PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

J. C. PHILLIPS

APRIL 1980
FINAL REPORT

Prepared for
U.S. DEPARTMENT OF TRANSPORTATION
MATERIALS TRANSPORTATION BUREAU
OFFICE OF HAZARDOUS MATERIALS REGULATIONS
WASHINGTON, D.C. 20590
PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

Part VI: Mass Loss and Effective Carbon Atom Number Measurements

by

Joseph C. Phillips
Polymer Science and Standards Division
National Measurement Laboratory
National Bureau of Standards
Washington, D. C. 20234

For

U.S. Dept. of Transportation
Materials Transportation Bureau
Office of Hazardous Materials Regulation
Washington, D. C. 20590

Research Contract DOT AS-50074

April 1980
# Table of Contents

1. Introduction................................. 6  
2. Materials................................. 7  
   A. Ladings................................ 7  
   B. Polyethylene Bottles................... 7  
3. Experimental.............................. 7  
4. Results and Discussion.................... 8  
   A. Mass Loss................................ 8  
   B. Effective Carbon Atom Number......... 9  
5. Conclusion................................ 12
Abstract

This report describes the mass loss through polyethylene bottles of two n-alkyl series (n-alcohols and n-carboxylic esters) and a group of miscellaneous compounds. The experiments were performed at 50 °C using both low density and high density polyethylene bottles. The backbone chain length, $N_A$, for each series of n-alkyl's was extended to 16 in order to characterize more fully the dependence of loss rate from PE on chain length of permeant.

The results suggest that the effective carbon atom number for a given permeant may be determined from a single density resin bottle using the n-alkane series as the standard lading. Once the effective carbon atom number has been determined under chosen conditions, the permeability performance of the permeant for another resin density may be predicted with reasonable accuracy. These results seem to complement the "permachor" method to minimizing the number of tests required for the determination of the performance of full-scale containers.
Preface

This report is part VI of a series prepared for the Office of Hazardous Materials Operations under Research Contract DOT AS-50074. This work deals with the establishment of criteria for predicting permeation performance of various kinds of ladings in polyethylene bottles. This study verifies, at least for the permeants and containers studied herein, the validity of the effective carbon atom number as a parameter for transferring results of permeation measurements among various shipping containers made from various PE resin. The present work extends the concepts presented in Part IV of this series.
List of Tables

1. Polyethylene (PE) Bottles Used for Mass Loss Measurements

2. Loss Rate at $t = 50 \, ^\circ C$ for various classes of compounds using low density (CPE) and high density (LPE) bottles.

3. Average Effective Carbon Atom Number for Various Classes of Compounds (Based on Skeletal Chain Length).

4. Predicted Loss Rate at 50 $^\circ C$ for High Density Bottle From Loss Rate of Low Density Bottle.
List of Figures

1. Mass-Loss Data, n-Hexane
2. Mass-Loss Data, n-Alcohols (c₁ - c₄)
3. Mass-Loss Data, n-Alcohols (Decyl and Dodecyl)
4. Mass-Loss Data, n-Cetyl Alcohol
5. Mass-Loss Data, n-Carboxylic Esters (Ethyl, Butyl, and Amyl Acetate)
6. Mass-Loss Data, n-Carboxylic Esters (Methyl Heptanoate and Methyl Tetradecanoate)
7. Mass-Loss Data, 1,2-Dichloroethane, Acetone, Methyl Ethyl Ketone, and Acetonitrile [Low Density PE]
8. Mass-Loss Data, 1,2-Dichloroethane, Acetone, Methyl Ethyl Ketone, and Acetonitrile [High Density PE]
9. Loss-Rate Data, Low Density PE
10. Loss-Rate Data, High Density PE
11. Loss-Rate Data Versus Effective Carbon Atom Number
12. Loss-Rate Data Versus Density of PE
Introduction

The permeation rate of vapors and gases through a given barrier material depends on parameters such as thickness, density of the material, and the compatibility of the permeant and the barrier [1]. Various attempts at correlating permeability with these barrier parameters have proven successful in many instances and have also made possible the prediction of the transmission performance of a given barrier and the permeant [2,3]. In a previous report to DOT (Part IV, DOT AS-50074), an effective carbon atom number was introduced as a parameter for predicting permeation performance of n-alkanes in PE bottles [4]. This present report has attempted to establish the validity of the effective carbon atom number by: (1) studying other homologous series; and (2) looking at a wider range of densities of the PE resin.

