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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RECEIVED for review May 23, 1955; resubmitted April 7, 1958. Accepted November 10, 1958.

Properties of Urethane Foams Related to Molecular Structure

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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, allophanate, and isocyanate trimer formations and maintained the influence of these side reactions as uniform as possible from prepolymer to prepolymer. The 5000 molecular weight triol prepolymer was prepared under somewhat different conditions to obtain a suitable foam sample. In all cases, a "total prepolymer" was prepared which involves the addition of diisocyanate to all of the polyether glycol.

FOAMING

All prepolymers were foamed by the Mobay foam machine (*7*). Additional diisocyanate was added at the time of foaming if the amount of free isocyanate in the prepolymer was not enough to give the desired foam density. The activator mixture was composed of a tertiary amine catalyst, water, and silicone oil. The catalyst and silicone oil concentrations were adjusted slightly in some cases to give the best foam obtainable from each prepolymer. Foams from the prepolymers were allowed to cure at 70° to 75° C. until tack-free, crushed to open the cells, and cured overnight at 70° to 75° C. before testing.

Foams from polyesters were prepared by the "one-shot" method, whereby measured amounts of polyester, diisocyanate, and activator mixture were metered simultaneously to a common mixing chamber. The activator mixture was composed of a typical tertiary amine catalyst, emulsifiers, and water. The catalyst and emulsifier levels were adjusted to give foams having the best properties, while the water concentration was maintained at 95% of the theoretical requirement. Polyester foams were allowed to cure overnight at room temperature before testing.

TEST METHODS

The following tests were conducted according to methods approved by the Cellular Plastics Division of the Society of Plastics Industry (*10*): density, tensile strength, elongation, constant deflection compression set (calculated on original thickness), and compression load deflection. An Instron tester was used for tensile, elongation, and compression-deflection tests. Other tests similar to standard ASTM procedures were conducted: rebound elasticity (similar to ASTM D 1054-55), Yerzley resilience (similar to ASTM D 945), and Clash-Berg torsional stiffness (similar to ASTM D 1043-51). Two improvised tests were also used: "swell index," allowing a 1.0 x 1.0 x 0.25 inch foam sample to swell to the maximum, immersed in dimethylacetamide for 24 hours at room temperature, and calculating the per cent volume swell from the per cent area swell, and "point load indent," indenting a foam sample to 90% deflection with a rod 1.13 inches in diameter for 5 minutes, removing the rod, determining the time for the foam to recover completely.

The Yerzley resilience test was inapplicable to firmer polyether foams, because test conditions greatly influenced the results.

CALCULATION OF BRANCHING

Calculations were made assuming that all materials were 100% of their reported functionality. The hydroxyl number of the material was used to calculate the equivalent weight. Knowing the amounts and functionality of each ingredient used in preparing a foam, the number of branch points per 100 parts of foam polymer was calculated correcting for the gas loss due to carbon dioxide evolution. It was assumed that one mole of carbon dioxide was produced from each mole of water used in foaming. One tetrafunctional branch point was assumed present for each mole of tetrol.

The calculated molecular weight per branch point is assumed to be the maximum probable weight since any cross linking due to biuret, allophanate, and trimer formations would decrease this value. Probable deviations of the polyethers from their assumed functionality—e.g., due to terminal unsaturation—would tend to increase the value, thus compensating for side reactions during foaming.

The weight percentages of structural factors such as aromatic (C_6H_3—) urea (—NHCONH—) and urethane (—NHCOO—) were also calculated. These factors have a contributing influence on some physical properties. The amount of water in the formulation was held nearly constant, so the weight per cent urea (calculated on the basis that one mole of urea was produced from one mole of water) remained fairly constant. The urethane content was calculated assuming that one urethane group was formed from each hydroxyl group in the polyether or polyester.

