

Dependence of Physical Properties on Composition in a Series of High Load-Bearing Polyurethane Foams

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Synopsis

Data are presented on the physical characteristics of a polyether-based urethane foam developed as a highly specialized shock-cushioning material. The effect of changes in catalyst ratio and concentration on load deflection and density are shown—also the correlation between foam density and tensile strength. In general, load bearing and density increased nonlinearly with increasing tin catalyst concentration and decreased with increasing amine catalyst. Desired load-bearing properties were obtained by using a blend of di- and higher-functional isocyanates and by the inclusion of ethylene glycol with a polyol of about 4000 average molecular weight. Hydroquinone was used to inhibit autoxidation and scorching during normal exotherms of foaming. Open cells were obtained by the use of trimerized fatty acids.

Introduction

A polyurethane foam was designed for a packaging application involving protection of certain instruments against shock and various lower frequency vibrational motions that occur during their conveyance. The required mechanical properties of the foam were presented to us after being determined by various groups of mechanical engineers and physicists who performed computer studies of the mechanical analyses.

The most salient features of the requisite engineering specifications require that the foam have high load bearing properties, good resilience or quick recovery from distortion, a moderate tensile strength, good breathability, low glass transition temperature, and high hydrolytic stability.

Properties and Their Measurement

An Instron universal tester or a Southwark Tate Emery testing machine with automatic cycling controls and a recorder was used to measure the load bearing capacity of the foam. The specimen, usually $6 \times 6 \times 2$ in. or $4 \times 4 \times 2$ in., was centered between two parallel flat plates that cover the entire sample area and a total load of 1 lb. applied to the specimen surface. The distance between plates was measured to the nearest 0.01 in., and the sample was loaded to 25% of its initial height and then

unloaded without pause. A total of four deflection cycles, applied at the rate of 1 ± 0.1 in./min./in. of initial thickness, were imposed on the sample with essentially zero time lag between cycles, the zero point on the chart being determined from the first loading curve. Compression-deflection data reported were obtained from the fourth loading cycle. Typical raw

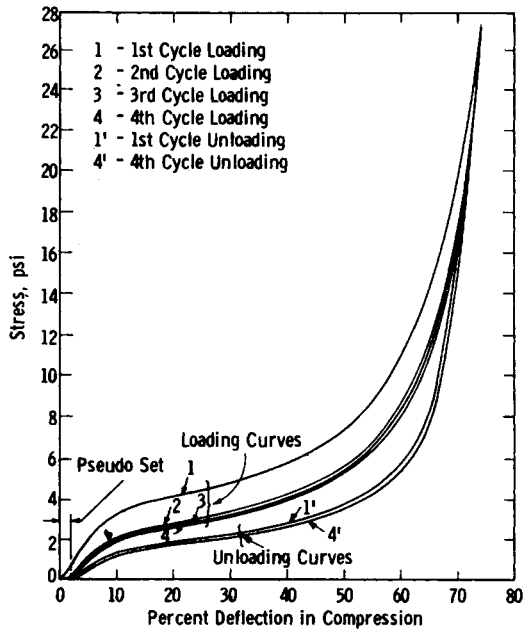


Fig. 1. Typical stress-strain data for four-cycle test.

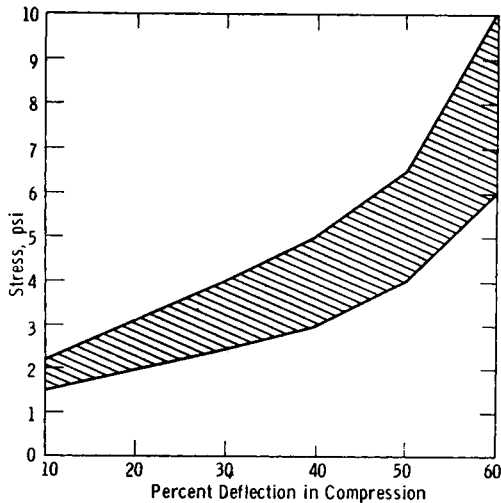


Fig. 2. Stress-strain requirements for load bearing.

data obtained directly from the tester that illustrate the loading characteristics and the hysteresis loops are shown in Figure 1.

The specified properties of the foam required that the compression-deflection curve (fourth cycle) fall within the limits shown in Figure 2. In addition the unloading value for deflections of 20, 30, 40, and 50% were required to be not less than 25% nor more than 85% of the loading values.

