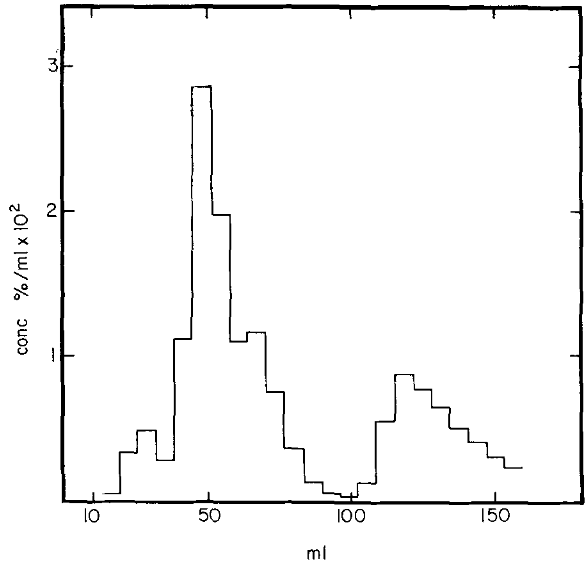

FIG. 6. Chromatogram of a mixture of isomeric sodium phenyl-n-decane sulfonates on charcoal using methanol containing 8% benzene, 1% ammonia, 2% water. Four of the possible five isomers are resolved.

Fig. 5 shows the chromatography of a synthetic mixture of three alkyl sulfates which could be completely resolved and the presence of impurities indicated. It is clear, however, that if impurities in the linear C_{15} surfactant were to be determined, a better solvent, i.e., one containing more benzene, should be used.

Fig. 6 shows the chromatogram of 3.11 mg. of a synthetic mixture of n-C_{10} alkyl benzene sulfonates. Twenty-eight per cent of the mixture had the benzene ring attached to the terminal carbon atom, and formed the last peak. Seventy-two per cent of the mixture that was formed by the other isomers and three of these are clearly resolved. The total recovery was 96%.

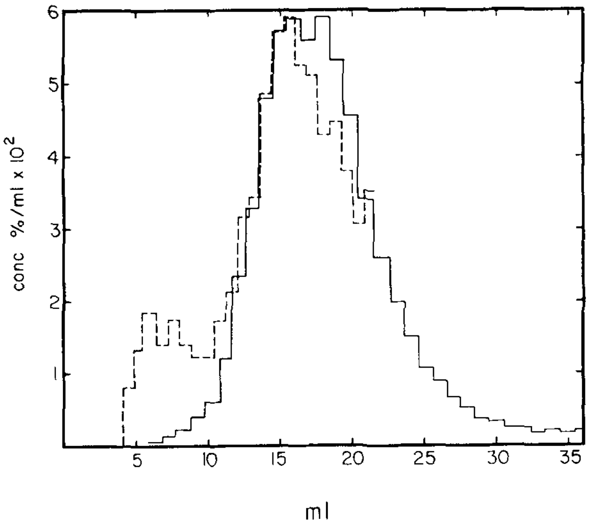

FIG. 7. Chromatograms of 1-mg. samples of two commercial sodium dodecyl benzene sulfonates on charcoal using methanol containing 4% benzene, 1% ammonia, and 2% water.

Fig. 7 shows the chromatograms of 1-mg. samples of two different commercial alkyl benzene sulfonates. Since exactly the same analytical technique was used in both runs, it is clear not only that they are quite different in composition, but also that one is much more complex than the other.

Acknowledgment

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Solvent-Blown, Rigid Urethane Foams from Low Cost Castor Oil-Polyol Mixtures[1]

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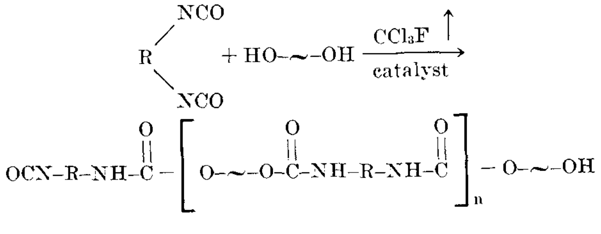
The preparation of solvent-blown rigid urethane foams from low cost castor oil-polyol mixtures was investigated. Solutions of triisopropanolamine, and of mixtures of triisopropanolamine and triethanolamine in castor oil, were used as the polyol component of these foams. Foams were prepared by reacting these polyol mixtures, in the presence of catalyst, surfactant, and trichlorofluoromethane, with prepolymers prepared from toluenediisocyanate and certain polyether polyols or mixtures of these polyether polyols with castor oil. The effect of polyol and prepolymer composition and blowing agent concentration on such foam properties as density and compressive strength was investigated. The properties of the castor oil-based foams were comparable to those of foams obtained from more costly polyols.