A sample calculation of the average molecular weight per branch point and the weight percentages of structural factors is described for a typical polyether foam sample. The prepolymer was prepared from 50 parts by weight of diol, hydroxyl number 56 (0.025 mole, 0.05 equivalent); 50 parts of triol, hydroxyl number 56 (0.0167 mole, 0.05 equivalent); to 10.5% NCO content, and was foamed with 2.2 parts of water per hundred of prepolymer:

Wt. of triol per branch point 3000 (triol mole wt.)
Wt. of diol per branch point 3000
Hydroxyl equiv. per branch point 6
Equiv. of NCO in prepolymer (x) $\dfrac{10.5}{100} = \dfrac{42x}{6000 + 87(x + 6)}$
$x = 20.9$
Total isocyanate $87(6 + 20.9) = 2340$
Water for 8340 parts prepolymer $8340 \times 2.2/100 = 183$
CO lost/branch point
CO_2 lost/branch point $183 \times 44/18 = 447$
Net weight/branch point $6000 + 2340 + 183 - 447 = 8076$
Wt. % aromatic, C_6H_3 (MW 75)

$$\frac{2340}{8076} \times \frac{75}{174} \times 100 = 12.5\%$$

Wt. % urea, —NHCONH— (MW 58)

$$\frac{183}{18} \times \frac{58}{8076} \times 100 = 7.3\%$$

Wt. % urethane, —NHCOO— (MW 59)

$$\frac{6}{8076} \times 59 \times 100 = 4.4\%$$

STRUCTURE AND FOAM PROPERTIES

Polyether Foams. Table I shows the relation between the physical properties and the calculated molecular weight per branch point and other structural features for foams from pure polyether triol prepolymers. Increasing the molecular weight per branch point increased elongation, softness, both Yerzley resilience and rebound elasticity, rate of recovery from indentation, and the swelling by a solvent, and reduced hysteresis and tensile modulus, and decreased torsional stiffness (Clash-Berg) at lower temperatures as urethane and aromatic contents were decreased. A commercial latex foam rubber sample is used as a comparison. The compression-deflection values at 25% de-

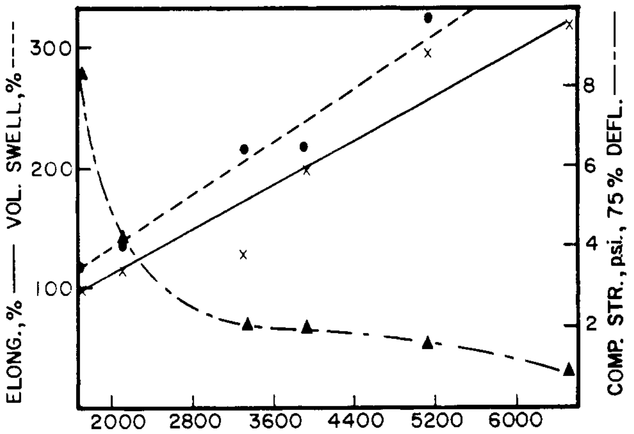

Figure 1. Weight per branch point vs. swell, elongation, and compression strength of polyether triols

Table I. Relationship between Structure and Physical Properties for Polyether Urethane Foams

(Pure triols system)

Weight per branch point	1650	2175	3375	3900	5175	6525
Aromatic, %	16.2	14.9	12.6	11.2	11.0	11.0
Urethane, %	10.5	8.3	5.3	4.5	3.4	2.7
Urea, %	7.9	7.6	6.6	6.6	6.7	6.6
Density, lb./cu.ft.	2.4	2.2	2.5	2.5	2.8	2.4
Tensile strength, p.s.i.	30.0	21.0	18.0	20.0	22.0	15.0
Tensile mod., 100% elong., p.s.i.	. . .	16	12	10	7	6
Elongation, %	100	130	155	200	295	340
Compression strength, p.s.i.						
25%	1.9	0.9	0.5	0.5	0.5	0.3
25%R[b]	0.7	0.6	0.5	0.4	0.4	0.3
50%	2.8	1.3	0.7	0.7	0.7	0.4
75%	8.3	4.3	2.1	1.9	1.6	0.9
Compression set, %	7.0	3	4	3.0	. . .	14
Rebound elasticity, %	16	15	44	49	42	. . .
Yerzley resilience, %	N.A.[c]	N.A.[c]	47	63	50	. . .
Point load indent, sec.	7100	130	1	1.0	1	. . .
Swell index, vol. %	145	170	237	240	350	. . .

[a] Prepolymer prepared under different conditions.

[b] Measured after 1-minute rest.

[c] Not applicable.

flection and at the same deflection after a one-minute rest (25R) may be considered a measure of hysteresis. Ultimate tensile strength and compression set were influenced very little. The effects upon elongation, compression strength, and swelling in a solvent are presented in Figure 1.

