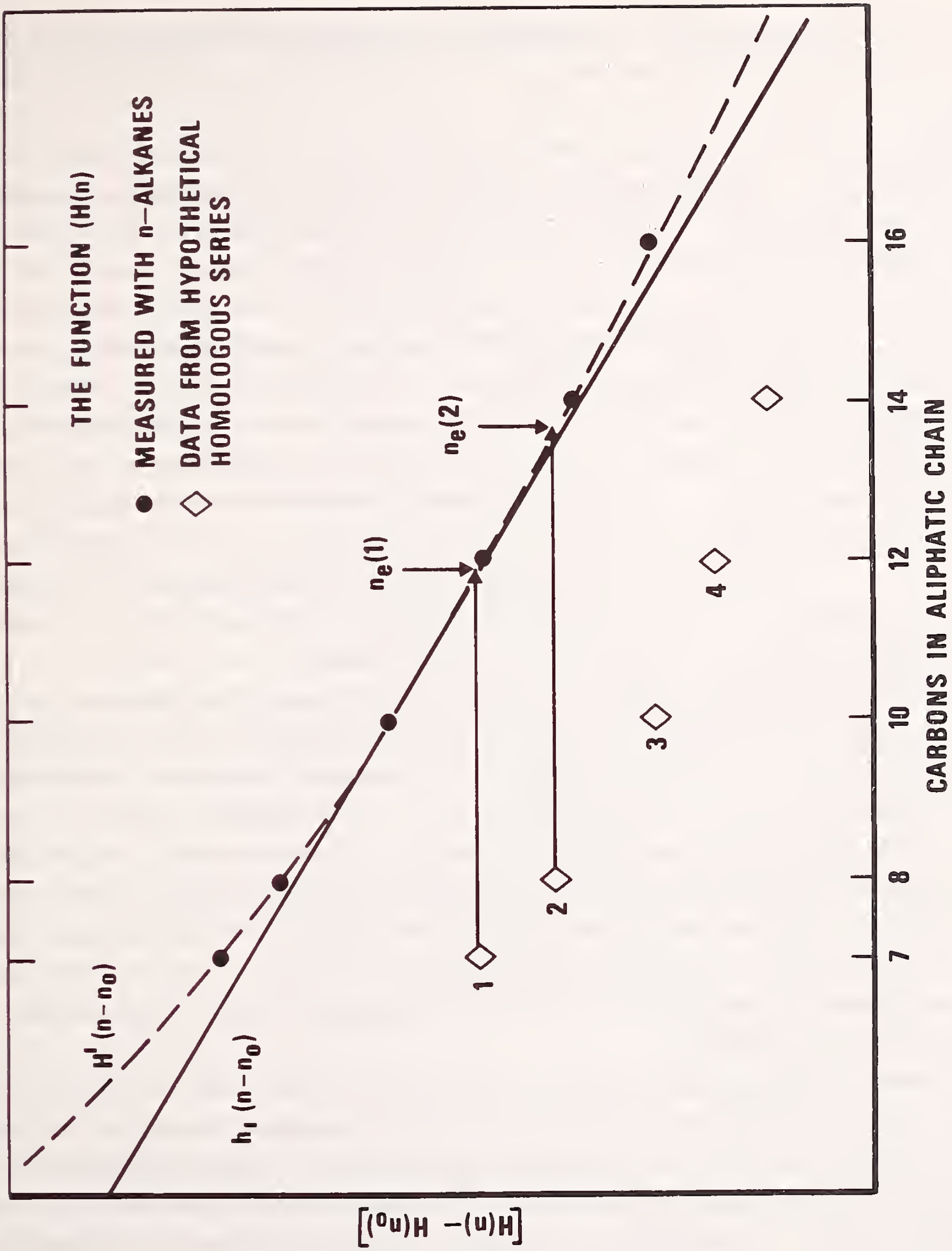

Figure 9: Calculation of Effective Carbon Atom Numbers from measurements on substances other than n-alkanes. The ordinates for points 1,2... represent values of H'(x) obtained from eqn. 18. The abscissae are determined by the number of aliphatic carbon atoms present in the substance. Note that the presence of other chemical groups causes the points to fall off of the line for the n-alkanes. By drawing a line through H' parallel to the abscissa an effective carbon atom can be defined as the point of intersection of this line and the curve for the n-alkanes.

The experimentally determined value of B(T)H'(x) can then be compared with Eq. 17. A value of n_e which, when inserted into Eq. 17, gives $B(T)H'(n_e) = B(T)H'(x)$ is what is desired.

