

## Some Relationships between Water Vapor Permeability and Chemical/Physical Structure in Rigid Urethane Foams

C. J. HILADO and R. H. HARDING, *Research and Development Department, Union Carbide Chemicals Company, South Charleston, West Virginia*

### INTRODUCTION

Thermal insulation is installed to maintain a large temperature differential across the insulated wall. This thermal driving force is often accompanied by a potential for water vapor transfer, since warm air normally contains more vapor than colder air. Because the conductivity of liquid water is 10-40 times that of the insulation itself, thermal short circuits due to excessive condensation could be serious. The designer therefore considers not only heat transfer, but also whether moisture will enter the wall, and if so whether it will pass out again or condense within the insulation.

Rigid urethane foams are finding increasing usage as thermal insulation. While the chemist usually does not design foams for specific applications (dimensions, skin materials, edge details, etc.), he is expected to define their heat and mass transfer characteristics. Further, since urethane foams are versatile materials, he may be asked to adjust these properties to preselected levels.

This paper summarizes one attempt to express the 23°C. water vapor permeabilities of rigid urethane foams in terms of their chemical and physical structures. The products studied were polymers obtained from polyether polyols, reacted with tolylene diisocyanate and blown to densities near 2 pcf using fluorotrichloromethane. Since urethane chemistry and foam manufacturing technology have often been discussed in existing literature,<sup>3,4,12</sup> it is assumed that the reader is already familiar with these subjects.

### PRELIMINARY CONSIDERATIONS

Closed-cell foams are physically unique among insulating materials because their dispersed gas phase is discontinuous. Plastic foams are distinguished further by the fact that they are largely gas, frequently containing only about 2% solids by volume.

When a heterogeneous material's gas phase is continuous, moisture can

transfer without entering the solid phase. Conversely, when the material's gas phase is discontinuous, moisture must diffuse through the solid phase and may diffuse alternately across many solid membranes and vapor cells.

Effective moisture transfer rates of plastic foams are thus established jointly by the permeability of each phase (a function of chemical structures) and by the distribution of phases in space (physical structures). The choice of criteria which describe these structures adequately is a fundamental problem in relating composition to performance. The remaining paragraphs of this section review the selective process followed in the present analysis. Table I summarizes pertinent nomenclature.

TABLE I  
Nomenclature

Symbol	Definition	Determined by
<i>d</i>	Foam specimen density, pcf. <sup>a</sup>	ASTM D1622-59T <sup>1</sup>
<i>e</i>	Average equivalent weight of a polyol, g./g. equiv.	Eq. (4), Table II
	Average functionality of polyol (blend) foamed: the number of reactive groups per average molecule	Starter <i>f</i> 's; eq. (6), Table II
<i>F</i>	Volume fraction of interconnected (open) cells within a foam (dimensionless)	Air displacement <sup>8</sup>
<i>h</i>	Average hydroxyl number of a polyol, mg. KOH/g. polyol	ASTM D1638-60T <sup>1</sup>
<i>m</i>	Molecular weight, g./g. mole	Eq. (1), Table II
<i>n</i>	Average number of alkylene oxide units per functional group in polyol (blend) foamed	Eq. (3) or (5), Table II
<i>r</i>	Average number of aromatic rings per molecule of polyol (blend) foamed	Starter composition; Eq. (7), Table II
<i>R</i>	Ratio of 25°C. compressive strengths within a foam,    psi/⊥ psi	ASTM D1621-59T <sup>1</sup>
<i>V</i>	Gas volume of the average closed cell within a foam, 10 <sup>-4</sup> cc.	Air displacement <sup>8</sup>
WVP	Water vapor permeability measured at 23°C., perm-in. <sup>b</sup>	ASTM C355-59T <sup>1</sup>

<sup>a</sup> Pounds per cubic foot.

<sup>b</sup> Grains of water vapor transferred per (hr.)(ft.<sup>2</sup>) (moisture vapor pressure differential/in. of thickness): the driving force for mass transfer (vapor pressure differential) is expressed in inches of mercury.

### General

Since the rigid urethane foams studied were expanded with fluorotrichloromethane blowing agent, their gas phase composition was not considered a variable. Neither were the nonreactive catalysts and surfactants used in foam manufacture considered directly. While fillers and plasticizers reportedly increase water vapor permeability,<sup>3</sup> other work with

urethane foams<sup>12</sup> suggests that the low concentrations of catalyst and surfactant employed make no significant contribution to WVP.