Table II shows a similar treatment of the physical properties obtained by Davis, McClellan, and Frisch (*2*) using polyether tetrols either alone or in mixtures with polyether diols. The results agree with the triol series with the addition that tear strength was decreased with increased branching.

Table III shows the properties of foams prepared from various mixtures of polyether diols and triols. The same general trends were followed except that the data were not as consistent as the pure triol series, because of the randomness of the amounts of structural factors such as aromatic and urethane contents of each foam. Two samples with nearly the same molecular weight per branch point but differing in amounts of these structural features, compared in Table III, show that greater amounts of aromatic and urethane groups cause a decrease in elongation and rebound elasticity.

Table IV shows the effect on torsional modulus of changing independently the molecular weight per branch point and the contents of urethane plus aromatic groups. Data on samples at 3375 to 3385 weight per branch point, show that greater amounts of aromatic and urethane groups increase the stiffness of the foam sample, since a given modulus is attained at a higher temperature. When the degree of branching is decreased within the same concentrations of structural factors, the stiffness of the foam is decreased.

Polyester Foams. Table V shows the properties of various adipic acid polyester foams and the relationship to their molecular structure. Two of the rigid foam samples were prepared from polyesters containing adipic acid and a small amount of phthalic anhydride. In the calculation of the aromatic content of such foam samples, the phthalic anhydride is included.

The trends established in Table V generally agree with those of the polyether series. At similar weights per branch point, the polyester samples were firmer than those obtained from polyethers. Figure 2 shows the low temperature flexibility of a flexible and a semi-rigid sample, with the former being considerably stiffer at a given temperature than a more cross-linked polyether sample (Figure 3). A greater degree of intermolecular forces due to the presence of the ester linkages in polyester foams is considered to be the principal reason for their greater compressive strengths and greater apparent moduli at certain temperatures.

"Semiflexible" polyester and polyether foams were obtained in the range of 750 to 2500 molecular weight per branch point.

Table II. Relationship between Structure and Physical Properties of Polyether Urethane Foams[a]

(Tetrol plus glycol system)

Weight per branch point	3100	4560	5730	7270	10350	13440	16520
Aromatic, %	13.1	11.5	10.9	11.3	11.9	12.2	12.3
Urethane, %	7.6	5.2	4.1	4.9	5.7	6.1	6.4
Urea, %	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Density, lb./cu.ft.	2.2	2.3	2.4	2.4	2.4	2.4	2.5
Tensile, p.s.i.	12.0	10.0	8.0	11.0	12.0	13.0	20.0
Elongation, %	110	100	117	147	197	237	292
Compression strength, p.s.i.							
25%	0.6	0.6	0.4	0.5	0.4	0.4	0.4
50%	0.9	0.8	0.6	0.7	0.6	0.6	0.6
75%	3.2	2.2	1.8	1.8	1.7	1.6	1.6
Tear strength, lb./in.	0.6	0.6	0.8	1.4	1.7	2.3	3.1

Catalyst mixture
N-methylmorpholine = 1.0
Triethylamine = 0.2
Water = 2.34 (115%)
Silicone oil = 0.4
%NCO = 9.0 (theoretical)

[a] Data from (*5*).

Table III. Relationship between Structure and Properties of Polyether Urethane Foams

(Triol plus diol system)