This work investigated the loss rate for an n-alcohol series ($N_A = 1$ to 16) and an n-carboxylic ester series ($N_A = 5$ to 16) in PE bottles of two different densities ($\rho \sim 0.92$ g/cm and $\rho \sim 0.94$ cm) at 50 °C. The effective carbon atom number was determined for each permeant and found to be relatively insensitive to the density of both PE resin bottles [4]. By using the average effective carbon atom number, the loss rate in the high density PE bottle was predicted for a group of miscellaneous compounds (1,2-dichloroethane; acetone; methyl ethyl ketone; acetonitrile) from the loss rate measurements in the low density PE bottle with rather good agreement to the experimental data. These results tend to support the statistical linear model for transmission rate as outlined in part IV of the permeation report DOT AS-50074.
Materials

A. Ladings

The n-alcohols ($N_A = 1$ to 16), n-carboxylic esters ($N_A = 5$ to 16), and a group of miscellaneous compounds used in this study are listed in Table II. All samples were either A.C.S. certified, reagent or technical grade and were used without any further purification.

B. Polyethylene Bottles

Table I lists some information on the PE bottles used in this study. The low density (CPE, $\rho \sim 0.92 \text{ g/cm }$) and high density (LPE, $\rho \sim 0.94 \text{ g/cm }$) bottles were manufactured by the Nalge Company. The actual densities, as determined by a flotation method using ethanol and distilled water at 25 °C, were found to be $\rho = 0.9235 \text{ g/cm}^3$ and $\rho = 0.9453 \text{ g/cm}^3$. Some high density PE bottles made by Phillips Petroleum Company were found to have a density of $\rho = 0.9430$. The mean wall thickness of the CPE and LPE bottles were, respectively, 0.1062 cm and 0.0950 cm and the "Phillips" bottles had a mean thickness of 0.0671 cm. The CPE bottles as shown in Table I showed the greatest variation in thickness over its wall surfaces while the "Phillips" bottle had the least variation. Such density and thickness fluctuations for a given bottle contributes to the uncertainty in the mass loss measurement.

Experimental

Mass loss measurements were performed in a safety-designed air circulating oven maintained at 50.0 °C ± 0.4 °C. Marked positions within the oven were calibrated for temperature variations and during the experiment, the oven temperature was monitored by a thermistor probe. The zero time of the experiment was taken as the initial placement of the bottles.
(filled with ~100 m\(\text{L}\) of sample) into the oven[4]. At subsequent times, the bottles were removed and weighed on a top-loading balance sensitive to about .01 g. From the change in mass versus time, the loss rate for each sample was determined.

Results and Discussion

A. Mass Loss

Typical curves for mass loss measurements are shown in Figs. 1-8. All the curves seem to possess the same general mass-time behavior, i.e., as the time increases beyond the induction period, the curves tend to asymptotically approach linear behavior. From permeation theory [5] such behavior may be represented as

\[
\Delta m = \left[\frac{\partial \Delta m}{\partial t}\right] (t - \eta (t/\tau))
\]

(1)

where \(\Delta m\) is the amount of permeant lost after time \(t\), \(\frac{\partial \Delta m}{\partial t} = \dot{Q}\) is the steady-state rate of loss, \(\eta\) is a parameter which depends on the molecular transport process and the initial experimental conditions and \(\tau\) is the time-lag which is proportional to the thickness of the container wall, \(\lambda\), and inversely proportional to the diffusivity of the permeant, \(D\), i.e., \(\tau = \lambda^2 / 6D\).

The mass-time data for this study have been analyzed only in terms of the steady-state rate, \(\dot{Q}\), and is summarized in Table II and Figs. 9 and 10. As can be seen in Fig.1, Figs. 3-6, and in Table II, an increase in PE density tends to diminish the amount and rate of permeant passing through the container walls. If the diffusion process is truly Fickian, then the steady-state rate should be inversely proportional to the effective thickness for a constant area [4]. The results in Fig.1 and
Table I and II for the "Phillips" bottle do indeed suggest an inverse
dependence of \( \dot{Q} \) on \( \ell \), but a small difference in density (as will be shown
later) could also appreciably increase the loss rate.