This is essentially the same procedure Salame used in his original work on polyethylene [2]. In that sense, the n_e values we describe are nothing but another name for his "permachors". Salame went farther in his work in an effort to find a systematic molecular basis for calculating permachors from chemical structures. We are content to regard the n_e as experimental observables. For that reason, we sometimes describe our scheme as a "modified permachor" approach. Once the effective carbon atom number of a permeant has been determined, the function $B(T)H'(n_e)$ can be evaluated for a temperature other than the test temperature and the value can be inserted into Eq. 14 to predict the transmission rate of the permeant through a production container. The only information which is needed with regard to the polymer in the production container is the transmission rate of a standard permeant (n_0) at the temperature of interest. This is the basis for our statement that most measurements for predicting permeation performance can be carried out on reference containers and only a small number of measurements are needed on polymer from production containers.

A lot of new parameters were introduced in the paragraph leading up to eqn. 17. $B(T_0)h_1$, b, and h_2 are expansion parameters which can be used to link a standard condition with a closely related condition. The standard condition to which they refer is contained in the value of $G(T,C,n_0)$. Since the transmission rate is the product of three materials properties ($G = \Delta pDS$) it is unreasonable to expect that these expansion coefficients can be stated in terms of simple molecular quantities. Our data on the diffusion coefficient could, in principle, be linked to a free volume theory [8] but we have not yet had the opportunity to do so. It would be interesting to see what effects molecular composition and thermodynamic state of the polymer have on the expansion parameters.

The effective carbon atom number is a quantity of a different sort. It is partly a fundamental physical constant and partly a measurable property of the polymer-permeant pair. Since the n_e are measurable quantities the degree of agreement among values obtained by different observers helps to characterize the performance of the measurement system. If good precision is found, the n_e values can be tabulated and the table widely distributed; then the only users who need to make measurements are those who wish to introduce new commodities into the measurement system. As long as there is no significant chemical change in the resin, n_e values should remain sensibly constant. If there is a chemical difference between resins there may be a large-scale reordering of the n_e values relative to one another. Salame's publications on polyethylene [2], PVC [9], and oxygen in a variety of polymers [10] illustrate the complexities of describing the association between permachor values and chemical structure.

5.3 SOME ADDITIONAL COMMENTS ON MATERIALS PROPERTIES

In our data the function B(T) accounts for the fact that the temperature coefficient of permeability for n-alkanes differs from one alkane to another. As Eq. 17 shows, the temperature coefficient increases as the chain length increases. The universality of B(T) can be tested by measuring the temperature coefficient for all permeants. We have no data to indicate how serious this problem is. If the function B(T) is different for different homologous series, calculations and correlations using the modified permachor scheme would become considerably more complex. Our evidence that B(T) is independent of the state of the polymer is not convincing. Data must be gathered from a much wider range of polymer states before such a conclusion can be put forth.

Before leaving the issue of materials properties, we would like to state the equation which can be derived from our experimental data:

$$G(T,C,x) = G(T_0,\sigma,n_0)\exp[X(T,C)-X(T_0,\sigma) + B(T)H(x)-B(T_0)H(n_0)] \qquad 19$$

Equation 19 links the transmission rate for a permeant x at a temperature T for a polymer in a state C with a transmission rate of a different permeant at a different temperature in a different polymer. As we have noted above, the function H(x) depends upon the choice of permeant. In previous paragraphs, we have discussed the possibility that H(x) is a universal function if we use an appropriately defined effective carbon atom number as the entering argument. In our experiments, we determined values of H(x) for a few n-alkanes. The significance of B(T) was discussed in the preceeding paragraph. Equation 19 is attractive because it allows us to describe a very large number of situations by using a rather compact set of functions. Unfortunately, we have verified its validity only under highly restricted conditions and many more experiments are needed before we can use it in its full generality.

We have used X(T,b) to characterize the state of the polymer without saying much about what we mean by that usage. So far as we know, it is not possible to calculate the function X(T,b) *a priori*. Some insight into the significance of such a function can be gained by considering semicrystalline polymers as being made up of impermeable domains embedded in a permeable matrix. The molecular properties of the permeable matrix (which is the non-crystalline part of the polymer) are governed by the flexibility of the chains, their chemical character, and the available free volume. However, the size, shape, orientation, and volume fraction of the impermeable domains (crystallites) will strongly affect the permeability [11]. In this context, it is not surprising that there is a function like X(T,b) which is insensitive to the particular choice of permeant. Another clue to the nature of the state function is that it accounts for most, but not all, of the temperature coefficient of permeability. This is an activated process, but we have not yet estimated an activation energy because the transmission coefficient is a composite of three distinct processes, each of which has its own activation energy. The temperature range we have used is also too narrow to get good values of activation energies.

In order to obtain a clear understanding of the meaning of the state function, we would have to do experiments on a series of polymers whose states are easily derivable from one another (by annealing, for example). The correlations obtained from such measurements might be expressible in terms of simple expansion parameters. We have been careful to couch our argument in terms of differences between two states, $X(T,C)-X(T,\sigma)$, without ascribing too much significance to the numerical values of the state functions.