### Polymer Chemistry

Since all polyether polyols foamed were reacted with the commercial 80:20 blend of tolylene diisocyanate isomers, this latter important fraction of the overall polymer system varied only in amount from one foam to the next. While this fact simplifies analysis, it might still be proposed that the mechanisms by which polyol and isocyanate react could vary with catalyst type and concentration, with formulated isocyanate excess, or with manufacturing process (one-shot *vs.* quasi-prepolymer). The literature suggests, however, that such variables exert a minor influence on polymer structure,<sup>9</sup> at least as reflected by the foam's WVP.<sup>12</sup>

It thus appeared that the urethane polymers under consideration might be described adequately by parameters defining the average polyol molecules from which they were obtained. Although not always apparent, this is an approach often used by urethane foam chemists.<sup>2,10</sup> Polymer crosslinking is so difficult to measure directly,<sup>5,6,11</sup> particularly in foam, that it is commonly calculated from the functionality and equivalent weight of polyol and isocyanate by assuming that two functional groups extend chains while the rest provide crosslinking. Except for nomenclature and auxiliary calculations, this is equivalent to describing the polymer's precursors. Both approaches assume complete reaction and ignore crosslinking that might occur through rearrangements or by allophanate or biuret formation. The more direct approach was selected for present use because it requires fewer numerical manipulations (see Table II).

A foamable polyether is manufactured by adding alkylene oxide(s) to one or more "starter" molecules, each containing  $f$  active-hydrogen reaction sites. The resulting polyol's hydroxyl number  $h$  is measured to specify its stoichiometric isocyanate requirement. Higher  $h$  requires more tolylene-bonded isocyanate, thus increasing the final polymer's content of both

TABLE II  
Material Balances Describing Polyol Composition

A. For single polyols*
1. $m = ef$
2. $m = m_s + fnm_o$
3. $e = e_s + nm_o$
4. $e = 56,100/h$
B. For composite polyols*
5. $n = n_1(e - e_2)/(e_1 - e_2) + n_2(e_1 - e)/(e_1 - e_2)$
6. $f = f_1f_2(e_1 - e_2)/[f_2(e - e_2) + f_1(e_1 - e)]$
7. $r = [f_2r_1(e - e_2) + f_1r_2(e_1 - e)]/$ $[f_2(e - e_2) + f_1(e_1 - e)]$

\* Subscripts in these equations are defined as follows:  $s$  = Starter molecule to which alkylene oxide is added to form a polyether;  $o$  = Alkylene oxide; 1 = The first polyol in a blend of two; 2 = The second polyol in a blend of two.

hydrophobic aromatic nuclei and polar urethane groups. Since the solubility of moisture in the solid is reduced by the first constituent but probably increased by the second, hydroxyl number can be expected to influence WVP. Earlier work<sup>4</sup> suggests that its effect may be small.

Calculating a polyol's effective equivalent weight  $e$  is simple when  $h$  is known (eq. 4, Table II). Calculating average molecular weight  $m$  and ether chain length  $n$  is also straightforward when the raw materials processed are well defined chemically. Among these parameters, only  $n$  contributes independently to an improved understanding of polyol structure. Within a starter/oxide family  $n$  is defined by  $h$ , but as the starter or oxide is changed both  $n$  and  $h$  are needed to define the starter's equivalent weight. Perhaps more significant is the fact that higher  $n$ 's simultaneously increase a polymer's ether oxygen content and the distance between its branch points. Both effects can contribute to higher WVP, since polar groups promote solubility and loose-knit structures facilitate molecular diffusion.

Starter functionalities  $f$  also have an important influence on the number of crosslinking sites available in the polymer. As  $f$  rises above 2 the urethane network can become a progressively greater barrier to molecular diffusion.<sup>2</sup> There is, however, a limit to this effect since  $h$  must be finite. Steric requirements will insure some space between chains, and might also be such that complete reaction is a remote possibility. Thus, while increasing  $f$  should reduce WVP, it can be expected to do so at a decreasing rate.

The foregoing paragraphs have worked from the hydroxyl groups terminating the polyol chains toward the starter itself, defining its equivalent weight and functionality in the process. The starter can, of course, incorporate other molecular variants. It might be essentially hydrocarbon or might contain more polar elements, commonly oxygen and nitrogen. Its branch points and polar elements may cluster or be uniformly distributed in space. It may be aliphatic or aromatic in nature.

Since this starter comprises a large fraction of the total polyether designed for rigid foams, its structure should affect foam performance. Unfortunately, the only additional feature that can readily be described quantitatively for purposes of analysis is aromatic content  $r$ . By a treatment similar to that used with  $f$ , increasing  $r$  can be expected to reduce WVP at a decreasing rate. The aromatic effect<sup>2,3</sup> may be appreciable.

This review of chemical variables influencing WVP led to four potentially significant factors:  $h$ ,  $n$ ,  $f$ , and  $r$ . While not completely definitive, these approximate the polyether's structure closely enough that further work seemed justifiable. It was recognized that effects due to the other chemical variables mentioned could only appear pooled with experimental errors.

### Physical Structure

Polyols are defined chemically before foam is made. The distribution of the urethane polymer in space also affects foam properties, and is es-

established by the physical chemistry and foaming mechanics of each system. It seems impractical to predict or measure viscosities and surface tensions within foaming systems as functions of time and temperature. In addition, effects of mold configuration on the structure of rising foam are not well understood. Attempts to describe the mechanisms of cell formation are therefore necessarily qualitative.<sup>9</sup>

In the absence of suitable data within foaming systems, it becomes necessary to study the microstructures of finished products. While this alternative expedites progress, it has limited utility in the sense that measurements can be made only after a foam is available.