RIGID URETHANE FOAMS are cellular plastics which are being used in increasing amounts as insulating material, in low density structural panels, and in flotation gear such as life rafts and buoys. These materials can be foamed in place or in some cases sprayed on.

These foams are polyurethane polymers produced by the reaction of polyisocyanates with polyhydroxy compounds or polyols as shown in the equation



$$R\begin{matrix}\nearrow NCO\\ \searrow NCO\end{matrix} + HO\text{-}\sim\text{-}OH \xrightarrow[\text{catalyst}]{CCl_3F\uparrow} OCN\text{-}R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}-\left[O\text{-}\sim\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\right]_n-O\text{-}\sim\text{-}OH$$

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The reaction of isocyanates with polyols is exothermic. In solvent-blown foams, the heat generated is used to vaporize a dissolved low boiling solvent which expands or blows the plastic to a foam. The solvent most commonly used for blowing is trichlorofluoromethane. This boils at about room temperature (24°C.). For simplicity, only two hydroxyl groups of the polyol are shown in this equation. Actually, polyols possessing three or more hydroxyl groups are used in making rigid foams. These additional hydroxyl groups cause branching and crosslinking of the polymers. Castor oil, which is composed chiefly of glycerol triricinoleate, is a trihydroxy compound that has often been used for the preparation of urethane foams (1–5).

It is often convenient to prepare the foam in two steps and that is the procedure reported here. A prepolymer was first prepared from toluene diisocyanate and part of the polyol. This isocyanate terminated prepolymer was then reacted with the remainder of the polyol to produce a foam.

The preparation of strong rigid solvent-blown foams from mixtures of castor based polyols and some low molecular weight polyols such as trimethylolpropane has been described (6). These foams have good properties but are slightly more expensive, at present, than competitive foams made from polyether polyols. Our present investigation was concerned with the preparation of solvent-blown rigid urethane foams from polyols containing castor oil itself rather than its more expensive derivatives.

Experimental and Discussion

The experimental foams were prepared by reacting an isocyanate containing prepolymer with a polyol using an isocyanate to hydroxyl ratio of 1.05. Generally the total polymer weight was 10 g. exclusive of the CCl_3F blowing agent, catalyst, and surfactant, but larger samples of some of the better foams were prepared. For the 10-g. batches the prepolymer was weighed into a 9-oz. hot drink paper cup and mixed with 0.15 g. silicone surfactant (Union Carbide L-520) and 1.6 g. trichlorofluoromethane. To this mixture was added a polyol solution containing the catalysts: triethylenediamine (0.06 g.) and stannous octoate (0.005 g.). The two solutions were mixed rapidly with a spatula for about 15 sec. and then allowed to foam in place. Foaming was complete in 40 to 60 sec. No serious problems were encountered in scaling up this procedure 10 to 30 fold, but the amount of catalysts used was adjusted to allow more time for mixing and pouring the foam components. Foam testing was done on cylindrical pellets made from 1 in. thick horizontal sections cut from the center of the samples as described previously (6).

Castor oil, when used as the sole polyol in foams of this type, does not produce sufficient crosslinking to yield strong, nonshrinking foams. It must be mixed with a lower molecular weight, or more highly functional, polyol. Mixtures of castor oil with triisopropanolamine were found to be very suitable. Most other low cost, low molecular weight polyols are not sufficiently soluble in castor oil. The polyol mixtures used in this work are listed in Table I. The average compressive strength of foams calculated to 2 lb./ft.^{3} density is plotted *versus* average polyol equivalent weight. The castor oil content of the polyols used is indicated below the curve. The prepolymer used was the same as that described previously (6) and contained 10.3% pentaerythritol monoricinoleate, 10.3%

TABLE I
Castor Oil-Triisopropanolamine Polyol Mixtures

Polyol composition		Average polyol equivalent weight
Castor oil[a]	Triisopropanolamine	
%	%	
10.9	89.1	70
24.9	75.1	80
35.8	64.2	90
44.5	55.5	100
51.6	48.4	110
57.5	42.5	120

[a] The DB grade of castor oil of the Baker Castor Oil Company was used.

equivalent weight of the polyol mixtures was varied from 70 to 120 and castor oil content from 11 to 58%.