These differences are easy to evaluate experimentally as is shown by:

$$X(T,C)-X(T,\sigma) = \ln[G(1,C,x)/G(T,\sigma,x)]. \qquad 20$$

Evaluating the above ratio for a number of permeants of different types should provide a critical test of the universality of the state function. Permeants which alter the state of the polymer should not be expected to fit into this scheme.

6. STANDARDIZED BOTTLES FOR PERMEABILITY TESTING

One of the best ways to ensure agreement among measurers of materials properties is through the use of appropriate reference materials [12]. NBS already distributes a number of Standard Reference Materials for this purpose [13]. None of the present SRM's are suitable for permeability measurements. In order to better understand the role of a reference material in permeability testing, consider the reference state, σ, which was introduced in Section 5.1. Recall that $G(T,\sigma,x) = \dot{Q}(T,\sigma,x)/[(A/\ell)_{eff} + \lambda I_2]$. If we are dealing with a homogeneous material I_2 can be neglected. $\dot{Q}$ is used in this context to indicate any method of measuring the transport of matter across the barrier and not just a mass-loss measurement. If the material is homogeneous, measuring G is simply a matter of measuring $\dot{Q}$ and $(A/\ell)_{eff}$ accurately. Persons who have access to a material in the reference state should be able to make a measurement of G and arrive at the same values as other users of the same material. In order to guarantee that there is enough material to go around, a central organization stockpiles a supply of a suitable material. They prepare and characterize it as carefully as they can so as to minimize differences between old and new batches of material. The physical properties of interest are measured using techniques designed to keep bias and error to a minimum. The results of these measurements together with such other information as is needed to use the material properly are supplied to interested parties.

A reference material can be distributed in a raw form or in a finished form. In the former case, the purchaser must follow some prescription supplied by the distributor (ASTM D1928 is an example) to fabricate test specimens. For materials like polyethylene, which are sensitive to thermal history, it is preferable for the supplier to use a carefully controlled process to form the material into shapes from which tests pieces can be made by simple cutting. It is worthwhile to put considerable effort into characterizing the material when the material will be widely used or when the measurements are important from an economic or regulatory point of view.

Measurements on reference materials serve to reveal errors which can arise from many different sources. As these errors are found and eliminated, the user's measurements on the materials that interest him become more meaningful.

As we have discussed previously, samples in sheet or tube form offer the most promise as a way to distribute a highly precise and accurate reference material. A reference material in either of these forms requires fixtures to define the area through which permeation is taking place. Cups, similar to those used in ASTM E-96, could be used for sheet or film specimens. Impermeable plugs are needed to seal off lengths of tubing to make permeation tubes [14]. In both cases, it has been found difficult to make seals between polymers and impermeable surfaces.

Few organizations are in a position to use such a reference material effectively. The measurement system would be better served with a less accurate standard which could be used by a great many people. Our experience indicates that a reference material in the form of a small bottle might be very useful. It is necessary to find out how widely such a reference material would be accepted before actually producing it.

The principal disadvantage of a bottle is that there is likely to be bias in the measurements. The sources of this bias include: (1) imperfect closure performance, (2) variations in wall thickness from one part of the bottle to another, (3) ambiguity in the value of the effective area, and (4) inhomogeneous material properties.

Poor closure performance will lead the user of a bottle test to overestimate $G(T,\sigma,x)$. Items 2, 3, and 4 will be discussed later when we demonstrate that this bias can be removed by a calibration step which is part of the certification procedure.

One strong advantage of the bottle shape is that a small container exposes a large area for permeation. A cup equivalent to a 120 ml bottle would have an exposed surface 15 cm in diameter. The metal or glass parts of the fixture would weigh at least 200 to 300 grams. Another advantage of the bottle as a standardized container is that it requires only a minimum of manipulation and auxiliary equipment to use.

Table 3 lists some of the specifications which are crucial to the design of a suitable standardized bottle. We have avoided making specific recommendations in this table because some of the items are best taken up in negotiations with potential fabricators of bottles. The table is divided into factors which depend on quality control and mold design (architectural factors) and factors which affect performance (performance factors). Careful quality control in the architectural area is essential to good reliability in the performance area.