It has been noted that the polymeric solid within a foam provides its major resistance to moisture transfer. The volume fraction of solids is indicated by foam density  $d$ , which therefore constitutes a base for any description of physical structure.<sup>3,7</sup>

Other structural features independently affect the efficiency with which available solids are used to reduce moisture transfer. Perhaps the most obvious of these is open cell content  $F$ . When there are no solid membranes between foam cells, the polymer simply minimizes the convection and transfer approaches the characteristic rate for stagnant air (WVP = 120 perm-in.). When all cells are closed, moisture must repeatedly: (1) dissolve in solid, (2) diffuse through the solid, (3) revaporize, and (4) diffuse across the cell's vapor phase to the next membrane. When most cells are closed, this mechanism combines with diffusion through air-filled capillaries formed by chains of open cells. Effects of small open cell fractions are logically and reportedly<sup>3,4</sup> significant.

A third criterion, effective cell diameter, determines how often the above four-step mechanism repeats as water molecules traverse an inch of foam. However, since foam cells are usually elongated, effective diameter is not simply proportional to the cube root of cell volume  $V$ . Auxiliary microscopic studies, too cumbersome for routine application, suggested that compressive strengths might conveniently provide the desired measure of cell elongation: it had been observed that when the cell height-to-width ratio was near 1/1 the corresponding strength ratio  $R$  was also 1/1, and as the height-to-width ratio rose toward 5/3 the strength ratio approached 3/1. It was therefore proposed that both  $V$  and  $R$ , which can change independently of each other, would be required to describe effective cell diameter.

Cells tend to elongate in the direction they move while foaming. The foaming liquid is subjected to oriented mechanical forces, both internal and external, and to drainage imposed by interactions of viscosity and surface tension with gravity. These mechanisms suggest, again with limited microscopic support, that "vertical" and "horizontal" cell walls and edges may contain unequal thicknesses of the polymer in that cell. It is possible to calculate an average membrane thickness from  $d$ ,  $F$ ,  $V$  and  $R$ , but only an average. Since this average does not correctly describe effective wall thicknesses, it may prove necessary to isolate WVP's measured

parallel to the foam rise ( $\parallel$ ) from those measured in the perpendicular ( $\perp$ ) direction.

### EXPERIMENTAL

WVP data on rigid foams have been accumulated for applied and exploratory studies conducted by these laboratories over a period of several

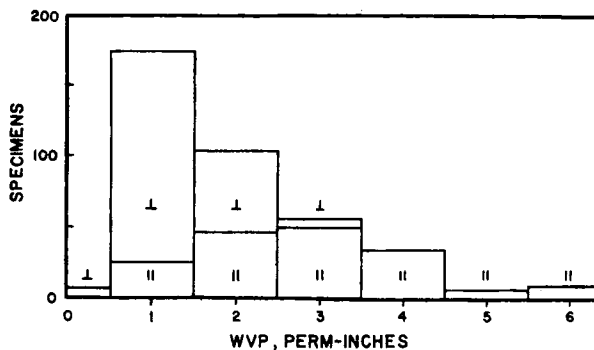


Fig. 1 Permeability distributions studied.

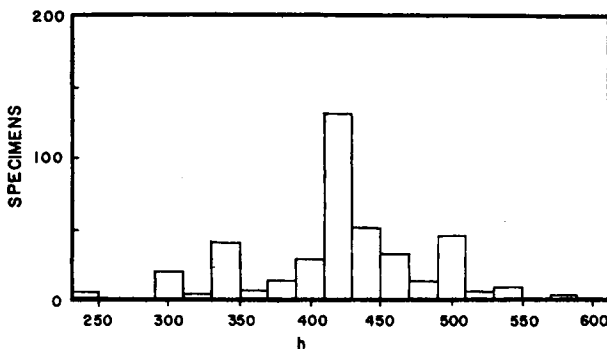


Fig. 2. Test data as a function of polyol hydroxyl number.

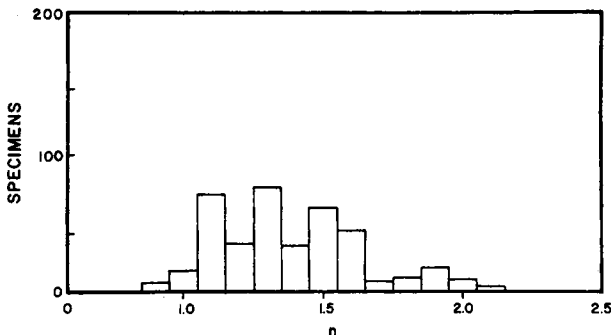


Fig. 3. Test data as a function of polyol chain length.

years. Nearly 400 results were supported by the desired minimum of chemical and physical measurements, and so were available for use in the present empirical investigation.

