

# Solvent Barrier Property for Fluorinated Polyethylene

L. J. HAYES and D. D. DIXON, *Corporate Research and Development, Air Products and Chemicals, Inc., Allentown, Pennsylvania 18105*

## Synopsis

Solvent barrier studies for fluorinated polyethylene have shown that the fluorinated surfaces reduce the rate of permeation for many solvents. The barrier property has been related to physical and chemical properties of the solvent. For instance, solvents having a dielectric constant between 7 and 10 were not retained as well as solvents with a dielectric constant less than 7.

## INTRODUCTION

Since the discovery by Rudge<sup>1</sup> that fluorination of polyethylene yields a surface resembling Teflon in certain properties, various polymeric materials have been fluorinated.<sup>2-7</sup> The reported results of the reaction of elemental fluorine and polyethylene have led us to investigate the solvent barrier property for fluorinated polyethylene bottles. Tanner has recently proposed a mechanism by which the fluorination process occurs.<sup>8</sup>

In order for a solvent to permeate a polymer substrate, the solvent must first dissolve in the polymer, diffuse through the resin, and finally evaporate.<sup>9</sup> As the solubility of the solvent increases, permeation through the polymer will increase. Diffusion depends mainly on solubility and diffusivity of the vapor. This means that a surface treatment of a polymer resin will only affect the first step of permeation—solution formation.

Solubility depends on the surface tension of both the polymer and the solvent.<sup>10</sup> If a solvent does not permeate a polymer resin, then a surface treatment will have no effect on its permeation rate. If, however, the solvent does dissolve in the polymer, then the permeation rate will be dependent on the solubility of the solvent in the surface coating.

According to the activated diffusion theory of permeation, it is assumed that if a solvent is not dissolved readily in the solute (polymer) it will not permeate it easily.<sup>11</sup> In order to determine if a solvent will dissolve in a polymer, the solvent's solubility parameter is compared to the polymer's solubility parameter. Those solvents with solubility parameters close to, or identical with, that of the polymer will be soluble in the polymer.

The solubility parameter is the square root of the cohesive energy density<sup>12</sup>:

$$\delta = (\text{cohesive energy density})^{1/2}$$

where cohesive energy density = cohesive energy/molar volume. Cohesive energy arises from both permanent dipole molecular interactions and London "dispersion" atomic interactions and thus encompasses many properties of the solvent such as dielectric constant, dipole moment, and polarizability.<sup>13</sup>

In addition to the solubility parameter, various other properties are involved in permeability.<sup>14</sup> Not only are the physical and chemical properties of the polymer important, but also the physical and chemical properties of the solvent.<sup>9</sup> Using a variety of liquids, Pinsky and coworkers introduced a  $P$  factor from permeation data of solvents through polyethylene bottles.<sup>15</sup> More recently, Salame has developed a method by which the permeation rate can be predicted for polyethylene bottles.<sup>16</sup> By assigning certain values to the various atoms or groups of atoms present in the solvent molecule, he arrived at what is called the Permachor ( $\pi$ ) value.

### EXPERIMENTAL

The polyethylene bottles used in this study are made of high-density polyethylene resin. The bottles were 4-ounce containers with a wall thickness of about 25 mils. Fluorinations were carried out using a modification of the procedure reported by Schonhorn and Hansen<sup>6</sup> for a period of 10 min. ESCA analysis indicates that the depth of fluorination is approximately 50 Å.

Permeation data were obtained by measuring the weight of solvent placed in the polyethylene bottle sealed using a 3M polyethylene seal. The bottle was placed in an oven at the desired test temperature and then weighed periodically. The percent weight loss was then calculated by the following equation:

