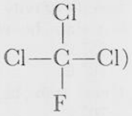
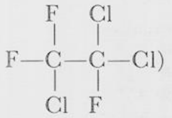
Effect of Fluorinated Refrigerants on Cured Polyester Resins

JOSEPH GAYNOR[1] and GEORGE W. BLUM[2]
Case Institute of Technology, Cleveland 6, Ohio

The advantages inherent in the use of polyester resins for the fabrication of storage tanks, pipelines, ducts, and other structural shapes are rapidly being recognized by consumers and manufacturers alike. Therefore, knowledge of the degree to which these polymers are affected by solvents of various kinds is extremely important. Polyester resins are condensation products of relatively low molecular weight saturated or unsaturated dibasic acids and polyfunctional alcohols which are cross-linked via an addition mechanism employing monomers such as styrene, diallyl phthalate, or triallyl cyanurate. Many refrigerants are fluorinated organic compounds. When such materials are shipped, stored, or metered in equipment which is made of polyester resins, it is imperative that the effect of these fluorine containing organic compounds on the resins be known.

There have been few data showing the effect of fluorinated organic compounds on polymers (*2*) and none with respect to polyesters. Therefore, a study of the effects of two refrigerants, Freon 11 (Du Pont) (trichloromonofluoromethane,  $\mathrm{Cl{-}\overset{\displaystyle Cl}{\underset{\displaystyle F}{C}}{-}Cl}$) and Freon 113 (trichlorotrifluoroethane,  $\mathrm{F{-}\overset{\displaystyle F}{\underset{\displaystyle Cl}{C}}{-}\overset{\displaystyle Cl}{\underset{\displaystyle F}{C}}{-}Cl}$) on four polyester resins, Vibrins 112, 121, 132, and 142 (U. S. Rubber Co.) was undertaken.

EXPERIMENTAL

Quantitative Analysis of Vibrin Resins. To correlate polyester composition with degree of attack of Freon solvent on the cured resins, resin content, free acids, phthalic acid, sebacic acid, succinic acid, maleic, and/or fumaric acid, and total dibasic acids were determined quantitatively (*1,5*).

Sample Preparation. One per cent benzoyl peroxide was dissolved in the polyester resins. The mixture was permitted to stand for 48 hours under slight vacuum to remove all air bubbles. Then samples, 1 × 3 × ¼ inches, were cast in the nine-cavity aluminum mold shown in Figure 1. The lubricant used was Aquadag, casting temperature was 80° C. for all resins except Vibrin 132, which was cast at 70° C. Three cure times were investigated. Upon removal from the curing oven, the samples were demolded, cleaned of carbon, and stored in airtight, dry containers until ready for use.

Exposure of Resin Samples to Freon Solvents. The apparatus employed in this study is shown in Figure 2. Figure 3 shows schematically the manner in which material flowed into and out of the equipment. All surfaces including the tubing (1/4 inch in inside diameter) in contact with the Freon compounds were of stainless steel. The bombs were provided with hangers for the resin samples and could withstand pressures up to 5000 p.s.i.g. (Figure 4). Pressures from 0 to 3000 p.s.i.g. were measurable. Each test unit was immersed in a constant temperature oil bath.

The resin samples, with 1/8-inch holes drilled in one end, were labeled, weighed, and hung in the units (two to a unit). The bombs were sealed with aluminum gaskets and sufficient solvent (250 ml.) admitted so that 1 inch of the sample was immersed in liquid at all times. The baths were heated to 50°, 75°, or 100° C., respectively. The valves leading to the atmosphere were left open for a short time during the heating period to permit air to be displaced by solvent vapor. Time at temperature was 2 hours. Thereafter, the units were permitted to cool. The samples were removed and the rate of loss of solvent was determined with the aid of a Chainomatic balance. The duplicate samples were totally immersed in the appropriate Freon solvent while readings on the first one were recorded.

RESULTS AND DISCUSSION

Quantitative Analysis of Resins. The results of the analyses are presented in Table I. Table II lists the general properties of Vibrin resins as given by the manufacturer (*4*). Vibrin 121 is a flexible resin. Examination of Tables I and II shows that a high concentration of maleic and/or fumaric acid results in a flexible cured resin. The concentration of phthalic acid appears to control hardness, that of sebacic acid to control toughness.

