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DEVELOPMENT OF IMPROVED PLASTIC FOAM GENERATING AGENTS AND TECHNIQUES FOR SATURN APPLICATIONS

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MONSANTO RESEARCH CORPORATION
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TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

This report was prepared by Monsanto Research Corporation under contract no. NAS8-11373, Development of Improved Plastic Foam Generating Agents and Techniques for Saturn Applications, for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with John Schell acting as project manager.

This report covers the work carried out between July 1964 to July 1965.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation by C. L. Bellanca, R. T. Jefferson, and B. R. Hickman, with I. O. Salyer serving as project leader.

The authors are indebted to Messrs. N. E. Jones and C. L. Church who conducted the compound preparation and testing throughout the program.

ABSTRACT

MONSANTO RESEARCH CORPORATION

Dayton, Ohio

DEVELOPMENT OF IMPROVED PLASTIC FOAM GENERATING AGENTS AND TECHNIQUES FOR SATURN APPLICATIONS

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A mathematical analysis of the compressive strength of foam systems was conducted and a factor was derived which allowed foam strength to be evaluated independently of foam density.

Solid urethane castings were prepared in order to screen candidate polymer systems so that the more promising high strength and modulus products for further evaluation as foams could be selected.

Prepolymer and "one-shot" methods of foam preparation were investigated. A "one-shot" foam system was developed encompassing the one-to ten-pound per cubic foot density range.

Heterogeneous foams, consisting of a low density foam matrix reinforced with "strands" of high-density foam and foams containing low-density fillers or holes, were prepared and tested for strength-at-density properties.

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I. INTRODUCTION

Every pound of extra weight carried into orbit by spacecraft reduces useful payload; therefore, materials of construction utilized in space applications should ideally possess a high strength-to-weight ratio. Foamed plastics are especially useful in space structures because of their high strength, light weight, and excellent insulation properties. However, to further improve their utility it is desirable that these foam materials have even higher strength, for a given weight, than they have at present.

This research study was directed toward the development, evaluation, and characterization of improved plastic foams suitable for use on current and advanced Saturn flight vehicles and ground support equipment. The specific objective of the research effort was directed toward producing uniform, essentially closed-cell foams in the density range of 1 to 10 lbs/ft^3 (pcf). The foams should be capable of being foamed in large masses of 150 pounds or more for foam in place applications with low exotherms, or non-uniform areas. Additionally, the foams should have physical properties which equal or exceed the best urethane foams now commercially available; i.e., the properties of foams with densities of 4 lbs/ft^3 should equal or exceed those specified below:

Compressive strength	225 psi (75° ± 5°F)
Tensile strength	225 psi (75° ± 5°F)
Shear strength	125 psi (75° ± 5°F)

Our initial approach involved the preparation of dense polymers rather than foams to investigate the effect of material and process variables on strength properties. It was felt that basic strength data could be obtained from each polymer system without the obscuring variables of foam structure and/or additives.

Our final approach to obtaining an improved foam was the investigation of foam variables, i.e., materials, stoichiometry, and processing conditions.

A literature search was begun prior to the initial work on the project, and was continued throughout the program. The search was conducted in order to keep abreast of the state-of-the art, and to unearth information of value in solving the problem.

Research on this project was carried out in the Dayton Laboratory of Monsanto Research Corporation during the period of July 1964 to July 1965.

II. SUMMARY

A. Theoretical Analysis of Limiting Foam Strength

A mathematical analysis of the compressive strength of a foam system was conducted. Analysis of the compressive strength of a model foam system in which all of the material is uniformly distributed in the wall was compared to that of foams containing all of the material in corner struts. A "factor" was derived from the experimental data which permits a quantitative comparison of the relative merit of foams of different density.

B. Solid Urethane Castings

Solid urethane castings were prepared in order to screen candidate polymer systems so that the more promising high strength and modulus products for further evaluation as foams could be selected. Tests conducted were Vicat softening and flexural strength. Evaluated were polyether polyols of aliphatic, aromatic, and heterocyclic type structures of varying functionality and hydroxyl number. Aromatic diisocyanates of varying functionality were also investigated.

C. Prepolymer Foam Preparation

The prepolymer approach to foam preparation was investigated. Prepolymers were prepared from various polyols and diisocyanates and possessed varying levels of free isocyanate.

D. "One-Shot" Foam Study

A "one-shot" foam system was developed encompassing the one-to ten-pound per cubic foot density range. The formulation representing the four pcf foam was investigated in large scale batch and machine pours. During the course of this research, numerous materials were evaluated as to their effect on foam strength. Polyols, diisocyanates, catalysts, pneumatogens, and fiberous and particulate fillers were among those studied.

Early in the program, we became aware that neither foam composition variables, nor foam processing variables were significantly affecting the strength-at-density or "characteristic" cellular structure of the experimental foams. Consequently, new and different foaming processes were investigated in an attempt to exert some control over the cellular geometry.

Cell nucleation and growth were observed in experiments carried out under specialized conditons. We were able to control cell size without changing the density of the foam. However, we quickly learned that cell size was only important in a statistical sense in determining the strength of the foam. By this, we mean that the probability of obtaining a uniform arrangement of cells, or nearly the same size, becomes greater as the average cell size becomes smaller; and, uniformly is important in determining foam strength.

Other specialized experiments were conducted in pressure vessels in an attempt to inhibit or control foaming by means of pressure, and thereby improve the cellular geometry.

We found that the only consistent method for improving foam strength involved manually changing foam density in part of the foam product.

E. Heterogeneous Foams

Heterogeneous foam systems were prepared and evaluated as to relative strength-to-density ratios. The systems consisted of incompatible foam formulations of high and low densities. The goal was to obtain in the composite, an intermediate density and a compressive strength approaching that of the higher density foam.

Foams containing low-density fillers and/or holes were also prepared and tested for strength and were compared with "uniform" foam of equivalent overall density.

III. CONCLUSIONS

A. Theoretical Analysis of Limiting Foam Strength

The mathematical analysis of the compressive strength of a rigid foam system indicated that the strength should be a direct function of the density of the foam. Strength should also be dependent on the modulus of the material.

Cell size should be immaterial as long as the characteristic gas-blown, closed cell structure is maintained.

Further, the mathematical analysis indicated that the compressive strength of a model foam structure, in which all of the material is in the corner struts, should be approximately one order of magnitude stronger than one in which all of the material is equally distributed in the walls.

B. Strength/Density Relationships in Gas-Blown Rigid Foams

From the experimental results complied during the course of this research, it was found that foam compressive strength is dependent only upon the density of the foam. As density increases, compressive strength increases. Variables in foams and foam systems investigated showed no effect on strength, i.e., catalyst type and level, pneumatogen type, stoichiometry. Neither particulate nor fiberous reinforcing fillers were effective in improving the compressive strength-at-density and were, in most cases, detrimental. Further, variation in cell size is inconsequential in its effect on foam strength.

The compressive strength of urethane and other gas-blown rigid foams can be quantitatively predicted from the equation, compressive strength, psi = $5 \times D^2$ (where D = pounds per cubic foot).

The direct correlation of compressive strength with density is believed to result from the "characteristic" cell structure of gas-blown foams, wherein the material available is subdivided into many masses of relatively small cross-sections and a high length/diameter ratio, in which the structural support members are randomly oriented with respect to each other. Consequently, there is very poor distribution of surface applied load through the cellular matrix and there follows progressive failure of the material (layer by layer), starting at some plane of weakness (usually at the surface at which the load is applied).

The effect of modulus on foam strength may be masked by the geometrical configuration of the foam cells or by variation from the theory of elasticity by extremely small cross-sectional members. Accordingly, in urethane or other gas-blown rigid foams it is not possible to achieve the strength/density goals originally specified in this research (compressive strength, 225 psi at 4 lbs/ft^3 density). We can expect at best to achieve only about 1/2 of the specified compressive strength (225 psi) in any closed-cell, rigid foam envisioned at present.

C. Effect of Chemical Composition and Process Variables

No correlation was found between the strength of the solid urethane castings and the corresponding rigid foams.

The highest strength-to-density ratio was obtained from a prepolymer based foam; however, the system was too reactive to be practical.

Attempts to decrease the reaction rate while maintaining strength proved unsuccessful.

Test results obtained from Vicat softening and flexural tests of solid urethane castings indicated that functionality appears to impart the greatest effect on temperature sensitivity and flexural strength. Additionally, polyol structure significantly affected heat softening properties. The heterocyclic polyols showed the highest resistance to heat softening; aliphatic based polyols showed the lowest.

As isocyanate and polyol functionality increases, flexural strength and resistance to heat softening increases.

Other variables, such as hydroxyl number, reaction temperature, and stoichiometry, appeared to have little, if any, effect on solid body strength characteristics.

D. Heterogeneous Foams

Compressive strength and other physical properties of higher merit than those indicated by the general equation given above can be obtained in heterogeneous foams. These heterogeneous foams may consist of either a low density foam matrix reinforced with "strings" of higher foam randomly dispersed therein, or a relatively high density matrix containing a substantial volume of very low density fillers or holes (zero density filler). Orientation of the highest strength of the foam in the direction of the applied load is also advantageous. The limiting case for this approach to high strength "foam" is obviously honeycomb composites.

The heterogeneous foam system offers some promise of approaching the desired strength-at-density level. The resultant compressive strength approaches that of the higher density component foam; however, this method would require great care in preparation and mixing and, consequently, possesses some limitations in its use.

The specified strength of 225 psi at 4 pcf "foam density" should be both theoretically and practically achievable in honeycomb structures in which the load bearing members are through-going and effectively distribute the load throughout the composite.

Since it is usually desirable to have the highest strength in the direction of applied stress, the unidirectional strength character of the heterogeneous system is not a serious limitation. Heterogeneous foam structures can be very conveniently made by the polystyrene bead foam process, since beads of different densities can be prepared and arranged in a predetermined pattern within the mold.

IV. DATA AND DISCUSSION

A. Mathematical Analysis

1. Strength evaluation factor. A factor was calculated which allowed relative evaluation of foam strength characteristics independent of foam density. The numerical value of the factor was determined in the following manner.

The strength of a foam may be described by this equation:

$$S = c\rho^{N} \qquad (1)$$

where c = factor being sought (encompases all the variables affecting foam strength, independent of density, ρ^N).

N = exponential constant of density, which has assumed to be approximately 2 for this calculation.

The strength/density (S/ρ) ratio was calculated for all the foams prepared under this program up to that time, and these values were plotted against their respective densities. A straight line was drawn through the average of these points (assumption: N = 2) and the slope of this line was taken to obtain the average value of C for our experimental foams.

$$C = S/\rho^2 = 4.25$$

Although this value of C is not absolute, it is valid for the evaluation of foam strength characteristics relative to MRC's average foams. It is applicable only within the density range of the foams used for the calculation, namely from 2 to 20 lbs/ft^3 density.

Since the above calculation was made, the following compressive strength/density relationship has appeared in the literature (Ref.1). According to the reference, this relationship

$$S = 12.77\ \rho^{1.416}$$

is valid, within 90% confidence limits, throughout the range of 0-60 lbs/ft^3. There is not indication in the reference as to how the relationship was derived, however, the exponential value of ρ suggests an empirical derivation.

2. On the compressive strength of foams. When we consider the stress-strain relationship that occurs in the crushing of foams, we find a type of collapse quite different from the usual compression curve where the material gradually increases in cross-sectional area and the compressive strength increases in proportion. The cells do not appear to fail gradually, but, rather, they fail by the buckling of the cell walls. The buckling is progressively passed from one cell to another until the whole structure has collapsed, at which point the stress-strain curve shows a characteristic elastic increase.

The fact that rigid foams fail in progressive buckling suggests that we examine the stability of the cell walls for an evaluation of the factors that are involved in the strength of cellular structures. If we examine a foam microscopically, we see a group of cells separated by cell walls. Where the cell walls are a small part of the total volume of the foam, we can obtain essentially two distinct types of foam, the wall or the rod type. In the wall type foam, the great majority of the material forms the walls of the cells, and in the rod-type nearly all the material of the foam is in the shape of rods along the cell edges. If we further examine the nature of these foams, we will find that the walls of the wall type foams are of a uniform thickness, and are relatively flat so that they join at their edges to form the actual cells. In the rod type of foam, the edges of the cells are in the form of cylindrical rods of essentially uniform diameter and these join at the corners to give the cell structure.

By examining the parameters governing the stability of structures formed of rods and of walls, or platelets, we can obtain insight into the factors controlling the compressive strengths of foams. Let us consider the effect of density upon strength for an idealized cubical cell of each of the above types. A cubical type structure is assumed for mathematical simplicity.

a. Foams with rod type cells. Idealize a foam into uniform cubical cells of $1/N^3$ length, such that we have N^3 cells per unit cube of foam. Each individual cell is defined by uniform struts, or rods, about the perimeter, and may be represented as in Figure 1.

If we consider square ends (neglecting volume effect of ends), the volume of each rod is V_R,

$$V_R = \frac{\pi d^2}{4} \ell$$

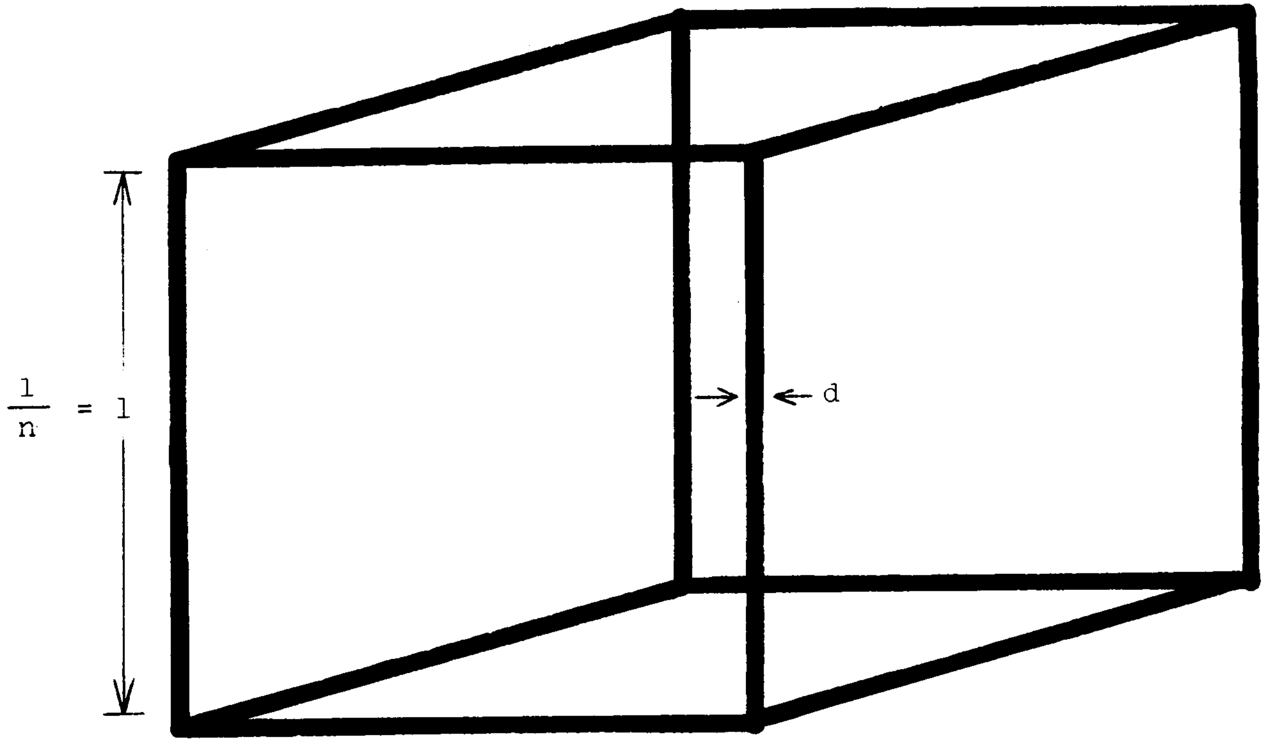


Figure 1. Cubical Rod-Type Cell

where ℓ = length of cell edges

d = diameter of cell edges

and the volume of the cell is V_c,

$$V_c = \ell^3 = 1/N^3$$

The total volume of rods in a single cell is V_{RT}:

$$V_{RT} = M \frac{\pi d^2}{4} \ell = \frac{12}{4} \pi d^2 \ell = 3\pi d^2 \ell$$

where M = no. of rods/structure = 12 for a cube

The density of a single cube, ρ_c, is then:

$$\rho_c = \frac{M_c}{V_c} ;$$

but,

$$M_c = M_R = \rho_p \times V_{RT}$$

where M_c = mass of cell

M_R = mass or rods

ρ_p = density of material (plastic)

$$\therefore \rho_c = \frac{\rho_p 3\pi d^2 \ell}{\ell^3} = 3\pi \rho_p (\frac{d}{\ell})^2 \qquad (1)$$

Since the density of the material is constant, the density of the cell is proportional only to $(d/\ell)^2$.

The same density analysis can be used for the total foam system. The density of a single cell of this type is related to the density of the foam by a factor of 1/4 since each edge is shared by four cells, thus the density of the foam is:

$$\rho_F = \frac{3\pi\rho_r}{4} (\frac{d}{\ell})^2$$

The ultimate strength of a rod type structure such as described is determined by the buckling strength of each individual strut. The theoretical basis for buckling of struts, or beams, is well documented (3,4). An analysis was made of the strength of the cubical cell foam system using this approach.

The buckling of struts, or columns, occurs through an elastic instability that is independent of the inherent strength of the material in slender columns, such as are typical of a foam cell skeleton. The critical buckling stress of long columns with built-in ends is given by Euler's formula:

$$\sigma_{CR} = \frac{P_{CR}}{A} = 4\pi^2 E \left(\frac{r}{\ell}\right)^2 \tag{2}$$

where E = Young's modulus

r = radius of gyration, and for solid rods along the long axis = d/4

P_{CR} = critical load

A = area of resisting surface = $\frac{\pi d^2}{4} \cdot 4$ for an elemental cell undergoing axial compression

$$\begin{aligned} \therefore P_{CR} &= \sigma_{CR} \cdot A_{resisting} \\ &= 4\pi^2 E \left(\frac{r}{\ell}\right)^2 \cdot \frac{\pi d^2}{4} \cdot 4 \\ &= 4\pi^2 E \frac{d^2}{(4\ell)^2} \cdot \frac{\pi d^2}{4} \cdot 4 \\ &= \frac{\pi^3 E}{4} \left(\frac{d}{\ell}\right)^2 d^2 \end{aligned}$$

The buckling strength of a cubic cell in terms of load per unit surface area is:

$$\begin{aligned} S_m &= \frac{\text{critical load}}{\text{projected area of cell}} \\ &= \frac{\frac{\pi^3 E}{4} \left(\frac{d}{\ell}\right)^2 d^2}{\ell^2} \\ &= \frac{\pi^3 E}{4} \left(\frac{d}{\ell}\right)^4 \end{aligned} \tag{3}$$

From the equation for the density of an edge type cell, we have:

$$\left(\frac{d}{\ell}\right)^2 = \frac{1}{3\pi} \frac{\rho_c}{\rho_p}$$

Substituting this into equation (3), we get:

$$S_m = \frac{\pi^3 E}{4} \left(\frac{1}{3\pi} \frac{\rho_c}{\rho_p}\right)^2$$

$$= \frac{\pi E}{36} \left(\frac{\rho_c}{\rho_p}\right)^2$$

$$= .0875\ E\left(\frac{\rho_c}{\rho_p}\right)^2 \qquad (4)$$

The values predicted by this equation are somewhat higher than those actually experienced with rigid foams. This may be due to the fact that the cell model used for calculations is a perfect cube, whereas in an actual foam the cells are irregular polyhedra. The normal irregularities of a foamed structure may also account for part of the difference. Table 1 compares the values for the strength of foam systems based on (a) equation (4), (b) our experimental data, (c) our empirical equation for strength ($S = 4.25\rho^2$), and (d) the equation for strength given in Ref. 2 ($S = 12.77\rho^{1.416}$).

As previously stated, the l/d ratio of the support members of a foam cell is determined only by the density of the foam. Now from equation (4), we see that the strength of a foam of any particular geometry is a function only of the modulus of elasticity and the density ratio ($\rho c/\rho p$). Since the modulus of elasticity for any particular material does not vary greatly, it is safe to say that the strength is a function only of the density ratio.

b. Foams with platelet structure type cells. If we consider that that majority of the material of the foam lies in the walls, a condition which never actually exists but which may be approached; we may idealize the structure as being composed of unit cells as shown in Figure 2.

If we let t = depth of platelet (thickness)

$\ell = 1/N$ = length = width of platelet

the volume of one platelet = $\ell^2 t$, and the total volume of all plates in one cell = $6\ \ell^2 t$, then the density of a cube composed of this type of wall would be:

$$\rho_c = \frac{M_c}{V_c}$$

TABLE 1

STRENGTHS OF FOAM SYSTEM

	Strength Basis	ρ=1#/ft^3	ρ= 2#/ft^3	ρ= 4#/ft^3	ρ= 6#/ft^3	ρ= 8#/ft^3	ρ= 10#/ft^3	ρ= 20#/ft^3
1)	$S=.0975E\,(\rho_c/\rho_d)^2$ (Struts for cubes)	7.15	28.5	114	256	457	712	2,850
2)	Experimental Data	10	25-30	70-90	125-225	250-300	350-400	-
3)	$S=12.77\rho^{1.416}$ (from Ref. 1)	15	35	90	-	250	350	900
4)	$S=4.25\rho^2$	4.25	17	68	153	272	425	1,700

used ρ_p = 64

$E = 3 \times 10^5$

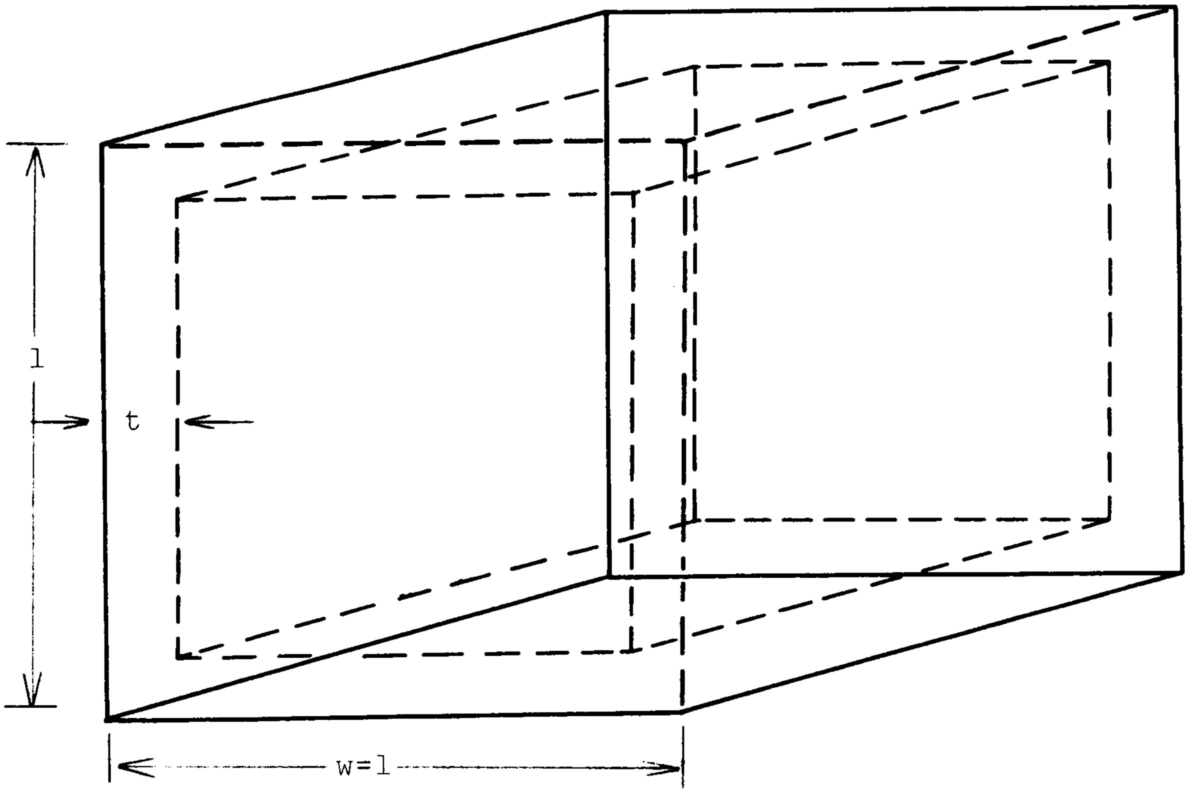


Figure 2. Cubical Platelet-Type Cell

but,

$$M_c = \rho_p \times V_{walls}$$

$$\therefore \rho_c = \frac{\rho_p 6\ell^2 t}{\ell^3} = 6\rho_p (\frac{t}{\ell}) \qquad (5)$$

If the analysis is continued to include a unit cube foam comprised of the platelet type cubic cells, the density of the foam is:

$$\rho_F = 3\rho_p (\frac{t}{\ell})$$

as one half of the thickness of each wall may be associated with a neighboring cell.