Tensile strength of the foam was required to exceed 30 psi when tested in accordance with ASTM-D1564-62T. While elongations were not specified, it was desirable that their values exceed 70%.

It was also required that the compression set values, expressed as percentage of original height, did not exceed 8%. These tests were performed as described in ASTM-D1564-62T (compression set test, method B).

Hydrolytic stability requirements were stringent and will be discussed in a later publication.

Breathability is defined here as the pressure drop observed when passing an air flow of 5 ft.³/min. through a doughnut-shaped specimen, 6 in. O.D., 1 in. I.D., and 2 in. high, while the doughnut is compressed to 1 in. in height. Air was introduced at the center of the doughnut and permitted to pass through only in a radial direction due to the external fixture that contains two parallel plates that press on the faces of the sample. Specifications required that the foam have a maximum pressure drop of 4 psi. Typical results for most of the foams described here were of the order of 1-2 psi.

Since the shock protection provided by the foam at high impact rates, such as 12 ft./sec., is correlatable with the glass transition temperature by a time-temperature superposition relationship, it was specified that the glass transition temperature should not exceed -40°C . Dilatometric determinations were performed by evacuating the sample and replacing the gas with isooctane which does not appear to cause noticeable swelling of the foams described here. The filled dilatometer was cooled to -80°C . and the temperature permitted to rise at $0.5^{\circ}\text{C}/\text{min}$. Typical T_g values for most of the foams described here were about -55 to -60°C .

While this paper is primarily concerned with load-bearing characteristics, certain limitations dictate other characteristics of the foam. The curves in Figure 2 require that the stress should not rise too rapidly with increasing strain. In order to conform to the specified range it is necessary that the pseudo set on the fourth cycle be small, generally less than 3%. The pseudo set is defined as the location on the abscissa (Fig. 1) where the stress value for the fourth cycle loading curve begins to depart from zero. Since the testing apparatus operates essentially continuously for the four cycles, foams having slow rates of elastic recovery cannot keep up with the movement of the platens. A typical slow recovery foam may have recovered only 90% of its original thickness between the third unloading curve and start of the fourth load cycle and thus show a zero value for the stress at 10% compression. Materials exhibiting moderate rates of recovery may have pseudo sets of 5%. If such a material

were to have a sufficiently high modulus to meet the 10% deflection requirements, it would probably exceed the upper stress limits at the higher deflections.¹ Foams having greater resiliencies display lower pseudo set values, thus providing an inherent advantage in meeting the requirements of Figure 2. While compression set simultaneously measures a number of different properties, lack of resilience generally gives high values which exceed specifications. Since the foam is used to surround certain instruments and protect them from vibrational motions of various frequencies, it becomes apparent that use of nonresilient materials can result in development of temporary rattle spaces.

Good breathability is an important requirement, since it permits air to escape sufficiently rapidly at high frequency vibrations and under shock conditions. If the gas cannot escape, its *PVT* characteristics will tend to raise the stress values at high deflections beyond the specified range in Figure 2.

There were no requirements regarding cell structure or size except that the structure should be free of striations and be uniform in order to avoid discontinuities in properties. Foam prepared according to the formulation in Table I, which met the required physical properties, had a "bread"

TABLE I
Typical Formulation of Protective Foam

Stream	Components	Parts of components	Total parts of stream
1	Polyoxypropylene triol (mol. wt. approx. 4000) ^a	35	45.2
	Tribasic fatty acids ^b	10	
	<i>N</i> -Ethyl morpholine (NEM)	0.2	
2	Ethylene glycol	5.00	5.8 + X
	Hydroquinone	0.80	
	Water ^c	X	
3	Tall oil fatty acids ^d	3.0	0.27
	Stannous octoate (SnOct)	1.0	
4	Polymethylene polyphenyl isocyanate ^e	19.6	30.3
	Toluene diisocyanate-80 ^f	12.0	

^a Polyoxypropylene triol was Voranol CP-4000 (Dow Chemical Co.). Similar results are expected with the use of other 4000 mol. wt. polypropylene ether triols.

^b Tribasic fatty acids were trimer acids, Empol 1040 (Emery Industries), consisting of approx. 90% of C₆₄ tribasic acids and 10% of C₈₆ dibasic acids.