Resin content was determined by heating a known weight of material at 150° C. to constant weight. The composition of the material volatilized during this heating period (approximately 1 to 2 hours) was not determined. Because plasticizers exhibit high boiling points and low vapor pressures, it seems unlikely that the nonresinous material was plasticizer. From data on Vibrin resins (*4*), temperature of resin content determination, time required to reach constant weight and odor of uncured resins, it

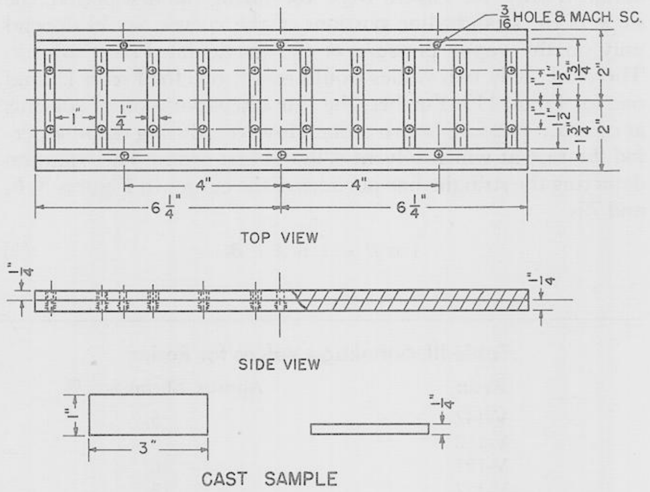


Figure 1. Multicavity mold design for casting polyester resins

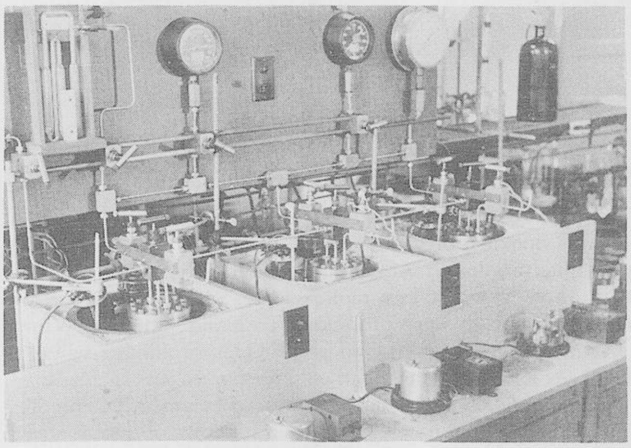


Figure 2. Apparatus

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[1] Present address, General Engineering Laboratory, General Electric Co., Schenectady, N. Y.