Again, observation shows that failure occurs through buckling of the individual walls composing the cell. Plate buckling theory states that a simply supported plate undergoing compression will fail at the critical stress, σ_{CR}, given by the formula below, (Refs. 3,4).

$$\sigma_{CR} = \frac{\beta\pi^2 E t^2}{12\ \ell^2 (1 - \mu^2)} = \frac{P_{CR}}{A_{resisting}} \qquad (7)$$

where

β = coefficient, dependent upon the length to width ratio. For square plates ($\ell/w = 1$) $\beta = 4.0$

μ = Poisson's ratio, and is approximately 0.5 for polymeric materials

$$\therefore \sigma_{CR} = \frac{P_{CR}}{A_{resisting}} = \frac{4}{12} \frac{\pi^2}{\ell^2} \frac{E\ t^2}{(1 - .25)}$$

$$= \frac{\pi^2\ E}{3\ (0.75)} (\frac{t}{\ell})^2$$

$$= \frac{\pi^2 E}{2.25} (\frac{t}{\ell})^2 \qquad (8)$$

or, in terms of the critical load, P_{CR},

$$P_{CR} = \sigma_{CR}\ A_{resisting}$$

$$P_{CR} = \frac{\pi^2 E}{2.25} \left(\frac{t}{\ell}\right)^2 \quad A_{resisting}$$

$$P_{CR} = \frac{4\pi^2 E}{2.25} \left(\frac{t}{\ell}\right)^2 \; w \; \ell$$

$$P_{CR} = \frac{4\pi^2 E}{2.25} \; \frac{t^3}{\ell} \qquad (9)$$

The applied stress on the foam surface is:

$$S_m = \frac{P_{CR}}{A_{measured}}$$

$$S_m = \frac{\frac{4\pi^2 E}{2.25} \; \frac{t^3}{\ell}}{\ell^2}$$

$$S_m = \frac{4\pi^2 E}{2.25} \left(\frac{t}{\ell}\right)^3 \qquad (10)$$

But from the equation for density we have:

$$\frac{t}{\ell} = \frac{1}{6} \; \frac{\rho_F}{\rho_P}$$

Substituting, we get:

$$S_m = \frac{4\pi^2 E}{2.25} \left(\frac{1}{6} \; \frac{\rho_F}{\rho_P}\right)^3$$

$$S_m = \frac{4\pi^2 E}{(2.25)(108)} \left(\frac{\rho_F}{\rho_P}\right)^3$$

$$S_m = 0.162 \; E\left(\frac{\rho_F}{\rho_P}\right)^3 \qquad (11)$$

Again, we have an expression for the strength of a cubical structure in terms of the density ratio. However, in the above equation (11), the strength is proportional to the cube of the density ratio; whereas for the rod type cubical cell, the strength is proportional to the square of the density ratio. Since the density ratio is always a fraction, this would indicate that the strength of a rod type structure should be greater than that of a plate type structure of the same density. This difference is quite large for low density structures (eg. <10 lbs./ft^3) but becomes increasingly less as density increases. At about 30 lbs./ft^3, where the two strengths begin to approximate each other, the systems depart from the cellular structure and become solids with irregular voids. Table 2 compares the strengths of both types of cells for several densities.

The two equations for the buckling strengths of foams composed of rod type and platelet type cells may be compared:

$$\sigma_{CR} = A\ E\ (\frac{\rho_F}{\rho_M})^2\ \frac{S_M}{S_F} \qquad \text{(rod type)}$$

$$\sigma_{CR} = A'E\ (\frac{\rho_F}{\rho_M})^3\ \frac{S_M}{S_F} \qquad \text{(platelet type)}$$

Expressing these equations in terms of measured strength, they could be written,

$$S_M = B\ E\ (\frac{\rho_F}{\rho_M})^2 \qquad \text{(for rod type)}$$

$$S_M = B'E\ (\frac{\rho_F}{\rho_M})^3 \qquad \text{(for platelet type)}$$

where B and B' are constants containing the surface ratios. These are then equivalent to the numerical values of equations (4) and (11), respectively.

It should also be noted that nowhere in the above analysis does the cell size show any effect upon strength. This will be considered further in the following section.

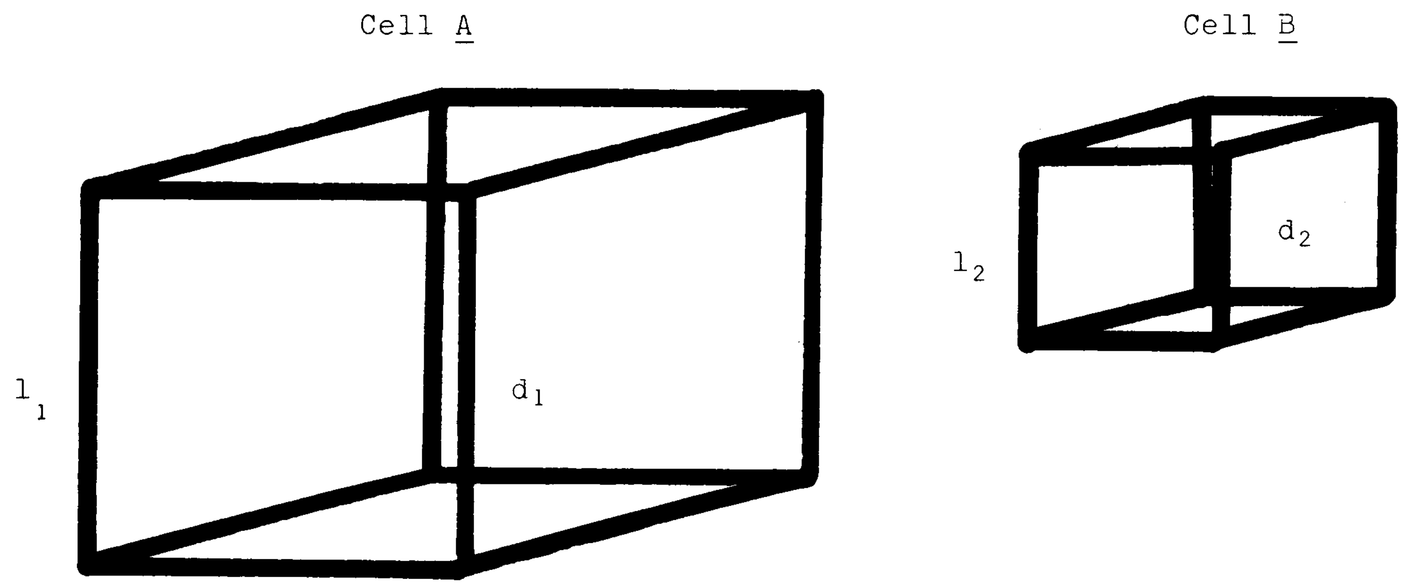
c. Effect of cell size upon strength. First, let us consider two foams of exactly similar geometry, but of differing cell size. (Figure 3). This implies that foam A will be an exact enlargement of foam B, so that the angles between cell walls and edges will be similar in both foams, and there will be a one to one correspondence between the two foams. Let the ratio of the cell size be k_c, so that an edge in foam B will have k_c times the length of the corresponding edge in foam A.

TABLE 2

ROD VS PLATELET TYPE CELL STRENGTHS

	ROD $S = .0875\ E\ (\rho_c/\rho_p)^2$	PLATELET $S = 0.162\ E\ (\rho_c/\rho_p)^3$
1 lb/ft^3	7.15	very small
2 lb/ft^3	28.5	1.47
4 lb/ft^3	114	11.80
8 lb/ft^3	457	94.5
10 lb/ft^3	712	184
20 lb/ft^3	2,850	1,475

using $E = 3 \times 10^5$



$$l_1 = k_c\, l_2 \quad \text{or} \quad k_c = \frac{l_1}{l_2}$$

$$d_1 = k_t\, d_2 \quad \text{or} \quad k_t = \frac{d_1}{d_2}$$

Figure 3. Identical Geometry Cells of Different Size

Similarly, let the ratio of the wall thickness in foam B to those in foam A be k_t, the rod diameter ratio be k_d and the density ratio be ρ_r. If all of the material is incorporated in the rods comprising the edges of the cells, as may be assumed in a rod-type foam, then in a unit cube of foam we can expect that the weight of material in foam B will be k_d^2/k_c^2 that in foam A as the sectional area of the rods is in the ratio of k_d^2, the total number cells in the ratio $1/k_c^3$ and the length of edge in each cell k_c. So $\rho_r = \frac{(k_d)^2}{(k_c)^2}$ for rod-type foams.

Similarly, the actual cross-sectional area of the plastic material in a unit cube will be in the ratio k_d^2/k_c^2 as the area ratio of the individual rods will be k_d^2 and the number of rods crossing any transverse plane will be in the ratio $1/k_c^2$.

The end load needed to cause a rod to buckle in compression is given by kEI/ℓ^2 where k is a constant depending on the form of end anchorage restraining the rod, E is the modulus of the material, I the moment of inertia of the section of the rod and ℓ its length. This corresponds to a stress on the end proportional to $kEI/\ell^2 d^2$ where d is the diameter of the rod. This expression can be rearranged to give $k''Ed^2/\ell^2$ by substituting for I in terms of d. The ratio of the stress needed to buckle a rod in foam B compared to that in foam A will be k_d^2/k_c^2 when the ratio of the end loads on the unit cube will be $(k_d/k_c)^4$ to cause the rods to fail in buckling.

This ratio is $\rho_r{}^2$. This shows that the crushing strength of foams of similar geometries are dependent only on their densities and are independent of the size of cells or on the ratio of the rod diameters. Any change in these structural dimensions are reflected in the density and we can therefore expect the cell size to be of secondary importance in the strength of rod type foam structures.

This argument can be repeated for foams where the majority of the material comprises the walls of the structure: here the density ratio ρ_r is k_t/k_c. The sectional area ratio is k_t/k_c. The buckling stress to cause a wall of thickness to fail depends on $E(t/l)^2$ where t is the thickness of the wall and l its length so that the ratio of buckling stress in foam A to that in foam B will be $(k_t/k_c)^2$ or, as the sectional area ratio of k_t/k_c, the buckling load ratio will be $(k_t/k_c)^3$ or ρ_r^3 for wall-type foams.

This analysis for both the rod and the wall forms of foam show that, in either case, the collapse load of the foams will be a function of their densities and not be related specifically to the cell sizes, the wall thicknesses or the rod diameters provided the foams are of identical geometry and of the same material. These conditions are reasonable in the case of extensive structures with many cells, provided there is no unusual change in the cell material properties as a result of the foaming.

B. Dense Urethane Castings

The objective in this phase was to screen candidate polymer systems in solid castings in order to select the more promising high strength and modulus products for evaluation in foams. It was felt that basic strength data could be obtained on each polymer system without the obscuring variables of foam structure and/or additives.

1. Preparation of dense urethane castings.

A basic procedure was established for the preparation of bubble- and flaw-free dense castings:

> The polyols were outgassed overnight under 1 mm. vacuum, at 60°-120°C.
>
> The isocyanates were outgassed overnight under 1 mm. vacuum at room temperature.

The stirring apparatus consisted essentially of a rotating base for the mixing container (400 ml. beaker), and a stationary, baffle-type stirring blade. A powerstat was used to control the speed of the container. The purified isocyanate was weighed into the mixing container and an amount of hot, purified polyol added to give the desired NCO/OH ratio. The beaker was rotated for 1-4 minutes, depending on the reactivity of the system, with the stirring blade in a fixed position. Mixing was maintained at 180 rpm. Above this speed, air bubbles were caused to enter the solution. Stirring time varied according to viscosity: for example, efficient mixing was obtained in 15-20 seconds if the solution viscosity was below 500 cps. This result is consistent with the reactivity of the system.

Solutions were then placed into 4 oz. polypropylene bottles and heated for one hour at 50°C. under dry nitrogen at 30 psi. Bubbles present in the liquid were squeezed out at this high pressure. The solidified castings were postcured 16 hours at 100°C.

2. Physical tests and evaluation. Tests conducted on solid urethane castings in order to determine the most promising foam resins were flexural strength (ASTM D790-63) and Vicat softening (ASTM D1525-58T). Data obtained from flexural tests were: flex strength at yield and break, modulus of elasticity, and deflection at break.

Flex strength at break was calculated from the load-deflection curve by the following equation:

$$S = \frac{3PL}{2bd^2}$$

where:

S = Stress in the outer fiber at midspan in pounds per square inch,

P = Load at a given point, or break, in pounds,

L = Span, in inches,

b = Width of beam tested, in inches,

d = Depth of beam tested, in inches.

Flexural yield strength was also calculated from the above equation for those polymers exhibiting load-deflection curves showing a point, Y, at which the load does not increase with an increase in deflection. This point, Y, is the yield point and, in such cases, the flexural yield strength is calculated by letting P equal the load at point Y.

The modulus of elasticity is the ratio, within the elastic limit, of stress to corresponding strain and is expressed in pounds per square inch. It is calculated by first drawing a tangent to the steepest initial straight-line portion of the load-deformation curve and using:

$$E_B = \frac{L^3m}{4bd^3}$$

where:

E_B = Modulus of elasticity, in pounds per square inch,

L = Span, in inches,

b = Width of beam tested, in inches,

d = Depth of beam tested, in inches,

m = Slope of tangent, in pounds per inch.

Deflection at break is taken directly from the load-deflection curves.

The Vicat softening test consists of loading the polymer with 1000 grams on an indentor having a foot with an area of one square millimeter. The temperature of the surrounding air is raised at the rate of 50°C. per hour. The degree of the indentor's penetration into the specimen is measured as the temperature is increased. The temperature at which the indentor has penetrated 1 mm is known as the Vicat softening point. Plotting penetration versus temperature indicates the modulus-temperature relationship of the sample. The curve thus shows a physical property behavior over a wide temperature range, such as the glass transition temperature, Tg, or second order transition point. The polymer becomes elastomeric at temperatures above Tg due to rotation of chain lengths causing a reduction in modulus. Rigid foams and solid castings should have Tg values well above room temperature and flexible foams and elastomers should have Tg values below room temperature. Additionally, it has been shown that polymers with low softening temperatures show low dimensional stability when foamed (4).

3. Discussion of results. Polyols selected for evaluation as dense castings were of the polyether type and represented aliphatic, heterocyclic, and aromatic nuclei. Polyols evaluated are shown in Table 3.

Polyol functionality varied from three to eight; hydroxyl number ranged from 380 to 660. Isocyanates used in this work were tolylene diisocyanate(TDI), polyphenylmethane polyisocyanate (Mondur MR), and polymethylene polyphenyl isocyanate (PAPI) possessing functionalities of 2, 2.5, and 3 respectively.

a. Vicat softening test. Six polyol-isocyanate systems were evaluated, as follows:

Sample No.	System
33	RS-375 - Mondur MR
111	CP-260 - Tolylene diisocyanate (TDI)
126	LK-380 - TDI

TABLE 3

POLYOLS EVALUATED IN DENSE POLYMERS

Trade Name	Manufacturer	Chemical Classification	Molecular Weight	Hydroxyl Number	Functionality
LK-380	Union Carbide Chemicals Co.	Aromatic based Propylene Oxide	440	380	3
HP-410	Corn Products	Heterocyclic - Methyl Glucoside Polyethe		410	4
HP-450	Corn Products	Heterocyclic - Methyl Glucoside Polyethe		450	4
RS-375	Dow Chemical	Heterocyclic - Sucrose Polypropylene Oxide		374	8
RS-410	Dow Chemical	Heterocyclic - Sucrose Polypropylene Oxide		410	8
RS-450	Dow Chemical	Heterocyclic - Sucrose Polypropylene Oxide		443	8
RS-430	Dow Chemical	Heterocyclic - Sucrose Polypropylene Oxide		528	8
TP-440	Wyandotte Chemical	Aliphatic - Trimethyalpropane		400	3
CP-260	Dow Chemical	Aliphatic - Trishydroxypropylglycerine	255	660	3
PEP 550	Wyandotte Chemical	Aliphatic - Polyether	500	450	4
PEP 650	Wyandotte Chemical	Aliphatic - Polyether		375	4
LS-490	Union Carbide Chemicals Co.	Aliphatic - Sorbitol-propylene oxide	700	490	6
SP-560	Wyandotte Chemical	Aliphatic - Sorbitol-propylene oxide		657	6
Atpol 2566	Atlas Chemical	Aliphatic - Polyoxypropylene Sorbitol	530	620	6
Atpol 2571	Atlas Chemical	Aliphatic - Polyoxypropylene Sorbitol		450	6
Atpol 2468	Atlas Chemical	Aliphatic - Polyoxypropylene Sorbitol		450	6

Sample No.	System
132	LK-380 - Mondur MR - tin catalyst
136	LK-380 - TDI - tin catalyst
137	LK-380 - Mondur MR

Polyol RS-375 is an octafunctional, heterocyclic reaction product of sucrose and propylene oxide. Polyol CP-260 (tris hydroxypropylglycerine) is a trifunctional, aliphatic polyether; LK-380 is a trifunctional, aromatic based propylene oxide polyol. Mondur MR is diphenyl methane diisocyanate and is polyfunctional (f = 2.5).

The samples were selected to evaluate the effects of structure and the relative merits of each system. Additionally, the effect of catalyst on softening characteristics was determined. The results of these tests are shown in Table 4 and are shown graphically in Figure 4.

Generally, it appears that urethane castings based on Mondur MR are superior in heat-distortion properties to those made with TDI. This is probably due to the higher functionality of the MR resulting in a greater degree of crosslinking and more extensive network.

The heterocyclic RS-375 showed the greatest resistance to heat softening compared to the aliphatic and aromatic polyols evaluated. The RS-375/Mondur MR polymer had the highest Vicat softening point (243°C.); the best aromatic based polymer had a softening point of 240°, and the aliphatic based polymer, 215°C.

The temperatures representing the mid-points of the transition portions of the Vicat curves shown graphically in Figure 4 were evaluated for comparative second order transition temperatures. Here again, the heterocyclic based polymer had the highest temperature (213°C.). However, this temperature is not considered a midpoint, since this polymer did not exhibit a transition curve as found in the others. The recorded temperature (213°C.) is actually the point at which the indentor penetrated 0.1 mm. and was chosen for comparative purposes only. Very little difference in mid-point temperature was observed between the aliphatic and aromatic systems reacted with TDI; however, the aromatic system reacted with Mondur MR showed an increase in mid-point temperature (150°C. vs. 160°C.). This increase in the mid-point temperature is probably due to increased functionality found in Mondur MR over TDI (2.5 vs. 2.0)

TABLE 4

VICAT HEAT DISTORTION TESTS

Sample	Polyol - Type		Isocyanate	Mid Point	One MM. Indention
33	RS-375	Heterocyclic	Mondur MR	0.1mm @ 213°C	243°C
111	CP-260	Aliphatic	TDI	150°	215°
126	LK-380	Aromatic	TDI	145°	212°
132	LK-380	Plus Tin Cat	MR	155°	234°
136	LK-380	Plus Tin Cat	TDI	144°	200°
137	LK-380		MR	160°	240°

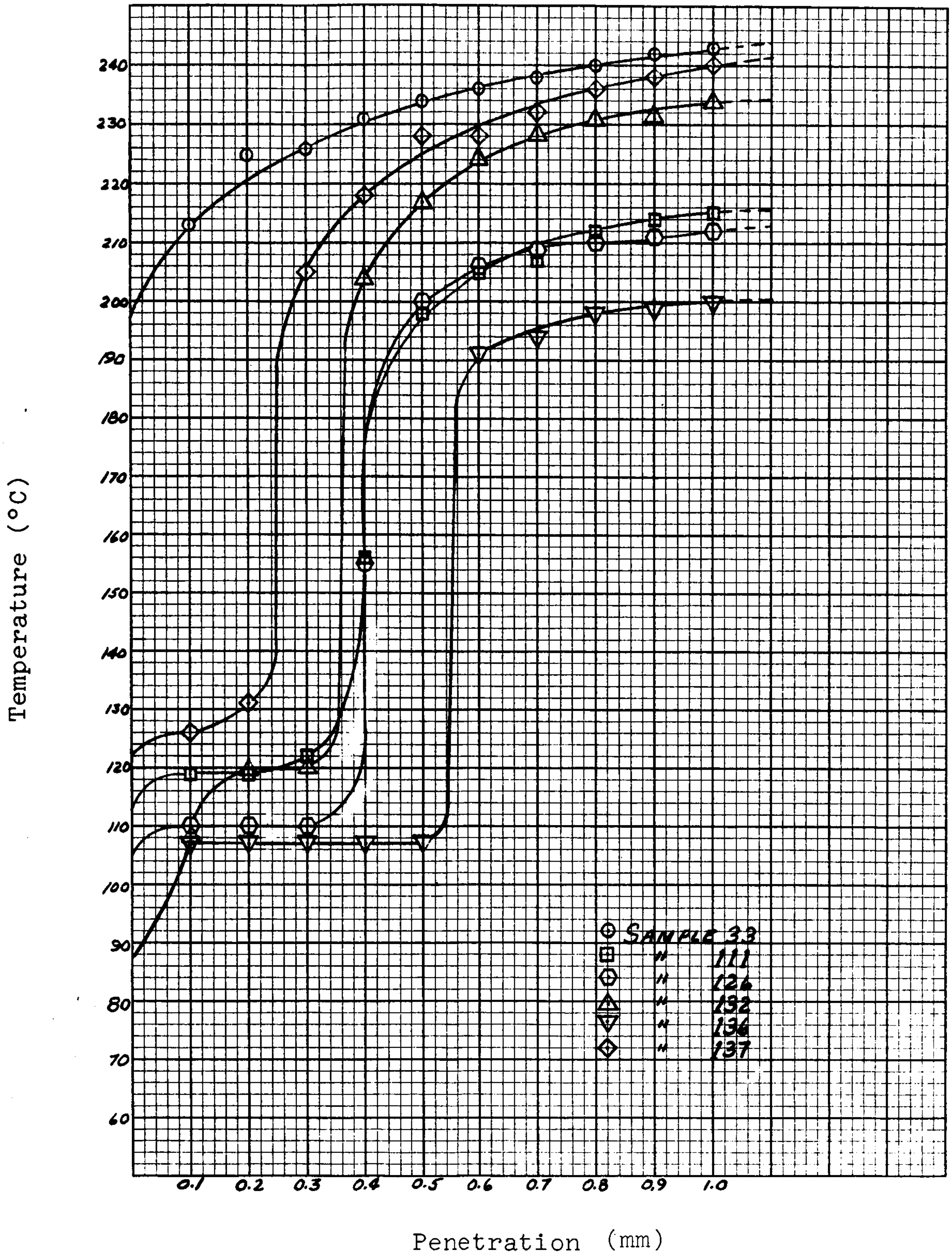


Figure 4. Vicat Softening Temperature of Rigid Urethane Dense Castings

resulting in higher degree of crosslinking.