^c X = quantity of H₂O added adjusted to give desired compression-deflection properties. Most common values are 0.38-0.41 parts water.

^d Tall oil fatty acids were in the form of Acintol FA-1 (Arizona Chemical Co.). Other fatty acids can be substituted.

^e Polymethylene polyphenyl isocyanate was Mondur MR (Mobay Chemical Co.). Similar results are expected from PAPI (Carwin Co.). Material believed to have an average functionality of about 2.7.

^f Toluene diisocyanate-80 consists of approximately 80% of 2,4-tolylene diisocyanate and 20% of 2,6-tolylene diisocyanate.

structure when prepared with a low-pressure, high-shear Martin Sweets machine and a "caviar" structure when a high-pressure, low-shear Hennecke UBT machine was used.

The results reported in this study are on foams prepared by a Martin Sweets machine on variations of the basic formulation shown in Table I. Typical properties are shown in Table II. Since properties of foams can be affected by their curing conditions and environment, all results were determined on foams that were cured for a least 7 days in an environment of 50% R.H. and $25 \pm 2^\circ\text{C}$.

TABLE II
Typical Properties of Protective Foam*

Tensile strength, psi	30-60
Elongation, %	70-100
Compression set, %	4-7
Glass transition temperature, $^\circ\text{C}$.	-55 to -60
Breathability, psi	1-2
Density, lb./ft. ³	7.0-8.5
Load bearing	Within limits of Figure 2
Pseudo set, %	1.5-2.5
Cream time, sec.	30-40
Rise time, min.	2.5-3.5

* Values pertain to measurements performed or described in text.

Composition of Foam

In order to meet the above described properties, we found that we could not employ conventional formulations. Firstly, castor oil-based formulations which have found success in some shock protection and high load-bearing applications could not be used here since they lacked the required resilience. Polyester-based foams can be prepared so as to have good load bearing and recovery properties; however, they had to be eliminated because of their poor hydrolytic stability. Conventional flexible polyethers generally give load-bearing properties that are too low for this application, whereas the rigid polyether formulations are obviously lacking in their cushioning qualities. As a result we chose an ethylene glycol-polyether combination for the base polyols. Table I illustrates a typical formulation that meets the requirements of the specifications which we shall discuss in detail.

High molecular weight polyethers, as the sole polyol source, gave foams that were low in load-bearing ability. Use of higher hydroxyl number polyethers gave foams of increased load-bearing ability but imparted poor resilience. Use of ethylene glycol and other very low molecular weight polyols improved the rigidity of the foam and yet gave good resilience when used with polyethers having molecular weights above 3500. The added stiffness can be attributed to the large increase in hydrogen bonding and also to the resultant dilution of the polyether groups with the aromatic

urethanes formed by the reaction of the glycol and isocyanates. Large numbers of hydrogen bonds generally give polymers having slow rates of recovery. The high resilience obtained despite the large number of hydrogen bonds might be attributed to the long uninterrupted polyether chain segments between the hydrogen bonds. This is consistent with our findings that intermediate molecular weight polyethers, used in place of the combination of ethylene glycol and high molecular weight polyethers and having the same total NCO requirements, give about the same total number of hydrogen bonds but yet have poorer resilience.¹

Trimer acids were incorporated into the formulation in order to provide a high percentage of open cells. We speculate that this effect is of a kinetic nature based on the different rates of reaction of carboxylic and

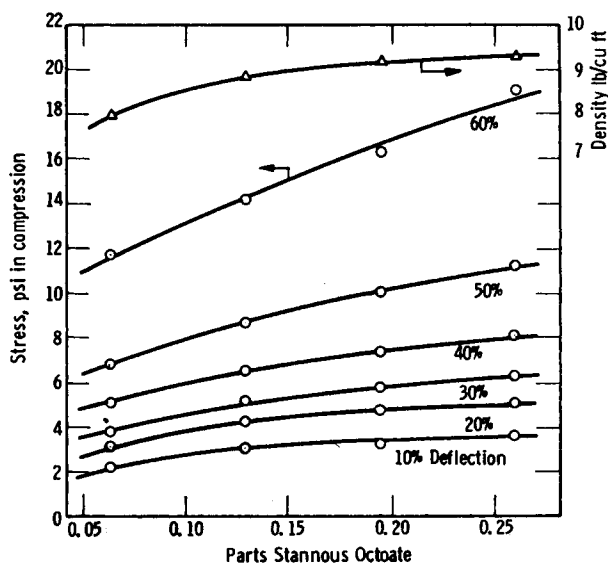


Fig. 3. Effect of stannous octoate concentration on load bearing and density. NEM concentration, 0.2 part.

various hydroxyl groups with isocyanates. Carboxylic groups enter into the reaction at a slower rate than that of the water and most of the hydroxyls of the polyols. Thereby CO_2 could be generated from the acids after the foam has been partially formed, causing many of the cells to burst.