TABLE 3

PARTIAL SPECIFICATIONS FOR A STANDARDIZED BOTTLE FOR USE IN PERMEABILITY TESTING

Architectural Factors

Total Volume of Contents	: 120 - 500 ml
Outside Diameter	: Commensurate with above
Closure	: Subject to definition
Wall Thickness	: 2.00 ±.05 mm
Mass Variability	: ±.06 g
Shape	: See Text

Performance Factors

Effective thickness, l_{eff}	: To be established using time-lag measurements and geometrical measurements
Ratio of A_{eff} to l_{eff}	: To be established by normalizing to measurements on sheet stock
Resin density	: To be established by measurement (ASTM D1505 or ASTM D792)
Rate of mass loss for selected permeants	: To be established by measurement

The volume of the bottles is established by the interplay between several competing factors. For example, the effects of closure performance are minimized on larger bottles. Small bottles of a given wall thickness tolerate stresses better than large ones do. The amount of permeant used in testing should be kept to a minimum, particularly if the permeant is hazardous. The sensitivity of the mass-loss test, as defined by the ratio of surface to volume, is better for smaller bottles. The size range we have given in table 3 is such that the smallest bottles are not too small to be useful and the large ones are not too unwieldy.

The shape and volume of a standardized bottle are partly determined by what is available in the way of molds. Some effort should be devoted to insuring that the standardized bottle is similar to ones made on laboratory-scale molding machinery. Similarity in this attribute will encourage more comparisons with resins which are in a state of development. The bottle shapes depicted in ASTM methods D2561 and D2684 are representative of common shapes.

One of the most difficult areas to specify is the bottle closure. The key to making good seals appears to be care. There is some leeway in specifying the nature of the cap liner and the finish on the bottle mouth. A smooth seating surface is essential. A good finish on the threads should help to insure smooth operation of the closure. ASTM D2684 goes to great lengths to specify the method of sealing. A heat-sealable barrier film is required for the bottle mouth and a torque wrench is used to obtain uniform torque on the closure.

Any procedure for using a standardized bottle must include instructions for making and testing closure seals.

We have touched on the performance of containers in the preceding section. The disadvantages of a complex shape like a bottle are that $(A/\ell)_{eff}$ is difficult to estimate and resin homogeneity is difficult to maintain. In order that the state of the material in the bottle can be well-defined, it is best to use the polymer in the side walls as being representative of the state of the polymer in the bottles. The side wall areas are reasonably uniform and they are the dominant contributors to permeation mass-loss. The transmission properties of the side wall material can be characterized by cutting off the ends of the bottle, flattening the side wall section, and putting it in a test fixture for sheet specimens. Once the materials properties (G and D) are determined in this way, normalization constants can be derived which can be used to give correct values from measurements made on intact bottles. $(A/\ell)_{eff}$ can be fixed so as to give the correct transmission rate from the steady-state rate of mass-loss. The thickness can be fixed so as to give the correct diffusion constant from time-lag measurements. The resin density should be measured at a number of points on the bottle walls as a check on the homogeneity of the resin state. These checks should be supported by appropriate morphological observations including optical microscopy and x-ray diffraction.

The functions X(T,b), B(T), and H'(n) are needed to estimate effective carbon atom numbers using the standardized bottles, and to transfer results among differing states of the polymer. The procedures we followed in Section 3 serve as a model for performing these calibration measurements. It may be desirable to include selected permeants in addition to n-alkanes in the list of permeants used in calibration.

Polymeric materials are not noted for their long-term chemical and physical stability. There are a number of processes which cause the state of the material to change with time. The result of such change is a drift in the measured value of $G(n_0)$ as depicted in figure 10. Values of ne are expected to be relatively insensitive to the state of the material and should be much more stable with time. In order to achieve this stability, the measured values of G on the right hand side of Eq. 18 must be corrected for drift.

One way to do this is to make measurements on one or more standard ladings at the same time measurements are being made on the unknown lading.