The addition of tin catalyst to the LK-380/TDI and LK-380/Mondur MR systems proved detrimental to the Vicat softening point. As shown in Table 4, the addition of tin catalyst to the LK-380/TDI system decreased Vicat softening point 12° (212° to 200°); the Vicat softening point of the LK-380/Mondur MR system decreased 6° upon addition of catalyst (240° to 234°C.). These results were unexpected since the addition of catalyst should accelerate the polymerization and crosslinking reactions. However, it appears possible that premature gelation in the catalyzed systems caused incomplete reaction and a lower degree of crosslinking.

b. Flexural strength tests. Test data obtained from flexural strength tests are shown in Table 5 in addition to the polyol-isocyanate systems and reaction conditions. The reaction temperature for a given polyol-isocyanate system was determined by trial to give a mixing viscosity of approximately 500 cps. Certain systems were too reactive at the selected temperature and since mixing was inefficient, the experiments were repeated at lower temperatures. Hence, the difference in reaction temperature between a number of evaluated polymer systems.

Flexural (yield) strengths up to 27,000 psi and flexural moduli of 0.55 x 10^6 psi were obtained from the best polyol-isocyanate systems investigated. These strengths and moduli compare very favorably with data obtained from other high modulus (non-reinforced) plastic materials. A number of plastic materials are listed in Table 6, together with their flexural strengths and moduli.

The polyol-isocyanate system giving consistently high strength values was LK-380/TDI. This system generally showed strengths of 22,000-25,000 psi. Highest flexural yield strength was obtained from equal parts of polyols LK-380 and SP-560 with TDI (27,200 psi).

The highest breaking strength was exhibited by the SP-560/TDI polymer system (27,500 psi).

A polymer prepared from equal parts of RS-350 and CP-260 with TDI possessed a flexural strength of 25,700 psi and modulus of 0.56 x 10^6 psi.

Other polyol-isocyanate systems giving high modulus castings were SP-560/TDI (0.55 x 10^6 psi), RS-450/TDI, and CP-260/TDI (both with a modulus of 0.52 x 10^6 psi).

TABLE 5

FLEXURAL PROPERTIES OF DENSE POLYMERS

AROMATIC

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
28	LK - 380	Mondur MR	1.02	120	19,088	16,365	0.33	0.59
29	"	"	1.02	120	20,242	17,973	0.38	0.57
30	"	"	1.02	50		20,320	0.47	0.39
35	"	"	1.16	120	21,000	17,700	0.38	0.60
36	"	"	0.99	120	19,900	16,990	0.37	0.60
45	"	"	0.99	25	18,300	15,310	0.38	0.62
46	"	"	0.99	25	18,700	15,700	0.39	0.63
57	"	"	1.02	120	19,300	16,000	0.19	1.11
58	"	"	1.02	120	20,000	16,200	0.19	1.33
59	"	"	1.02	120	19,600	15,000	0.20	1.51
60	"	"	1.02	120	19,000	14,000	0.20	1.59
114	"	"	1.00	60	-	19,700	0.44	
132*	"	"	1.00	25	-	19,700	0.44	
49	"	TDI	1.03	120	23,000	16,500	0.47	0.68
50	"	"	1.03	120	23,400	17,900	0.49	0.66
54	"	"	1.03	120	22,400	15,800	0.43	0.68
55	"	"	1.03	120	22,700	17,500	0.46	0.61
56	"	"	1.03	120	23,100	17,400	0.48	0.60

TABLE 5 (Continued)

AROMATIC

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
64	LK - 380	TDI	1.03	35	24,200	18,600	0.48	0.58
65	"	"	1.03	35	24,100	20,200	0.47	0.53
66	"	"	1.03	35	24,800	22,500	0.48	0.41
67	"	"	0.94	35	23,000	22,000	0.47	0.56
69	"	"	1.03	120	23,800	17,800	0.45	0.63
70	"	"	1.03	120	23,100	19,200	0.42	0.54
71	"	"	1.03	120	22,700	17,500	0.44	0.63
72	"	"	0.94	120	22,300	18,100	0.45	0.55
91	"	"	1.03	50	22,600	18,200	0.43	0.41
98	"	"	1.03	100		26,000	0.49	0.51
101	"	"	1.03	50	23,100	17,200	0.49	0.58
99	"	"	1.19	100		21,200	0.41	0.34
126	"	"	1.03	25	24,400	19,700	0.49	
94	"	PAPI	0.68	50	18,500	15,400	0.49	0.56

* Catalyzed

TABLE 5 (Continued)

HETEROCYCLIC

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
33	RS - 375	Mondur MR	1.00	120		16,900	0.28	0.46
34	"	"	1.00	120	19,475	16,600	0.32	0.64
41	"	"	1.00	80		11,800	0.37	0.18
42	"	"	1.00	60	16,520	16,100	0.37	0.51
47	"	"	1.00	120	14,975	14,208	0.35	0.56
37	RS - 410	"	1.00	120		12,840	0.36	0.20
43	"	"	0.91	60	19,516	15,407	0.41	0.72
104	"	TDI	1.00	80		22,000	0.44	0.45
105	"	"	1.09	80		22,300	0.45	0.40
38	HP - 410	Mondur MR	1.00	120	17,610	13,075	0.36	0.66
31	HP - 450	"	0.90	120		18,475	0.42	0.50
44	"	"	1.00	60		12,720	0.40	0.18
92I	RS - 530	TDI	1.00	120		16,800	0.48	0.17
92J	"	"	1.12	120		18,700	0.51	0.18
103	RS - 450	"	1.00	90		22,200	0.44	0.38
80	"	"	1.01	120		25,900	0.52	0.46

TABLE 5 (Continued)

ALIPHATIC

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
97	ATPOL 2566	TDI	1.00	100	-	23,700	0.48	0.29
107	"	"	1.00	75	-	22,300	0.45	0.29
92H	"	"	1.12	120	-	21,300	0.51	0.21
116	"	Mondur MR	1.03	70	-	16,700	0.44	
118	TP-440	"	1.01	65	17,000	10,600	0.38	
117	PeP 650	"	1.00	70	16,300	13,600	0.39	
113	LS-490	"	1.00	60	-	19,700	0.42	
63	"	"	0.87	35	19,900	18,100	0.38	0.58
61	"	TDI	1.00	35	24,800	24,100	0.48	0.44
62	"	"	1.00	35	24,100	22,100	0.46	0.49
85	"	"	1.00	60	23,600	23,900	0.48	0.40
86	"	"	1.13	55	-	24,600	0.51	0.34
87	"	"	1.26	60	-	17,800	0.53	0.17
109	SP-560	"	1.02	75	-	23,739	0.51	0.27
75	"	"	0.85	120	-	27,500	0.51	0.33
76	"	"	0.76	120	-	26,100	0.53	0.41
78	"	"	0.85	73	-	21,500	0.46	0.39

TABLE 5 (Continued)

ALIPHATIC

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
92F	SP-560	TDI	1.02	50	23,600	22,200	0.55	0.22
92C	CP-260	"	1.03	70	27,000	22,700	0.52	0.49
100	"	"	0.98	50	25,100	19,000	0.49	0.61
110	"	"	1.03	65	22,304	17,678	0.52	0.63
95	Pep 550	"	1.01	100	22,500	15,500	0.47	0.68
96	"	"	1.01	50	21,800	15,800	0.47	0.63
115	CP-260	Mondur MR	1.00	60	21,300	17,600	0.43	
121	Atpol 2571	"	1.00	120	-	18,700	0.38	
122	Atpol 2408	"	1.02	120	-	22,700	0.41	

TABLE 5 (Continued)

POLYOL BLENDS

Sample No.	Polyol	Isocyanate	NCO/OH	Temp. Polyol, °C	Flexural Yield, psi	Flexural Break, psi	Modulus of Elasticity, X106 psi	Deflection at Break inches
92D	LK-380(50) w/SP-560(50)	TDI	0.83	50	27,200	26,500	0.51	0.40
92E	"	"	0.94	50	-	25,200	0.52	0.28
68	LS-490(90) LA-475(10)	"	1.00	50/25	23,000	22,000	0.44	0.45
92L	CP-260(50) RS-530(50)	"	1.14	120	-	25,700	0.56	0.29

TABLE 6

FLEXURAL STRENGTHS AND MODULI OF PLASTIC MATERIALS (1)

Plastic Material	Type (2)	Flexural Strength (3) (1000 psi)	Modulus of Elasticity (3) in Flexure (10^6 psi)
Acrylic Castings	General Purpose	15 - 17	0.4 - 0.5
ABS Mouldings	Medium Impact	11.5-13.5	0.4 - 0.5
Alkyd Mouldings	General Purpose, (granular)	7 - 10	2.2 - 2.7
Epoxy Castings	General Purpose	8 - 20	0.4 - 1.5
Melamine Mouldings	-	11 - 14	1.3
Phenolic Mouldings	-	7 - 12	0.7 - 1.5
66 Nylon Injection Mouldings	General Purpose (0.2% H_2O)	13.8	0.41
Polyester Castings	Styrene Type (Rigid)	7 - 19	0.3 - 0.9
Polystyrene Mouldings	General Purpose	8 - 15	0.4 - 0.5
Polypropylene Extrusions	General Purpose	8.5 - 8.8	0.26- 0.27
Polycarbonate Mouldings	-	13.5	0.34
PVC/PVCA	Rigid - Normal Impact	12.5 - 16	0.38- 0.54
Polyvinyl Formal	-	13 - 18	0.5 - 0.6

(1) The test data presented here was obtained from "Materials in Design Engineering," Materials Selector Issue, Vol. 58, No. 5, pp. 198-225 (Oct. 1963).

(2) No reinforcing material or filler was used in these test specimens.

(3) ASTM D790.

The effects of variables on flexural properties are discussed below.

Effect of mixing temperatures. As can be seen in Table 5, there appears to be an increase in flexural strength as the mixing temperature is increased, although this does not hold true for all systems. The polymer system based on SP-560-TDI showed the highest flexural strength at break of those evaluated (27,500 psi) when the reaction temperature was increased from 73°C. to 120°C. at an NCO/OH ratio of 0.85. Flex strength at the lower temperature was 21,500 psi. Decreasing the NCO/OH ratio to 0.76 while maintaining the reaction temperature at 120°C. had little effect on flex strength (26,100 psi); however, at an NCO/OH ratio of 1.02, decreasing the reaction temperature to 50° and 75°C. resulted in significant decreases in strength (22,200 and 23,739 psi respectively).

A significant increase in yield strength and break strength was realized in the CP-260/TDI system (NCO/OH = 1.03) when the reaction temperature was increased from 60° to 70°C. Strength at yield increased from 22,304 to 27,000 psi; strength at break increased from 17,678 to 22,700 psi.

The effect of mixing temperature on the LK-380/TDI system followed no pattern although the highest breaking strength obtained from this system (26,000 psi) was obtained at a relatively elevated temperature (100°). An NCO/OH ratio of 1.03 was maintained and the mixing temperature varied as follows: 35°, 50°, 100°, and 120°C. As seen in the table, increasing the mix temperature from 35° to 50° resulted in a decrease in both yield and break strength; however, increasing the temperature to 100° resulted in a significant increase in breaking strength and eliminated the yield point. Further increase in breaking strength (26,000 psi vs. 17,000 psi avg.) and the development of a yield characteristic at 23,000 psi. This general increase in strength characteristics as the mixing temperature is increased is probably due to a highly crosslinked network structure and indicates the degree of reaction is nearing completion. Crosslinking is facilitated by an increase in temperature as the reaction rates of the two NCO groups present tend to be equal as the temperature is increased. At low mixing temperatures, the polyol is probably "capped" by the isocyanate through the para NCO group. As the temperature is increased, either through external means or reaction exotherm, the reaction proceeds through the less reactive ortho NCO group resulting in a crosslinked structure.

Effect of polyol structure. The effects of polyol structure on the flexural properties of cast polymers are shown in Table 7. In general, it appears that aromatic and aliphatic based polyols impart higher strength values than the heterocyclic type. The aromatic polyol, LK-380, showed yield values of 20,000 to 23,000 psi and ultimate strengths of 16,500 to 26,000 psi depending on the type of isocyanates used in the polymerization reaction. Polymers based on aliphatic polyols exhibited high yield strengths (16,000-23,000 psi) and breaking strengths ranged from 16,000-27,000 psi. The polymers based on heterocyclic polyols showed relatively low yield and strength values (16,000-19,000 psi and 12,000-24,000 psi respectively).

Unexpected was the fact that the modulus of elasticity showed no dependence on polyol structure. It was expected that the bulky heterocyclic and aromatic groups which limit rotation of the polymer chain would cause increased modulus compared to the aliphatic chains. However, this was not the case; no direct relationship between modulus and structure was found.

It must be kept in mind that polymers based on heterocyclic polyols did not consistently have lower flexural properties than aliphatic and aromatic based castings but only in general. Variables such as hydroxyl number, polyol functionality, type of isocyanate, isocyanate functionality, and degree of polyol-isocyanate reaction all contribute in determining the ultimate physical properties of the casting.

Effect of functionality. The relationship between reactant functionality and flexural properties was investigated. Polyol functionality ranged from 3 to 8; isocyanate functionality varied as follows: 2-TDI, 2.5-Mondur MR, and 3-PAPI.

Generally, polyol functionality had little effect on flexural properties. As seen in the table, there appears to be no direct correlation between level of polyol functionality and flex strength.

Isocyanate functionality appeared to have a definite effect on flex strength; as NCO functionality increased, flex strength decreased. Very limited data was obtained from PAPI-cured systems; an LK-380/PAPI system was the only polymer evaluated. However, comparing the flex properties of this polymer versus polymers based on LK-380/Mondur MR and LK-380/TDI systems indicates a definite degradation in flex strength as isocyanate functionality is increased.

TABLE 7

EFFECT OF POLYOL STRUCTURE ON FLEXURAL PROPERTIES

Polyol - Type		Yield, psi (3)	Break, psi (3)	Modulus of Elasticity, X10^6 psi (3
		MR/TDI	MR/TDI	MR/TDI
LK-380	Aromatic	20,000/23,000	17,000/16,500-26,000	0.35/0.48
HP-410	Heterocyclic	17,000/ (1)	13,000/	0.36/
HP-450	"	(2) -/	12,-18,000/	0.41/
RS-375	"	16,-19,000/	12,-16,000/	0.35/
RS-410	"	19,000/ -	13,-15,000/22,000	0.38/0.44
RS-450	"	/ -	/24,000	/0.48
RS-530	"	/ -	/17,000	/0.49
TP-440	Aliphatic	17,000/	10,000/	0.38/
CP-260	"	21,000/25,000	17,500/19,000	0.43/0.50
PEP-550	"	/22,000	/15,500	/0.47
PEP-650	"	16,000/	13,500/	0.39/
LS-490	"	19,000/23,000	19,000/20,000	0.40/0.48
SP-560	"	/ -	/21,-27,000	/0.52
Atpol-2566	"	/ -	/16,700	/0.48
Atpol-2571	"	- /	18,700/	0.38/
Atpol-2408	"	- /	22,700/	0.41/

(1) Where no data exist, none was obtained.
(2) Where dash is noted, no yield was present.
(3) Values are approximate averages.

As shown in the table of results, practically all polymers based on polyols reacted with both Mondur MR and TDI show higher flex strengths in the TDI system.

Darr et al (4) calculated the per cent degree of reaction at gel point of resin-isocyanate systems utilizing Flory's statistical explanation covering gelation and critical conditions for the formation of infinite networks (5). Assuming that all functional groups present are of equal reactivity regardless of size or structure, the results are as follows:

Calculated Degree of Reaction at Gel Point

Functionality of Resin, f (Resin):	2	3	4	6	8
Functionality of Isocyanate, f(NCO)	Degree of Reaction at Gel Point,%				
2	∞	72	58	45	38
3	72	50	33	20	14

The above data show the effects of functionality on the degree of reaction at gelation and indicate that as f (resin, NCO) increase, the degree of reaction decreases. Further, the same work showed that as functionality of the reactants increased, the exotherm temperature at gelation decreased indicative of premature gelation. Consequently, it is felt that premature gelation observed as functionality increases, causes incomplete reaction resulting in degradation of physical properties.

Effect of polyol hydroxyl number. The data indicate no effect of polyol hydroxyl number on flexural strength. Although no significant effect on yield or ultimate strength was expected from varying OH number, surprising was the fact that no correlation between modulus of elasticity and hydroxyl number existed. An increase in modulus as hydroxyl number increased was expected, due to, not only increased crosslinking sites but also an increasing number of stiff urethane blocks and decreased concentration of flexible ether linkages in the final polymer. The increasing chain stiffness should, obviously, impart increased modulus characteristics. These data could possible indicate that the reaction between available isocyanate and hydroxyl groups is incomplete.

Effect of stoichiometry. The evaluation of flexural properties of polymers based on polyol-isocyanate systems with varying stoichiometric amounts of NCO/OH indicate that there appears to be no correlation between stoichiometry and flexural properties.

As seen in the table of results, LK-380-TDI polymers were prepared in which NCO/OH was varied from 0.94 to 1.19 and no trend in flexural properties was evident. Polymers prepared from RS-410/TDI(NCO/OH = 1.00 and 1.09) at 80°C. showed no significant difference in flexural properties. The NCO/OH ratio was varied from 0.99 to 1.16 in polymers prepared from LK-380/Mondur MR and no effect on flex strength was observed.

C. Foam Preparation and Evaluation

The objectives, as outlined in the Introduction, are that the physical properties should equal or exceed the best polyurethane foams now commercially available. However, the selected formulation, or series of formulations, should consist of commercially available ingredients and should offer simple, practical methods of foam preparation that demand no special equipment.

Generally, two types of processes are used in urethane foam preparation; namely, the "one-shot" process and the "prepolymer" method. In the one-shot method, the resin, diisocyanate, pneumatogen, etc., are mixed simultaneously and foamed. In the prepolymer process, the polyol resin reacts with excess isocyanate resulting in -NCO terminated resins. The terminal isocyanate groups are available for subsequent reactions, i.e., with water for foaming and chain growth, and branched resins for crosslinking purposes. Since the "one-shot" method is by far the simpler of the two, considerable effort was expended along these lines during the course of the program. Raw materials utilized during the course of the program are listed in the Appendix and the results of foam investigation are discussed below.

1. "One-Shot" Foam System

The foams were prepared in a powerstat-controlled Waring Blendor, using the one-shot technique as described below.

The polyol or polyol mixture was weighed into the Blendor jar. The foam stabilizer or nucleating agent and pneumatogen were added and the mixture stirred until it was homogeneous. The required amount of isocyanate was quickly added to the jar, and the formulation was stirred at high speed (90 volt powerstat setting) for 30 seconds. When stirring had proceeded for 3-5 seconds, a preweighed amount of catalyst was added. After stirring for 30 seconds, the formulation was quickly poured into a cardboard box (8" x 8" x 6"), where it expanded and became rigid. Foam rise time was recorded, at which time a thermometer was inserted into the rigid foam to measure the exotherm. Finally, the foam was placed in an oven at 75°C. overnight to accelerate maximum cure.

Test specimens measuring 3" x 3" x 2" were cut from each of the cured foams. The specimens were accurately weighed, and their density was calculated. Then, the compressive strength of each specimen was determined in the direction of foam rise, according to ASTM D1621. Foam formulations and physical properties are tabulated in Table 8.

Evaluation of Compressive Strength Test Methods

When a standard compressive sample is cut with a saw, many dissected cells are present on the test surface, resulting in extremely high-point loadings during compression. It was postulated that due to cell rupture and crack propagation resulting from the high-point loadings, perhaps the strengths being measured were not actually the true strengths of the foams. To test this hypothesis, the following work was conducted.

(a) From the same foam, compressive samples were prepared by:

(1) foaming upward through a 2" x 1" open-end, Teflon-coated mold; and

(2) sawing by the standard method.

The skin was removed from the 1" sides of the molded specimen, leaving a standard test sample with a skin on the test surfaces. These samples were compression-tested, and the results are shown in Table 9. As can be seen, there is no significant difference between the samples. It was later decided that this test was not completely valid, since the mold was acting as a heat sink, and the foaming conditions may have been different for each sample.