The results in Table II and Figs. 9 and 10 further suggests a de-
pendence of loss rate on chain length as expected. Here the chain length
is defined as the backbone or skeletal chain length, \( N_A \), which includes
all atoms in the primary chain [6] exclusive of atoms at the chain end
that constitute a chemical group (e.g., CN, NH\(_2\), OH, etc.). The loss
rate, \( \dot{Q} \), may be empirically defined [3] as:

\[
\dot{Q} = \dot{Q}_0 e^{-E_p/RT}
\]

(2)

where \( \dot{Q}_0 \) is a constant, \( E_p \) is the apparent activation energy, \( R \) is the
gas constant, and \( T \) is the absolute temperature. Since the apparent
activation energy generally increases as the chain length increases,
the loss rate according to Eq.(2) should decrease. For chain lengths
below some critical value, \( (N_A \sim 5) \) the loss rate may not be a monotonic
function due to polarity effects [3] as shown in Figs. 9 and 10 for
the n-alcohol and n-carboxylic ester series. Two members of the ketone
series (acetone and MEK) also seem to show polarity effects for the early
members of the series. The results in Figs. 9 and 10 also suggest that
as the chain length increases, the loss rate for each series tend to
approach that of the n-alkanes.

B. Effective Carbon Atom Number

The effective carbon atom number, \( n_e \), is just a shift parameter
that characterizes the loss rate of a given permeant to that of some
standard or reference permeant [4]. This concept is analogous to that
of the "permachor" approach [3]. In order to account for all atoms in
the primary chain, the backbone or skeletal chain length, $N_A$, is used
in this study rather than only the number of carbon atoms in the chain.
The choice for the former appear to be small and roughly constant.

Figure 9 for low density PE may be used to illustrate the determina-
tion of $n_e$ for a given permeant. For example, the effective carbon atom
number for n-amyl acetate is found by shifting at constant loss rate
to the n-alkane curve (note dotted line in Fig.9). The abscissa at the
intersection of the two curves is defined as $n_e$. Hence, the determina-
tion of $n_e$ may be given mathematically as:

$$n_e = \log \left( \frac{\dot{Q}_A}{\dot{Q}_0} \right) / k$$

(3)

where $\dot{Q}_A$ is the loss rate for a given permeant, $\dot{Q}_0$ and $k$ are parameters
that may be determined from the loss rate equation for the n-alkanes,
i.e.,

$$\log \dot{Q} = \log \dot{Q}_0 + kN_A$$

(4)

By using Eqs.(3) and (4), the effective carbon atom number was calculated
from the results in Figs. 9 and 10. In Fig.11 a semi-log plot of loss
rate and $n_e$ for both PE density bottles does indeed yield parallel lines
within experimental error. The average $n_e$ values for both PE density
bottles are assembled in Table III with a maximum deviation of about
10% which occurred in the alcohol series. The lines in Fig.11 may be
represented as:

$$\log \dot{Q}_A = F(\rho_p,T) + k_o n_e$$

(5)

where $F$ is a function of PE density and temperature and $k_o$ is apparently
independent of PE polymer density. By using Eq.(5) and loss rate results
for the miscellaneous compounds in Table II for the low density PE bottles, the loss rate for the high density PE bottle was predicted as shown in Table IV. The results are in rather good agreement with the experimental values and tend to reaffirm the validity of the effective carbon atom number [4]. Similar calculations may also be done for the other compounds with comparable agreement. Figure 12 further illustrates the fact that for $N_A > 5$ the nature of the steady-state diffusion process in the PE polymer matrix is somewhat similar for each series of permeants.

If Eq.(5) is now combined with the results of Fig.11, the loss rate of the permeant at constant temperature becomes:

$$\log \dot{Q}_A = F(\rho_p, T) + k_o n_e = \log \dot{Q}_{A_o} + C(\rho_p - \rho_{p_0}) + k_o n_e$$  (6)

where $C$ is a constant, $\rho_{p_0}$ and $\rho_p$ are, respectively, the density of PE for the reference or standard state and $\rho_p$ is some other PE density of interest. Thus at constant temperature, the loss rate for a given permeant may be estimated by Eq.(6) from a knowledge of only $n_e$ and $\dot{Q}_{A_o}$. The latter quantity is determined from the n-alkanes in the standard state. As discussed above, the effective carbon atom number of a given permeant may be experimentally determined from some standard permeant in a given polymer resin.
Conclusion

This work has presented data at constant temperature on mass loss and loss rate for n-alcohols and n-carboxylic esters and a group of miscellaneous compounds of two different densities in PE resin bottles. From the data an effective carbon atom number, $n_e$, for each permeant was determined and found to be roughly independent of the density of the PE polymer matrix. By measuring loss rate of the n-alkanes as standard permeants in PE bottles of a given density, the loss rate of other permeants may be predicted at some other PE density with reasonable accuracy by using $n_e$ values.