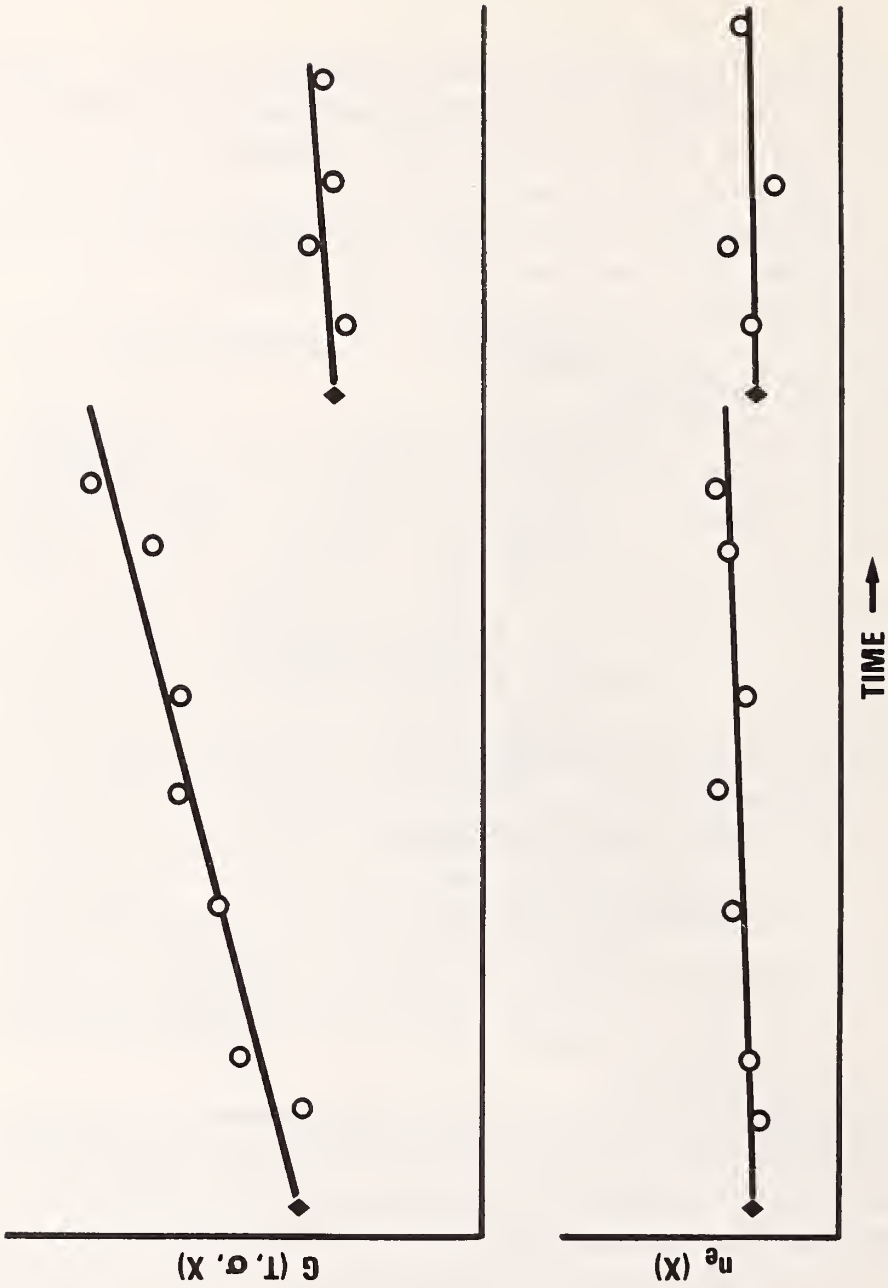

Figure 10: Schematic illustration of the effects of aging of standards on measured values of effective carbon atom number. The drift for the effective carbon atom number is less than that for the transmission rate because the effect of the changing state of the polymer is partially compensated for by taking the ratio between two transmission rates.

7. USING PERMEATION MEASUREMENTS FOR SCREENING PURPOSES

DOT-OHMO has an urgent need for a set of standards to be used in screening out dangerous or ill-advised combinations of ladings and packages. Such screening necessarily depends on meaningful measurements and in the preceding sections we have addressed a variety of measurement questions. In this section, we will address screening questions.

There are three situations which suitable screening procedures should detect: (1) cases where the lading is incompatible with the container, (2) cases where the lading is released from an otherwise acceptable container so rapidly as to create a hazard, and (3) cases where the resin has been processed so poorly that its barrier properties are inadequate. Incompatibility as we have defined it above implies that the lading has damaged the container to such an extent that its lifetime is reduced. These questions are addressed in other reports in this series [15,16]. Permeability testing may play only a minor role in this kind of screening, although a test result indicating a high permeability should spur a search for damage.

7.1 SCREENING FOR UNSUITABLE LADINGS

We will restrict ourselves to cases 2 and 3 above. In these cases, the failures we wish to avoid are due to releases of hazardous material as a result of permeation through the walls of the container. In order to demonstrate how we can arrive at quantitative criteria, we will consider N shipping containers, each of volume V_s, in an enclosed space whose volume is V. There is no way for permeant in V to escape to the outside. Let Q(t) be the mass of permeant lost from each container in time t. The concentration, C, of permeant which has escaped from the shipping containers is given by:

$$C(t) = Q(t)/((V/N) - V_s) \qquad 21$$

At some time, the concentration will exceed some critical value and a hazard will have been created. Let us label the critical concentration C_{crit} and the critical time t_{crit}. C_{crit} can be in the ppb range or it can amount to several percent. As long as t_{crit} is much longer than any time element in the transportation cycle, the risk from this release is acceptable. There is a potential for serious incident if t_{crit} is comparable to the duration of a road trip, a trip in a rail car, or a sea voyage. Some of these times are long enough that even a very slow rate of release can create a hazard potential.