(b) To further prove or disprove the original theory, several samples were saw-cut from an experimental foam:

On half of these samples, the 2"-square test surfaces were coated with paraffin to a depth of 1/16" in order to eliminate high-point loadings. The remaining samples were left uncoated. Compression testing revealed no significant

TABLE 8

FOAM FORMULATIONS AND PROPERTIES

Foam Number	Foam Stabilizer (gr.)	Polyol Component (1)				Isocyanate Component (2)		NCO/OH Ratio	Freon F-11 (gr.)	Water (gr.)	Catalyst Component		Exo-therm (°C)	Foam Rise Time (min.)	Density (lbs./ft.^{3})	Compressive Strength (psi)
		Polyol	(gr.)	Polyol	(gr.)	Isocyanate	(gr.)				Catalyst	(gr.)				
30.8	DC-113 7	LK-380	157	-	-	Mondur TD-80	93	1.00	47	-	C-16	1.5	115	6	2.07	16.7
32.3	8	"	161	-	-	"	95	1.00	40	-	"	1.5	114	6	2.25	28.0
30.7	8	"	161	-	-	"	95	1.00	40.3	-	"	1.5	115	6.5	2.34	22.2
30.11	8	"	160	-	-	"	103	1.09	32	-	"	1.5	134	6	2.63	36.2
32.2	8	"	166	-	-	"	98	1.00	33	-	"	1.5	141	5	2.78	29.8
30.6	8	"	166	-	-	"	98	1.00	33	-	"	1.5	128	5	2.90	31.4
30.12	8	"	171	-	-	"	92	0.91	34	-	"	1.5	137	6.5	3.03	39.5
35.1	8	"	171	-	-	"	101	1.00	26	-	"	1.5	125	5.5	3.04	47.2
32.1	8	"	171	-	-	"	101	1.00	26	-	"	1.5	135	5	3.15	43.0
35.2	8	"	173	-	-	"	103	1.01	21	-	"	1.5	134	6	3.58	62.8
30.4	8	"	171	-	-	"	101	1.00	26	-	"	1.5	114	5	3.61	57.8
35.0	8	"	175	-	-	"	104	1.01	17.5	-	"	1.5	135	5	4.33	78.8
30.3	8	"	175	-	-	"	104	1.01	17.5	-	"	1.5	134	5	4.66	92.1
32.0	8	"	175	-	-	"	104	1.01	17.5	-	"	1.5	123	4	4.76	77.5
30.9	8	"	170	-	-	"	110	1.09	17	-	"	1.5	146	3.5	4.92	101.7
30.10	8	"	180	-	-	"	97	0.92	18	-	"	1.5	123	5	5.03	86.0
30.5	8	"	182	-	-	"	107	1.00	9	-	"	1.5	120	4	7.81	213.8
31.5	8	LK-380	119	-	-	Mondur MR	174	1.07	-	4.8	Tin Oleate	0.5	126	18	2.38	28.0
31.3	8	"	119	-	-	"	174	1.07	-	4.8	C-16	1.5	144	3	2.43	27.1
31.4	8	"	119	-	-	"	174	1.07	-	4.8	Tin Oleate	0.1	103	20	2.46	27.4
31.6	8	"	119	-	-	"	174	1.07	-	4.8	"	1.0	137	11	2.48	29.5
31.2	8	"	119	-	-	"	174	1.07	-	4.8	-	-	-	19	2.53	31.9
31.0	8	"	136	-	-	"	161	1.08	-	2.7	C-16	1.5	124	-	4.16	72.5
65.0	7	SP-560	75	CP-260 Quadrol	60 15	TDI	154	1.00	10	-	-	-	-	-	5.1	99
65.1	L-520 1.5	Quadrol	20	LHT-34	180	"	138	1.00	14	-	-	-	-	-	27.5	260
71.2	1.5	CP-260	142	TP-440	8	"	148	1.00	14	-	-	-	-	-	7.7	154
71.3	1.5	Quadrol	20	PEP-550	180	"	146	1.00	14	-	-	-	-	-	6.1	112
71.4	1.5	Quadrol	20	LA-475	180	"	152	1.00	14	-	-	-	-	-	4.95	60
71.5	1.5	Quadrol	20	RS-375	180	"	126	1.00	14	-	-	-	-	-	8.2	175
*58.4	DC-113 -	Quadrol	100	-	-	Mondur MR	215	1.00	-	-	-	-	-	-	5.6	117.5
*58.5	2	LS-490	100	-	-	MR/PAPI	74/76	1.00	-	-	-	-	-	-	5.51	112.2

*Contains 2.5 gm Syton 250.

TABLE 8 (Continued)

Foam Number	Foam Stabilizer (gr.)	Polyol Component (1)				Isocyanate Component (2)		NCO/OH Ratio	Freon F-11 (gr.)	Water (gr.)	Catalyst Component		Exo-therm (°C.)	Foam Rise Time (min.)	Density (lbs./ft.^{3})	Compressive Strength (psi)
		Polyol	(gr.)	Polyol	(gr.)	Isocyanate	(gr.)				Catalyst	(gr.)				
31.1	8	LK-380	136	-	-	Mondur MR	161	1.08	-	2.7	-	-	100	12	4.33	73.2
32.4	8	LS-490	145	-	-	Mondur TD-80	114	1.04	36	-	C-16	1.5	138	6	1.98	24.0
36.2	8	"	150	-	-		116	1.02	26	-	"	1.0	130	8.5	2.94	44.4
36.3	8	"	150	-	-	"	116	1.02	26	-	"	0.5	134	10	3.35	49.1
36.0	8	"	156	-	-	"	119	1.00	16	-	"	1.0	145	6.5	4.33	84.4
32.5	8	"	156	-	-	"	119	1.00	16	-	"	1.5	126	4.5	4.75	97.5
36.1	8	"	156	-	-	"	119	1.00	16	-	"	0.5	134	10	4.97	103.3
33.1	8	LS-490	119	LA-700	30	Mondur TD-80	129	1.05	35	-	-	-	130	-	5.01	101.8
34.3	4	CP-260	126	-	-	Mondur TD-80	135	1.23	31	-	C-16	1.5	134	3	2.37	28.3
34.4	12	"	126	-	-	"	135	1.23	31	-	"	1.5	164	3	2.71	29.0
34.2	8	"	126	-	-	"	135	1.23	31	-	"	1.5	160	3	2.73	28.0
34.7	12	"	126	-	-	"	135	1.23	31	-	"	0.5	148	8.5	2.76	28.0
34.5	16	"	126	-	-	"	135	1.23	31	-	"	1.5	160	3	2.78	30.5
34.6	8	"	134	-	-	"	145	1.24	14	-	"	0.5	160	4.5	4.33	75.0
34.0	8	"	134	-	-	"	145	1.24	14	-	"	1.5	155	3	4.33	77.5
34.1	4	"	134	-	-	"	145	1.24	14	-	"	1.5	162	3	5.08	85.5
33.2	8	SP-560	63	CP-260	63	Mondur TD-80	135	1.23	31	-	C-16	1.5	176	3	2.15	24.5
33.6	8	"	32	"	94	"	135	1.24	31	-	"	1.5	172	3.5	2.19	26.0
33.4	8	"	94	"	32	"	135	1.24	31	-	"	1.5	159	3	2.37	25.0
33.3	8	"	67	"	67	"	145	1.25	14	-	"	1.5	177	2.5	4.56	93.8
33.7	8		33	CP-560	101	Mondur TD-80	145	1.25	14	-	C-16	1.5	188	3	4.71	77.5
33.5	8	"	101	"	33	"	145	1.25	14	-	"	1.5	186	2.5	5.13	102.5
37.1	8	G-2566	130	-	-	TDI	125	1.00	25	-	"	0.5	134	10	2.51	27.2
37.0	8	"	141	-	-	"	134	0.99	16	-	"	1.5	150	4	4.31	85.6
37.3	8	"	69	CP-260	69	"	129	0.94	36	-	"	0.5	122	12	2.22	24.4
37.2	8	"	69	"	69	"	138	1.00	16	-	"	0.5	167	6.5	4.59	92.2
C45.0	8	LS-490	150	-	-	"	116	1.02	20	-	"	0.5	-	-	4.06	71.0
C45.2	8	"	150	-	-	"	116	1.02	40	-	"	0.5	-	-	2.80	33.3
46.0	8	"	150	-	-	"	145	1.09	-	3	"	-	140	11	2.90	44.4
C46.3	8	"	150	-	-	"	138	1.08	-	2.25	"	-	-	-	4.80	114.3
46.2	8	"	150	-	-	"	138	1.08	-	2.25	"	0.5	153	7.5	3.80	80.3

TABLE 9

EVALUATION OF COMPRESSIVE STRENGTH TEST METHODS

Sample Identification (4 sq. in. size)	Density (lbs./ft.^{3})	Max. Load (lbs.)	Strength (psi)	Evaluation Factor (psi/d^2)
Foamed in Mold	5.026	283	71	2.81
Specimen Cut	4.481	260	65	3.23
" "	4.454	278	70	3.40

differences between coated and uncoated samples, as shown in Table 10. However, the force deflection curves for the paraffin-coated specimens differed significantly from the uncoated specimens. Although yield occurred for both types of samples at approximately the same load level, it occurred for the coated samples at about 50% less deflection than for the uncoated samples (5% vs. 10% deflection). This would indicate different rupture mechanisms occurring in the two types of samples.

From the above tests, it was concluded that although the rupture mechanism is affected by the saw cut, the strength measured from this type of sample is indicative of the true compressive strength of the foam.

To further investigate whether the measured strengths were the true strengths of the foams, compressive samples were coated with Adiprene L-100 urethane elastomer and epoxy to eliminate high-point loadings.

Compression testing revealed no significant differences between coated and uncoated samples, as shown in Table 11. The data are in agreement with the results reported above, further proving that the strength measured from an uncoated sample is indicative of the true compressive strength of the foam.

In order to determine the effect of mixing conditions on foam structure and strength, 18 experimental foams were prepared by the one-shot method in a Waring Blendor. Half of these foam formulations were stirred with the standard high shear (Blendor) blade for periods of 10 seconds, or 30 seconds, using powerstat settings of 40 volts (2000 RPM), 80 volts (5000 RPM), or 120 volts (8,000 - 10,000 RPM).

We found no conclusive evidence that one set of mixing conditions produced stronger foams than another. The other half of the foam products were prepared in a Waring Blendor fitted with a paddle-type (low shear) stirring blade. Stirring time was varied from 15 to 60 seconds at powerstat settings of 40 to 120 volts. The results were the same. There was no significant improvement in foam strength with either high-shear or low-shear stirring under any of the mixing conditions tested.

The foam products are listed in the approximate increasing order of total mixing energy involved in the preparation.

TABLE 10

COMPRESSIVE STRENGTH PROPERTIES OF COATED VS UNCOATED SPECIMENS

Sample Identification (4 sq. in. size)	Density (lbs./ft.^{3})	Max. Load (lbs.)	Strength (psi)	Evaluation Factor (psi/d^2)
Top side - Left (with paraffin)	Coated before weighing	98	24.5	-
Top - Center (with paraffin)	2.156	88	22	4.75
Bottom side - Left (with paraffin)	2.146	108	27	5.85
Top side - Right (without paraffin)	2.144	97	24	5.21
Bottom - Center (without paraffin)	2.108	92	23	5.17
Bottom side - Right (without paraffin)	2.131	103	26	5.72

TABLE 11

COMPRESSIVE STRENGTH PROPERTIES OF ADIPRENE L AND EPOXY COATED FOAMS

Run No.	Polyol	Isocyanate	Coating	Apparent Density (lbs/ft^3)	Compressive Strength (psi)	Strength Factor
E-1	LK-380	TD-80	Adiprene Urethane Rubber Room Cured	4.974	102	4.13
E-1 Control	LK-380	TD-80	Uncoated	5.017	101	4.02
E-2	LK-380	TD-80	Epoxy Patch Kit Room Cured	4.517	81	3.97
E-2 Control	LK-380	TD-80	Uncoated	4.514	85	4.18

Coatings of comparable thickness and on both sides (in direction of compression).

Mixing Conditions			Freon 11 Content			
			25 parts		10 parts	
Time Sec.	Volts	Blade Type	Density lbs./ft.^{3}	Comp. Strength psi	Density lbs./ft.^{3}	Comp. Strength psi
15	40	Low Shear	-	-	4.7	92
30	40	Low Shear	2.1	27	4.4	81
10	90	High Shear	-	-	4.5	89
30	90	High Shear	2.1	21	4.7	97
60	40	Low Shear	-	-	4.5	88
30	80	Low Shear	2.2	26	4.4	85
15	120	Low Shear	-	-	4.5	84
30	80	High Shear	2.1	20	4.7	97
30	120	Low Shear	2.3	25	4.9	102
60	120	Low Shear	-	-	5.2	103
30	120	High Shear	2.3	27	4.5	89

As described above, our initial approach to this program involved the evaluation of polyol and isocyanate materials in the form of dense polymers and the selection of promising systems for investigation in rigid foam formulations. During the course of the program, it became apparent that no correlation existed between the strength of the dense urethane polymers and the compressive strength of corresponding rigid urethane foams. We found that a dense polymer having a flexural modulus of 200,000 psi produces the same foam strength (at 4 pcf) as one having twice this modulus. For example, the modulus of elasticity of a polymer prepared from LK-380/Mondur MR was 200,000 psi; a polymer prepared from LK-380/TDI exhibited a flexural modulus of 480,000 psi. Rigid foams (nos. 31.1 and 35.0) based on these systems were of equivalent density (4.3 pcf) and compressive strength (73 and 78 psi, respectively). Further a polymer based on CP-260/TDI possessed a flexural modulus of 520,000 psi; however, two rigid foams prepared from this polyol/isocyanate system were of 4.3 pcf density and had compressive strengths of 75 and 77 psi (nos. 34.6 and 34.0). In order to investigate the effect of system variables on foam density and compressive strength, the following areas were studied and are discussed below:

Stoichiometry

Pneumatogen Type

Foam Stabilizers and Nucleating Agents

Lower Modulus

Fillers

Pressure Effects

a. Investigation of Foam System Variables

Effect of Stoichiometry on Foam Density and Strength

Eight experimental foams were prepared using water as the pneumatogen. The formulation is given below:

60 Parts	LK-380 (Union Carbide Chemicals Company)
40 "	LA-700 (" " ")
5 "	Water
2 "	DC-113 (Dow Corning Corporation)
184-200 "	Mondur MR (Mobay Chemical Company)

The NCO/OH ratio in this group of foams was varied from 0.99 to 1.06. The experimental data are shown in Table 12. Foam compressive strength ($\sim$ 60 psi) was not significantly affected as a result of the variations in composition. Also, cell

TABLE 12

EFFECT OF STOICHIOMETRY

Foam Number	LK-380 (grams)	LA-700 (grams)	Polyol Temp. (°C.)	Water (gr.)	DC-113 (grams)	Mondur MR (gr.)	NCO/OH Ratio	Stirring Conditions Voltage	Stirring Conditions Time (Sec.)	Exotherm (°C.)	Foam Rise Time (Sec.)	Density (lbs/ft^3)	Compressive Strength (Psi)
29.0	60	40	25	5	2	200	1.06	90	6	148	80	3.49	62.4
29.1	"	"	"	"	"	192	1.02	"	"	136	90	3.36	61.0
29.2	"	"	"	"	"	186	0.99	"	"	133	70	3.41	64.5
29.3	"	"	"	"	"	184	0.98	"	"	142	65	3.07	52.9
29.4	"	"	"	"	"	196	1.04	"	"	166	90	3.44	62.6
29.5	"	"	"	"	"	200	1.06	"	12	132	75	3.13	57.9
29.6	"	"	"	"	"	200	1.06	130	"	158	80	3.23	59.4
29.7	"	"	50	"	"	200	1.06	90	6	168	45	3.09	51.0

size and structure, and foam density remained essentially constant (3.07 - 3.49 lbs./ft.^{3}).

Effects of Pneumatogen on Foam Density and Strength

In unrelated, classified AEC research, we had considerable success in developing extremely lightweight, rigid urethane foams with high strength (8 psi at 0.6 lb./ft.^{3}) and good dimensional stability. These foams were prepared from commercially available materials. It was reasonable to expect that these same materials would give strong foams at the higher densities (1-10 lbs./ft.^{3}) specified in NASA's contract.

The materials under consideration are an aromatic polyether triol (LK-380, Union Carbide Chemicals Company), an amine-based polyether pentol (LA-700, Union Carbide Chemicals Company), and polyphenylmethane polyisocyanate (Mondur MR, Mobay Chemical Company) in the following proportions:

60	Parts LK-380
40	Parts LA-700
122	Parts Mondur MR
2	Parts DC-113

(The NCO/OH ratio is 1.02 in this polymer system.)

A preliminary investigation was made of foam formulations based on the above polymer system with Freon F-11 (E. I. duPont de Nemours & Company, Inc.) and/or water as the blowing agents. The purpose of this investigation was to determine the amount of blowing agents required to give a 4 lb./ft.^{3} foam density, as well as the strength-density relationship obtained with this polymer system. Four groups of experimental foams were prepared using:

a. Varying amounts of Freon F-11 (10-150 parts) as the only blowing agent;

b. Varying amounts of water (2-5 parts) as the only blowing agent;

c. Varying amounts of Freon F-11 (30-90 parts) with constant water (2 parts) in a mixture of blowing agents; and

d. Varying amounts of water (1-6 parts) with constant Freon-11 (30 parts) in a mixture of blowing agents.

Each foam was prepared by the one-shot polymerization method, using high-speed Waring-type blending equipment. Also, the required amounts of raw materials were calculated to give a constant (300 grams) formula weight in order to assure comparable stirring conditions.

Each formulation was stirred at high speed (100 volt powerstat setting) for exactly 6 seconds, and then cast into a cardboard box measuring 8" x 8" x 10", where it expanded and became rigid in less than 3 minutes. Although previous work with this polymer system showed good foam strength with no postcure, the foams were nevertheless cured overnight at 75°C in order to accelerate maximum cure.

The compositions of the experimental foams in the four groups described above are given in Table 13. Figures 5 through 8 show the strength-density relationship existing in each of the four groups of experimental foams. It was found that 4-5 parts of water, or 20 parts of Freon-11 (per 100 parts of polyol), are required to give a 4 lb./ft.^{3} foam density with this formulation, and that the compressive strength at 4 lbs./ft.^{3} is below 100 psi.

The formulation viscosities were quite high at less than 30 parts of Freon F-11 or less than 5 parts of water. In addition, 6 seconds was about the maximum time available for stirring these formulations. Under these conditions, it was difficult to obtain efficient and reproducible mixing, which could explain the single outstanding foam shown in Figure 6 with a compressive strength of 160 psi at 3.3 lbs./ft.^{3} density.

An additional investigation was made of foam formulations based on the LK-380 - Mondur TD-80 urethane system. Included in this work was an evaluation of varying amounts of Freon 113 and Freon 11, used (separately) as blowing agents, and their effect on foam structure and strength.

TABLE 13

COMPOSITION OF RIGID FOAMS OF VARIABLE PNEUMATOGEN

Foam Number	LK-380	LA 700	Mondur-MR	DC113	Water	Freon-11-
F-1-	60 grams	40 grams	120 grams	2 grams		10 grams
F-2-	" "	" "	" "	" "		20 "
F-3-	" "	" "	" "	" "		30 "
F-4-	" "	" "	" "	" "		40 "
F-5-	" "	" "	" "	" "		50 "
F-6-	" "	" "	" "	" "		100 "
F-7-	" "	" "	" "	" "		150 "
F-11-	77.3 "	51.6 "	154.6 "	2.6 "		12.9 "
F-11-A-	77.3 "	51.6 "	154.6 "	2.5 "		12.9 "
F-12-	74.1 "	49.4 "	149.3 "	2.5 "		24.7 "
F-13-	71.3 "	47.6 "	143.4 "	2.4 "		35.3 "
F-14-	66.0 "	44.0 "	133.0 "	2.2 "		55.0 "
F-15-	57.5 "	33.2 "	116.0 "	1.9 "		86.4 "
F-16-	61.5 "	41.0 "	124.0 "	2.0 "		71.7 "
W-2-	70.9 "	47.3 "	177.0 "	2.4 "	2.4 grams	
W-3-	67.0 "	44.6 "	183.0 "	2.2 "	3.4 "	
W-4-	63.3 "	42.3 "	188.0 "	2.1 "	4.2 "	
W-4-A-	63.3 "	42.3 "	188.0 "	2.1 "	4.2 "	
W-5-	60.3 "	40.2 "	192.5 "	2.0 "	5.0 "	
20	62.4 "	42.3 "	158.4 "	2.1 "	2.1 "	31.7 grams
21	59.2 "	39.5 "	148.0 "	2.0 "	2.0 "	49.3 "
22	55.6 "	37.0 "	138.9 "	1.9 "	1.9 "	64.8 "
23	52.3 "	34.9 "	127.2 "	1.7 "	1.7 "	78.5 "
24	66.9 "	44.6 "	151.7 "	2.2 "	1.1 "	33.4 "
25	63.2 "	42.3 "	158.5 "	2.2 "	2.2 "	31.6 "
26	60.0 "	40.0 "	164.5 "	2.0 "	3.0 "	30.0 "
27	57.3 "	38.2 "	170.0 "	1.9 "	3.8 "	28.6 "
28.1	70.9 "	47.3 "	177.0 "	2.4 "	2.4 "	
28.2	67.0 "	44.6 "	183.0 "	2.2 "	3.4 "	
28.3	63.3 "	42.3 "	188.0 "	2.1 "	4.2 "	
28.4	60.3 "	40.2 "	192.5 "	2.0 "	5.0 "	
28.5	57.3 "	38.2 "	196.5 "	1.9 "	5.7 "	