Since laboratory measurements were either standardized (Table I) or directly available only to the polyol manufacturer, comments on test procedures can be minimized. It might be noted that 23°C. WVP's were

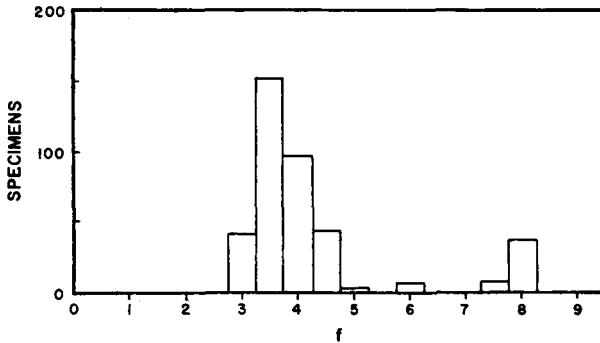


Fig. 4. Test data as a function of polyol functionality.

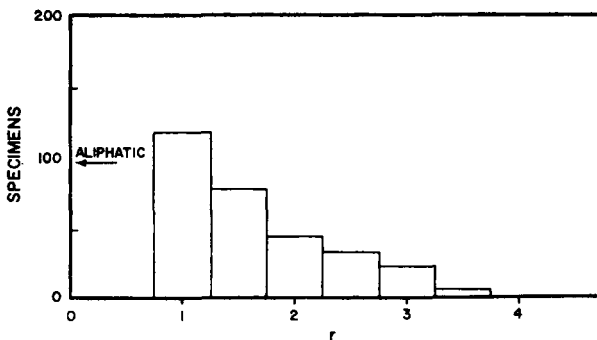


Fig. 5. Test data as a function of polyol aromatic content.

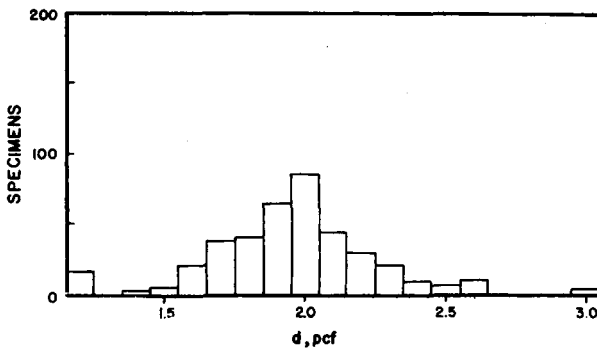


Fig. 6. Test data as a function of foam density.

measured on inch-thick foam specimens with all surfaces cut. The ASTM C353<sup>1</sup> "water method" was selected when independent auxiliary studies suggested that minor procedural errors would lead to higher and more conservative design figures. The "desiccant method" might yield equal or lower WVP's, and tests specifying less vigorous air circulation appeared significantly biased toward optimistically low results.

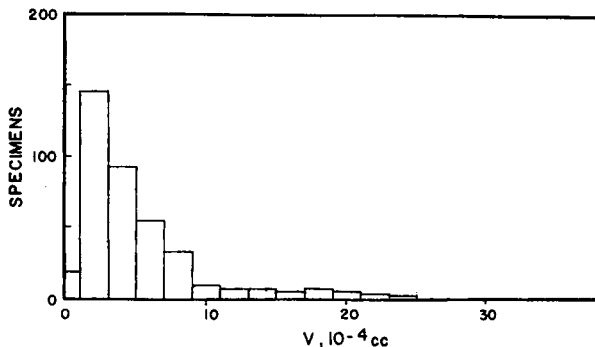


Fig. 7. Test data as a function of cell volume.

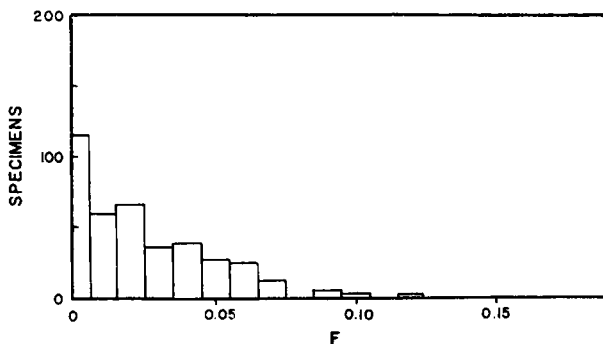


Fig. 8. Test data as a function of open cell content.

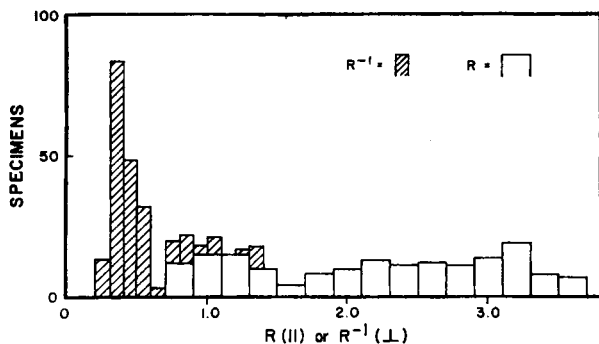


Fig. 9. Test data as a function of foam strength ratio.