The denominator of Eq. 21 is simply the volume available for each container to release its contents into. This estimate is not conservative enough, if, for example, the vapor has a tendency to settle. Q(t) is just the total mass released from each container in time t. The smaller the denominator, the smaller t_{crit} will be (Q(t) is a monotonically increasing function). Q(t) can be expresses simply as:

$$Q(t) = \int_0^t \dot{Q}(y)\, dy \qquad 22$$

$\dot{Q}$ must include all of the environmental factors which regulate the loss rate. The most important of these is temperature. Since the loss rate increases with temperature, episodes of high temperatures during transportation may create hazardous conditions even though most of the transportation cycle is carried out at a safe temperature. Such considerations can lead to complicated models for the environmental conditions during transportation. This kind of modeling is beyond the scope of this work. It should be possible to establish that there is an upper temperature limit which is approached for only a few hours at a time and is almost never exceeded. This upper use temperature would be the appropriate one to use in calculating $Q(t_{crit})$. An upper bound can be placed on $\dot{Q}$ by assigning it the steady-state value. This is equivalent to neglecting the time-lag in Eq. 22. In that case, $Q = \dot{Q}t$. The following simple equation can then be used to calculate t_{crit}:

$$t_{crit} = [(V/N)-V_s]C_{crit}/\dot{Q} \qquad 23$$

Eq. 11 is the expression to use in evaluating $\dot{Q}$. Since most shipping containers resemble one another as to their design, we can assume that $(A/\ell)_{eff}$ does not vary over a wide range. The same thing is true (except for a few very special cases) of the state of the material. Estimates to within an order of magnitude can, therefore, be obtained by replacing $\dot{Q}$ by $G(T,\sigma,x)(A/\ell)_{eff}$. The ratio of C_{crit} to G can then be used as a screening criterion and ladings for which this ratio is too low would not be acceptable for shipment in plastic containers.

This screening criterion offers the advantages that it is simple, it is based on an objective measurement, and it is uniform. The procedure offers the disadvantages that ladings which are acceptable in some shipping container designs would be rejected while ladings which are unacceptable in other shipping container designs would be accepted. Such marginal cases should be decided on their own merits. One difficult part of the screening process is finding suitable values of C_{crit}. The critical concentrations are set using toxicological or other safety criteria. The levels have been known to change as new data is developed and DOT-OHMO's screening system should be responsive to these changes.

The effective carbon atom number can be directly employed as a screening parameter for unsuitable ladings. As an example, such a screening criterion might state: "No lading containing a component whose effective carbon atom number is less than (limiting value) shall be shipped in (description) container. The effective carbon atom number shall be determined by (test description) using (material description) as a reference material." This criterion is based on the finding that any substance which permeates a polymer at a substantial rate tends to damage the polymer. It is also presumed that the damage done by a slowly permeating substance is acceptable. At the present time, there is no way to draw the line between acceptable and unacceptable damage. The method for determining the effective carbon atom number and the nature of reference materials have been described in earlier sections of this report.

The limiting value of the effective carbon atom number will depend strongly on the nature of the container. A greater level of damage can be tolerated in a non-reusable polyethylene liner used in conjunction with a rigid overpack than can be tolerated in a reusable, free-standing drum. It is not necessary to perform holding tests using production containers because the effective carbon atom number can be more readily determined in a small-scale reference container. If the above screening criterion is written into container specifications, the level of performance which is used to establish the cutoff will tend to be the lowest common denominator of the existing industrial practice. A petitioner for an exemption can demonstrate that containers made by his process exceed this level of performance using permeation data. Decisions regarding the granting of exemptions can then be based on quantitative data.

7.2 SCREENING FOR MATERIALS SUITABILITY

The present Hazardous Materials Regulations make use of materials properties to screen out unsuitable resins. The materials properties used in this way include the resin density, the melt index, and certain tensile properties. The observation that the transmission rate, G, is very sensitive to the state of a resin indicates that G values could be used to screen out unsuitable materials. The materials screened out would be those whose barrier properties are not up to some standard value. It should be possible to designate a standard lading, which we shall call x_0, for such a test. If we recall that C is used to label the state of the resin in a production container, our screening criterion is that $G(T,C,x_0)$ may not exceed some limiting value. If a sufficiently rapid way to measure G(T,C,x0) could be found it should be possible to use this test for quality control purposes as well as for design qualification purposes. As we have noted in previous reports, the success of a materials screening parameter rests on whether or not the measurements are made on specimens from production containers.

In closing our discussion of screening criteria, we must, once again, return to the matter of units. Current industrial practice calls for using a 5 percent weight loss on storage over an extended period as a screening criterion. In part II of this series of reports, we discussed this issue and stated that this was not an acceptable way to use permeation data. The only kind of data which can be meaningfully used to predict the performance of a large number of combinations of containers and ladings are quantities like the transmission rate, G, which are materials properties.