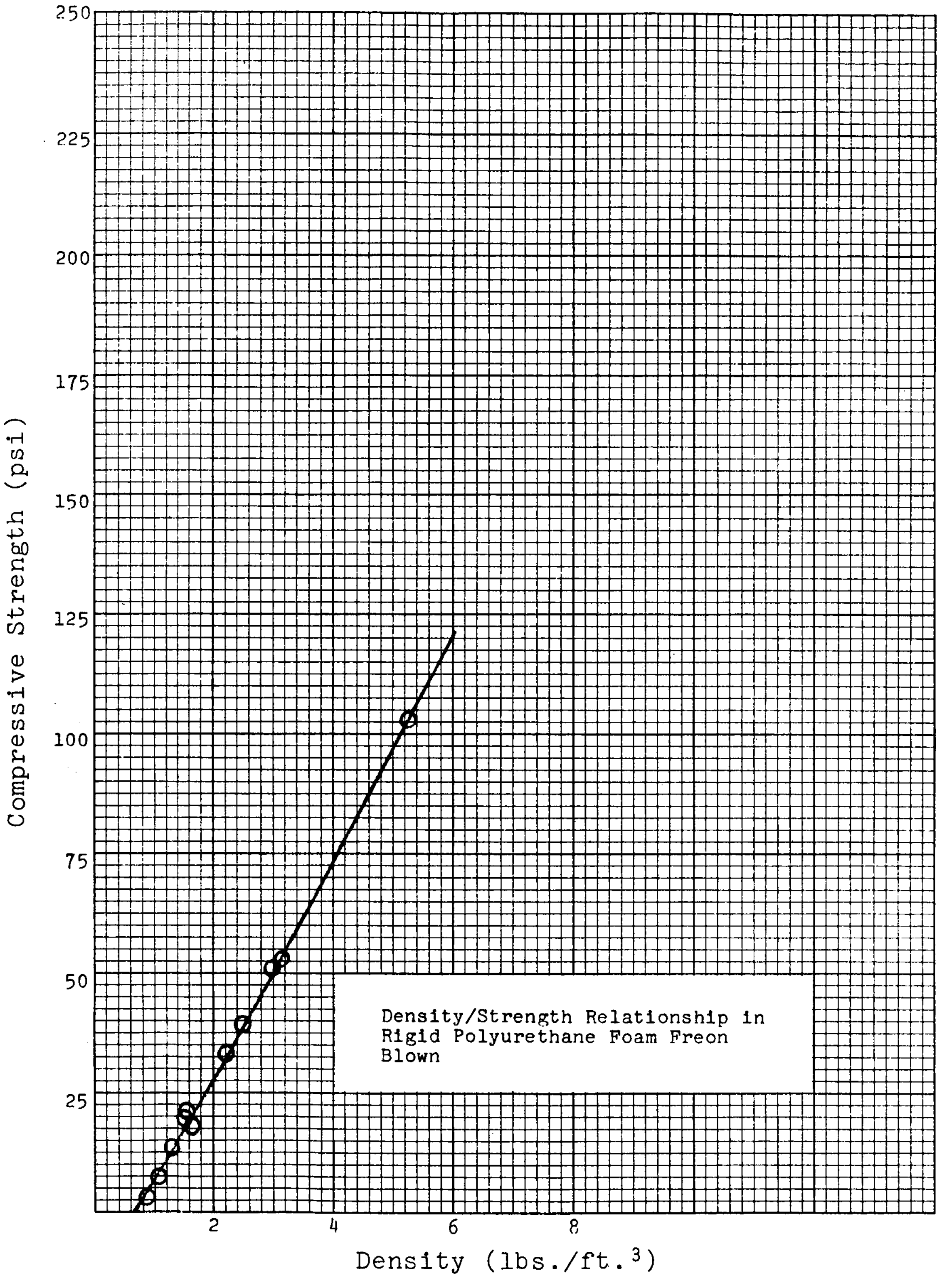


Figure 5. Density/Strength Relationship in Rigid Polyurethane Foam Freon Blown

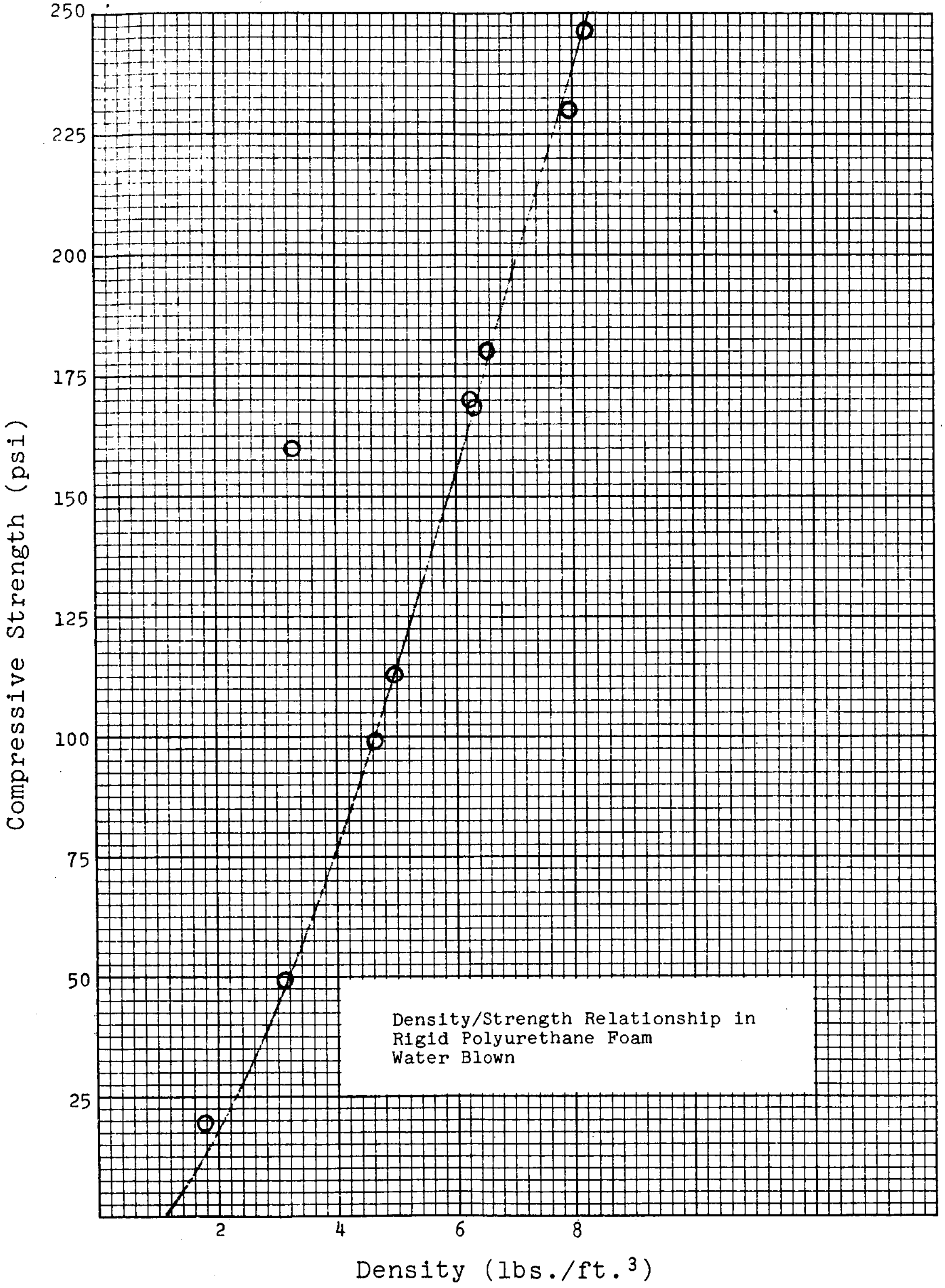


Figure 6. Density/Strength Relationship in
Rigid Polyurethane Foam
Water Blown

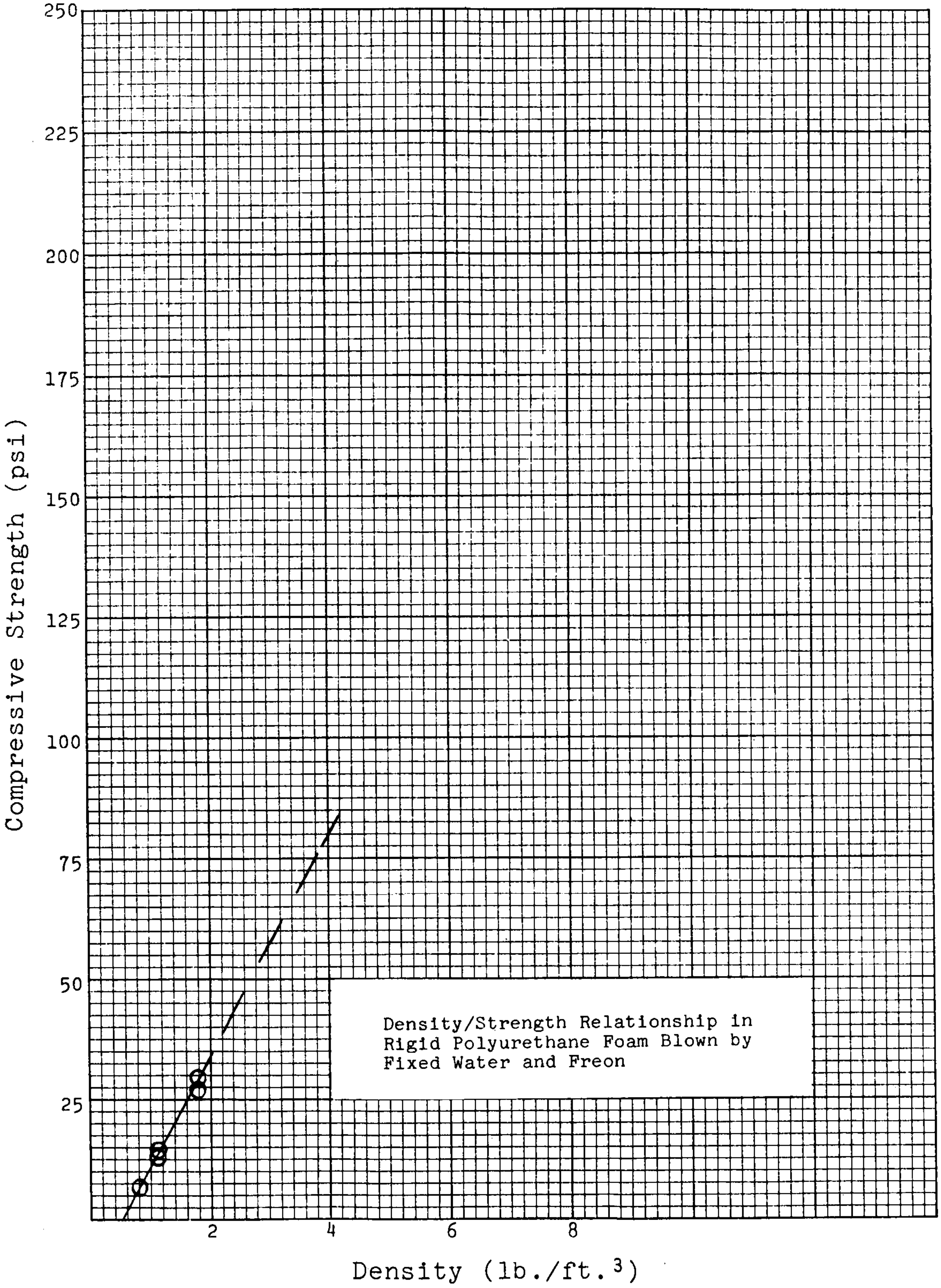


Figure 7. Density/Strength Relationship in Rigid Polyurethane Foam Blown by Fixed Water and Freon

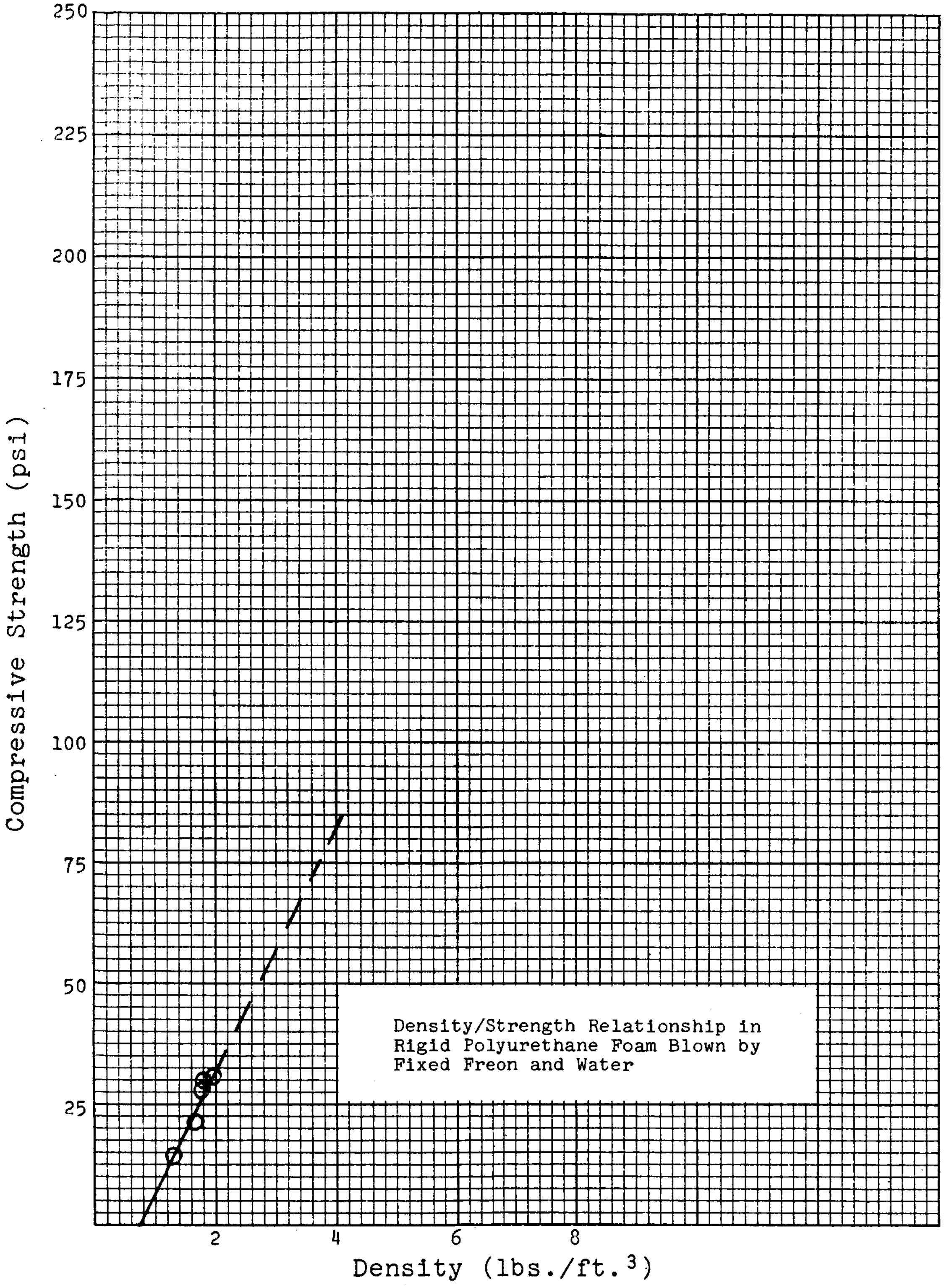


Figure 8. Density/Strength Relationship in Rigid Polyurethane Foam Blown by Fixed Freon and Water

The basic formulation used in this investigation is shown below:

100 parts	LK-380
8 parts	DC-113
n parts	Freon
61 parts	Mondur TD-80 (Tolylene diisocyanate)
1 part	C-16

The two Freons were each evaluated at 5.7% concentration (10 parts), and 13.0% concentration (25 parts). The lower concentration gave foam densities of 4.5 lbs./ft.^{3} and foam compressive strengths of 80-100 psi. The higher Freon concentration gave densities of 2-3 lbs./ft.^{3} with compressive strengths of 25-35 psi. No significant difference was noted upon changing from Freon 11 to Freon 113.

The composition of each foam formulation is given in Table 14, together with test data.

Pneumatogen Mixtures Investigation

It was observed through the course of the program that foams obtained from formulations which have a relatively long rise time (ca. 10 minutes) often have good strength-density values. Also, the rise is continuous and uniform from its initiation until the foam has set. These foams generally exhibit a uniform, small-cell structure.

Consequently, a series of foam formulations was prepared in which the pneumatogen content was varied in amounts of Freon F-11 and F-113, keeping total pneumatogen constant. The two fluorocarbons have respective boiling points of 75° and 95°F. Additionally, foams were prepared which contained fluorocarbon mixtures and "Vazo", a solid blowing agent which, at its decomposition temperature of 103°C releases nitrogen gas. All of the foams were of very uniform, small-cell structure.

Formulations and data are shown in Table 15. As can be seen in the Table, no increase in strength properties was realized from any of the systems. Consequently, this approach was discontinued.

TABLE 14

PNEUMATOGEN INVESTIGATION-FREONS F-11 AS F-113

Foam Number	Foam Stabilizer		Polyol Component (1)		Isocyanate Component (2)		NCO/OH Ratio	Freon		C-16 Catalyst (gr.)	Stirring Conditions		Exotherm (°C.)	Foam Rise Time (min.)	Density (lbs./ft.^{3})	Compressive Strength (psi)
	Identity	(gr.)	Polyol	(gr.)	Isocyanate	(gr.)		Type	(gr.)		Time (Sec.)	Voltage				
38.6	DC-113	8	LK-380	156	Mondur TD-80	95	1.03	F-113	39	1.5	30	90	123	7	2.65	28.9
38.5	"	2	"	156	"	95	1.03	"	39	1.5	30	90	126	7.5	2.67	34.4
38.1	"	8	"	156	"	95	1.03	"	39	1.5	30	90	124	8	2.70	36.7
38.3	"	4	"	156	"	95	1.03	"	39	0.5	30	90	96	19.5	3.05	36.7
38.2	"	4	"	170	"	103	1.03	"	17	1.5	30	90	136	5	4.95	98.9
38.0	"	8	"	170	"	103	1.03	"	17	1.5	30	90	128	5	5.03	95.6
38.4	"	2	"	170	"	103	1.03	"	17	1.5	30	90	147	5.5	5.04	97.8
38.7	"	8	"	170	"	103	1.03	"	17	1.5	30	90	158	5.5	5.72	131.1
38.10	"	8	"	156	"	95	1.03	F-11	39	1.5	30	90	144	9.5	2.30	25.6
38.9	"	8	"	170	"	103	1.03	"	17	1.5	30	90	155	7	6.03	135.6
39.6	"	8	"	170	"	103	1.03	"	17	1.5	15	40	146	5	4.68	92.3
39.3	"	8	"	156	"	95	1.03	"	39	1.5	30	40	117	9.5	2.14	26.8
39.0	"	8	"	170	"	103	1.03	"	17	1.5	30	40	145	5	4.37	81.1
39.7	"	8	"	170	"	103	1.03	"	17	1.5	60	40	146	5.5	4.51	87.7
39.4	"	8	"	156	"	95	1.03	"	39	1.5	30	80	114	9.5	2.23	26.1
39.1	"	8	"	170	"	103	1.03	"	17	1.5	30	80	143	5	4.39	85.0
39.8	"	8	"	170	"	103	1.03	"	17	1.5	15	120	144	5.5	4.45	84.4
39.5	"	8	"	156	"	95	1.03	"	39	1.5	30	120	134	8	2.31	25.0
39.2	"	8	"	170	"	103	1.03	"	17	1.5	30	120	144	5	4.91	102.2
39.9	"	8	"	170	"	103	1.03	"	17	1.5	60	120	146	5.5	5.17	102.7
40.3	"	8	"	156	"	95	1.03	"	39	1.5	30	40	121	9	2.08	21.1
40.0	"	8	"	170	"	103	1.03	"	17	1.5	30	40	138	6	4.72	96.7
40.4	"	8	"	156	"	95	1.03	"	39	1.5	30	80	107	9	2.09	20.0
40.1	"	8	"	170	"	103	1.03	"	17	1.5	30	80	148	5	4.71	96.7
40.5	"	8	"	156	"	95	1.03	"	39	1.5	30	120	116	8.5	2.26	26.9
40.2	"	8	"	170	"	103	1.03	"	17	1.5	30	120	144	5.5	4.52	89.4
41.2	"	8	"	170	"	103	1.03	"	17	1.5	10	90	126	6	4.47	88.9
41.3	"	8	"	170	"	103	1.03	"	17	1.5	15	90	138	6.5	3.84	65.0
41.0	"	8	"	170	"	103	1.03	"	17	1.5	30	90	138	6	4.63	91.1
41.1	"	8	"	170	"	103	1.03	"	17	1.5	60	90	138	6	4.80	95.6
40.9	"	8	"	170	"	103	1.03	"	17	1.5	30	90	140	6	4.25	81.1
40.7	"	8	"	170	"	103	1.03	"	17	1.5	30	90	146	6	4.21	81.7
40.8	"	8	"	170	"	103	1.03	"	17	1.5	60	90	154	6	4.88	102.2
40.6	"	8	"	170	"	103	1.03	"	17	1.5	30	90	146	6	4.5	91.1

TABLE 15

MIXED PNEUMATOGEN INVESTIGATION

Base Formulation

LK-380	170 gms
DC-113	8
TDI	103
C-16	0.5
Pneumatogen	Varied

Foam No.	Freon 11	Freon 113	Vazo	F-11:F-113	Density, lbs/ft^3	Strength, psi	psi/d^2
73.0	10 gms	--	--	10:0	4.88	92	3.84
73.1	8	2	--	4:1	4.91	94	3.93
73.2	6	4	--	3:2	4.80	86.5	3.84
73.3	4	6	--	2:3	5.76	126	3.79
73.4	2	8	--	1:4	5.86	126	3.66
73.5	--	10	--	0:10	5.59	110	3.52
73.6*	8	2	--	4:1	4.90	87	3.65
73.7*	6	4	--	3:2	4.95	98	4.00
73.8*	4	6	--	2:3	5.10	100	3.88
73.9*	2	8	--	1:4	5.92	124	3.57
73.10	5	--	5	--	4.63	63.5	2.98
73.11	2.5	2.5	5	1:1	4.70	62	2.76
73.12	--	5	5	--	4.82	61	2.63

*Pneumatogen premixed before incorporating into formulation.

Solid Pneumatogen Investigation

At least two solid pneumatogens that release nitrogen gas at the relatively low temperatures generated in the urethane foam reaction are commercially available. The pneumatogens are azoisobutyronitrile produced by duPont (tradename VAZO) and by Fison House, England (tradename AZDN-FF), and N,N'-dimethyl-N,N'-dinitrosoterephthalamide, which decomposes at 105°C. and is also produced by duPont (tradename Nitrosan). A series of fourteen experimental foams were prepared, using the solid pneumatogen as the sole source for foam expansion. The purpose of this investigation was to determine whether the particle size of the pneumotogen affected the cell size of the rigid foam. The basic foam formulation was the same as shown above, except that the Freon pneumatogen was replaced by VAZO, Nitrosan, or AZDN-FF at concentrations of 3 - 13%. The desired amount of solid pneumatogen was added to a mixture of LK-380 and DC-113. The viscous mixture was passed between the rolls of a paint mill to break up the agglomerates and uniformly disperse the solid in the polyol.

The particle size of the solid pneumatogens was initially measured in the pure (dry) state as well as in the polyol mixture. A Hegman (Fineness of Grind) gage was used for this purpose. We found that the largest particle size in VAZO and AZDN-FF (dry) was 1.5 mils. The particle size could not be measured in the case of pure Nitrosan because of excessive agglomeration. After two passes through the paint mill, the largest particle size of all three pneumatogens (in the polyol mixtures) was still 1.5 mils. The LK-380 - DC-113 - pneumatogen mixtures were passed through the mill as many as seven times, with the rolls closed for maximum shear, yet the size of the solid particles remained at approximately 1.5 mils. In spite of the fact that pneumatogen particle size could not be varied by the paint mill technique, we proceeded with the investigation in order to determine which solid pneumatogen gave the strongest foams.

Eight foams were prepared with varying amounts of VAZO, ranging from 3 to 13%. The C-16 Catalyst concentration was also varied in these foams. We found that the heat generated by the LK-380 - Mondur TD-80 polymerization was sufficient to utilize 6 - 7% VAZO in the formulation.

Adding more than 7% VAZO had very little effect on foam density. Also, there was a correlation between catalyst concentration and foam density, as expected. Lower densities were obtained at constant VAZO concentration when the catalyst level was increased. In general, however, the foam products based on VAZO were not as strong as earlier foams produced with Freon or water.

Two additional foams were prepared using AZDN-FF which were comparable to the VAZO products in both composition and strength.

Four experimental foams were prepared at two Nitrosan concentrations of 3.3% and 6.6%. Nitrosan appears to be the most effective solid pneumatogen, since smaller amounts were required to produce a given foam density. We also observed that the LK-380 - Nitrosan mixtures were quite unstable. After standing only one to two hours, nitrogen bubbles began to rise throughout these mixtures.

The strongest foams were prepared with Nitrosan at densities up to 3.9 lbs./ft.^{3}. However, the compressive strengths obtained were below 30 psi, which is significantly lower than comparable Freon-blown or water-blown foams. The complete data for these solid pneumatogen foams are shown in Table 16.

Ten foams were prepared using the low-shear stirrer. We were not able to observe the foaming process in detail in these formulations, since they were nearly opaque. The cardboard mold was moderately warm before the first bubbles appeared (10-15 minutes). We could not determine whether the individual bubbles formed about individual particles of solid pneumatogen, but it was apparent that all of the bubbles were nearly the same size and that there was very little movement of the individual bubbles with respect to one another. Eight of these ten foams were prepared using 20 grams of VAZO. The densities of these products were very similar (3.5-3.9 lbs./ft.^{3}), but they differed considerably in compressive strengths (33-46 psi). Also, the compressive strengths of these foams were much lower than comparable foams containing Freon pneumatogen.