TABLE III  
WVP Test Data as a Function of Formulation and Foam Manufacture

Variable	Specimens
A. Formulation: <sup>a</sup>	
Foam based entirely on aliphatic polyol(s)	100
Foam-including aromatic polyol(s)	290
	<u>390</u>
B. Process:	
One-shot foam	90
Quasi-prepolymer foam	300
	<u>390</u>
C. Manufacture:	
Machine-molded foam	30
Slabstock machine foam	90
Laboratory-molded foam	270
	<u>390</u>
D. Test Orientation:	
WVP parallel to foam rise (  )	170
WVP perpendicular to foam rise (⊥)	220
	<u>390</u>

<sup>a</sup> All fluorocarbon-blown, polyether-based foams met the following limitations: (1) tolylene diisocyanate excesses ranged from 0 to 10% above stoichiometric; (2) concentrations of tin and amine catalysts, and of silicone surfactant, ranged from 0.02 to 0.8 wt.-% of total charge; (3) no nonreactive ingredients other than catalyst, surfactant, and fluorocarbon were present.

Distributions of the raw data analyzed are summarized in Table III and Figures 1-9. Ideally, the distributions of Figures 2-9 should approach rectangles to give each variable equal opportunity to influence the correlations.

Raw data were submitted to stepwise multiple regression analysis so WVP, the dependent variable, could be expressed as a function of  $h$ ,  $n$ ,  $f$ ,  $r$ ,  $d$ ,  $V$ ,  $F$ , and  $R$ . On the basis of earlier discussion, however, it would be unreasonable to limit the functions to first order terms. Thus  $V^{1/3}$  was employed, and the remaining variables were studied in both the first and second orders (e.g.,  $h$  and/or  $h^2$ , etc.). Since it was noted that  $h$  and  $n$  can be related in special cases, an  $h$ - $n$  interaction term was also included. Since  $R$  helps define effective cell diameter, terms containing  $R$  correlate directly with || WVP and  $1/R$  terms can be shown correct for use with ⊥ WVP.

Regressions that attempted to treat || WVP and ⊥ WVP jointly were discarded because their precision was found to be unsatisfactory. Separate regressions were therefore prepared for data falling within each category of Table III (e.g., quasi-slab based on aliphatic polyols tested perpendicular to foam rise). The various correlations for parallel WVP were found equivalent, so these data were pooled to yield a single regression for || WVP.

According to statistical tests, the variances of the fractional regressions equalled that of the overall regression. This procedure was repeated for  $\perp$  WVP with the same result.

Variance checks on coefficients of individual variables showed that: (1) second order  $d$ ,  $F$ , and  $R$  terms did not improve regression quality; (2) among the  $h$  and  $n$  terms used, all coefficients other than that for  $h$  itself were zero; (3) both first and second order terms were needed to describe the effects of  $r$  and  $\parallel f$  on WVP, although  $\perp f$  coefficients were zero.

As anticipated in the "Preliminary Considerations" section, increasing  $f$  or  $r$  across the ranges studied (see Figs. 4 and 5) reduced WVP at a diminishing rate. For convenience in application, new functions of  $f$  and  $r$  were sought to present these effects in simpler form with no sacrifice of precision. Suitable functions were obtained when  $(f - 3)$  and  $(f - 3)^2$  were replaced by  $1/f$ , and when  $r$  and  $r^2$  were replaced by  $1/(r + 1)$ .

The final equations relating foam WVP to three chemical and five (including transfer direction) physical variables, all of which are mathematically significant, appear in Table IV.

TABLE IV  
23°C. WVP of Rigid Urethane Foam  
(Polyether Reacted with Toluene Diisocyanate and Blown with Fluorocarbon-11;  
Foam WVP measured by ASTM C355 "wet cup.")

Foam rise direction	WVP, perm.-in.	Correlation coefficient	Standard error of estimate $s$ , perm.-in.
$\parallel$	$2.03 - 0.0080h + 2.69/f + 5.39/(r + 1) - 0.859d + 0.390V^{1/2} + 9.28F + 0.642R$	0.94	$\pm 0.43$
$\perp$	$1.98 - 0.0033h + 2.16/(r + 1) + 0.601d + 0.201V^{1/2} + 5.44F + 4.07R$	0.90	$\pm 0.24$

## DISCUSSION

Inquiry into the practical utility of these regressions should be preceded by a review of their physical significance.

### The Regressions

Within the variable ranges studied, 90% confidence limits on a WVP predicted from Table IV are  $\pm 0.7$  ( $\parallel$ ) or  $\pm 0.4$  ( $\perp$ ) perm.-inch. These limits combine random errors of measurement of all variables studied, and therefore strictly apply only to the laboratory methods actually used.

Independent reproducibility studies showed that 90% confidence limits for a local WVP measurement average about  $\pm 0.6$  ( $\parallel$ ) or  $\pm 0.3$  ( $\perp$ ) perm.-in. Agreement between these figures and the regression limits suggest that further improvement in precision of the regressions is unlikely, at least until significant changes are made in the standard WVP test method.

It may therefore be deduced that: (1) the chemical and physical variables considered describe WVP adequately; (2) changes in polymer structure that might occur through the action of different catalysts, reaction temperatures, or curing environments have negligible effects on WVP; and (3) WVP changes observed when a given formulation is foamed by different techniques are due to the different physical structures imposed on products.