8. SOME UNRESOLVED ISSUES

In the preceding sections, we have presented data and analyses which suggest a fairly compact way to describe permeation phenomena. There are a number of experiments which remain to be performed and there are situations which obviously do not fit into the scheme we have developed. The purpose of this section is to point out some areas where more answers are needed.

8.1. THE PROBLEM OF MIXTURES

In the previous sections, we have considered ladings to be pure molecular substances. Many industrial commodities are mixtures of such substances or ionic solutions and it is unreasonable to expect that they can be characterized by an effective carbon atom number. The simplest basis for calculating the transmission rate for a mixture is to use simple additivity:

$$G(T,C,AB) = \phi_A G(T,C,A) + (1-\phi_A)G(T,C,B) \qquad 24$$

where ϕ_A is the mole fraction of compound A in the mixture and $1-\phi_A$ is the mole fraction of compound B. Fels and Li have shown that this simple law is violated in at least one case [17].

Fractionation can cause the mass-loss rate to change with time. It is also possible that there is a mutual enhancement of the permeation rate due to changes in the state of the polymer brought about by the presence of the permeants. This appears to be the case in the paper by Fels and Li. We have not directly verified any of these phenomena. The effect they would have on the screening criterion for unsuitable ladings which we introduced in section 7.1 is not clear. The most conservative approach is to test the permeation properties of each component of the lading and if an unsuitable substance is present the lading should be ruled unsuitable because the rapidly permeating species may cause too much damage to the polymer. This tendency may be revealed on measurements of a lading of unknown composition if the products which permeate can be captured and identified.

Small-scale permeation tests using reference containers are simple enough that no unreasonable burden is placed on shippers of proprietary mixtures by asking them to test each component of their mixture against screening criteria for unsuitable ladings. Problems which are encountered can be settled on their individual merits.

Measurements in which each component of a permeating mixture is captured on the downstream side of the membrane are needed before we can construct general models for the behavior of mixtures.

8.2. THE CUP TEST AS AN ALTERNATIVE TO BOTTLE TESTS

We have made frequent reference to a "cup test" as an alternative means of measuring transmission rates of permeants. ASTM Method E-96 is an example of such a test which is used for measuring the water vapor transmission rate (WVTR) of plastics in sheet form. The literature on ASTM E-96 and our own experience using organic liquids as permeants indicate that there are severe problems with this method. In most cases, it appears that the permeant flux is greater when the liquid phase is in contact with the polymer film than it is when the vapor phase is in contact with the film. This result is difficult to understand because the chemical activity of a liquid and a saturated vapor are the same and the chemical activity gradient drives permeation.

Our tests using bottles tend to demonstrate that the rate of loss is the same no matter how much the liquid covers the surface of the bottle. We can obtain a very small dependence of loss rate on filling ratio if we fill bottles with varying amounts of permeant at the start of the experiment. One simple hypothesis which may account for these differences between the "vapor" and the "liquid" permeability is that air above the liquid forms a barrier to the diffusion of vapor. This hypothesis needs to be investigated.

We have also experienced difficulty making good seals betwen polymers in sheet form and the surfaces of metal cups. Elastomeric O-rings are attacked by many solvents and many semi-crystalline polymers do not deform easily enough to smooth out their surface roughness. This problem is especially acute for those who wish to test sections from production containers because such sections are often very thick and possess curved shapes. A means of thinning sections from industrial containers must also be found because the walls are so thick that a permeant having a time lag of 1/4 day when tested in a bottle may have a time-lag of 9 days or more in a thick section.

8.3. EXOTIC RESINS

Because polyethylene is not a good barrier to many kinds of molecular substances, other resins with improved barrier properties have come into use. These may be resins which are used to make complete containers, like poly(vinyl chloride) (PVC) or they may be resins which are applied as coatings (saran is an example). Several processes have been developed recently which chemically modify polyethylene to produce a better barrier layer *in situ*. In all of these cases the barrier resin is chemically different from polyethylene and the relationships between permeability and molecular structure have to be reexamined. Salame has already demonstrated that ranking schemes must be rearranged when the resin chemistry is changed [9]. Data from a fluorine treatment for blow-molded containers [18] further demonstrates that permeation depends on resin chemistry.

The practice of using measurements on reference containers should still be valid, but the tests to devise a ranking scheme may have to be very wide-ranging indeed. The introduction of a new resin will generally require the establishment of a new system for ranking and screening permeants.