The two remaining products were prepared using 10 grams of VAZO. The densities and compressive strengths of these foams were 5.6 and 5.7 lbs./ft.^{3} and 130 and 118 psi, respectively. Again, there was a wide variation in compressive

TABLE 16

INVESTIGATION OF SOLID PNEUMATOGEN

Foam Number	Foam Stabilizer		Polyol Component (1)				Isocyanate Component (2)		NCO/OH Ratio	Pneumatogen (3)		C-16 Catalyst (gr.)	Stirring Conditions		Exotherm (°C.)	Foam Rise Time (min.)	Density (lbs./ft.^{3})	Compressive Strength (psi)
	Identity	(gr.)	Polyol	(gr.)	Polyol	(gr.)	Isocyanate	(gr.)		Type	(gr.)		Time (Sec.)	Voltage				
42.5	-	-	LK-380	156	-	-	Mondur TD-80	95	1.03	VAZO	39	1.5	30	90	134	5.5	3.60	47.8
42.3	DC-113	8	"	170	-	-	"	103	1.03	"	20	0.5	30	90	149	8	3.80	48.9
42.1	"	8	"	170	-	-	"	103	1.03	"	20	1.5	30	90	169	3.5	4.13	51.7
42.4	-	-	"	170	-	-	"	103	1.03	"	17	1.5	30	90	142	5	5.53	127.8
42.2	DC-113	8	"	170	-	-	"	103	1.03	"	10	0.5	30	90	152	7.5	6.70	182.0
42.0	"	8	"	170	-	-	"	103	1.03	"	10	1.5	30	90	166	3.5	7.34	209.4
44.4	"	8	"	170	-	-	"	103	1.03	"	10	1.5	30	90	160	5	4.75	126
44.5	"	8	"	170	-	-	"	103	1.03	"	10	0.5	30	90	147	10	4.93	107
44.2	"	8	"	170	-	-	"	103	1.03	Nitrosan	20	1.5	30	90	164	5	2.25	22.2
44.3	"	8	"	170	-	-	"	103	1.03	"	20	0.5	30	90	170	6.5	2.72	29.1
44.0	"	8	"	170	-	-	"	103	1.03	"	10	1.5	30	90	156	3.5	3.15	42.9
44.1	"	8	"	170	-	-	"	103	1.03	"	10	0.5	30	90	158	6	3.86	65.8
44.6	"	8	"	170	-	-	"	103	1.03	AZDN-FF	10	1.5	30	90	164	4	5.45	151.4
44.7	"	8	"	170	-	-	"	103	1.03	"	10	0.5	30	90	152	10	5.81	146.7

strength, but these higher-density foams are now as strong as 5.7 lbs./ft.^{3} Freon-blown foams based on the same urethane formulation. The compositions and physical properties of the experimental foams are given in Table 17.

Investigation of Solid Pneumatogen Particle Size

A study of pneumatogen (VAZO) particle size was included in the series of ten foams prepared with the low-shear stirrer. The VAZO was first sieved and collected in three particle sizes: 4-6 mils, 3-4 mils, and 2-3 mils. Foams were prepared using 20 grams of each of these particle classifications. Each foam possessed a uniform cellular structure composed of very small cells. There was no significant variation in cell size. Also, the densities and compressive strengths of these products were not affected by the change in VAZO particle size.

Effect of Nucleating Agents and Foam Stabilizers

In the preparation of a foam, the first step is the formation of a gas bubble in the liquid system (Ref. 7). This formation is a result of generated gas reaching its supersaturation point in solution and coming out of solution in the form of a bubble. This bubble formation is termed "nucleation." The nucleation phenomenon is often assisted by the presence of a finely divided solid known as a nucleating agent. An example of a nucleating agent is finely divided silica.

A newly formed bubble is in the form of a sphere surrounded by a polymer phase. As bubbles grow and the foam volume increases, the polymer phase becomes thinner until the spherical shape is lost. The bubbles form dodecahedral structures surrounded by polymer membranes joined together by struts or ribs.

A number of experiments were conducted with slow-rising foam formulations to study the formation and growth of bubbles and cells. For this work the low-shear stirrer, developed for the dense polymer program, was used to mix the foam formulations.

TABLE 17

SOLID PNEUMATOGEN FOAMS UTILIZING LOW SHEAR STIRRER

Foam No.	DC-113 Gm.	Polyol		Isocyanate,		Pneumatogen,		Catalyst,		Stirring		Exotherm °C	Foam Rise, Min.	Density, lbs/ft3	Compressive Strength, psi
		Type	Gm.	Type	Gm.	Type	Gm.	Type	Gm.	Time, Sec.	RPM				
50.3	8	LS-490	170	TDI	103	Vazo	20	C-16	0.5	120	180	154	16	3.49	36.7
50.4	8	"	170	"	103	"	20	"	0.5	120	180	134	15	3.52	35.0
50.1	8	"	170	"	103	"	20	"	0.5	120	180	155	15	3.56	34.4
50.8	8	"	170	"	103	"	20	"	0.5	120	180	153	15	3.58	33.3
50.7	8	"	170	"	103	"	20	"	0.5	120	180	146	15	3.66	40.0
50.2	8	"	170	"	103	"	20	"	0.5	120	180	142	15.5	3.72	42.2
50.10	8	"	170	"	103	"	20	"	0.5	120	180	164	14	3.85	38.9
50.[illegible]	8	"	170	"	103	"	20	"	0.5	120	180	156	15	3.88	45.6
47.4	8	"	170	"	103	"	10	"	0.5	120	180	120	13	5.62	130.0
47.	8	"	170	"	103	"	10	"	0.5	120	180	140	14	5.71	117.8

The various formulations were efficiently mixed without trapping bubbles in the liquid. Each bubble-free formulation was gently poured into a cardboard box which contained a sight glass. We observed that, in the absence of a nucleating agent, the bubbles initially form at the interfaces between liquid and cardboard and primarily at the bottom of the box. The viscosity of the liquid remained relatively low for 2-3 minutes in these slow-foaming formulations. During this time, the buoyancy of the bubbles caused them to rise to the surface. We observed that the bubble diameter increased with distance traveled and that near-spherical shape was retained until the bubbles reached the surface.

During the first three minutes of foaming, as the volume of bubbles increased, the liquid level dropped to about half its initial height. As the polymerization reaction proceeded, the viscosity and temperature of the liquid increased. Bubbles began to form within the liquid because of the higher vapor pressure of the pneumatogen. Since these bubbles had only a short distance to travel before reaching the surface, they remained relatively small. Finally, after 6-8 minutes, the viscosity increased to the point where the bubbles were trapped in place. These final bubbles were the smallest in spite of the fact that the temperature of the liquid was rising rapidly at this stage in the foaming process. The composite structure continued to expand with increasing temperature for an additional 3-5 minutes until the polymer became rigid.

The above foaming experiment was repeated using a similar formulation containing 0.1% Cab-O-Sil as a nucleating agent. In this case, the bubbles formed uniformly throughout the liquid and rose to the surface in a random manner. The boundary line of the liquid disappeared very quickly (1 minute), after which the foam structure appeared to expand everywhere simultaneously. (Actually, the foam could move in only one direction, since it was being contained by the walls of the box.) The basic cellular structure of the rigid, nucleated foam appeared basically the same as before. However, there was a significant difference in cell size, as the nucleated foam was composed of smaller cells. Both foams possessed the characteristic close-packed, twelve-sided, thin-walled, cellular configuration.

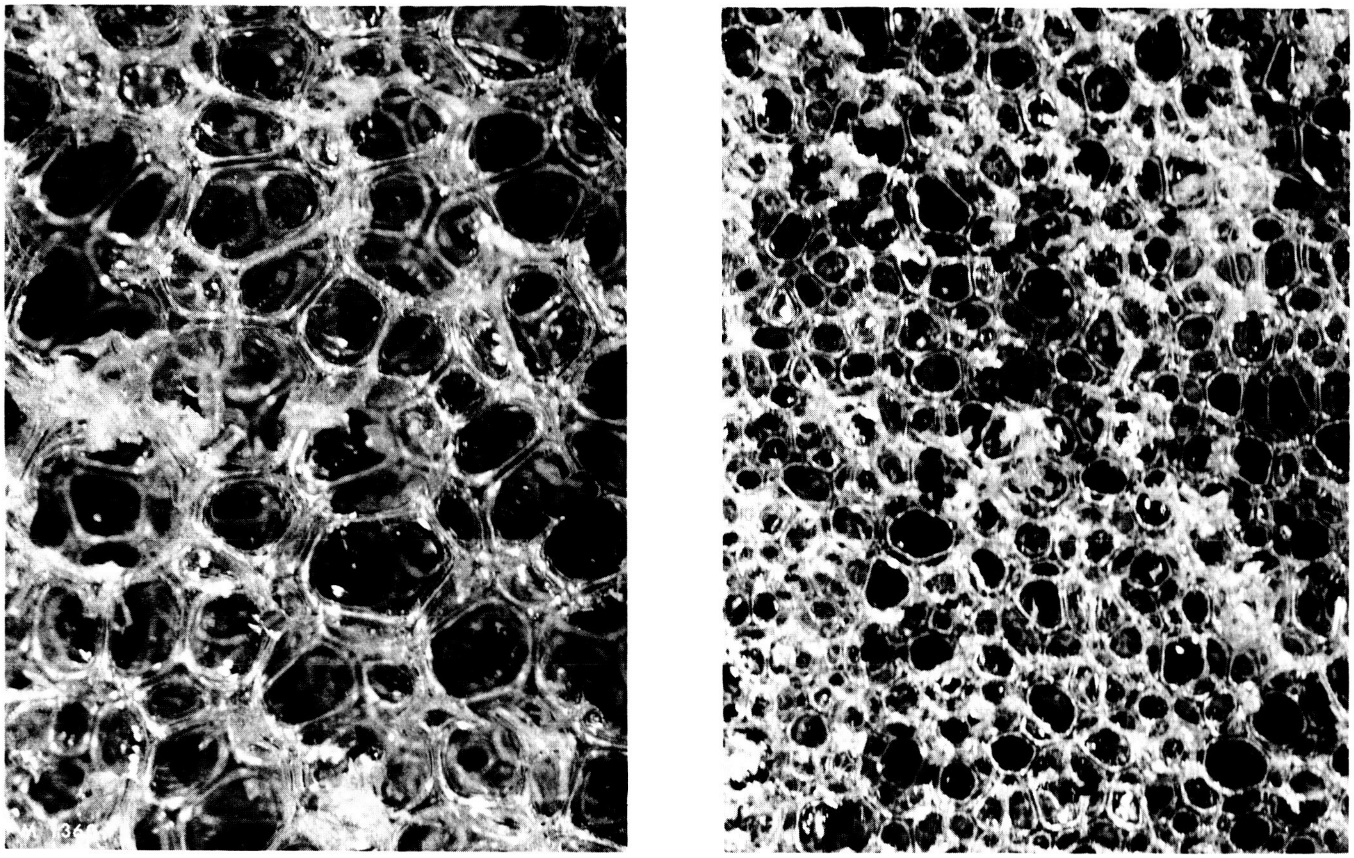
Photographs taken of the two foams described above are included in Figure 9. The photographs show that both foams possessed uniform cell size, with significantly smaller cells in the nucleated product. The density was the same for both foams (4.1 lbs./ft.^{3}). Also, the compressive strengths for these two foams were the same (72.8 psi). This substantiates an earlier theoretical analysis which concluded that cell size should have no effect on foam strength, other factors being equal. It was felt that perhaps large (1/4"), coarse foam cells should contain proportionally larger amounts of polymer in the struts compared to finer cell structures, resulting in smaller l/d ratios and increased strength. A series of foam experiments was run investigating the effect of increasing amounts of nucleating agent on foam cell structure and compressive strength. The investigation was conducted with and without foam stabilizers. The experiments were run under slow stir conditions using the paddle-type stirrer used in the dense casting work to eliminate entrapment of air bubbles.

As seen in Table 18, increased nucleating agents resulted in increased density and decreased evaluation factor, psi/d^2. In general, as seen in Figure 10, foams 66.0 - 66.4 cell size becomes smaller as the amount of nucleating agent increases. Foam 66.0 (no foam stabilizer or nucleating agent) made a very irregular foam of high density, but lowest strength/density quality.

The addition of silicone oil, which serves as a foam stabilizer, resulted in relatively finer cell structure. However, at a constant level of foam stabilizer (Figure 11, foams 66.5 - 66.9), the trend toward larger cells with decreased nucleating agent continued.

The data shown in Table 18 also indicate that the presence of foam stabilizer in the foam systems results in relatively constant densities and strengths, regardless of the level of nucleating agent present. Also of interest is the fact that the cell size was the largest where no nucleating agent was present. In no case was the cell structure as large as desired (1/4").

Reduced amounts of silicone oil stabilizer (.5 and 1.0 parts) were added to separate basic foam formulations. To each of these, 1/8 and 0.5 parts of Santocel nucleating agent were added. The addition of nucleating agent to



47.5 Without nucleating agent

47.6 Contains 0.1% Cab-O-Sil for improved nucleation

Figure 9. Effect of Nucleation on Foam Cell Size

TABLE 18

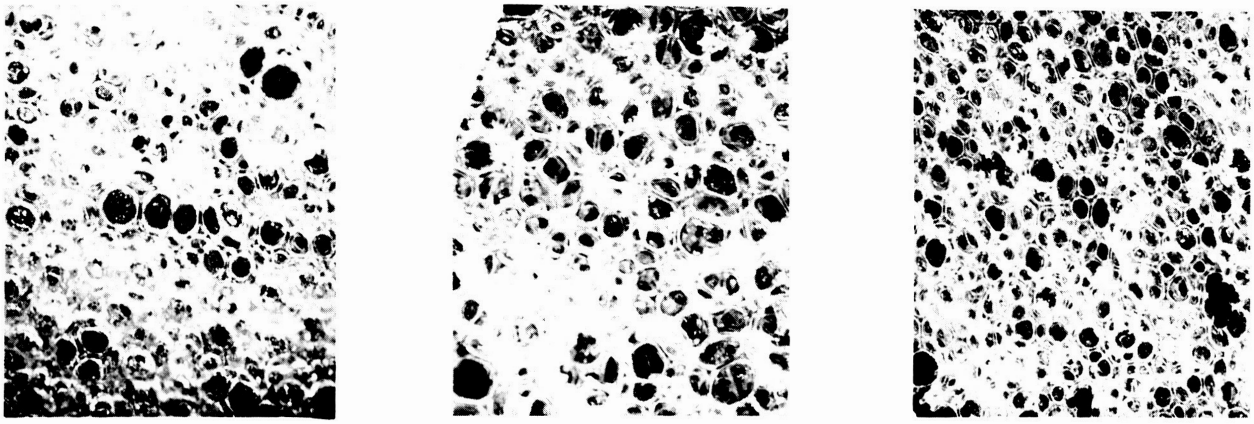
NUCLEATION TEST DATA

Basic Formulation

LK-380	200 grams
Freon 11	20 grams
TDI	114 grams
C-16	1.5 grams
Santocel FR-C	varied
L-520	varied

	66.0	66.1	66.2	66.3	66.4*	66.5	66.6	66.7	66.8	66.9	67.0	67.1	67.2	67.3	67.4	67.5
Santocel FR-C		1	2	3	4	4	3	2	1				1	0.25	1	0.25
L-520						4	3	3	3	3	2	1	2	2	1	1
Density, lbs/ft^3	8.50	3.93	4.86	9.19	10.038	4.12	3.92	3.88	3.75	4.18	4.50	3.910	3.173	4.275	4.367	4.438
Strength, psi	208	57	86	253	299	69.8	68	65	61	75	69	59.5	72	69	71.5	78
Constant, psi/d^2	2.87	3.6	3.85	3.23	2.99	4.12	4.44	4.34	4.32	4.34	3.58	3.92	4.09	3.73	3.98	3.85

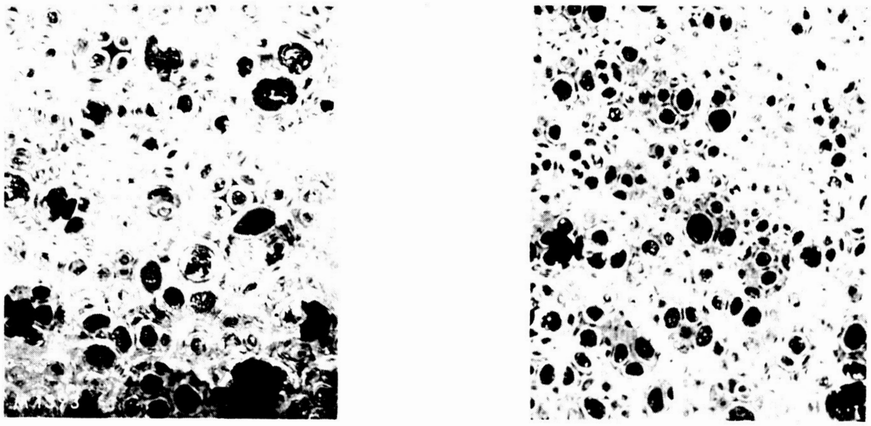
*Collapsed



66.0
No Santocel

66.1
0.5 phr Santocel

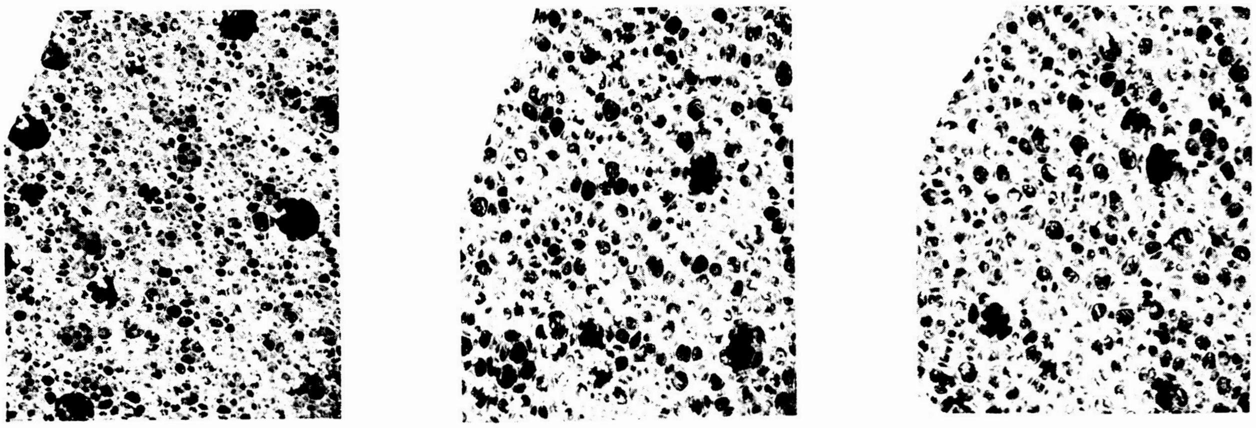
66.2
1 phr Santocel



66.3
1.5 phr Santocel

66.4
2 phr Santocel

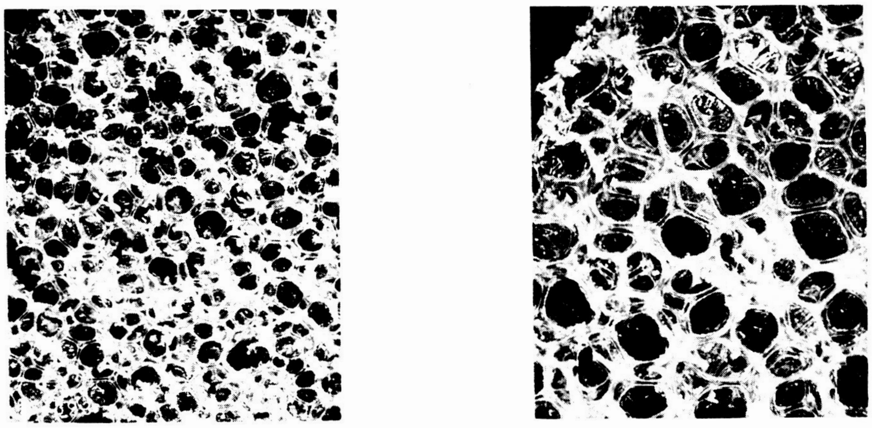
Figure 10. Effect of Nucleating Agent on Cell Size



66.5
2 phr Santocel/
2 phr LS-520

66.6
1.5 phr Santocel/
1.5 phr LS-520

66.7
1 phr Santocel/
1.5 phr LS-520



66.8
0.5 phr Santocel/
1.5 phr LS-520

66.9
1.5 phr LS-520

Figure 11. Effect of Nucleating Agent and Foam Stabilizer on Cell Size

the formulations decreased cell size (Figure 12, foams 67.0 - 67.5); however, very little difference in compressive strength was realized (Table 18).

In further attempts to obtain large cell size, Freon-blown, water-blown, and nitrogen-blown foams were evaluated, with and without nucleating agent (Santocel), utilizing non-degassed and degassed polyol. Additionally, other foam stabilizers were evaluated, such as DC-200 (50 Centistoke silicone oil), Selcon 150 (organic foam stabilizer available from Houdry), and Mobay's Additive A-5 (soap).

In no case was the cell structure as large as desired and, as expected, the systems with no Santocel were of the largest cell size. As seen in Table 19, no significant improvement in strength was realized from this approach. Additionally, no apparent difference in strength was noticed between foams based on non-degassed and degassed polyol. Since the nucleation approach appeared to offer no significant improvement in strength, further work was discontinued.

Evaluation of Syton Nucleating Agents

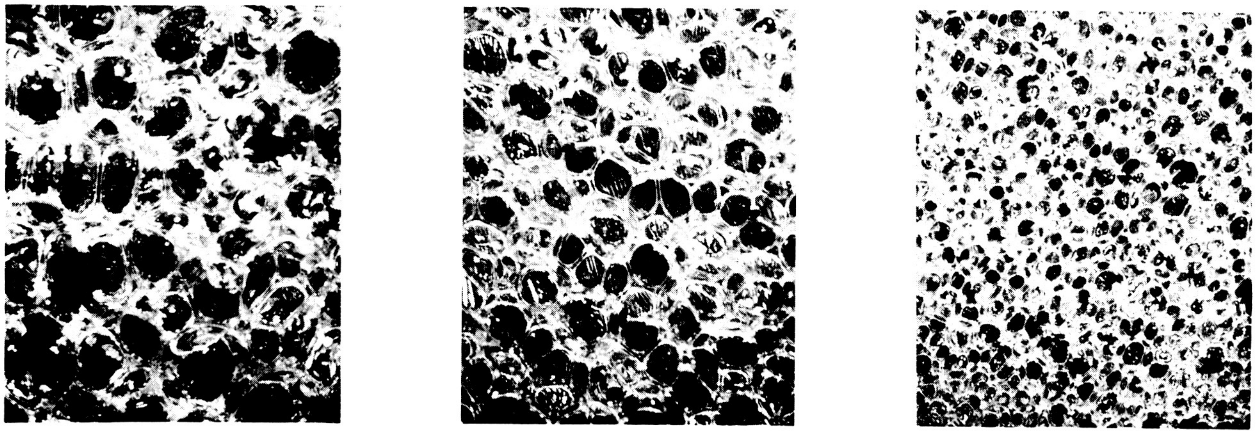
A series of twelve foams were prepared to test the effectiveness of Monsanto's line of colloidal silica dispersions (Sytons) as nucleating agents. The Sytons are aqueous suspensions of extremely small silica particles (150 - 300 angstroms diameter). The water was utilized as the pneumatogen.