While confidence limits may seem broad for use in predicting WVP, the correlations do yield probable—not idealized—values because of their empirical nature. Trends in and relative magnitudes of the various effects remain meaningful. Perhaps the most important conclusion to be drawn from the limits themselves is that measurements parallel to foam rise may not be desirable for routine usage: approximately four “identical”  $\parallel$  WVP's must be averaged to yield the narrower confidence limit available from a single  $\perp$  WVP measurement.

### Variable Effects

Examining the equations in Table IV will show that WVP can be reduced by increasing  $h$ ,  $f$ ,  $r$ , or  $d$ , or by decreasing  $V$  or  $F$ . It can also be determined that  $\parallel$  WVP is higher than  $\perp$  WVP in the same foam, and that the difference between the two rate constants increases with foam orthotropicity  $R$ . These qualitative observations have been anticipated, however, and the magnitudes of the effects are of major interest at this point.

Variance ratios for individual coefficients were examined to estimate the relative contribution of each to the regressions. It was found that the coefficients fell into three distinct groups. The most important group included  $r$  and  $R$ . Terms involving  $h$ ,  $d$ ,  $V$ ,  $F$ , or  $1/R$  formed the intermediate group. The least important effect was that attributed to  $\parallel f$ , as expected when  $\perp f$  coefficients were found so small that they empirically equalled zero.

These groupings are meaningful only if the corresponding variables can be adjusted over sufficiently broad ranges to have a practical effect on WVP. Changes in foam structure which generate small WVP reductions appear in Table V, where nonlinear effects are solved at two arbitrarily selected levels. Figures 2-9 provide a guide to ranges over which the various factors have been manipulated in practice. Table VI estimates the overall WVP change associated with these approximate ranges.

Tables V and VI, as solutions of the regressions from two viewpoints, jointly tend to confirm the above groupings. They also point out that  $\parallel$  WVP responds more strongly to a given change in foam structure than does  $\perp$  WVP.

Other interesting points will occur to the foam chemist reviewing these tables. Perhaps, for example, the cause underlying the apparent  $h$  effect is the corresponding change in overall polymer aromaticity due to variable isocyanate demands. The assumption seems reasonable because the effect of aromaticity in the polymer's polyol fraction is strong. On this basis, it could be anticipated that foams made from an aliphatic isocyanate would

TABLE V  
Relative Effects of Chemical and Physical Variables on the 23°C. WVP of Rigid Urethane Foams

Variable (Table IV) <sup>a</sup>	Change which reduces WVP by	
	0.1 perm.-in. (⊥)	0.2 perm.-in. (  )
Chemical (polyol):		
Hydroxyl number, <i>h</i>	+30.0 units	+25.0 units
Functionality, <i>f</i> = 5	impractical	+3.0
<i>f</i> = 3	impractical	+0.9
Aromaticity, <i>r</i> = 2	+0.48 ring	+0.37 ring
<i>r</i> = 0	+0.05 ring	+0.04 ring
Physical (foam):		
Density, <i>d</i>	+0.17 pef	+0.23 pef
Cell volume, <i>V</i> = 10	-5.5	-5.6
<i>V</i> = 1	-0.9	-0.8
Open cells, <i>F</i>	-0.02	-0.02
Orthotropicity, <i>R</i> = 2	+1.9	-0.3
<i>R</i> = 1	+0.3	-0.3

<sup>a</sup> In reading across any row, assume that all other factors in this column are constant.

TABLE VI  
Net Effects of Practical Changes in Basic Variables on the 23°C. WVP of Rigid Urethane Foams

Variable	Range	Calculated WVP change, perm.-in.	
		⊥	
Chemical			
<i>h</i>	300-600	-1.0	-2.4
<i>n</i>	1-2	nil	nil
<i>f</i>	3-8	nil	-0.6
<i>r</i>	0-4	-1.7	-4.3
Physical			
<i>d</i>	1-3	-1.2	-1.7
<i>V</i>	0-25	+0.6	+1.1
<i>F</i>	0-0.1	+0.5	+0.9
<i>R</i>	1-4	-0.3	+1.9

provide far higher WVP's than would be the case when tolylene diisocyanate was reacted with the same polyol.