Density of the foam greatly affects the load-bearing characteristics. While all of the ingredients have some effect on the density, we chose to control it primarily by adjusting the water and catalyst content. Increased quantities of water and amine catalyst gave decreased densities, whereas the density increased with the stannous octoate (SnOct) concentration. These variables were adjusted so as to provide a foam having the desired load bearing properties. Such adjustments are highly specific for given temperatures and machine conditions.

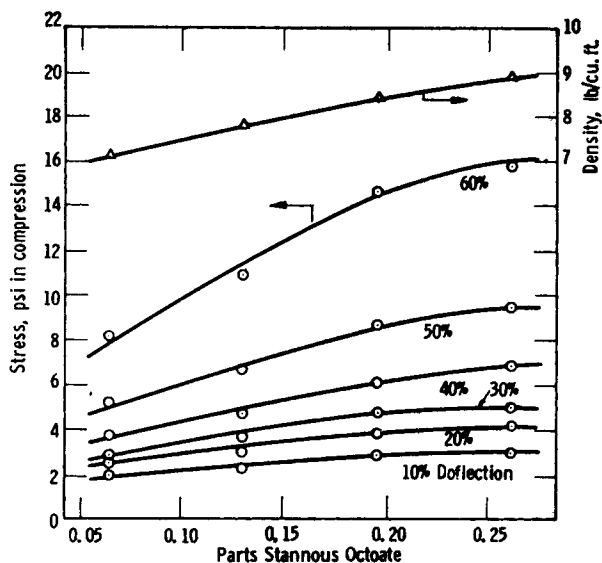


Fig. 4. Effect of stannous octoate concentration on load bearing and density. NEM concentration, 0.4 part.

In order to improve control of metering, the SnOct was diluted with a carrier, tall oil fatty acids. Other liquid fatty acids or unreactive carriers such as dibutyl phthalate or perchloroethylene can also be used, provided that they do not behave as surfactants. They do not show any noticeably different effects due to their use in small concentrations.

The ratio of polymethylene polyphenyl isocyanate to toluene diisocyanate was adjusted to give the required stiffness. Increased ratio of toluene diisocyanate gives a foam having a higher elongation and greater flexibility due to fewer crosslinks.

Addition of hydroquinone greatly reduced the scorch. Runs greater in volume than 4 ft.³ attain their maximum exotherm temperature of about 150–160°C. ca. 1–4 hr. after pouring. If buns without hydroquinone are cut open shortly after the foam is prepared the entering air autoxidizes the foam, causing a rather severe darkening of the material. Uncut buns show a much lighter brown scorch in the interior, the intensity of which is dependent on the integrity of the skin. Autoxidative degradation is expected when one considers the high temperature resulting from the exotherm and that the substrate consists largely of a polyether containing tertiary hydrogen atoms. In a study¹ of the effects of many autoxidants, we found that hydroquinone was very effective in inhibiting the oxidation and yet had a minimum effect on the physical properties of the foam. Even early cutting of hot freshly poured buns of foam, prepared with hydroquinone, did not result in significant deterioration of the foam.

Almost all of the commercially available silicone surfactants were studied and none of them gave improved properties.¹ In general, most surfactants

gave a slightly lower density, finer cells, and reduced breathability. Since the foam is normally quite breathable and highly open-celled, reduction in cell size by surfactants could cause an increased pressure drop for flow and thus reduce the breathability. Actually the formulation can be consid-