[2] Present address, Goodyear Tire and Rubber Co., Akron, Ohio

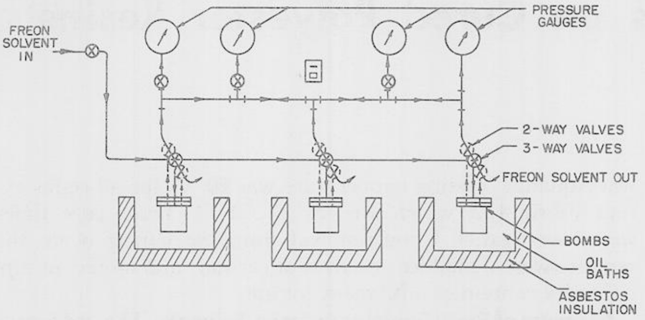


Figure 3. Schematic flow diagram of apparatus

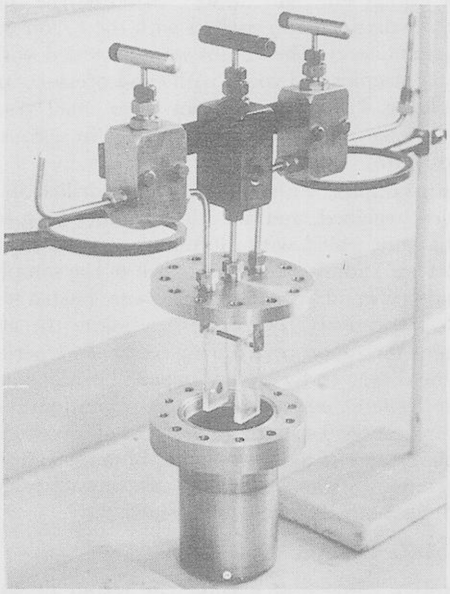


Figure 4. Bomb with hangers for resin samples

Table I. Quantitative Analysis of Vibrin Resins

Resin	V-112	V-121	V-132	V-142
Resin content, %	93.28	65.65	79.25	83.70
Total dibasic acids, %	59.87	74.74	60.33	75.61
Phthalic acid content, %	37.80	3.29	32.61	14.89
Phthalic anhydride content, %	33.70	2.94	29.10	13.28
Sebacic acid content, %	1.29	14.25	2.57	35.32
Maleic and/or fumaric acid content, %	20.78	57.20	25.15	25.40
Succinic acid content, %	0.00	0.00	0.00	0.00
Free acids, mg. KOH/g. resin	26.90	17.58	25.54	30.79
Molecular weight	4160	6368	4384	3640

Table II. General Properties of Vibrin Resins

Vibrin	112	121	132	142
Type	General purpose	Flexible	Hard non-styrene	Fire-resistant
Uncured resin				
Appearance	Clear straw			
Odor	Styrene	Styrene	DAP	Styrene
Visc., poises	10.0	0.6	12.0	150.
Specific gravity	1.18	1.05	1.19	1.35
Cat. stab., hours (min.),				
25° C.	48	48	48	48
70° C.	. . .	. . .	. . .	. . .
Uncat. stab., hours (min.),				
70° C.	48	48	48	48
Cure rate, sec.				
110° C.[a]	70	. . .	80	68
100° C.[a]	. . .	. . .	150	. . .
80° C.[c]	430	. . .	. . .	400
Gel test[b] (sec.)				
100° C.	. . .	150	. . .	. . .
Flame resistance vertical test	NG	NG	NG	OK

[a] 1 × 1 × 1/8 inch cell.
[b] 10 × 75 mm. tube.
[c] 25 × 250 mm. tube.

was inferred that the volatile material was styrene. Concentration of maleic and/or fumaric acid was determined by subtraction, assuming that no other dibasic acids were present.

The monomer unit molecular weights were computed from the free acids concentration. Assuming that the terminal group on both ends of each chain is a carboxyl group, there are one half as many moles of monomer present as moles of base required for titration. A knowledge of the weight of potassium hydroxide required to neutralize 1 gram of uncured resin leads directly to a number average molecular weight. To illustrate,

$$\text{Free acids found in Vibrin 112} = \frac{0.0269 \text{ gram KOH}}{\text{grams resin}}$$

$$\frac{\text{Moles KOH}}{2} = \text{moles resin; moles KOH} = \frac{0.0269}{56}$$

$$\text{Moles resin} = \frac{0.0269}{56\ (2)} = \frac{1 \text{ gram resin}}{\text{mol. wt. resin}}$$

$$\text{Molecular weight of Vibrin 112 monomer unit} = 4160$$

Sample Casting. The mold employed was constructed so that cleaning, lubrication, and removal of samples were easily and quickly accomplished. Aquadag, a colloidal dispersion of graphite in water, gave the best mold release. Sample shrinkage and bubble formation were problems. To avoid cracking, Vibrin 132 was cast at 70° C. instead of 80° C. Approximate values of shrinkage for each of the resins are given in Table III.