### Applications

It is interesting to note that reducing WVP by increasing *h* or *d* necessarily yields a more costly product, and usually poses a more difficult manufacturing problem. The foam chemist will recognize that these observations are based on the following facts: (1) isocyanates cost more than polyethers, and higher *h* requires a larger formulated level of the former ingredient; (2) heavier foams contain more solids per cubic foot; (3) within most homologous series of rigid foam polyols, viscosity rises with

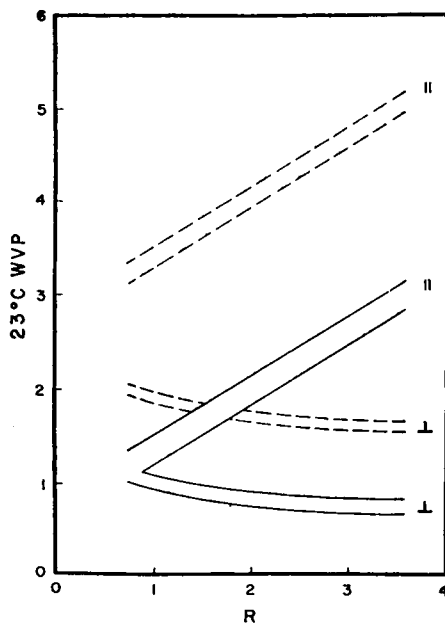


Fig. 10. Illustrative solutions of WVP correlation: (---) foamed NIAX polyol LS-490; (—) foamed NIAX polyol LK-380. Constants:  $d = 2$ ,  $V = 2$ , and  $F = 0$ .

$h$ ; (4) polyol/fluorocarbon solution viscosities rise with target foam density because the fluorocarbon concentration is lower.

Reducing WVP by employing polyols with  $f$  much larger than 3 may cost little or nothing, but such a change is practically useless in itself. Improved adaptation of processing technology to a given foaming system might reduce WVP significantly if  $V$ ,  $F$ ,  $R$ , and/or transfer direction were affected favorably. The necessary process changes may or may not require capital expenditure, formulation changes for improved cell structure control, or increased material losses from trimming.

Apparently the only approach which reduces cost and WVP simultaneously is the use of aromatic polyols. Figure 10 helps illustrate this point among others. WVP's of foams based on commercial aliphatic (Union Carbide NIAX polyol LS-490) and aromatic (Union Carbide NIAX polyol LK-380) polyethers appear as functions of  $R$  and transfer direction at constant  $d$ ,  $V$ , and  $F$ . Although  $h$ (aliphatic) exceeds  $h$ (aromatic) by more than 100 units, WVP's of the aliphatic foam exceed those of the aromatic by about 1 ( $\perp$ ) to 2 ( $\parallel$ ) perm-inches at equivalent  $R$ .

The WVP regressions suggest that this differential could be eliminated by increasing the aliphatic foam system's density about 2 pcf, or halved by increasing its density about 1 pcf above the other. Assuming that material costs of these formulations were equal originally, the aromatic system remains a superior barrier to moisture transfer at much lower density and proportionally lower cost per unit foam volume.

Band heights on Figure 10 enclose the maximum WVP variations permitted within current polyol manufacturing specifications. The slopes of these bands, particularly in the parallel orientation, suggest one means by which a given formulation may seem to yield the greater variability sometimes observed in the laboratory.  $R$  can range from 1 to 2 within a piece of slabstock and from 1 to 3 or even 4 within a molded panel. Its exact value is primarily a function of location, but also of the foam's original size and shape, reaction kinetics, and other manufacturing conditions. Directly comparable WVP's can be obtained only at corresponding  $d$ ,  $V$ ,  $F$ ,  $R$ , and test orientation. Tests at equivalent locations in similar molds do not guarantee that these conditions have been met if formulations or manufacturing conditions are changed. It is probable that these conditions have not been met if a given formulation is foamed by a fixed process but in different molds.

This discussion has assumed that low WVP is desired. If some relatively high WVP is called for, the foam chemist would first select an aliphatic polyol with the lowest  $h$  yielding generally acceptable rigid products, and then recommend its use at the lowest foam density consistent with other performance requirements. If the predicted WVP remained below the design value, he would adjust surfactants or manufacturing conditions to provide higher  $V$  and  $F$ . Letting  $d = 1$  pcf,  $V = 25 \times 10^{-4}$  cc., and  $F = 0.15$  on Figure 10 as an example, the curves shown would shift upward by about 2 ( $\perp$ )-3 ( $\parallel$ ) perm-inches. Knowing the effective  $R$  obtained during production the chemist could predict WVP or, conversely, could set permissible limits on  $R$  from the WVP specification.

Some may wonder why  $V$  was increased only from 2 to 25 instead of 200, or why  $F$  was increased from 0-0.15 instead of 1. The explanation is that empirical correlations are not necessarily valid beyond the range in which data were studied. Trends established by the present regressions could be expected to hold, but calculated figures could incorporate too much error for design application. Had  $d$  and  $F$  been investigated over wider ranges, for example, it is possible that second-order terms might have been required to maintain existing precision: short sections of curves are approximated by straight lines where longer sections are not.

## CONCLUSIONS

Polymer chemists would theorize that water vapor permeabilities of rigid urethane foams should be reduced by higher functionality and aromaticity, and by lower equivalent weight and fewer polar elements, in polyols from which the foams are made. Foam chemists would add that product density and cell structure should also be important. The present work attempted to investigate these predictions quantitatively.

In no case was the effect expected from a basic variable reversed by this analysis of experimental data. It was found that total aromaticity of the polymer foamed was the most significant chemical variable, and should be

maintained at the highest possible level when low WVP is desired. Permeability of a closed-cell foam could easily vary fourfold at fixed polymer composition, however, as changes were made in effective cell diameter and transfer direction. Influences of foam density within the usual commercial limits, and of low open cell fractions, were appreciable but of lesser practical value. Crosslinking above the minimum required for suitably rigid products could be ignored as a WVP design criterion.