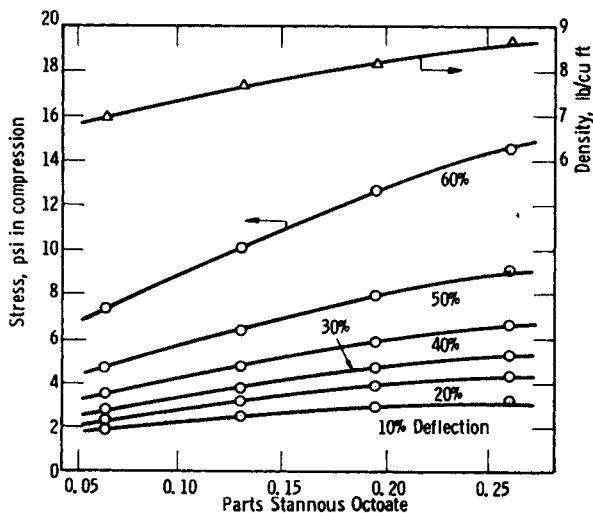


Fig. 5. Effect of stannous octoate concentration on load bearing and density. NEM concentration, 0.6 part.

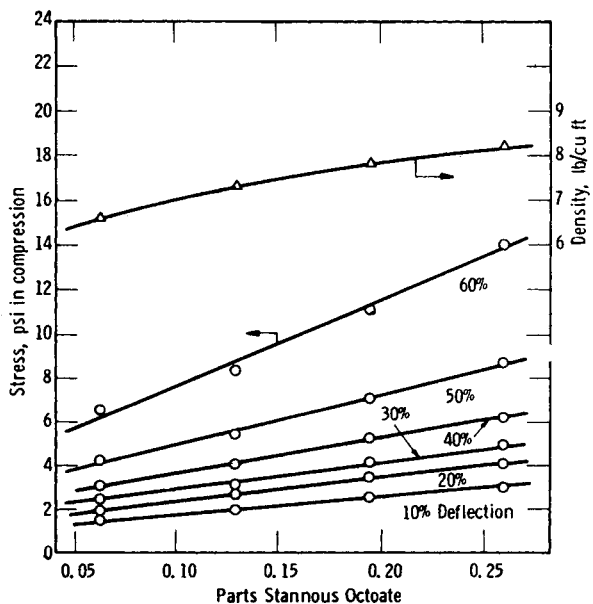


Fig. 6. Effect of stannous octoate concentration on load bearing and density. NEM concentration, 0.8 part.

ered to contain its own surfactant, since the ethylene glycol has miscibility with water and the organic ingredients. Surfactant activity could also result from the combination of the amine catalyst and fatty acids.

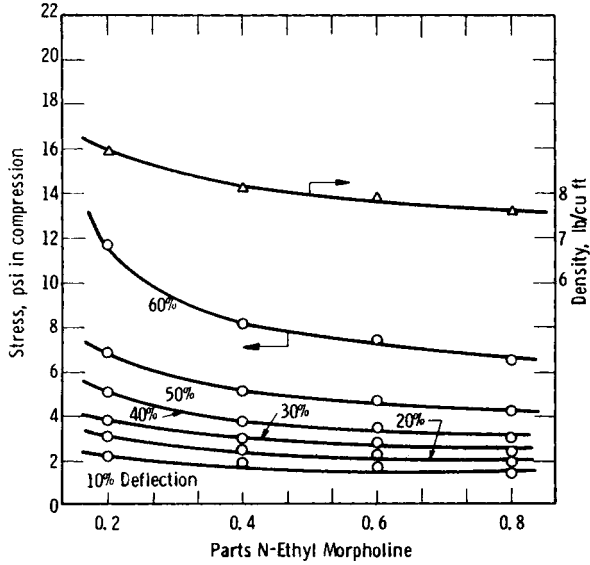


Fig. 7. Effect of *N*-ethyl morpholine concentration on load bearing and density. Stan-nous octoate concentration, 0.065 part.