The compressive strengths of foams prepared from these polyol mixtures are shown in Fig. 1. Here the trimethylolpropane and 79.4% toluenediisocyanate. As expected, there was a marked increase in compressive strength as the equivalent weight of the polyol was decreased.

In order to obtain lower cost foams, a series of lower cost prepalymers was prepared from toluenediisocyanate (80% 2,4- and 20% 2,6-isomers) and mixtures of castor oil with a commercial hexol, the adduct of sorbitol with six moles of propylene oxide. The composition of these prepolymers is shown in Table II. Ratios of hexol to castor oil used were: 1/0, 3/1, 1/1, 0/1. The prepolymers were all made to contain 26% free isocyanate. The viscosity of the prepolymers increased markedly with increasing hexol content.

The compressive strengths of foams prepared from these prepolymers and the castor-oil triisopropanolamine polyol mixtures are shown in Fig. 2. The castor oil content of the polyols used is indicated below the curves. Curves from top to bottom, are for foams prepared from prepolymers with hexol to castor oil ratios of 1/0, 3/1, 1/1, and 0/1. Compressive strengths increased with decreasing polyol equivalent weight and also with increasing hexol content of the prepolymer. Foams prepared from the hexol-toluenediisocyanate prepolymer and polyols with equivalent weights of 80 or less (represented by the top two points on the top curve of Fig. 2) were somewhat friable or brittle on the surface. Foams prepared from the castor oil-

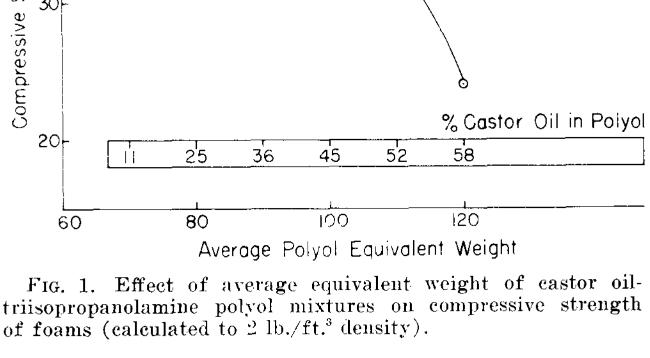

FIG. 1. Effect of average equivalent weight of castor oil-triisopropanolamine polyol mixtures on compressive strength of foams (calculated to 2 lb./ft.^{3} density).

TABLE II

Castor Oil-Hexol Prepolymers (26% NCO)

Hexol[a]/castor oil ratio	Composition[b]			Viscosity at 25°C.
	Hexol	Castor oil	TDI[c]	
	%	%	%	cps.
1/0	22.6	0	77.4	100,000
3/1	19.0	6.4	74.6	27,300
1/1	14.1	14.1	71.8	4,100
0/1	0	36.8	63.2	180

[a] Atlas G-2406 (Commercial adduct of sorbitol with 6 moles of propylene oxide).

[b] Components were mixed and heated for 1 hr. at 75°C. under nitrogen.

[c] Toluene diisocyanate (80% 2,4- and 20% 2,6-isomers).

toluenediisocyanate prepolymer (represented by the bottom curve) were unsatisfactory because of excessive shrinkage. A good combination of desirable properties and low cost is represented by foams in the center of the second curve from the top. For example a foam prepared from polyol with an equivalent weight of 100 and the 3 hexol/1 castor oil prepolymer had fine uniform cells, had a density of 2.12 lb./ft.^{3}, a compressive strength of 37 lb./in.^{2}, a closed cell content[a] of 95%, and a K factor[b] at 30°C. of 0.15.