The correlations offered will prove useful for selecting rigid foam systems which yield WVP in a desired range. They can further aid in optimizing the manufacturing processes used. Decisions based on these correlations will be conservative because: (1) no allowance was made for the natural urethane skin barriers found on all foamed-in-place products; (2) mean service temperatures are frequently lower than the test temperature and thus reduce WVP; (3) air circulation rates about the foam are normally lower in practice than under test (they equal zero whenever foam is installed behind another material), so effective WVP will be lower than the "true" calculated value.

Mr. L. J. Walker and Mr. C. J. Hendrix reviewed the statistical portion of this paper and made valuable suggestions for presentation.

### References

1. American Society for Testing Materials, 1916 Race Street, Philadelphia, Pennsylvania.
2. Barringer, C. M., *Rigid Urethane Foams, Chemistry and Formulation*, Bull. HR-26, E. I. du Pont de Nemours & Company, April 1958.
3. Barringer, C. M., *SPE J.*, **15**, 961 (1959).
4. Cear, S., G. C. Greth, and J. E. Wilson, Society of Plastics Engineers, Regional Technical Conference, Buffalo, N.Y., October 1961.
5. Cluff, E. F., and E. K. Gladding, *J. Appl. Polymer Sci.*, **3**, 290 (1960).
6. Cluff, E. F., and E. K. Gladding, *J. Appl. Polymer Sci.*, **5**, 80 (1961).
7. Cooper, A., *Plastics Inst. Trans.*, **26**, 299 (1958).
8. Harding, R. H., *Mod. Plastics*, **37**, 156 (1960).
9. Saunders, J. H., *Rubber Chem. Technol.*, **33**, No. 5, 1293 (1960).
10. Saunders, J. H., *Rubber Chem. Technol.*, **33**, No. 5, 1259 (1960).
11. Smith, T. L., and A. B. Magnusson, *J. Polymer Sci.*, **42**, 391 (1960).
12. Wilson, J. E., H. M. Truax, and M. A. Dunn, *J. Appl. Polymer Sci.*, **3**, 343 (1960).

### Synopsis

Low density rigid foams, reaction products of polyether polyols with tolylene diisocyanate, may transmit moisture vapor at rates from 0.3 to more than 8 perm-inches at 23°C. Analysis of experimental data provided conservative design correlations showing that rate constants could be predicted only when a foam's polymer composition and physical structure were considered jointly. Among commercially acceptable rigid foam systems, cell structure and polymer aromaticity dominated the control of permeability levels. Permeabilities were lowest when transfer was directed perpendicular to the rise of highly orthotropic closed-cell foams based on aromatic polyols of low equivalent weight. Permeabilities increased with effective cell diameter and also as foam density and closed-cell content were reduced.

### Résumé

Des mousses rigides de faible densité, produits de réaction de polyéther, polyols avec le diisocyanate de tolylène, transmet le vapeur humide à la vitesse de 0.3 à plus de 8 perm-inches à 23°C. L'analyse des données expérimentales démontre que les constantes de vitesses peuvent être évaluées uniquement lorsque la composition de la mousse de polymère et la structure physique sont considérées conjointement. Parmi les systèmes de mousses rigides, la structure cellulaire et l'aromaticité du polymère contrôlent les niveaux de perméabilité. La perméabilité est plus basse lorsque le transfert est orienté perpendiculairement à l'augmentation des mousses à cellules fermées, fortement orthotropiques, basées sur des polyols aromatiques à poids équivalent faible. Les perméabilités augmentent avec le diamètre effectif des cellules, avec la densité de la mousse et lorsque le volume des cellules fermées diminue.

### Zusammenfassung

Starre Schaumstoffe niedriger Dichte aus Reaktionsprodukten von Polyätherpolyolen mit Toluyldiisocyanat weisen eine Durchsatzgeschwindigkeit für Feuchtigkeitsdämpfe von 0,3 bis mehr als 8 Perminch bei 23°C auf. Eine Analyse der Versuchsdaten lieferte konservative Aufbaukorrelationen, was zeigt, dass Geschwindigkeitskonstanten nur bei gleichzeitiger Berücksichtigung der Polymerzusammensetzung eines Schaumstoffes und seiner physikalischen Struktur angegeben werden könne. Bei den handelsüblichen starren Schaumsystemen waren die Zellstruktur und der aromatische Charakter des Polymeren für die Permeabilität ausschlaggebend. Die Permeabilität war beim senkrechten Durchtritt durch Schaumstoffe mit hochgradig orthotropen geschlossenen Zellen auf Grundlage aromatischer Polyole von niedrigem Äquivalentgewicht am niedrigsten. Die Permeabilität nahm mit dem effektiven Zelldurchmesser und auch bei Herabsetzung der Schaumdichte und des Gehaltes an geschlossenen Zellen zu.

Received July 10, 1962