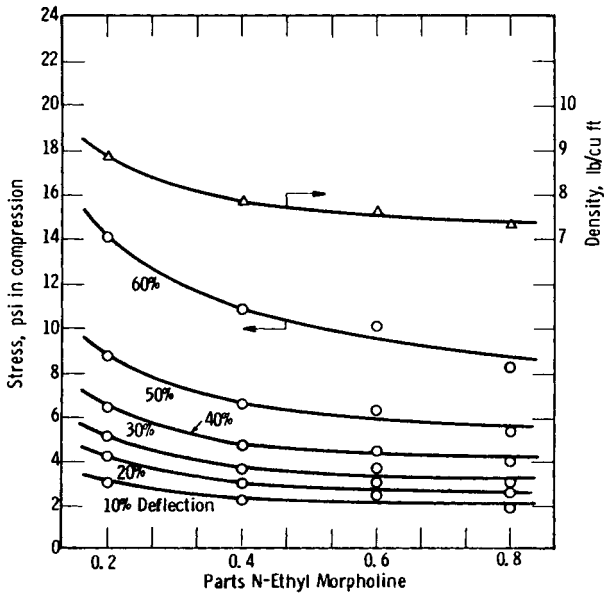


Fig. 8. Effect of *N*-ethyl morpholine concentration on load bearing and density. Stan-nous octoate concentration, 0.130 part.

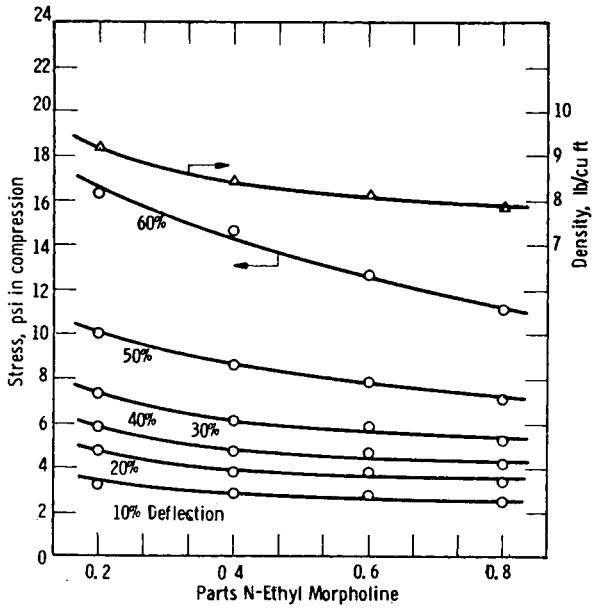


Fig. 9. Effect of *N*-ethyl morpholine concentration on load bearing and density. Stannous octoate concentration, 0.195 part.

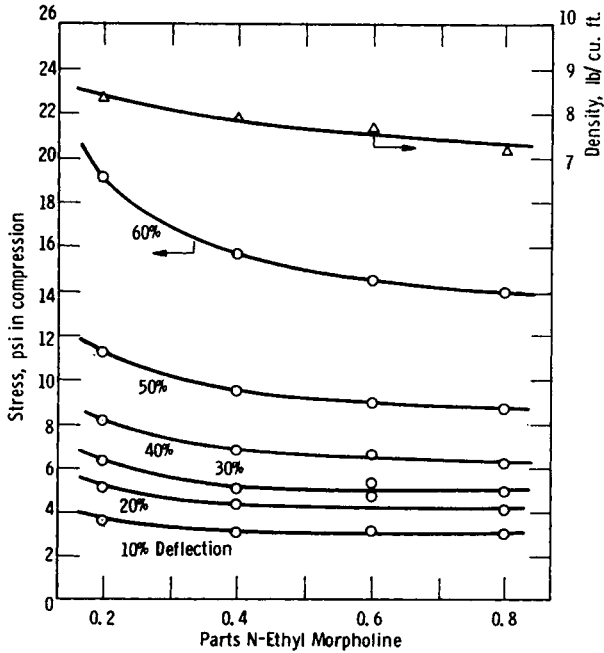


Fig. 10. Effect of *N*-ethyl morpholine concentration on load bearing and density. Stannous octoate concentration, 0.260 part.

A detailed study was made of the effect of catalyst concentrations on load-bearing characteristics and density. Since the amine catalyst favors the $\text{NCO-H}_2\text{O}$ reaction, that generates the CO_2 , increased quantities give lower densities and load bearing. The tin catalyst increases the rate of the NCO-OH reaction, relative to the water reaction, thus causing the polymer to gel faster. Therefore use of more SnOct gives a foam that can set before it attains the maximum expansion and thereby gives denser and higher load bearing foams. These effects are complex since each of the catalysts catalyzes all of the pertinent reactions and their concentrations also affect the exotherm while the foam is forming. (A good discussion of catalysis of polyurethane has been given by Saunders and Frisch.²)