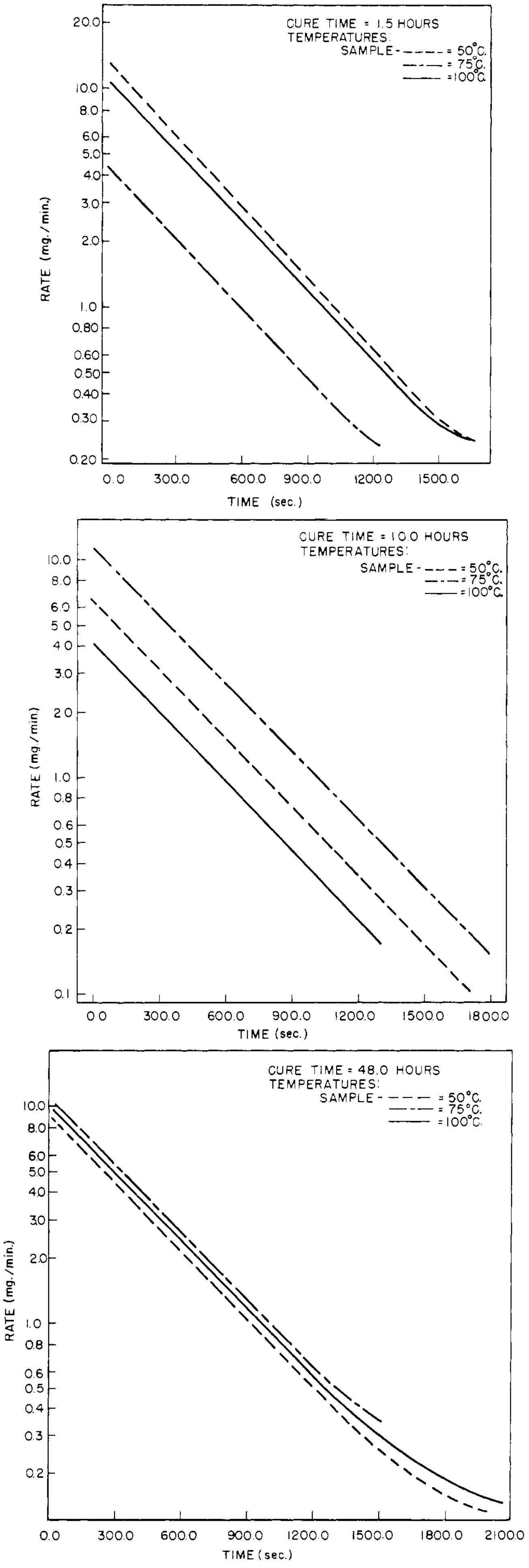
Effects of Freon Compounds on Cured Polyester Resins. The data on loss of Freon compound as a function of time for each of the samples were correlated, and rates of loss of solvent computed and plotted as a function of time semilogarithmically (Figures 5, 6, and 7). All such plots exhibited similar behavior. The first and major portion of the curve was a straight line, followed by a change in slope and a much slower loss of solvent which eventually became constant. This behavior is analogous to that exhibited by the drying of packed or porous solids. In such cases, there is a fairly rapid drying rate period followed by a much slower one. The generally accepted explanation is that the first drying period represents the loss of "free solvent," and the second one represents the loss of "bound solvent." Diffusion as well as deep capillary evaporation account for drying during this second period.

Although the analogy is reasonable, it does not correspond in detail. If only free solvent were lost during the first period, the slope of the straight-line portions of the curves would depend only on the vapor pressure of the particular Freon solvent. Therefore, only two values would result, one for Freon 11 and one for Freon 113. Further, the rate of evaporation of solvents at constant pressure is zero order. However, during the first period the rate at which solvent is lost is first order. The equation depicting the straight-line portions of the curves in Figures 5, 6, and 7 is

$$1\ n\ R = 1\ n\ A - Bt \qquad (1)$$

Table III. Shrinkage Values for Resins

Resin	Approx. Shrinkage, %
V-142	5
V-112	5
V-121	10
V-132	13



Figures 5, 6, and 7 (top to bottom).
Rate of loss of Freon 113 *vs.* time for Vibrin 142

where R = rate of loss of solvent mg. per minute, t = time, seconds, A = intercept, and B = slope.

$$R = \mathrm{Ro}e^{Bt} \text{ at } t = 0,\ R = A = R_0 \qquad (2)$$

Equation 2 is the integrated form of a first-order rate equation. The usual differential form is directly derivable by differentiation of Equation 1 with respect to R and t.

$$\frac{dR}{dt} = BR \qquad (3)$$

B is a first-order rate constant.

This evidence, coupled with the observation that the slopes differ considerably, indicates that the Freon solvents interact with surface molecules and then diffuse into the volume of the polymer. For the purposes of clarity, the first period, during which solvent is lost via a first-order rate process and the second period are discussed independently. Throughout, it is assumed that the solvent entry and exit mechanisms are identical.

Figures 8, 9, 10, and 11 are correlations of the average rate constants, derived from plots such as Figures 5, 6, and 7, with cure time and polyester composition. "Undercure," "medium cure," and "over cure" refer to the low, middle, and long cure times. "Changes in slope" are plots of $\frac{\text{ordinate}}{\text{abscissa}}$ *vs.* abscissa.