Av. weight per branch point	1650[a]	2175	2400[a]	2985	3385	3700	4040	4480	5085	5500	6170	6725	7580[a]	8075	8280	10200	10225	15185[a]
Aromatic, %	16.2	14.9	13.4	15.1	14.7	12.0	11.3	12.4	13.4	12.4	12.5	12.4	11.9	12.4	11.9	12.4	14.6	12.3
Urethane, %	10.5	8.3	7.3	8.8	8.1	4.8	4.3	4.4	6.0	4.5	4.5	4.4	3.6	4.4	4.8	4.3	7.9	6.0
Urea, %	7.9	7.6	6.8	7.2	6.9	6.9	6.9	7.0	6.8	6.6	6.6	7.3	7.3	7.0	6.8	7.4	6.6	7.0
Density, lb./cu. ft.	2.4	2.2	2.7	2.2	2.6	2.3	2.6	2.9	2.3	2.7	2.6	2.6	2.5	2.6	2.3	2.2	2.2	2.2
Tensile strength, p.s.i.	30.0	21.0	...	26.0	28.0	18.0	20.0	25.0	22.0	20.0	20.0	24.0	21	20.0	18	23	24	21.0
Elongation, %	100	130	...	125	180	180	165	185	220	235	260	250	280	240	225	340	270	375
Compression-strength, p.s.i.																		
25% def.	1.9	0.9	1.1	1.2	1.7	0.6	0.7	0.7	0.6	0.7	0.6	0.6	0.5	0.6	0.5	0.6	0.5	0.4
50%	2.8	1.3	1.5	1.7	2.4	0.9	1.0	1.0	0.8	0.9	0.9	0.8	0.7	0.8	0.7	0.7	0.7	0.4
75%	8.3	4.2	3.6	5.2	6.6	2.0	3.8	2.7	2.1	2.0	2.4	2.3	1.7	1.9	1.6	1.7	1.7	1.0
Compression set, %	7.0	3.1	...	30	15	...	4.0	3.0	4.0	...	...	6.0	8	2	5.0	6.0	3	6
Rebound elasticity, %	16	15	18	20	20	38	29	32	...	...	28	...	...	...	...	...	25	...
Yerzley resilience, % at 30% deflection)	N.A.[b]	N.A.[b]	11	30	22	30	...	38	...	...	51	...	...	...	...	...	21	...
Swell index, vol. %	145	170	...	175	205	270	...	237	...	...	350	...	...	...	...	...	390	...

[a] The catalyst concentration in this run was different from the standard amount.

[b] Not applicable.

Table IV. Effect of Structural Factors and Branching on Torsional Stiffness

(Clash-Berg)

Weight/branch point	3375	3385	10,225
% aromatic (C_6H_3—)	12.6	14.7	14.6
% urethane (—NHCOO—)	5.3	8.1	7.9
Temp., °C. at modulus 50 p.s.i.	-37	-10	-35
Temp., °C. at modulus 100 p.s.i.	-40	-30	-45

The compression sets of semiflexible polyether foams were better than those of the polyester semiflexible samples at similar weights per branch point. No rigid polyether samples were prepared.

SUMMARY

The molecular weight per branch point and other structural features for a number of polyether and polyester foams were calculated and related to some physical properties. The value calculated for molecular weight per branch point agreed qualitatively with the swell index.

Increasing the molecular weight per branch point favors greater elongation, tear strength, resilience, elasticity, and low temperature flexibility. Decreasing the molecular weight per branch point favors greater compression strength, hysteresis, tensile modulus, and stiffness at low temperatures.

Greater weight percentages of aromatic rings and urethane groups within similar degrees of cross linking appear to cause a decrease in elongation and rebound elasticity and favor greater stiffness at lower temperatures in polyether foams. The effect of the urethane, urea and, in the case of polyester foams, the ester groups, is presumed to be due to greater intermolecular attraction. Aromatic rings are believed to convey additional firmness by causing a hindrance to rotation within the polymer.

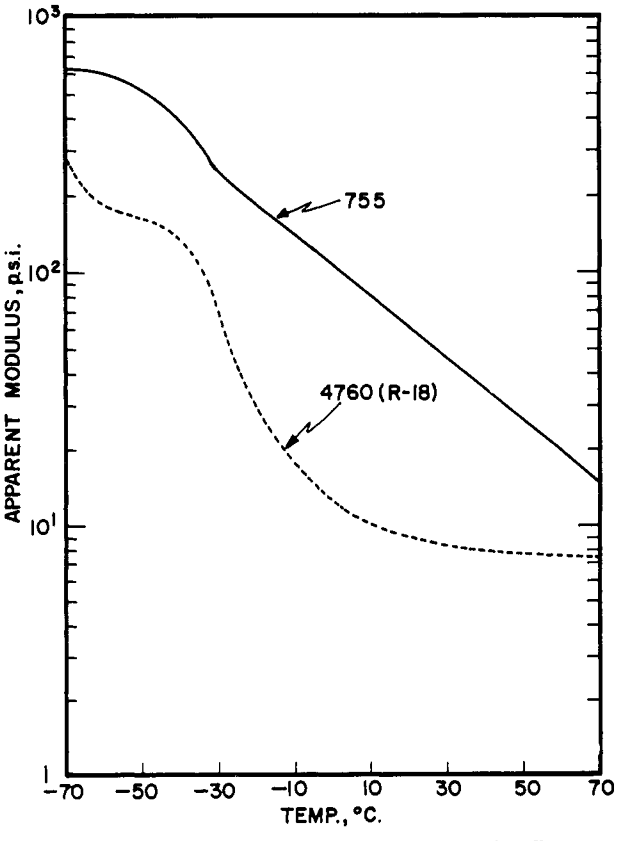

Figure 2. Weight per branch point vs. torsional stiffness vs. temperature for polyether triols