It is shown in Figures 3-10 that the load-bearing ability and density increase in a nonlinear manner with the tin concentration and decrease with increasing amine content. Since the stress values at increasing deflections are more sensitive to density, they showed the greatest dependency on the catalyst variations (Table IV). It can readily be seen that very similar load bearing properties can be obtained with a variety of catalyst compositions, since both the ratio of the partially competing catalysts as well

TABLE III
Load-Bearing and Density Characteristics of Protective Foam^a

Deflection, %	Stress \bar{X} , psi	Standard deviation σ	Density, lb./ft. ³ ($\pm \sigma$)
10	2.13	0.092	
20	2.85	0.164	
30	3.44	0.180	7.70 \pm 0.235
40	4.32	0.238	
50	5.85	0.346	
60	9.14	0.620	

^a Values were obtained from a formulation containing 0.38 parts H_2O . Seven runs were made, each on a different day using freshly prepared compositions for all the streams. Calculations were performed as indicated. $\bar{X} = \Sigma X/N$; $\sigma = \sqrt{\Sigma (X - \bar{X})^2/N}$.

as their absolute concentration and possible synergistic interactions govern the final properties. For example, Figures 4-6 show foams having densities of about 7.4 lb./ft.³ and stress values at 10 and 60% deflections of 2.0 and about 8.8 psi, respectively. These values were selected from catalyst compositions of 0.40 NEM with 0.083 SnOct (Fig. 4) and from the combination of 0.8 NEM with 0.13 SnOct (Fig. 6). Similarly, foams having densities of about 7.9 lb./ft.³ and stress values of 2.5 at 10% deflection and about 11.1 at 60% deflection were found for 0.33 NEM with 0.130 SnOct and 0.80 NEM with 0.195 SnOct from (Figs. 8 and 9), respectively. In general, it appears that comparable physical properties are obtained by simultaneously increasing or decreasing both catalysts; however, the relationship of the ratios and total catalyst quantities is quite complex.

TABLE IV
Effect of Catalyst Composition on Physical Properties of Foam

Parts NEM	SnOct	Stress, psi at various deflections					Density, lb./ft. ³	Tensile psi ^a	Elonga- tion, % ^a	
		10%	20%	30%	40%	50%				60%
0.2	0.065	2.24	3.09	3.81	5.16	6.82	11.73	7.95	44	78
0.2	0.130	3.02	4.24	5.15	6.48	8.75	14.15	8.85	54	87
0.2	0.195	3.25	4.74	5.79	7.33	10.03	16.28	9.15	62	85
0.2	0.260	3.66	5.14	6.33	8.14	11.25	19.11	9.30	60	80
0.4	0.065	1.96	2.46	2.98	3.78	5.16	8.12	7.15	42	80
0.4	0.130	2.26	3.01	3.64	4.72	6.65	10.87	7.80	51	90
0.4	0.195	2.85	3.83	4.74	6.08	8.60	14.65	8.40	52	77
0.4	0.260	3.11	4.31	5.02	6.85	9.50	15.75	8.90	58	75
0.6	0.065	1.89	2.30	2.79	3.50	4.73	7.40	6.95	44	93
0.6	0.130	2.46	3.14	3.77	4.75	6.37	10.05	7.65	53	87
0.6	0.195	2.81	3.85	4.66	5.84	7.96	12.66	8.15	59	83
0.6	0.260	3.23	4.38	5.28	6.62	9.03	14.50	8.70	63	83
0.8	0.065	1.49	1.98	2.44	3.07	4.21	6.52	6.60	41	95
0.8	0.130	2.00	2.63	3.18	4.01	5.40	8.31	7.32	49	90
0.8	0.195	2.58	3.42	4.15	5.21	7.06	11.13	7.81	55	90
0.8	0.260	3.04	4.05	4.90	6.21	8.62	13.98	8.18	60	83

^a Tensile and elongation values as averages of sets of three.

TABLE V
Effect of Catalyst Variations on Shape of Stress-Strain Curves

SnOct concn., parts	Stress ratio for 60:10 deflections			
	NEM = 0.2	NEM = 0.4	NEM = 0.6	NEM = 0.8
0.065	5.2	4.1	3.9	4.4
0.130	4.8	4.8	4.1	4.2
0.195	4.9	5.1	4.5	4.3
0.260	5.2	5.1	4.5	4.6

The sensitivity of the load-bearing properties to NEM variations was about the same overall the SnOct concentrations studied. Likewise SnOct variations had about the same magnitude of effect over the investigated range of NEM concentrations.