This work further suggests that a standard measurement system of bottles (constant wall thickness, density, type, etc.) and permeants (e.g., n-alkanes) could be chosen for obtaining quantitative mass loss information. Effective carbon atom numbers derived from such measurements could be compiled into a common data pool [4] and made accessible to the concerned community (manufacturers, shippers, users, etc.) for the purpose of ascertaining permeation performance. An assemblage of information of this kind could also aid rulemaking efforts in attempting to normalize such diversified community interests [4].

This investigation has not addressed the question of the dependence of loss rate on temperature. Such studies are highly desirable for ascertaining the activation energies as a function of chain length which enters directly into Eq.(2). Another question of equal importance is the dependence of loss rate on container wall thickness, $\lambda$. Limited results reported here do indicate an inverse dependence on $\lambda$, but more extensive and well-defined experiments need to be done in order to predict the permeation performance of full-scale containers with some degree of confidence.
List of References


<table>
<thead>
<tr>
<th>TYPE</th>
<th>Stated Density, g/cm(^3)</th>
<th>Found Density, g/cm(^3)</th>
<th>Average Thickness, cm</th>
<th>Volume Capacity, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE (Low Density)(^a)</td>
<td>.92</td>
<td>.9235 ± .0009</td>
<td>.1062 ± .0190</td>
<td>125</td>
</tr>
<tr>
<td>LPE (High Density)(^a)</td>
<td>.94</td>
<td>.9453 ± .0012</td>
<td>.0950 ± .0068</td>
<td>125</td>
</tr>
<tr>
<td>&quot;Phillips&quot; (High Density)(^b)</td>
<td>-</td>
<td>.9430 ± .0030</td>
<td>.0671 ± .0028</td>
<td>125</td>
</tr>
</tbody>
</table>

\(^a\) Malge Company

\(^b\) Phillips Petroleum Company
## TABLE II

Loss Rate at $t = 50 \, ^\circ C$ for Various Classes of Compounds

Using Low Density (CPE) and High Density (LPE) Bottles.

<table>
<thead>
<tr>
<th>$N_A^a$ Alkane (g/hr)</th>
<th>$\dot{Q}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CPE</td>
</tr>
<tr>
<td>7 Heptane</td>
<td>0.397</td>
</tr>
<tr>
<td>&quot;Phillips&quot; bottle</td>
<td>0.0837</td>
</tr>
<tr>
<td>16 Hexadecane</td>
<td>0.0254</td>
</tr>
<tr>
<td>&quot;Phillips&quot; bottle</td>
<td>0.00973</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$N_A^a$ n-Carboxylic Esters (g/hr)</th>
<th>$\dot{Q}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0696</td>
</tr>
<tr>
<td>7</td>
<td>0.0669</td>
</tr>
<tr>
<td>8</td>
<td>0.0540</td>
</tr>
<tr>
<td>9</td>
<td>0.0380</td>
</tr>
<tr>
<td>16</td>
<td>0.0135</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$N_A^a$ n-Alcohols (g/hr)</th>
<th>$\dot{Q}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00390</td>
</tr>
<tr>
<td>2</td>
<td>0.00290</td>
</tr>
<tr>
<td>3</td>
<td>0.00275</td>
</tr>
<tr>
<td>4</td>
<td>0.00380</td>
</tr>
<tr>
<td>6</td>
<td>0.00360</td>
</tr>
<tr>
<td>8</td>
<td>0.00301</td>
</tr>
<tr>
<td>10</td>
<td>0.000478</td>
</tr>
<tr>
<td>12</td>
<td>0.00248</td>
</tr>
<tr>
<td>16</td>
<td>0.000897</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$N_A^a$ Misc. Compounds (g/hr)</th>
<th>$\dot{Q}_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Aceto</td>
<td>0.00750</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>0.242</td>
</tr>
<tr>
<td>3 Acetone</td>
<td>0.0240</td>
</tr>
<tr>
<td>4 MEK</td>
<td>0.0450</td>
</tr>
</tbody>
</table>