TABLE I  
Solvents Used in Permeability Study<sup>a</sup>

Solvent	B.P., °C	$E$	$\epsilon$	$\pi$	% Wt loss F <sub>2</sub> -PE (11 days)	% Wt loss PE control (11 days)
<i>n</i> -Pentane	36	3	1.84	5.0	0.21	98.10
<i>n</i> -Hexane	69	2	1.88	6.0	0.19	61.29
<i>n</i> -Heptane	98	1	1.92	7.0	0.08	24.26
Isooctane	99	4	1.94	14.8	0.03	4.54
Cyclohexane	81	5	2.02	8.0	0.15	22.34
Carbon tetrachloride	77	6	2.24	5.8	0.05	28.26
Benzene	80	13	2.28	7.6	3.65	36.68
Toluene	110	9	2.38	6.4	1.80	41.23
<i>p</i> -Xylene	138	11	2.37	7.4	0.54	59.20
Mesitylene	165	10	2.27	10.6	0.18	15.83
Chlorobenzene	131	12	5.62	6.6	5.41	32.05
Glyme	80	16	7.20	8.8	13.20	12.37
Diglyme	160	15	—	10.2	1.73	2.14
Tetrahydrofuran	66	23	7.58	8.4	45.66	53.93
Dioxane	101	24	2.20	10.8	3.04	4.23
Chloroform	61	17	4.80	4.6	38.17	44.93
Methylene chloride	40	18	8.93	3.4	46.26	50.81
1,2-Dichloroethane	83	19	10.36	4.4	8.09	8.54
Acetone	56	22	20.70	13.8	2.58	2.51
Methyl ethyl ketone	80	22	18.51	12.5	2.68	2.81
Ethyl acetate	66	25	6.02	12.0	3.39	3.57
DMSO	189	26	46.68	—	0.12	0.09
Methanol	65	35	2.87	17.50	0.66	0.75
<i>n</i> -Propanol	97	33	20.33	18.50	0.35	0.34
Isopropanol	82	32	19.92	18.50	0.19	0.32
<i>n</i> -Butanol	118	31	16.56	18.00	0.27	0.30

<sup>a</sup>  $E$  = Elutropic value;  $\epsilon$  = dielectric constant;  $\pi$  = Permachor value.

$$\% \text{ weight loss} = \frac{\text{weight loss}}{\text{weight of solvent}} \times 100$$

Weight loss data could be altered by changes in the container geometry during the permeation tests. However, the exact change was not studied. For instance, the fluorinated container did not collapse as much as the control, but the fluorinated containers also showed significant reduced weight loss over the same test period.

If the collapsed container causes a negative internal pressure, the rate of permeation should decrease relative to a noncollapsed container. This would only serve to increase the effectiveness of the fluorination treatment since the rate of permeation for the control should actually be higher than noted.

### RESULTS AND DISCUSSION

Twenty-six common solvents were tested for containment by both control high-density polyethylene bottles and fluorinated high-density polyethylene bottles (Table I).

One goal of this study was to establish the solvent barrier properties of control

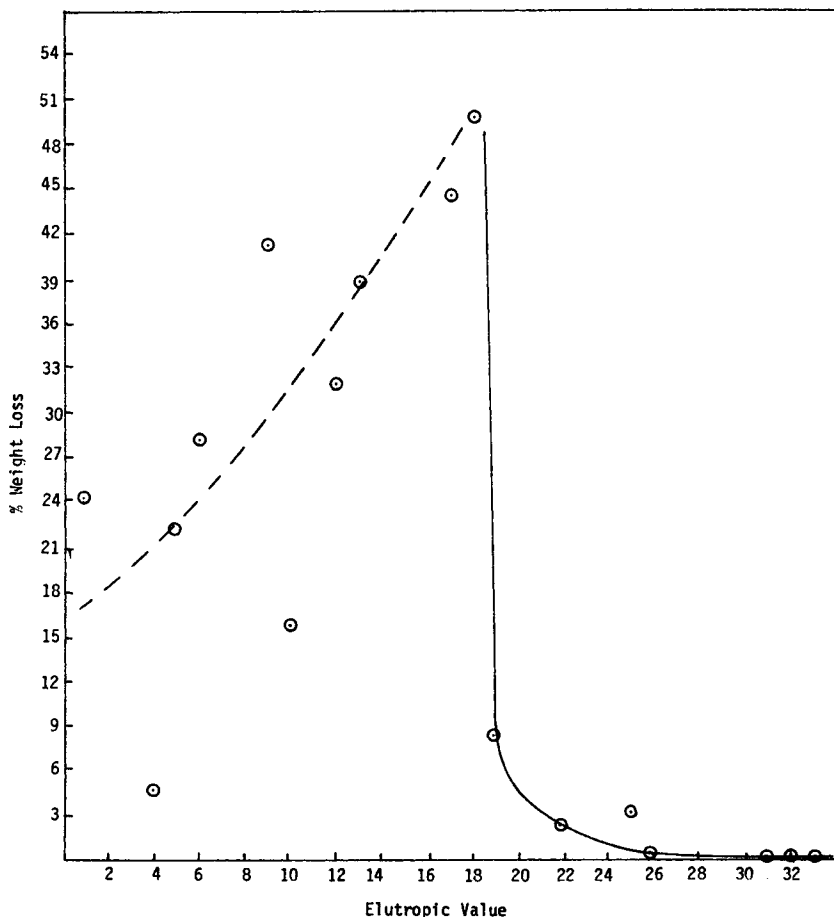


Fig. 1. Weight loss of solvent vs elutropic value—control bottles.