Because the rate constants showed no dependence on exposure temperature, they were averaged over all temperatures. Although there is a difference in rate constant which depends on the vapor pressure of the Freon used, this difference is not marked nor is the rate always higher for Freon 11 (vapor pressure, 693 mm. of mercury at 70° F.) than for Freon 113 (vapor pressure, 286 mm. of mercury at 70° F.). This would indicate that the size and nature of the molecule are more important than its vapor pressure. Certainly where vapor pressure differences are very large its effect might be correspondingly greater.

The effect of degree of cross linking seems to be minor except for the system Vibrin 121 and Freon 113. In this case, the rate constant increases with cure time to approximately 0.053 at 20 hours and thereafter remains virtually constant as the cure time increases. The major effect is clearly attributable to the con-

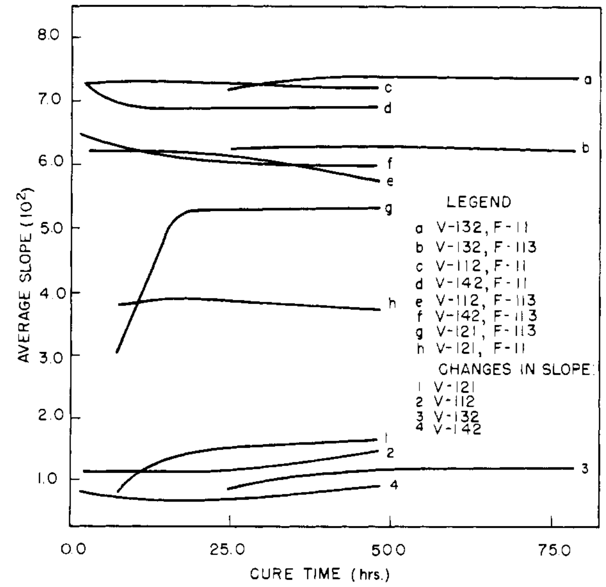
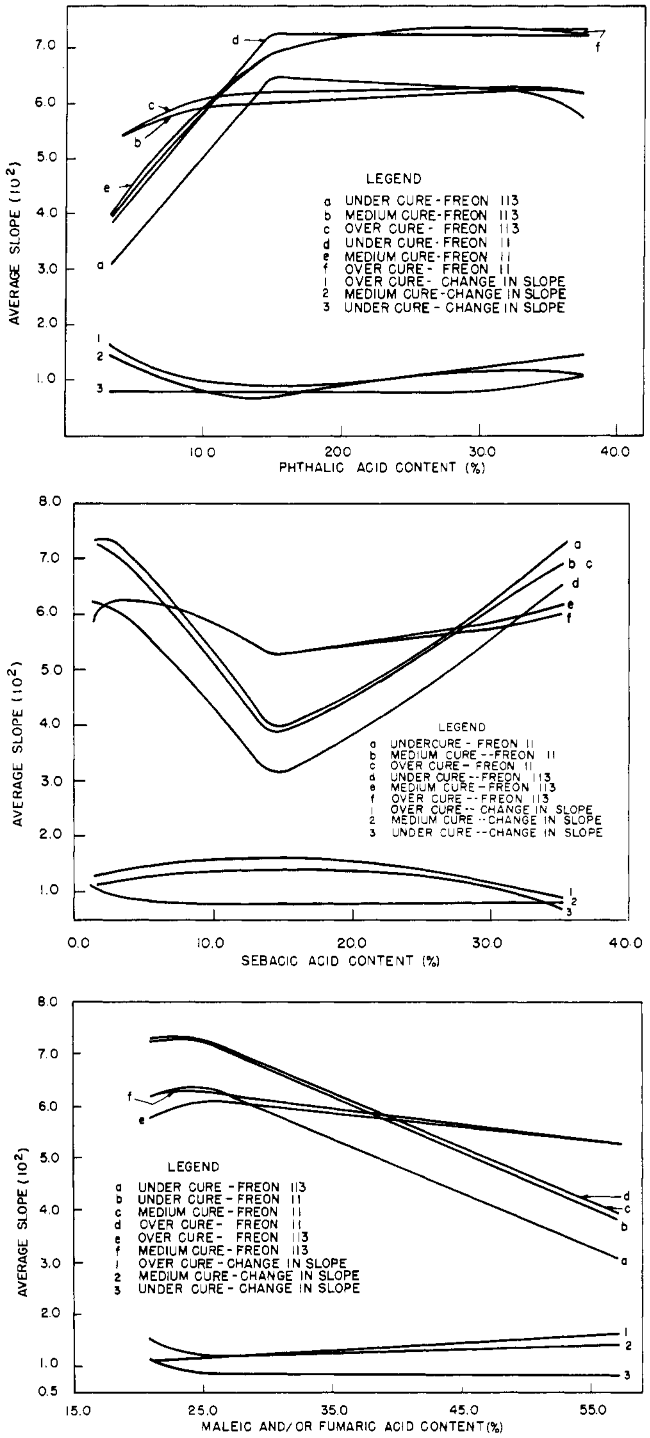