Table V. Relationship between Structure and Physical Properties of Polyester Urethane Foams

Weight per branch point	410	474	538	755[a]	1370	2170	2460	3760	4220	4760	6070	6700	8900	15,200
Aromatic, %	21.8	18.7	22.7	16.6	15.9	15.3	14.7	14.4	14.2	13.8	14.0	13.9	13.8	12.6
Urethane, %	16.6	11.1	17.3	7.7	7.9	6.8	5.8	5.2	4.7	4.5	4.4	4.2	4.0	3.7
Urea, %	5.2	4.0	5.0	4.8	6.8	7.0	7.1	7.2	7.2	7.1	7.3	7.3	7.3	7.1
Density, lb. cu. ft.	2	2	2	2.8	2	2.1	2	2.3	2	2	2.4	2	2.3	2.0
Tensile strength, p.s.i.	55	21	55	35	27	27.9	26	27.2	29	20	34.3	33	28.7	25
Elongation, %	10	. . .	10	60	160	145	270	300	300	200	450	380	385	350
Comp-strength at yield (10%), p.s.i.	20	9.1	20	8.7	. . .	. . .	. . .	. . .	. . .	0.7	. . .	. . .	. . .	0.6
Compression set, %	. . .	. . .	. . .	47	26	. . .	18	. . .	9	5	. . .	14	. . .	5

[a] Contains 4.0 pbw. plasticizer. Calculations based on actual foam components other than plasticizer.

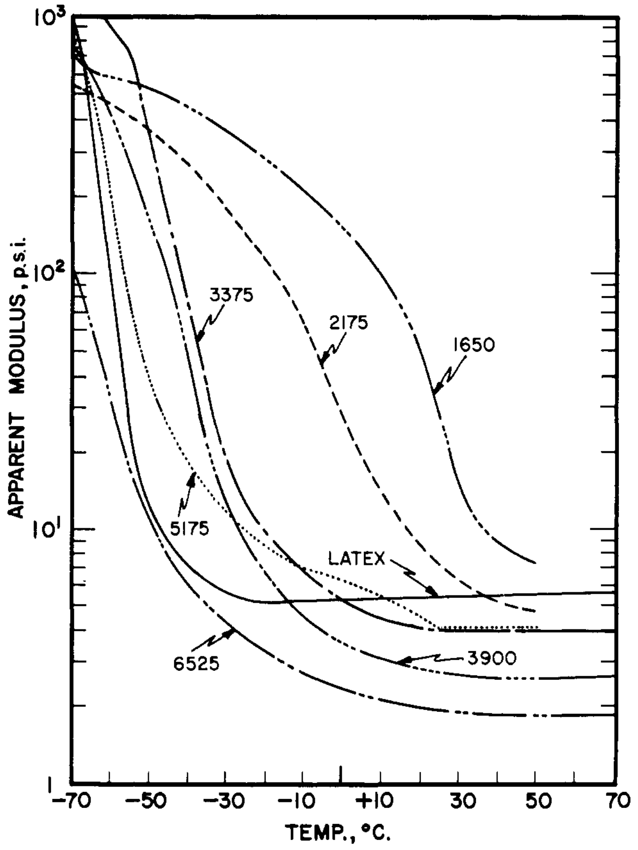

Figure 3. Weight per branch point vs. torsional stiffness vs. temperature for polyester foams

Polyester foams followed the same trends as polyether foams and are firmer than the latter within a similar molecular weight per branch point range. The compression set of semiflexible polyester foams was higher than that of semiflexible polyether foams. Ultimate tensile strength and compression set for both types of flexible foams did not appear to be affected significantly by the degree of cross linking.

ACKNOWLEDGMENT

The authors thank the Physical Testing and Evaluation Group at the Mobay Chemical Co., under the direction of Samuel Steingiser and William Darr, for testing the foams prepared.

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