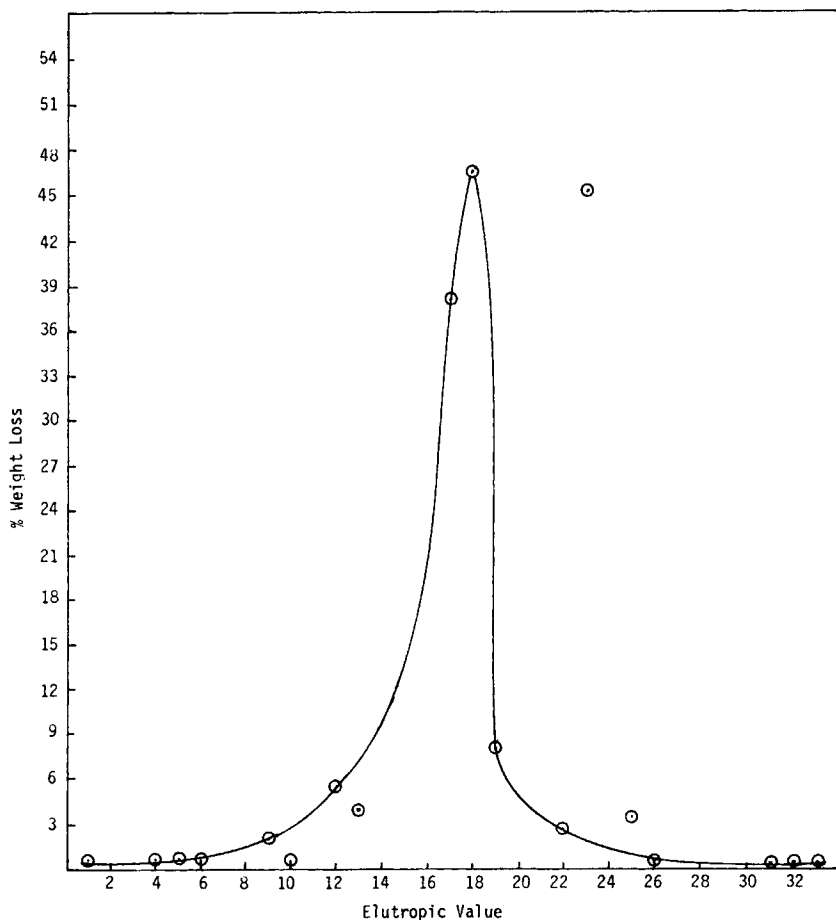


Fig. 2. Weight loss of solvent vs elutropic value—fluorinated bottles.

high-density polyethylene bottles since polyethylene resin has changed some over the years since Salame's work. Using Salame's method, Permachor values were calculated for the solvents listed in Table I. A general trend of increasing weight loss of the solvent with decreasing  $\pi$  values was found for the untreated bottles. In general, hydrocarbons, aromatics, chlorinated aromatics, chlorinated hydrocarbons, ethers, esters (high  $-\text{CH}_2-$  content), and ketones (high  $-\text{CH}_2-$  content) are capable of permeating high-density polyethylene. In fact, solvents having a  $\pi$  value less than 12 were not retained very well.

It should be noted that the Permachor method showed significant deviation with chloroform, methylene chloride, and 1,2-dichloroethane. Salame recognizes there are exceptions to his method, particularly in halogenated ethanes.

While the Permachor method attempts to take into account the size, shape, and polarity of the molecule, it can be seen from Figure 1 that the polarity of the solvent, elutropic value, alone is an important feature.<sup>17</sup> The highly branched molecules such as isooctane and mesitylene fall below the normal trend.

A second goal of this study was to establish the solvent barrier properties of fluorinated polyethylene bottles. Attempts to correlate permeability with  $\pi$  values gave a wide scatter of points. This result was not surprising since  $\pi$  values