Figure 8. Average slope of rate of loss of solvent *vs.* time curves *vs.* cure time for Freon 11 and Freon 113



Figures 9, 10, and 11 (top to bottom)
Average slope of rate of loss of solvent *vs.* time curves *vs.* acid content for Freon 11 and Freon 113 at various cures.

centration of each dibasic acid. Initially, the average slope increases sharply as the phthalic acid concentration increases. At 15% phthalic acid and higher, the slope remains virtually constant, decreasing in selected cases above 30%. The plot of average slope *vs.* sebacic acid concentration shows a minimum at approximately 13%.

Less affected by sebacic acid concentration are the rate constants for resins which have undergone fairly extensive cure and were exposed to Freon 113. The effect of increasing maleic and/or fumaric acid concentration is also marked but in a negative direction. There appears to be a concentration, approximately 25%, at which the average slopes are a maximum. Below this concentration, the slope does not change appreciably. Above it, however, the slopes decrease rapidly as the concentration increases. Again, resins which have been cured more extensively exhibit less concentration dependence when exposed to Freon 113.

The second "drying" period constitutes loss of solvent which has penetrated the volume of the polymers. The points at which the curves in Figures 5, 6, and 7 depart from linearity constitute the beginning of this second period. These points also indicate the amount of Freon solvent which the polymers have absorbed throughout their volume—i.e., the degree of swelling (Table IV). During this period, the rate at which solvent is lost decreases until it becomes constant. Readings were not taken to the point where solvent is lost at a constant rate. The degree of swelling is very low for all polyesters except Vibrin 121 (Table IV). Vibrin 112 imbibes less than Vibrin 132, which imbibes less than Vibrin 142. The values reported are not equilibrium ones, but those obtained by exposure to the Freon compound for a limited time (2 hours) at a given temperature. As with the rate constants, resin composition affects absorption more than any other variable. Swelling is minimized as the phthalic acid content increases and maximized as maleic and/or fumaric acid content increases. The effect of sebacic acid is not conclusive, although it does not exhibit the same effect on swelling as on the rate constant. The extent of cure influences the quantity of solvent imbibed. Longer cure time results in less solvent penetration; however, overcure can be detrimental. Exposure temperature assumes some importance, although its effect is not always consistent.

In general, at higher exposure temperatures the resins absorb more solvent. The inconsistencies are readily accountable if it is considered that during exposure, other processes, further cross linking, and thermal degradation, in addition to solvent penetration, are occurring. The effects of these additional reactions are particularly important for under- and overcured resins exposed to the higher temperatures. For all resins, much more Freon 11 is retained than Freon 113. Again, this is in reverse to what one might expect from a knowledge of their vapor pressures. There appears to be a partial dissolution of polymer when the resin has not been completely cured, which merely indicates that non-cross-linked polymer is soluble in the Freon compounds. The error encountered in neglecting the very small amount of material dissolved is low, when calculating the volume per cent of solvent present. Let x = volume of solvent present, y = volume of polymer dissolved, and v = volume of original polymer.

$$\frac{x}{v - y} \approx \frac{x}{v}$$

when $v >>> y$.

Resin content, total dibasic acids, free acids, and monomer molecular weight do not vary in a consistent manner and were not taken into account.

CONCLUSIONS

This study, though not aimed at theoretical knowledge of solvent-polymer interactions (*3*), has produced information of considerable practical utility, providing an insight into the mechanism of the absorption of solvents by polymers. The equipment can be used to study the effects of other solvents on other polymers. Solvent effects can be studied at high temperatures and pressures, and for very long times at constant conditions. That study would permit the determination of diffusion constants as well as molecular weight between cross links.