9. Establishment of a Permeation Measurement System

1. In this section we identify barriers to the incorporation of the measurement system given in the preceding sections into the transportation system. Activity on permeation standards should be stimulated within the consensus standards community. This is likely to prove the most rapid and economical approach to achieving test methods, recommended practices, and interlaboratory evaluations suitable for regulatory purposes. There are units of the ASTM which would be suitable for this task, but they require working participation from DOT-OHMO, NBS, shippers, container manufacturers, and other interests. Active liaisons should be established with others, such as the FDA, who have problems in the area of permeation. Present resources for these activities are underutilized.
2. Standard materials should be made available to the user community. The amount of such material needed will depend upon DOT-OHMO's rulemaking activities. The task of producing materials to DOT-OHMO's specifications could be delegated to others as could the task of distributing the reference materials. The assistance of some of the more sophisticated members of the measurement community will be needed with regard to resin selection, characterization, and molding. Section 6 of this report can be used as a basis for negotiating the design of reference materials and devices.
3. A screening criterion for materials suitability based on permeation performance (see section 7.2) should be incorporated into the appropriate paragraphs of part 178 of CFR 49. AQL's should be set in accord with current sound industrial practice. It may also be necessary to include materials suitability criteria in certain paragraphs of part 173 of CFR 49 as well as in some exemptions.
4. A standardized protocol for obtaining quantitative information on permeation performance and using that information in rulemaking needs to be developed. Each request should contain the complete chemical description of the lading. When the lading contains chemical species whose permeation properties are not known, the requestor should obtain data from tests on standard bottles. The present procedures are not specific enough as to the kind of data they require, and common practice has been to get by with data which is very qualitative. The data should be elicited in a standard format and encoded into a central data base (see item 6). The use of standard bottles and accelerated testing conditions will help to ensure that the data can be obtained cheaply,

accurately, and quickly.

5. In recognition of the fact that the existing list of hazard definitions is incomplete, a definition of a "permeating substance" should be developed and referenced at appropriate points within part 173 of CFR 49. This definition would use performance criteria which must be backed up by standard tests. It should be noted that a "permeating substance" is not necessarily hazardous in and of itself, but its presence may aggravate other hazards.
6. A central repository should be established for permeation data gathered as a result of activities under items 4,5, and 6 above. This should be a computer-searchable data base which could, if necessary, be used to develop tabulations of permeation data. Because such data is of fundamental value to industry, government, and universities, the support of other federal agencies and private interests could be sought.
7. Training aids should be developed which can be used to teach field personnel how to recognize permeation failures. It is difficult to analyze permeation failures in the present Incident Reporting System because they are so easily confused with other kinds of failures.
8. Continuing attention must be given to research to solve the unresolved questions in permeation performance. The rate at which new combinations of ladings and packages are coming into use is such as to swamp the system for dealing with them.

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Appendix A

List of ASTM Standards Referenced in this Report

Designation	Title	Part
D-792-66	Standard Method of Test for Specific Gravity and Density of Plastics by Displacement	35
D-1505-68	Standard Method of Test for Density of Plastics by the Density-Gradient Technique	35
D-1928-70	Standard Method for Preparation of Compression-Molded Polyethylene Test Samples	36
D-2188-70	Standard Recommended Practice for Statistical Design in Interlaboratory Testing of Plastics	35
D-2561-70	Standard Test Method for Environmental Stress-Crack Resistance of Blow-Molded Polyethylene Containers	36
D-2684-73	Standard Recommended Practice for Determining Permeability of Thermoplastic Containers	36
E-96-66	Standard Method of Test for Water Vapor Transmission Rate of Plastics in Sheet Form	35
E-104-51	Standard Recommended Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions	35
E-177-71	Standard Recommended Practice for Use of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material	35

"PART" refers to the part number of the Annual Book of ASTM Standards in which the complete text of a given standard is to be found. Further information with regard to the standards listed above may be obtained from: ASTM, 1916 Race St., Philadelphia, PA 19103.

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16. Abstract

This report describes experiments which confirm the essential features of the "permachor" method for estimating the permeability of polyethylene to various liquids. The variables controlled in these experiments were temperature, resin, and alkane chain length. A statistical analysis based on the Linear Model revealed that the data could be described by a function of the form:

$$G(T,\sigma,n) = \exp[X(T,\sigma) + B\ (T,\sigma) \times H(n)],$$

where $G(T,\sigma,n)$ is the transmission rate of lading n through resin σ at temperature T and B, X, and H are empirically determined functions. The broader implications of this result with respect to possible standard artifacts for use in permeability testing are described. A concept we have called the "effective carbon atom number" is introduced as a means of correlating data. Once the effective carbon atom number of a liquid is known from measurements on one kind of polyethylene, it should be possible to predict what its permeability performance will be in containers made from different polyethylenes. Procedures are presented for implementing a standard-based system for measuring effective carbon atom numbers of various liquids and using this information to make permeability performance predictions. The major advantage of such a system is that it minimizes the number of tests which must be made using full-scale containers.

17. Key Words
Effective carbon atom number; hazardous materials; packaging; plastics; standardization; transportation.

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