An attempt was made to determine whether the catalyst quantities had any significant effect on the shape of the compression-deflection curve (Fig. 1). This was examined by comparing the ratios of the stress at 60 and 10% deflections (Table V). Due to the scatter of the data, firm conclusions cannot be made; however, the overall data tend to reflect lower 60:10 stress ratios for higher NEM and lower SnOct contents. This can be attributed to the lower densities obtained with higher amine and lower tin which give a lower stress at the more highly density-sensitive 60% deflection value.

Tensile strength increases with density (Fig. 11) and is therefore affected by the catalyst composition. The elongation appears to be almost independent of density. It might show a slight decrease at higher densities due to the greater likelihood that the more dense foams are more highly

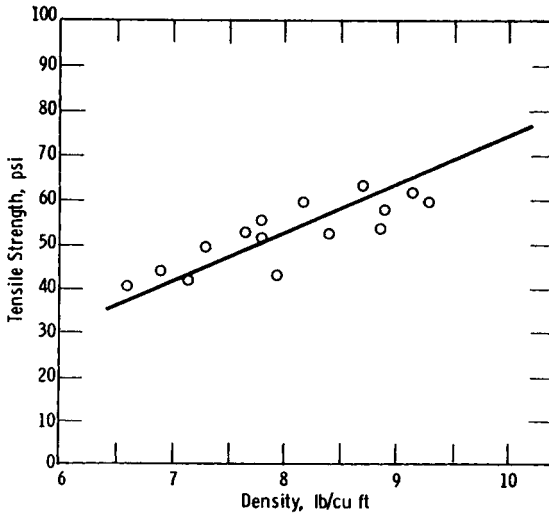


Fig. 11. Correlation between density and tensile strength.

crosslinked. However, the data showed too much scatter for the establishment of any relationships.

References

1. Mendelsohn, M. A., R. G. Black, H. F. Minter, and R. H. Runk, unpublished work, Westinghouse Research and Development Center, 1963-65.
2. Saunders, J. H., and K. C. Frisch, *Polyurethane Chemistry and Technology (High Polymers, Vol. XVI, Part I)*, Interscience, New York, 1962.

Résumé

On présente des résultats concernant les caractéristiques physiques d'une mousse d'uréthane à base de polyéther, fabriquée comme produit spécial d'amortissement au choc. On montre l'influence des changements dans le rapport du catalyseur et de sa concentration sur la déformation sous une charge et sur la densité; on a également montré la relation entre la densité de la mousse et la force de tension. En général, le pouvoir de supporter une charge et la densité augmentent d'une façon non linéaire avec une augmentation de concentration en amine comme catalyseur. On obtient des propriétés de support de charge désirées en utilisant un mélange d'isocyanates di- et plurifonctionnels et par l'introduction d'éthylène glycol avec un polyol possédant un poids moléculaire moyen d'environ 4000. L'hydroquinone a été employée pour inhiber l'auto-oxydation et la carbonisation pendant le processus exothermique. Des cellules ouvertes ont été obtenues par l'emploi d'acides gras trimérisés.

Zusammenfassung

Daten für die physikalische Charakteristik eines als hochgradig spezialisierten Stossdämpfungsmaterials entwickelten Urethanschaums auf Polyäthergrundlage werden vorgelegt. Der Einfluss einer Veränderung von Katalysatorverhältnis und -konzentration auf Belastungsverformung und Dichte wird gezeigt; ebenso die Korrelation zwischen Schaumdichte und Zugfestigkeit. Im allgemeinen nahm die Belastbarkeit und die Dichte mit steigender Zinnkatalysatorkonzentration nicht linear zu, und mit steigender Amin-katalysatorkonzentration ab. Wünschenswerte Belastbarkeitseigenschaften wurden durch Verwendung einer Mischung zwei- und höherfunktioneller Isocyanate sowie durch Einbau von Äthylenglycol mit einem Polyol mit einem mittleren Molekulargewicht von etwa 4000 erhalten. Hydrochinon wurde zur Verhinderung der Autoxydation und der Hitzeschädigung bei der normalen Wärmeentwicklung bei der Schäumung verwendet. Offene Zellen wurden durch Verwendung trimerer Fettsäuren erhalten.

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