\(^a\) $N_A$ is the backbone or skeletal chain length.
### TABLE III

Average Effective Carbon Atom Number for Various Classes of Compounds (based on skeletal chain length)

<table>
<thead>
<tr>
<th>N_A</th>
<th>n-Alcohols</th>
<th>n_e</th>
<th>N_A</th>
<th>n-Carboxylic Esters</th>
<th>n_e</th>
<th>N_A</th>
<th>Miscellaneous Compounds</th>
<th>n_e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl</td>
<td>21.8</td>
<td>5</td>
<td>Ethyl Acetate</td>
<td>12.9</td>
<td></td>
<td>Acetonitrile</td>
<td>21.1</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl</td>
<td>23.0</td>
<td>7</td>
<td>Butyl Acetate</td>
<td>13.2</td>
<td></td>
<td>1,2-Dichloroethane</td>
<td>8.4</td>
</tr>
<tr>
<td>3</td>
<td>Propyl</td>
<td>23.3</td>
<td>8</td>
<td>Amyl Acetate</td>
<td>14.2</td>
<td></td>
<td>Acetone</td>
<td>19.0</td>
</tr>
<tr>
<td>4</td>
<td>Butyl</td>
<td>22.7</td>
<td>9</td>
<td>Methyl Heptanoate</td>
<td>14.6</td>
<td></td>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>17.0</td>
</tr>
<tr>
<td>6</td>
<td>Hexyl</td>
<td>23.4</td>
<td>16</td>
<td>Methyl Tetradecanoate</td>
<td>15.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Octyl</td>
<td>24.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Decyl</td>
<td>26.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Dodecyl</td>
<td>25.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Cetyl</td>
<td>28.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE IV

**Predicted Loss Rate at 50 °C For High Density Bottle From Loss Rate of Low Density Bottle (Using Fig. 11)**

<table>
<thead>
<tr>
<th>( N_A )</th>
<th>Miscellaneous Compounds</th>
<th>Loss Rate, ( Q_A ) (g/hr) [High Density]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>Actual: 0.00210, Predicted: 0.0013</td>
</tr>
<tr>
<td>2</td>
<td>1,2-Dichloroethane</td>
<td>Actual: 0.0470, Predicted: 0.041</td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
<td>Actual: 0.00450, Predicted: 0.0041</td>
</tr>
<tr>
<td>4</td>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>Actual: 0.00820, Predicted: 0.0077</td>
</tr>
</tbody>
</table>
Fig. 1

- CPE Bottle
- "Phillips" Bottle
- LPE Bottle

Temperature: $t = 50^\circ C$

Time, Hours

Mass Loss, g
Fig. 3
Fig. 4

Cetyl Alcohol

- CPE Bottle
- LPE Bottle

$ t = 50^\circ C$

Time, Hours

Mass Loss, g
Fig. 5
Fig. 6

- Methyl Heptanoate
- Methyl Tetradecanoate
- Methyl Hexadecanoate

$t = 50^\circ C$

Mass Loss, g

Time, Hours

n-Carboxylic Esters: CPE, LPE
Fig. 8

Miscellaneous Compounds (LPE)

1,2-Dichloroethane
Methyl Ethyl Ketone
Acetone
Acetonitrile

$T = 50^\circ\text{C}$

Mass Loss, %

Time, Hours

0  60  120  180
- 1,2-Dichloroethane
- Methyl Ethyl Ketone
- Acetonitrile
- n-Alkanes
- n-Carboxylic Esters
- n-Alcohols

Loss Rate (LPE)

Fig. 10
Fig. 12

$\text{t} = 50^\circ\text{C}$

Loss Rate and Polyethylene Density

- $n$-Alkane, $N_A = 7$
- $n$-Carboxylic Esters, $N_A = 8$
- $n$-Alkane, $N_A = 5$
- $n$-Carboxylic Ester, $N_A = 16$
- $n$-Alcohol, $N_A = 16$
- $n$-Alcohol, $N_A = 8$

Log $Q_A$, (g/hr)

PE "Bottle" Density, g/cm$^3$