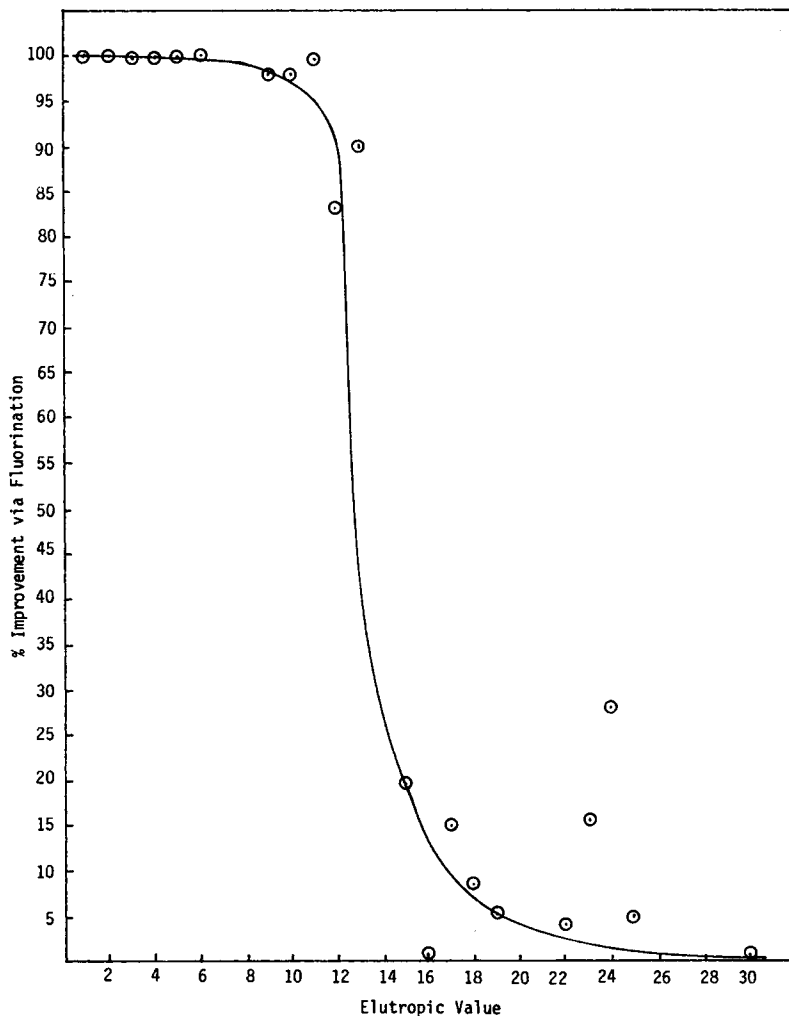


Fig. 3. Improvement of solvent retention via fluorination of polyethylene bottles.

TABLE II  
Barrier Properties for Commercial Products<sup>a</sup>

Fluid	Control bottle % wt loss	Fluorinated bottle % wt loss
Heavy gasoline	54.47	0.86
Turpentine	3.92	0.00
Snowmobile motor oil	0.30	0.00
Paint	2.22	0.06
Varnish	6.78	0.01

<sup>a</sup> Test was run at 122°F for 28 days.

were determined for nonpolar polymers and would not be expected to work on polar polymers or polar surfaces.<sup>18,19</sup>

The 26 solvents showed a definite relationship between their polarity and their permeability through the fluorinated polyethylene bottle. This relationship

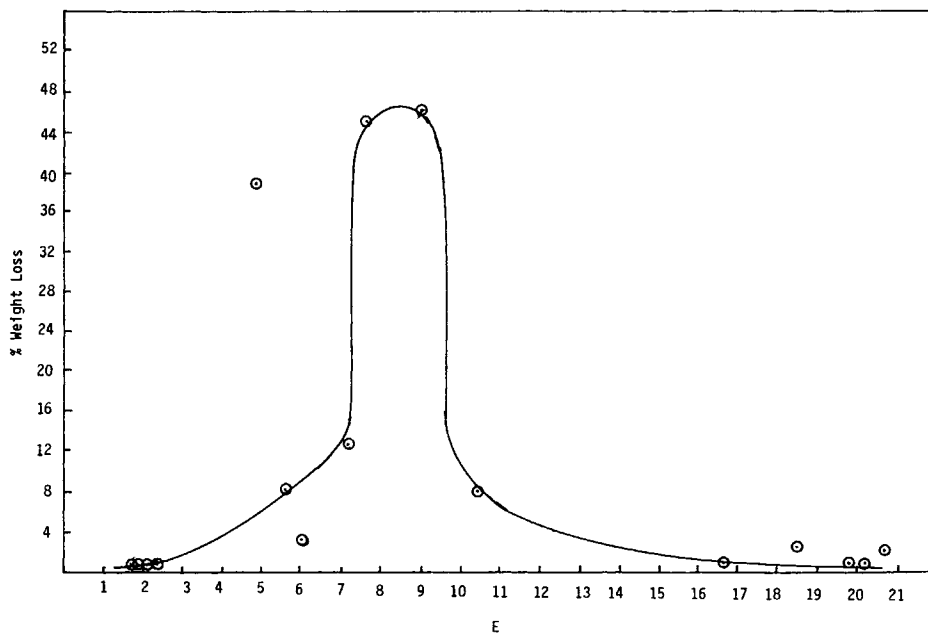


Fig. 4. Weight loss of solvent vs solvent dielectric constant—fluorinated bottles.