The formulations used in this work were based on two urethane systems:

(1) LK-380 (trifunctional polyol) - Mondur TD-80 (Tolylene diisocyanate)

(2) LS-490 (hexafunctional polyol) - Mondur TD-80 (Tolylene diisocyanate)

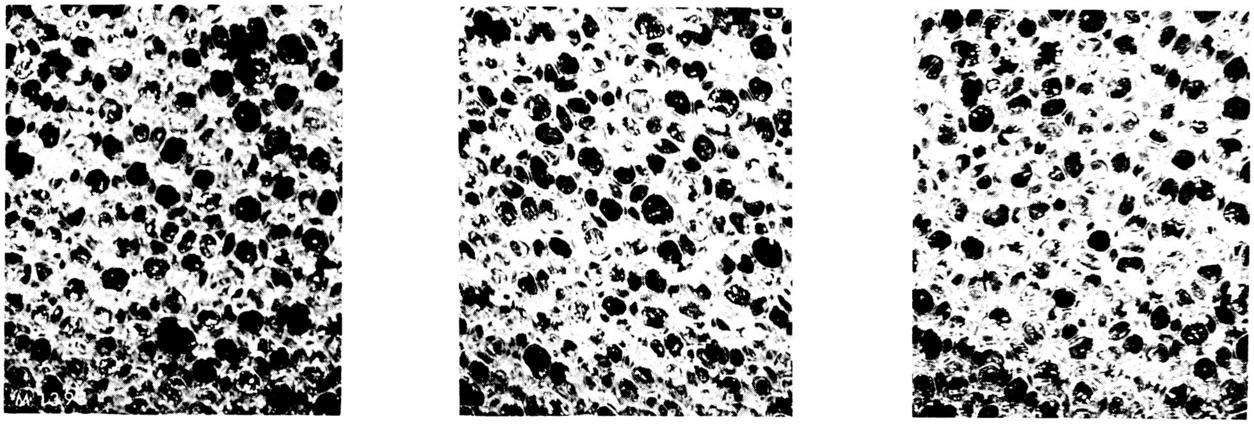
Syton content was varied to provide pneumatogen levels of 1 part water - 7 parts water (per 100 parts of polyol). The compositions and properties of the resulting foams are given in Table 20. Foam densities ranged from 1.4 - 4.6 lbs./ft.^{3}. The evaluation factor (psi/d^2) indicated that



67.0
1 phr LS-520

67.1
0.5 phr LS-520

67.2
0.5 phr Santocel/
1 phr LS-520



67.3
0.125 phr Santocel/
1 phr LS-520

67.4
0.5 phr Santocel/
0.5 phr LS-520

67.5
0.125 phr Santocel/
0.5 phr LS-520

Figure 12. Effect of Minimum Amounts of Nucleating Agent and Foam Stabilizer on Cell Size

TABLE 19

NUCLEATION TEST DATA

Foam No.	68.0	68.1	68.2	68.3	68.4	68.5	68.6	68.7	68.8	68.9	69.0**	69.1	69.2	69.3	69.4*	69.5*
LK-380	200gms	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Freon 11	20	20			20	20	20	20			20	20				
TDI	114	114	152	152	114	114	114	114	114	114	114	114	152	152	114	114
C-16	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5			1.5	1.5
Water			4	4									4	4		
DC-113	4	4	4	4	2						4	4	4	4	4	4
Santocel		0.25		0.25						0.25		0.25		0.25		0.25
Vazo									24	24					24	24
DC-200						4										
Selcon R-150							4									
A-3								4								
Density, lbs/ft^3	4.9	4.8	3.15	2.8	4.2	5.05	4.7	8.2	3.5	3.35	4.2	4.6	3.0	3.0	3.6	4.0
Strength, psi	92	89	44	29	67.5	73	82	158	36	38	71	81	39	30.5	37	50
psi/d^2	3.7	3.8	4.8	3.84	3.78	2.79	3.69	2.47	2.95	3.33	3.97	3.81	4.46	3.41	2.85	3.08

*Poor foam--voids, fissures.

**Foam nos. 69.0-69.5 utilized degassed polyol.

TABLE 20

INVESTIGATION OF AQUEOUS COLLOIDAL SILICA DISPERSIONS AS COMBINATION BLOWING AGENT AND NUCLEATOR

Foam Number	Polyol Component Name	Polyol Component (gms)	Foam Stabilizer Name	Foam Stabilizer (gms)	Syton (1) Type	Syton (1) (gms)	Mondur TD-80 (gms)	C-16 Catalyst (gms)	Density (lbs./ft.^{3})	Compressive Strength (psi)	(psi/d^2)
54.6	LK-380	170	DC-113	8	200	17	147	-	1.38	12.0	6.30
54.3	"	170	"	8	200	11	132	1.5	1.62	12.5	4.76
54.5	"	170	"	8	200	8	132	-	1.65	14.5	5.33
55.5	LS-490	160	"	8	250	8	166	-	1.78	16.0	5.05
54.9	LK-380	170	"	8	250	10	147	-	1.93	22.1	5.94
54.8	"	170	"	8	250	7	132	-	2.57	32.0	4.85
54.4	"	170	"	8	200	6	116	-	2.75	35.0	4.63
54.2	"	170	"	8	200	6	116	1.5	2.82	32.5	4.09
55.2	LS-490	160	R-150	8	200	5.5	136	-	3.01	40.5	4.47
54.7	LK-380	170	DC-113	8	250	3.5	116	-	4.14	70.0	4.09
55.4	LS-490	160	"	8	250	3.2	136	-	4.31	88.0	4.74
54.1 (2)	LK-380	170	"	8	Water	2.5	125	1.5	4.56	90.0	4.33

(1) Syton 200 is an aqueous 30% colloidal silica solution.
Syton 250 is an aqueous 50% colloidal silica solution. The silica particle sizes in both solutions are 150 - 300 angstroms (diameter).

(2) Control.

the Sytons produced a very slight improvement in foam strength within this range of densities. Since the nucleation approach appeared to offer no significant improvement in strength, further work was discontinued.

Foam Stabilizer Evaluation

Three silicone-type foam stabilizers, namely DC-113 and DC-199 (Dow Corning), and L-520 (Union Carbide), and one nonsilicone-organic foam stabilizer, R-150 (Houdry Process and Chemical Company), were tested at concentrations of 1% to 5%. One foam was prepared without foam stabilizer as a control. The pertinent data are given in Table 21.

The test results indicate that a commercially acceptable foam can be prepared from the LK-380 - Mondur TD-80 urethane system without the aid of a foam stabilizer. The control foam possessed a density of 4.6 lbs./ft.^{3} and a compressive strength of 99 psi. A very slight improvement in compressive strength was observed with either 1% DC-199 or 1% R-150.

Low Modulus Rigid Foam

The approach of obtaining significant increases in compressive strength had been directed toward building high moduli chemical structures. Work accomplished in obtaining solid urethane castings of increasing modulus showed no corresponding increase in compressive strength from rigid foams prepared from these high moduli urethane systems.

Compressive strength evaluation of foams based on high moduli systems shows a yield point prior to attaining 10% deflection. Plotting load-versus-deflection thus shows 10% deflection is seldom reached. This led to the belief that a somewhat lower modulus would be desirable. The lower modulus should eliminate the yield point characteristic of high moduli structures and, consequently, allow 10% deflection of the foam at increased load.

Incorporating low modulus characteristics into the structures was attempted through the reaction of straight

TABLE 21

EFFECT OF FOAM STABILIZER ON FOAM PROPERTIES

Base Formulation

LK-380	170 grams
TDI	103
Freon 11	17
C-16	1.5
Foam Stabilizer	As shown

Foam No.	Foam Stabilizer Type	Foam Stabilizer Gm.	Exotherm, °C	Density, lbs/ft^3	Compressive Strength psi
41.4	None		143	4.63	99.4
41.5	DC-113	3	146	4.87	104.4
41.6	DC-113	15	136	4.68	88.9
41.7	DC-199	3	143	4.85	111.1
41.9	L-520	3	143	4.37	86.7
41.10	L-520	15	130	4.02	65.0
41.11	R-150	3	147	4.90	113.3
41.12	R-150	15	130	4.59	91.1

chain aliphatic diols with diisocyanates at diol concentrations of 10 - 30%. Considerable reduction in the rigidity of the polymer backbone is obtained from diol chain extenders due to the lack of bulky aromatic groups. Aromatic groups produce an increase in the rigidity of a polymer chain by limiting its rotation.

Aliphatic diols evaluated were: ethylene glycol; 1,3-propanediol; 1,4-butanediol; and 1,5-pentanediol.

Using a 60/40 ratio of LK-380 (trifunctional aromatic polyether) and LA-700 (pentafunctional polyether of ethylene diamine-polypropylene oxide) as the basic formulation, specific percentages of diol were substituted while maintaining the 60/40 ratio of polyol.

The results based on the compressive strength/density constant discussed previously indicate no improvement in compressive strength was realized. The basic formulation gave the highest constant - 6.32 - while 10% 1,4-butanediol was the best diol, showing a constant of 5.74.

The data for this series of foams are given in Table 22. It will be noted that foam density varied from 1.8 lbs./ft.^{3} in the control to 3.5 lbs./ft.^{3} in the foam containing 30% 1, 4-butanediol, in spite of the fact that pneumatogen (water) level remained constant throughout. The anticipated effect of the diol additive on modulus (and compressive strength) may have been masked as a result of this density variation.

Since the possibility existed that we may have passed through a maximum at lower diol concentration, the effect of incorporating 2% and 5% of 1, 4-butanediol and 1,5-pentanediol into the basic formulation was investigated.

In general, as can be seen in Table 23, decreasing the diol levels resulted in significant decreases in strength-density constant.

In re-analyzing the data obtained from diol incorporation, density, compressive strength, and the evaluation factor were plotted versus the number of carbon atoms present in the diols substituted at the 20% level (ethylene glycol- 2C; 1,3-propanediol - 3C, etc.). As seen in Figure 13, although the density and strength values reach a maximum at the 3-4 carbon level, the evaluation factor is at

TABLE 22

INVESTIGATION OF POLYMER CHAIN EXTENDING DIOLS IN RIGID URETHANE FOAMS

Composition and Properties		Foam Number						
		57.6	57.0	57.1	57.2	57.3	57.4	57.5
Polyol Component	LK-380 (gms)	60	48	48	54	48	42	48
	LA-700 (gms)	40	32	32	36	32	28	32
	Ethylene Glycol (gms)	-	20	-	-	-	-	-
	1,3-Propanediol (gms)	-	-	20	-	-	-	-
	1,4-Butanediol (gms)	-	-	-	10	20	30	-
	1,5-Pentanediol (gms)	-	-	-	-	-	-	20
Pneumatogen	– Water (gms)	5	5	5	5	5	5	5
Foam Stabilizer	– DC-113 (gms)	2	2	2	2	2	2	2
Isocyanate	– Mondur MR (gms)	188	249	233	205	222	214	214
	Density (lbs./ft.^{3})	1.80	2.52	2.98	2.16	2.97	3.46	2.51
	Compressive Strength (psi)	20.6	33.2	41.2	26.9	41.8	52.9	32.9
	Evaluation Factor (psi/d^2)	6.37	5.24	4.64	5.77	4.74	4.42	5.23

TABLE 23

LOW MODULUS RIGID FOAMS

	59.0	59.1	59.2	59.3
LK-380	59	57	59	57
LA-700	39	38	39	38
DC-113	2	2	2	2
Water	2	2	2	2
Mondur MR	143	155	144	158
1,4-Butanediol	2	5	-	-
1,5-Pentanediol	-	-	2	5
Density, lbs/ft^3	3.90	4.55	4.08	3.96
Compressive Strength, psi	59	85	49	52.5
Evaluation Factor $(\frac{psi}{\rho^2})$	3.85	4.1	2.9	3.43

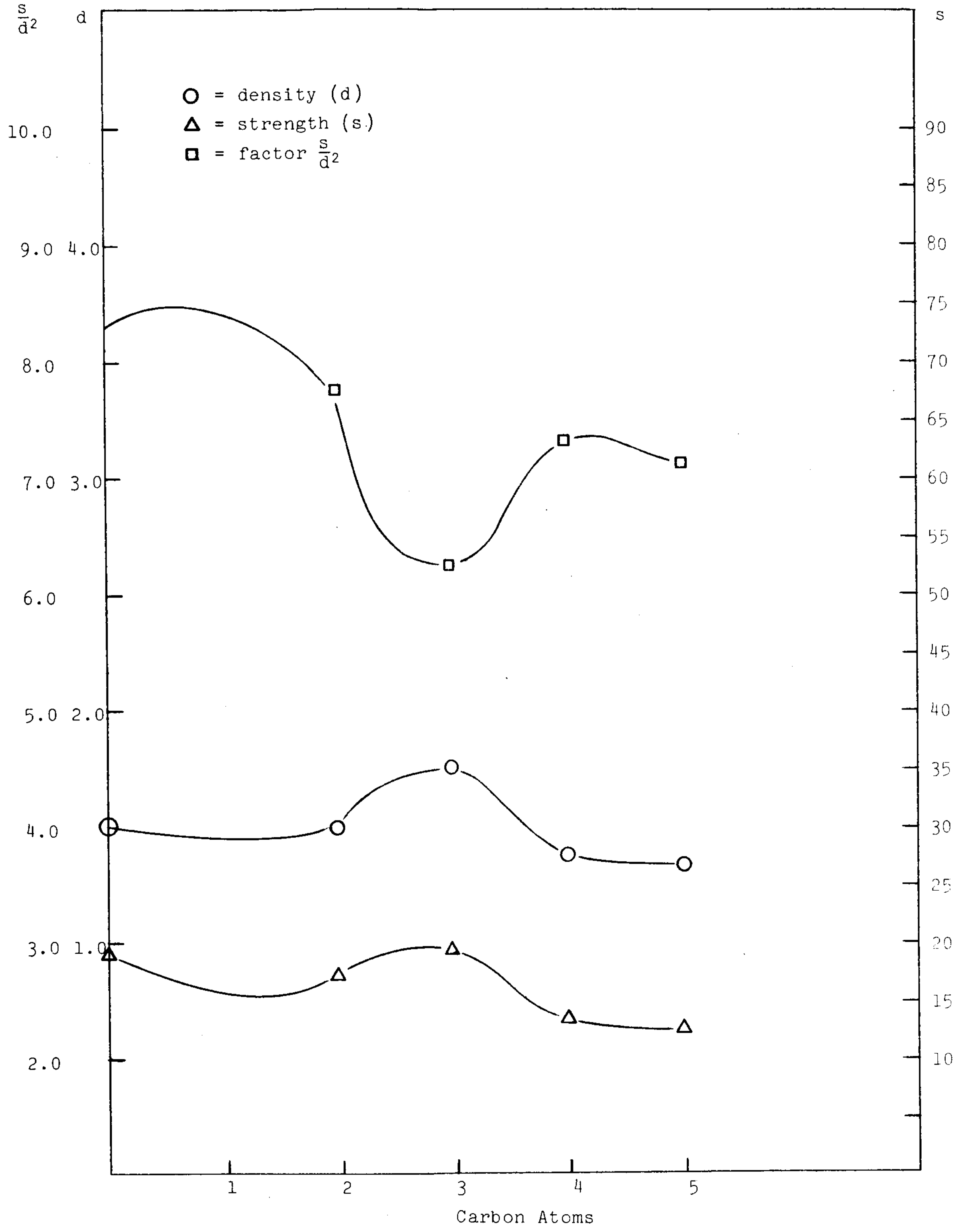


Figure 13. Effect of Number of Carbon Atoms Present in Incorporated Diols

a minimum at this point and begins to increase at the 5-carbon level. Longer chain diols (1,6- and 2,5-hexanediol, 1,10-decanediol) were compared to diols of 2 to 5 carbon atoms in a "standard" Freon-blown, rigid urethane formulation at the 20% substitution level. Additionally, 1, 4-butanediol and 1,6-hexanediol were evaluated at the 90% level.

As seen in Table 24, no significant differences were noted from diol incorporation. In general, most of the diols showed lower evaluation factors, psi/d^2, than the control. Foam Nos. 62.8 and 62.9, which contain 20% 2,5-hexanediol and 1, 10-decanediol, respectively, were slightly better from the compressive-strength standpoint than the control sample; however, the improvement is not significant.

To further investigate the effect of lower modulus on compressive strength, polypropylene glycols of 700 and 2000 molecular weight (PPG 700 and PPG 2000) were also evaluated. In addition, prepolymers normally used for elastomeric applications, Adiprene L-100 and L-315, were evaluated as polyols. The elastomeric prepolymers which are isocyanate-terminated are normally in the 2000-3000 molecular weight range. The comparatively longer chain lengths between crosslinks from the above polyol systems contribute to greater flexibility and lower modulus than found in polyfunctional, lower molecular weight, rigid foam polyols.

Polyglycol of 700 molecular weight (PPG700) was evaluated at the 40% level (60% LK-380) in Freon-blown systems utilizing TDI and Mondur MR. Additionally, blends of 60/40 PEP 550/PPG 700, 48/12/40 LK-380/LA-700/PPG 700 (TDI and Mondur MR), and 70/30 and 50/50 of LK-380/PPG 700 were evaluated.

As seen in Table 25, the polyglycol-based foams were of lower compressive strength than normally obtained from rigid foam polyol resins. The best foam in terms of strength properties was the 60/40 LK-380/PPG 700-Mondur MR system which showed an evaluation factor of 3.33 (4.25 = average foam).

Difficulties were encountered in attempting to produce foams based on polypropylene glycol of 2000 molecular weight. All foams prepared from this system collapsed. The foams were very slow-curing, even though excessive amounts of catalyst were used. The slow curing rate

TABLE 24

FREON BLOWN DIOL SUBSTITUTED RIGID FOAMS

Foam No.	62.0	62.1	62.2	62.3	62.4	62.5	62.6	62.7	62.8	62.9	64.0A	64.0B	64.1
LK-380	40	48	48	54	48	42	48	48	48	48	10	10	10
LA-700	60	32	32	36	32	28	32	32	32	32			
DC-113	2	2	2	2	2	2	2	2	2	2	5	5	5
Freon 11	50	50	50	50	50	50	50	50	50	50	10	10	10
Mondur MR	119	180	164	136	153	170	145	140	140	125	233	271	209
Ethylene Glycol		20											
1,3-Propanediol			20										
1,4-Butanediol				10	20	30					90	90	
1,5-Pentanediol							20						
1,6-Hexanediol								20					90
2,5-Hexanediol									20				
1,10-Decanediol										20			
C-16											1	1	1
Density, lbs/ft^3	1.516	1.486	1.764	1.515	1.378	1.915	1.348	1.482	1.427	1.543	5.25	3.26	3.56
Strength, psi	19	17	19.5	19.5	13.5	19	13	15.5	17	21.5	106	33	61
Constant, psi/d^2	8.30	7.75	6.25	8.70	7.32	5.17	7.13	7.18	8.41	8.90	3.84	2.77	4.80

TABLE 25

POLYPROPYLENE GLYCOL SUBSTITUTED RIGID FOAMS

Foam No.:	64.2	64.3	64.4	64.5	64.6	64.7	64.8
LK-380	90	90		72	72	105	75
PEP 550			90				
LA-700				18	18		
PPG CP-700	60	60	60	60	60	45	75
Freon 11	15	15	15	15	15	15	15
TDI	77		86	85			
Mondur MR		113			128	118	95
C-16	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DC-113	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Density, lb/ft^3	4.774	5.149	5.832	5.114	5.170	4.997	5.895
Strength, psi	44	88	40	30	84	84	32
Constant, psi/d^2	2.09	3.33	1.27	1.24	3.19	3.37	0.94

resulted in unstable cell structures, due to the low degree of crosslinking. Apparently, the cell structures were unable to maintain their configuration under the reduced pressure conditions existing inside the foam cells (as the foam cooled), resulting in foam collapse.

Adiprene L-100 prepolymer (4.25% free NCO) was evaluated in Freon-TDI and water-Mondur MR systems at 10, 20, 30, and 40% blends with LK-380 polyol. Adiprene L-315 prepolymer (ca. 9% free NCO) was evaluated in water-Mondur MR, water-TDI, and Freon-TDI systems at the 20% level.

As can be seen in Table 26, in no case was the blend of higher strength than the control. In general, the strength-to-density ratio appeared to decrease as the level of prepolymer increased.

Investigation of Reinforcing Fillers to Improve Foam Strength

Foam strength is optimized when the material is located entirely in the cell struts rather than in the thin membranes which are the cell walls. Additionally, foam strength is dependent upon the elastic modulus of the polymer and the L/D ratio of the struts. We obtained a number of high-modulus fibrous material for evaluation as fillers in rigid urethane foam formulations. These fibers were chosen on the basis of fiber length equal to the average cell diameter in 4 pcf rigid foam, with an L/D ratio such that the film has good stiffness. The fiberousmaterials include single crystal silicon carbide, fiberous potassium titanate, glass, fiberous colloidal alumina, fine nylon fiber, asbestos, acrilan, cotton, and cotton-rayon fibers. Foams were prepared to evaluate these fibers with Freon 11 used as the blowing agent. Fiber level was varied from 1-10% (based on formula wt.).

We found no evidence that the fibers were acting to reinforce the foam structure. In fact, in a few of the foams, the fibers appeared to be detrimental to compressive strength. One reinforced rigid foam was produced that contained 5% of a fibrous filler. Short lengths of narrow Mylar ribbon (0.5" x 0.015" x 0.002") were used for this purpose. The fibers were not uniformly distributed throughout this foam product, and therefore they did not improve

TABLE 26

ADIPRENE SUBSTITUTED RIGID FOAMS

Foam No.	63.0	63.1	63.2	63.3	63.4	63.5	63.6	63.7	63.8	63.9	63.10	63.11	63.12
LK-380	150	135	120	105	90	150	135	120	105	90	120	120	120
Adiprene L-100		15	30	45	60		15	30	45	60			
Adiprene L-315											30	30	30
DC-113	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Freon 11	15	15	15	15	15								15
TDI	89	80	70	60	51							98	68
Mondur MR						161	147.5	134	120	106	132		
Water						3	3	3	3	3	3	3	
C-16	1.5	1.5	1.5	1.5	1.5	1	2	2	2	2	2	1.5	1.5
Density, lbs/ft^3	4.05	4.94	5.24	5.18	5.91	3.98	3.79	4.06	3.26	3.54	3.73	3.35	4.94
Strength, psi	62.9	79	75.7	49.4	36.7	69.6	58.1	35.6	37.5	9.4	26	36	55
Constant, psi/d^2	3.84	3.23	2.74	1.83	1.06	4.41	4.05	2.22	3.53	0.740	1.88	3.21	2.26

its strength.

Difficulties were encountered in attempting to incorporate the fibrous materials into the foam formulations because of agglomeration of the fibers upon wetting.

The effect of very fine nylon fiber (0.030" long, 2.0 and 3.0 denier) on foam strength was investigated. The fiber length is the smallest evaluated during the program and was obtained from Microfibres, Inc. It was felt that if the fibers were oriented in the struts, the elastic modulus should increase and, in conjunction with low L/D ratio, the strength should increase. Also, since the organic fiber has the same density as the solid resin, separation of the reinforcing substrate during polymerization should be minimized.

Fiber levels of 10, 20, and 30 grams of each denier were studied. Formulations and test results are shown in Table 27. As seen in the table, foam strength decreases and density increases as the level of incorporated fiber increases. Fiber levels less than 10 grams will be evaluated, e.g., 2, 5, 7 grams.