An effort was made to reduce the cost of these foams further by using, as the polyol component, mixtures of triethanolamine, triisopropanolamine, and castor oil. Triethanolamine is not sufficiently soluble in castor oil to be used without the additional triisopropanolamine to solubilize it. The polyol mixtures, using 3 hexol/1 castor oil prepolymer, and the compressive strengths of foams obtained from them are shown in Table III. For a selected polyol equivalent weight (in this case 100), increasing the triethanolamine content permitted an increase in the castor oil content. Since castor oil is the lowest cost component of the mixture this would lower the cost of the foam. Low shrinkage, fine celled foams were obtained, but the compressive strength decreased somewhat as the triethanolamine content was increased.

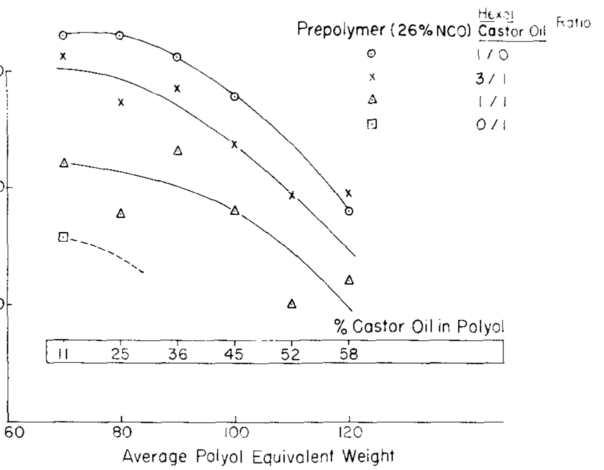

FIG. 2. Effect of average equivalent weight of castor oil-triisopropanolamine polyol mixtures on compressive strength of foams (calculated to 2 lb./ft.^{3} density) prepared from castor oil-hexol-TDI prepolymers.

TABLE III

Foams from Castor Oil-Triisopropanolamine-Triethanolamine Polyols (Equivalent Weight = 100)

Polyol composition			Compressive strength
Triethanolamine	Triisopropanolamine	Castor oil	Calculated at density of 2 lb./ft.^{3}
%	%	%	*lb./in.^{2}*
0	55.5	44.5	36
12.8	38.2	49.0	33
16.5	33.1	50.4	27
23.7	23.7	52.6	23
30.1	15.1	54.8	18

The experimental foams that have been described had densities of 2.0 to 2.6 lb./ft.^{3} The compressive strengths reported for these foams were those calculated for foams with densities of 2.0 lb./ft.^{3} so that the foams could be compared on a constant density basis. This calculation was made using the previously derived (6) empirical relationship between density and compressive strength in a given foam system

$$s = C\,d^{1.57}$$

$$s_{(d=2)} = s\,(2/d)^{1.57}$$

where: d = density in lb./ft.^{3}

s = compressive strength in lb./in.^{2}

$s_{(d=2)}$ = compressive strength of foam with density of 2 lb./ft.^{3}

The validity of this relationship was rechecked on foams prepared from a castor oil-triisopropanolamine polyol with an equivalent weight of 100 and the 3 hexol/1 castor oil prepolymer. The amount of trichlorofluoromethane blowing agent was varied as shown in Table IV to yield foams with densities ranging from 1.75 to 3.34 lb./ft.^{3} The observed compressive strengths and the compressive strengths calculated at a density of 2 lb./ft.^{3} are listed in the last two columns. The calculated compressive strengths are approximately constant as predicted by the above equation.

TABLE IV

Effect of CCl_3F Content on Properties of Foams Prepared from 44.5% Castor Oil-55.5% Triisopropanolamine Polyol

CCl_3F	Density	Compressive strength	
		Observed	Calculated at density of 2 lb./ft.^{3}
parts per 100 parts polymer	*lb. ft.^{3}*	*lb./in.^{2}*	*lb./in.^{2}*
11	3.34	74.2	33.0
13	2.81	59.1	34.7
15	2.27	43.1	35.2
19	1.91	34.3	36.7
21	1.75	28.7	35.3

Conclusion

Strong, low density, rigid solvent-blown urethane foams with low thermal conductivities can be prepared using as the polyol component low cost mixtures of castor oil with triisopropanolamine or with triisopropanolamine plus triethanolamine.

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[a] Determined by du Pont air displacement method.

[b] Thermal conductivity determined with Pittsburgh Corning Thermal Conductivity Probe on 4 in. x 4 in. x 12 in. foam block one day after preparation.

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