TABLE III  
Bottle Condition After Barrier Tests

Fluid	Control bottle condition	Fluorinated bottle condition
Heavy gasoline	Severe collapse	Severe collapse
Turpentine	Severe collapse	Slight collapse
Snowmobile motor oil	Collapse; dyed	Very slight collapse; not dyed
Paint	Severe collapse	Very slight collapse
Varnish	Severe collapse	Slight collapse

can be seen in Figure 2, where percent weight loss is plotted against the elutropic value,  $E$ . Elutropic values are a measure of polarity, and the higher the  $E$  value, the more polar the solvent.<sup>17</sup> The main deviation in this plot is tetrahydrofuran, whose permeation is high for the given  $E$  value. The published  $E$  value for tetrahydrofuran seems too high; i.e., it has value of 23 against a value of 16 for glyme (2 oxygens and open chain) and a value of 24 for dioxane (2 oxygens and cyclic). Also from Figure 3 it is seen that fluorination brings about significant improvement in barrier property of high-density polyethylene only when the  $E$  value is less than 14; for most practical purposes this would be hydrocarbons and aromatics.

A plot of percent weight loss versus dielectric constant ( $\epsilon$ ) also points up a relationship between solvent polarity and penetration for fluorinated polyethylene (Fig. 4). In this case chloroform does not fit the trend while tetrahydrofuran does.

In general, hydrocarbons and aromatics are readily contained, and thus a major permeability problem of polyethylene is solved through fluorination.

The permeation of chlorobenzene is drastically reduced by fluorination but

not as effectively as with toluene or benzene. The retention of *partially* halogenated aliphatics by polyethylene is not significantly improved, whereas completely chlorinated solvents such as  $\text{CCl}_4$  are readily retained. Fluorination of polyethylene does not significantly improve the retention of ethers. It may well be that higher ethers, such as dioctyl ether, will be retained. Lower ketones and esters are retained by both untreated and treated polyethylene, and thus fluorination does not affect the barrier property.

The barrier property of both untreated and treated polyethylene was determined for several commercial products. Table II shows that in all cases the barrier property is significantly improved. In addition, the treated bottles did not show the extreme paneling of the walls as was found in the untreated bottles (Table III).

In conclusion, it has been shown that fluorination of a polyethylene bottle improves the barrier property toward hydrocarbon and aromatic solvents.

The authors wish to thank D. Rissmiller for treating the samples and recording the solvent barrier data.

### References

1. A. J. Rudge, Br. Pat. 710,523.
2. J. Shimada and M. Hushino, *J. Appl. Polym. Sci.*, **19**, 1439 (1975).
3. M. Okada and K. Makunchi, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**(3), 334 (1969).
4. A. J. Otsuka and R. J. Lagow, *J. Fluorine Chem.*, **4**, 371 (1974).
5. R. J. Lagow and J. L. Margrave, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 177 (1974).
6. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **12**, 1231 (1968).
7. H. Shinohara, M. Iwasaki, S. Tsujimura, K. Watanabe, and S. Okazaki, *J. Polym. Sci. A-1*, **10**, 2129 (1972).
8. K. Tanner, *Chimia*, **22**, 176 (1968).
9. C. W. Hall, *Mod. Packag.*, **46**, 53 (1973).
10. M. Salame and J. Pinsky, *Mod. Packag.*, **36**, 153 (1962).
11. J. H. Parlman, *Mod. Packag.*, **22**, 198 (1948).
12. C. M. Hansen, *Chemtech.*, **2**, 547 (1972).
13. C. M. Hansen, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Wiley, New York, 1971, p. 889.
14. H. Yasuda and H. G. Clark, in *Encyclopedia of Polymer Science and Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 9, Interscience, New York, 1965, p. 794.
15. J. Pinsky, A. R. Nielsen, and J. H. Parlman, *Mod. Packag.*, **28**, 145 (1954).
16. M. Salame, *SPE Trans.*, 153 (1961).
17. G. P. Nilles and R. D. Schuetz, *J. Chem. Ed.*, **50**(4), 267 (1973).
18. L. J. Hayes and D. D. Dixon, *J. Appl. Polym. Sci.*, **22**, 1007 (1978).
19. L. J. Hayes, *J. Fluorine Chem.*, **8**(1), 69 (1976).

Received January 26, 1977

Revised February 24, 1977