This work, based on nonequilibrium values, has shown that some polyesters are suitable for contact with both Freon 11 and Freon 113 from 20° to 100° C. Vibrin 112 is better than Vibrin 132, which is better than Vibrin 142. Vibrin 121 is materially affected by both solvents at all temperatures and de-

Table IV. Residual Solvent[a] at Inflection Point

	50° C.		75° C.		100° C.		
Cure Time, Hr.	Freon 113	Freon 11	Freon 113	Freon 11	Freon 113	Freon 11	Resins
7.0	6.0	8.6	6.5	13.0	7.2	18.6	V-121
16	6.1	14.1	6.3	17.0	6.6	17.5	
48	1.9	12.2	2.4	16.7	3.3	20.1	
24	0.079	0.42	0.10	6.32	0.09	0.26	V-132
55	0.070	0.10	0.09	0.25	0.16	0.20	
79	0.058	0.16	0.09	0.24	0.13	0.19	
2.0	0.046	0.11	0.051	0.19	0.12	0.43	V-112
10	0	0.11	0.027	0.14	0.052	0.35	
48	-0.019	0.091	0.017	0.23	0.49	0.44	
1.5	0.098	1.4	0.069	1.4	-0.035	2.1	V-142
10	0.071	0.40	0.055	1.3	-0.024	1.8	
48	0.040	1.0	0.062	1.1	0.013	1.5	

[a] % by volume of original volume.

grees of cure; hence, it is not suitable for use with these compounds. Much more Freon 11 than Freon 113 is absorbed by all polymers at all exposure temperatures and cure times. The mechanism by which solvent enters the structure is interaction with the surface and then diffusion into the volume of the polymer. Solvent is lost via a route analogous to that attributed to the drying of porous or packed solids. Polyester composition, exposure temperature, and cure time affect solvent resistance. Overcure and undercure are detrimental; the latter is more serious. The overriding effect, however, is polymer composition

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Properties of Urethane Foams Related to Molecular Structure

R. E. BOLIN, J. F. SZABAT, R. J. COTE, ELAINE PETERS, P. G. GEMEINHARDT, A. S. MORECROFT, E. E. HARDY, and J. H. SAUNDERS

Research Department, Mobay Chemical Co., New Martinsville, W. Va.

Flexible urethane foams have been of commercial interest in this country for approximately three years. Extensive technology in the production of foams from polyesters and, lately, from polyethers has been developed. Variables in foaming have now become well enough recognized and controlled that attempts to correlate fundamental polymer structure and physical properties are meaningful.

Both chemical and mechanical factors influence the properties of urethane foams; some have been reported, such as the design and operation of machinery for foam production (*5*), the use of certain polyesters and polyethers (*3,8,9*), variations in the choice of polyether (*2*), different processing conditions used in the preparation of polyether prepolymers (*4*), and the choice of catalyst used in foaming (*1*).

The properties of the foam depend on controlling these and other variables so that two distinct features are provided: polymer growth toward a final structure compatible with the desired properties, and simultaneous formation of a cell structure realizing the inherent properties of the polymer. Sufficient knowledge of these many variables is available to permit the establishment of a realistic qualitative relationship between foam properties and structural features, especially the calculated average molecular weight per branch point.

Urethane foams based on polyethers and polyesters have been prepared illustrating a wide range of calculated molecular weights per branch point. The properties of these foams have been determined and related to characteristic structural features of the polymer molecules. Many of these foams are experimental only, and do not represent commercial foam systems.

RAW MATERIALS

For all polyether and polyester foam prepared within a molecular weight per branch point range of 1650 to 15,200, a commercial grade of 80-20 ratio of 2,4- and 2,6-tolylene diisocyanate, Mondur TD-80 (Mobay Chemical Co.) was used. For the preparation of polyester foams with a mole weight per branch point range of 410 to 1650, a commercial grade of 65-35 isomer ratio of tolylene diisocyanate, Mondur TD (Mobay Chemical Co.) was used.

Polyether resins were "urethane grade" polyoxypropylene triols, based on glycerol, with molecular weights of 750, 1100, 1500, 2500, 3000, 4000, and 5000 (Union Carbide Corp. and Dow Chemical Co.) and polyoxypropylene glycols of molecular weights 1200, 2000, and 3000 (Union Carbide, Dow, and Wyandotte). Polyester resins used were commercial resins: Multrons R-4, R-8, R-10, R-12, R-18, and R-68 (Mobay Chemical Co.).

PREPOLYMER PREPARATION

All prepolymers were prepared by modifications of techniques previously described (*6*). Conditions minimized biuret,