The effect of very fine polyester fiber (1 mm long, 1.5 denier) on foam strength was evaluated. The fibers were obtained from Chemstrand, a division of Monsanto. Fiber levels of 3, 13, 20, and 26 grams were studied. Formulations and test results are shown in Table 27. Formulations 84.2 and 84.3 containing 20 and 26 grams of fiber, respectively, were too dry to mix and were discarded.

Miscellaneous fillers investigated included unexpanded and pre-expanded polystyrene beads, powdered polystyrene, 1/8" strips of Mylar ribbon, urea-formaldehyde microballoons, aluminum, silver, gallium powder, mica, graphite, and cellulose. As seen in Table 27, no reinforcement was realized.

The limited data indicates that an increase in fiber content decreased the resultant density and strength. No improvement in properties was obtained; consequently, work was discontinued.

TABLE 27

EVALUATION OF FIBROUS AND PARTICLE FILLERS TO REINFORCE RIGID URETHANE FOAMS

Foam No.	Filler		Polyol		Isocyanate		Density, lbs/ft^3	Compressive Strength, psi
	Type	Amount	Type	Amount	Type	Amount		
C-1	Expanded Polystrene	10%	CP-260	-	TDI	-	4.07	26.0
61.0	Acrilan	1.18	LK-380	-	"	-	5.03	102.0
61.1	Cotton-rayon	10.0	"	-	"	-	4.03	42.0
61.2	Microballoons	13.5	"	-	"	-	3.22	20.0
61.3	Cotton	10.0	"	-	"	-	5.72	93.0
61.4	Unexpanded Polystrene	13.5	"	-	"	-	5.60	92.0
61.5	1/8" Mylar	10.8	"	-	"	-	3.91	44.0
58.6	Powdered Polystyrene	10.0	"	-	"	-	4.64	74.5
52.8	Cellulose	20 Gms.	"	170 Gms.	"	133 Gms.	3.33	46.7
55.1	Asbestos	17	"	"	"	103	3.37	38.0
52.9	Aluminum	120	"	"	"	"	3.48	40.8
52.4	Glass fibers	3	"	"	"	"	4.24	73.2
52.2	Gallium	10	"	"	"	"	4.52	81.0
52.1	Silver	15	"	"	"	"	4.59	43.0
53.0	Graphite	30	"	"	"	"	4.97	82.0
53.1	Mica	30	"	"	"	"	5.01	108.0

TABLE 27 (Continued)

Foam No.	Filler		Polyol		Isocyanate		Density lbs/ft3	Compressive Strength, psi
	Type	Amount	Type	Amount	Type	Amount		
52.0	Aluminum	15	LK-380	170 Gms.	TDI	103 Gms.	5.12	101.0
52.5	"	30	"	"	"	"	5.30	106.0
52.6	"	60	"	"	"	"	5.75	114.0
71.1	Silicon Carbide	5%	"	-	"	-	4.26	70.5
74.0	Fibrous Potassium Titanate	10	CP-260	-	"	-	3.60	47.0
74.3	"	15	"	-	"	-	3.06	41.5
74.1	Fibrous Colloidal Alumina	10	"	-	"	-	4.13	59.5
74.2	"	15	"	-	"	-	2.66	22.0
81.0	Nylon(1)	10 Gms.	SP-560 CP-260	40 Gms. 60 Gms.	Mondur MR	160	3.6	55.0
81.1	"	20(2)	"	"	"	"	4.0	54.0
81.2	"	20(3)	"	"	"	"	4.4	55.0
81.3	"	30(4)	"	"	"	"	5.1	35
81.4	Nylon(5)	10	"	"	"	"	4.2	73

TABLE 27 (Continued)

Foam No.	Filler Type	 Amount	Polyol Type	 Amount	Isocyanate Type	 Amount	Density, lbs/ft3	Compressive Strength, psi
81.5	Nylon(5)	20(3)	Sp-560/CP-260	40 Gms./60 Gms.	Mondur MR	160	4.2	56
81.6	"	30(4)	"	"	"	"	4.6	54
84.0	Polyester	3	"	"	"	"	2.8	42
84.1	"	13	"	"	"	"	1.7	11
84.2*	"	26	"	"	"	"		
84.3*	"	20	"	"	"	"		

(1) 2.0 denier

(2) 20 grams added to polyol

(3) 10 grams added to polyol; 10 grams added to Mondur MR

(4) 15 grams added to polyol; 15 grams added to Mondur MR

(5) 3.0 denier

*Discarded, too dry to mix

Effects of Pressure on the Structure of Rigid Urethane Foam

An investigation was conducted to determine whether cell wall uniformity could be improved by means of controlled pressure retardation of foaming. A Freon-blown foam formulation was poured into a pressure vessel and, at the moment the "cream" stage was reached, sufficient pressure was applied to prevent expansion. Polymerization proceeded normally, together with increasing viscosity. After a measured interval of time, the pressure was slowly released, permitting the foam to expand.

Preliminary experiments indicated that foam density is significantly affected by relatively low pressures of 10-20 psi.

A series of foam formulations were prepared by the usual one-shot Waring Blendor method. The foam composition is shown below:

150 grams	LS-490
8 grams	DC-113
20-50 grams	Freon 11
116 grams	Mondur TD-80
0.5 grams	C-16

Fifty grams of the foam formulation were poured into a cardboard carton, which was contained inside a pressure vessel in an oven. The remainder of the formulation was poured into a cardboard box and permitted to foam at atmospheric pressure to serve as a control. The formulation in the pressure vessel was foamed at various pressures and temperatures.

We found that relatively low pressures had a pronounced effect on foaming. At 30 psi (N_2 pressure), foaming was completely suppressed. At 15 psi, the foam expanded to give a uniform structure having twice the density of the control. These data are shown in Table 28. In these experiments, both water (CO_2) and Freon were used as the pneumatogens, with DC-113 or R-150 as foam stabilizer. Although no significant improvements

TABLE 28

EFFECT OF POSITIVE PRESSURE ON FOAM PROPERTIES

Base Formulation

LS-490	150 grams
TDI	116 (Freon Foams) or 138 (Water Foams)
C-16	0.5
Foam Stabilizer	8
Pneumatogen	As shown

Foam No.	Foam Stabilizer	Pneumatogen Type	Pneumatogen gms.	Pressure-Temperature psi	Pressure-Temperature °C	Density, lbs/ft	Compressive Strength psi
C45.5	DC-113	Freon	50	Atm.	25	2.70	30.8
*45.0	"	"	20	30	25	52.0	----
45.1	"	"	20	15	25	8.30	182
45.2	"	"	40	15	25	4.60	80
45.3	"	"	40	15	25	6.9	128
45.4	"	"	40	15	50	4.5	77.3
45.5	"	"	50	15	75	3.9	68.4
C46.3	R-150	Water	2.25	Atm.	25	4.8	114.3
46.3	R-150	"	2.25	15	50	8.8	286.3

*Foam rise inhibited under pressure

in strength-density were realized thereby, the experiments demonstrated that pressure can be an effective means of controlling density and cell size.

Foams prepared with 15 grams of Nitrosan have densities of 2.5 - 3.5 lbs./ft.^{3}, depending upon the amount of catalyst used. Comparable foam formulations, when foamed under 10 psi (positive) pressure, have densities near 5.5 lbs./ft.^{3}. Densities near 7.5 lbs./ft.^{3} are obtained when these same formulations are foamed under 20 psi pressure. This preliminary investigation of pressure did not produce a significant improvement in foam strength, but it established the fact that the principle was sound and workable. It is obvious that pressure is retarding bubble formation, whether Freon, water, or solids are used as blowing agents, while the viscosity of the formulation increases through polymerization. The most beneficial effects of this technique were expected to be realized in foams made with an initial positive pressure (to delay onset of foaming until polymer viscosity builds up), followed by reduced pressure to expand the foam to the desired volume. By this means, we hoped to prepare foams thicker and more uniform cell walls from the increased viscosity at the time of close packing, which minimizes the flow of material to the columns along the edges of the cell.

A series of foams were prepared using the foam formulation shown below:

170 grams	LK-380
8 grams	DC-113
N grams	Freon F-11
103 grams	Mondur TD-80
1.5 grams	C-16

Twenty grams of this formulation were placed in a pressure vessel, and positive pressure of 1 and 2 psi was applied to the closed system. The data from these experiments are shown in Table 29. In all cases, applying pressure to the foam resulted in increased density and strength. However, the evaluation factor, which allows evaluation of compressive strength characteristics independent of

TABLE 29

EXPERIMENTAL FOAMS PREPARED UNDER LOW POSITIVE AND NEGATIVE PRESSURES

Basic Formulation	
LK-380	170 grams
DC-113	8
Freon F-11	varied
Mondur TD-80	103
C-16	1.5

Run No.	Pressure	Freon, gms.	Density, lbs/ft^3	Compressive Strength, psi	Evaluation Factor
60.0	0 (Closed System)	17	4.42	86	4.4
	Control		3.96	70.7	4.45
60.1	2 psi (1)	17	5.16	112	4.5
	Control		3.93	68.5	4.4
60.2	2 psi	17	5.51	131	4.3
	Control		4.25	79	4.4
60.3	1 psi (2)	17	4.95	107	4.39
	Control		4.38	85.5	4.5
60.4	1 psi (2)	34	2.12	22	4.9
	Control		2.31	25.5	4.75
60.5 (3)	350 mm	8	-	-	-
60.6	400 mm	8	6.08	80.5	2.3
60.7	450 mm	8	6.59	90	2.07
60.8	500 mm	8	6.77	91.2	1.9
60.9 (4)	400 mm	8	-	-	-
60.10	350 mm	4	10.98	200	1.64

(1) Pressure increased to 4 psi during foaming then dropped back to 2 psi
(2) Pressure increased to 2.5 psi during foaming then dropped back to 1 psi
(3) Foam collapsed upon vacuum release
(4) Full of fissures and voids

density, was equivalent in all cases. Additionally, doubling the amount of pneumatogen (Freon F-11) resulted in decreased density in the control sample (foamed in atmosphere), as expected; however, it also resulted in decreased density under pressure with no improvement in strength.

A second series of foam experiments was run under decreased pressure conditions. Foams were subjected to decreased pressures of 350, 400, 450, and 500 mm Hg for 30 minutes. At this time, the vacuum was released. The data for this series are shown in Table 29.

As can be seen in Table 29, all foams had evaluation factors considerably below 4.25 commonly obtained from our average foams. These results are significant in that regardless of the foam compositions and conditions of foaming, the evaluation factor rarely varied significantly from 4.25. The only explanation at this time for the variance from the norm is that some collapse and shrinkage were noted in most of the foams prepared under vacuum and may have resulted in inferior foams.

b. Rigid foam systems of one to ten lbs./ft.^{3} density. In order to attain the goals of the program-that is, the development of a series of foam formulations giving a range of densities, 1 to 10 pcf - four foam formulations were selected for further evaluation, based on previous compressive strength data. The four systems, shown in Table 30, were considered the most promising "one-shot" foams prepared.

Formulation No. 75.0 showed a lower density than expected, based on previous preparation of this system. Indications are that properties from this particular formulation may be difficult to reproduce. Work conducted previously on this system indicated inconsistent densities in addition to erratic physical property values. Formulation No. 75.1 was of very high density; however, this was probably due to the lack of foam stabilizer (silicone oil) in the formulation.

Of the four formulations, Nos. 75.2 and 75.3 were selected as the base systems, and two variable density series were developed. The two base systems are blends

TABLE 30

PROMISING ONE-SHOT FOAM SYSTEMS

Foam No.	75.0	75.1*	75.2	75.3
LK-380	60	170		
LA-700	40			
SP-560			67	40
CP-260			67	60
Mondur MR	122			160
TDI		103	145	
DC-113	2		8	2
Water	4.5			
Freon 11		17	16	7
C-16		1.5	1.5	2
Density, lbs/ft^3	1.55	18	3.55	10.05
Strength, psi	11	680	58	335
psi/d^2	4.9	2.08	4.15	3.32

*Foam collapsed.

of CP-260 (trifunctional polyether, tris hydroxypropyl glycerine) and SP-560 (hexafunctional polyether, sorbitol-propylene oxide). In addition to varying in blend ratio, the two systems also differ in the type of isocyanate used; No. 75.2 is based on difunctional toluene diisocyanate and No. 75.3 based on Mondur (4,4-diphenyl urethane diisocyanate), which has a functionality of approximately 2.5. Both systems are Freon-blown. The wide variation in density obtained from the two formulations made it difficult to select the single best foam system. Foam No. 75.2 had a density of 3.55 lbs./ft.^{3}, and No. 75.3, a density of 10.05 lbs./ft.^{3}. Compressive strength data (58 psi and 335 psi, respectively) indicate both appear promising at their respective densities.

As shown in the formulations, the pneumatogen level was varied to obtain the desired density range. Series No. 78.0-78.9, based on formulation No. 75.2, is shown in Table 31. The fluorocarbon level was varied from 2 to 20 grams in two-gram increments. Rise times and strength-density data are shown in the table.

Series No. 79.0-79.10 is based on formulation No. 75.3. In this case, the Freon content was varied from 6 to 16 grams in one-gram increments. Foam rise times and strength-density data are shown in Table 32.

Series Nos. 79.0-79.10 showed consistently higher strength-at-density than Nos. 78.0-78.9. Therefore, further evaluations utilized this basic formulation.

As shown in Tables 31 and 32, small changes in Freon level produced relatively little change in density in the 3 to 4 lbs./ft.^{3} density range. Additionally, the short rise times of 2-1/2 to 3 minutes could present some difficulty in preparing large scale hand mixes.

In further experiments, the catalyst was removed entirely (No. 79.11) and reduced to one-half its original amount (Nos. 79.12-79.14). In No. 79.11, no rise was noted after 25 minutes. The foam was placed in an oven at 70°C; after 20 minutes, normal rise had occurred. This extremely slow rise time would be impractical in

TABLE 31

DENSITY SERIES INVESTIGATION

Base Formulation

SP-560	67 grams
CP-260	67
TDI	145
DC-113	8
C-16	1.5
Freon 11	Varied

FOAM NO.	78.0	78.1	78.2	78.3	78.4	78.5	78.6	78.7	78.8	78.9
Freon, gms.	2	4	6	8	10	12	14	16	18	20
Rise Time, Min.	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	3	3
Density, lbs/ft^3	9.5	9.1	7.9	5.6	4.7	4.2	3.4	3.1	3.2	2.8
Compressive Strength, psi	318	228	237	128	94	73	49	41	40	33

TABLE 32

DENSITY SERIES INVESTIGATION

Basic Formulation

SP-560	40 grams
CP-260	60
Mondur MR	160
DC-113	2
C-16	2
Freon 11	Varied

FOAM NO.	79.0	79.1	79.2	79.3	79.4	79.5	79.6	79.7	79.8	79.9	79.10
Freon, grams	6	7	8	9	10	11	12	13	14	15	16
Rise Time, min.	3	3	3	3	3	3	3	3	3	3	3
Density, lbs/ft.^{3}	9.87	7.6	7.2	6.5	6.6	6.4	5.8	5.2	4.6	4.5	4.4
Compressive strength, psi	334	218	201	171	177	165	143	120	102	94	90

actual service. As seen in Table 33, little effect on density was noted. However, a significant decrease in compressive strength occurred.

In Experiments No. 79.12-79.14, rise times were increased to 6-1/2 to 7 minutes, as shown in Table 33. This is a significant improvement compared to Nos. 79.0-79.11. Strength-density data are also shown in the table.

The effect of higher boiling pneumatogen, Freon 113, on foam rise time and density was evaluated in the original formulation. As seen in Table 33, little increase in rise time occurred. Additionally, at the pneumatogen levels investigated (6, 11, and 16 grams), the densities were considerably higher than those obtained from Freon 11-blown systems.

Since 1 gram of catalyst (C-16) allowed practical working times, the experiments were repeated in a continuing effort to obtain the desired density range series. Freon 11 levels of 7, 8, 9, 13, 22, 25, 40, 45, and 65 grams were investigated. The results are shown in Table 34.

Table 35 shows the projected density series from 1 to 10 lbs./ft.^{3}, compressive strengths, and the respective pneumatogen levels. All density levels appeared to be finalized, with the exception of the 10 lbs./ft.^{3} density formulation. The proposed formulation for this density level was repeated twice to determine its reproducibility. The results are shown in Table 36. As seen in the table, reproducibility was excellent. As a result of this, no further formulation development was conducted.

Further study of the foam series included catalyst level variation, reproducibility of foams at the 4 lbs./ft.^{3} density level, and large-scale pours. The investigations are as follows.

Variation in Catalyst Level

In view of the fact that it may often be desirable to control the foam rise, i.e., speed up or slow down, the effect of catalyst level on foam rise time was studied.

TABLE 33

DENSITY SERIES INVESTIGATION, EFFECT ON FOAM RISE RATE

FOAM NO.	79.11	79.12	79.13	79.14	79.15	79.16	79.17
SP-560	40	40	40	40	40	40	40
CP-260	60	60	60	60	60	60	60
DC-113	2	2	2	2	2	2	2
Mondur MR	160	160	160	160	160	160	160
C-16		1	1	1	2	2	2
Freon 11	6	6	11	16			
Freon 113					6	11	16
Rise Time, min.	45*	7	6.5	7	3	3.5	3.5
Density, lbs/ft.^{3}	9.6	11.0	5.8	4.3	14.6	8.4	5.9
Compressive strength, psi	261	384	134	84	656	249	145

*Twenty-five minutes at room temperature plus 20 minutes at 70°C.

TABLE 34

DENSITY SERIES DEVELOPMENT

Basic Formulation

SP-560	40 grams
CP-260	60
Mondur MR	160
DC-113	2
C-16	1
Freon 11	Varied

FOAM NO.	79.18	79.26	79.19	79.20	79.28	79.21	79.29	79.22	79.23
Freon, gms	7	8	9	13	22	25	40	45	65
Rise time, min.	6.5	5.5	6.5	6.5	8	10	11.5	10	17
Density, lbs/ft.^{3}	9.4	8.6	6.5	5.2	3.1	2.6	1.9	1.6	1.1
Compressive strength, psi	290	265	157	112	49	36	19	16	9

TABLE 35

PROJECTED DENSITY SERIES

Basic Formulation

SP-560	40 grams
CP-260	60
Mondur MR	160
DC-113	2
C-16	1
Freon 11	Varied

FOAM NO.	79.23	79.29	79.28	79.14	79.20	79.13	79.27	79.26	79.18	79.25
Freon, gm	65	40	22	16	13	11	9	8	7	6
Density, lbs/ft.^{3}	1.1	1.9	3.1	4.3	5.2	5.8	6.6	8.6	9.4	9.4
Compressive strength, psi	9	19	49	84	112	134	169	265	290	308

TABLE 36

TEN LBS/FT^3 DENSITY FOAM FORMULATION

SP-560	40 grams
CP-260	60
DC-113	2
Freon 11	6
Mondur MR	160
C-16	1

	Trial No. 1	Trial No. 2
Foam Rise Time, Min	6	6
Exotherm, °C	152	156
Density, Lbs/Ft^3	10.2	10.3
Compressive Strength, psi	345	345

Utilizing the 4 lbs./ft.^{3} density foam formulation as a base, the catalyst (C-16) level was varied from 0 to 2 parts. Foam rise time and temperature exotherm were recorded and are shown in Table 37. As expected, foam rise time decreased as the catalyst level increased. However, the fact that no rise was noticed after more than 16 hours with no catalyst present was surprising. The addition of 0.5 phr C-16 significantly decreased foam rise time to 17 minutes.

Reproducibility of Foam Formulation

To determine the reproducibility of the developed foam formulations, the foam system representing the 4 lbs./ft.^{3} level was repeated five times, and density and compressive strength determined. As seen in Table 38, excellent reproducibility of results was obtained; density ranged from 4.3 to 4.7 lbs./ft.^{3}, and strength was from 84 psi at 4.3 lbs./ft.^{3} to 99 psi at 4.7 lbs./ft.^{3}. Foam rise times ranged between 7 minutes to 7.5 minutes. Due to the favorable results, no further work along these lines was conducted.

Large-Scale Pours

As part of the program, the feasibility of scale-up from bench quantities to larger amounts in foam preparation was investigated. Hand mixing and machine processing were studied.

Hand Mixing

Initially, the formulations representing the one and four lbs./ft.^{3} densities were increased to three times the normal lab quantity (279 gms). Results correlated well with those obtained from standard quantities in both cases: 1.4 and 4.4 lbs./ft.^{3} densities versus 1.1 and 4.3 lbs./ft.^{3} from lab quantities, and 13 and 90 psi compressive strength compared to 9 and 84 psi.

The scale-up to pound quantities was carried out utilizing the 4 lbs./ft.^{3} density formulation as a repre-

TABLE 37

CATALYST LEVEL STUDY

Base Formulation

SP-560	40 grams
CP-260	60
DC-113	2
Freon 11	16
Mondur MR	160
C-16	Varies

Foam No.	83.8	83.9	79.14	83.10	79.10
Catalyst, grams	0	0.5	1	1.5	2.0
Foam Rise Time, Min.	No Rise >16 hrs	17	7.5	5	3
Exotherm, °C	---	135	156	149	164
Density, lbs/ft^3	---	4.4	4.3	4.6	4.4
Compressive strength, psi	---	86	84	99	90

TABLE 38

REPRODUCIBILITY OF FOAM SYSTEM

Formulation

SP-560	40 grams
CP-260	60
DC-113	2
Freon 11	16
Mondur MR	160
C-16	1

Trial No.	1	2	3	4	5
Foam Rise Time, Min.	7	7.5	7.5	7.5	7.5
Exotherm, °C	156	148	149	149	148
Density, lbs/ft^3	4.3	4.5	4.5	4.5	4.7
Compressive Strength, psi	84	90	92	92	99

sentative system. Quantities were as follows:

SP-560	8 lbs.
CP-260	12
Mondur MR	32
Freon 11	3.2
DC-113	0.4
C-16	0.2

The polyols were stirred by an air-driven stirrer until homogeneous. The Freon and DC-113 were added to the polyol mixture, stirred for 4 hours, and allowed to stand overnight. Approximately 1/4 to 1/2 lb. of Freon was lost through evaporation overnight. This loss was replenished.

Mondur MR was charged to a large container and the polyol-pneumatogen-DC-113 mixture added. The resultant mixture was stirred by an electrically driven stirrer for approximately 5 minutes and the catalyst, C-16, added. Stirring continued for 45 seconds and stopped. The mixture was poured into a box 1' x 4.25' x 4.25'. The pouring was initiated at one corner, continued across the front of the box, and then back to the original corner. Foaming initiated at 3 minutes after pouring, and the foam set at 6 minutes. Exotherm was 180°C.

Density and strength data from samples removed from the block are shown in Table 39. Densities were higher than expected; however, this may be due to pneumatogen loss prior to foaming. When cutting through the large pour foam, slight cracking was evident in the center portions. The cracks may be due to the high exotherm developed during foaming and subsequent curing. In order to reduce the developed exotherm, trichloroethylene was added as a heat sink. The following formulation was prepared in bench quantities:

SP-560	40 grams
CP-260	60
Mondur MR	160

TABLE 39

DATA FROM SAMPLES REVIEWED FROM LARGE-POUR

LOCATION	LEFT-BACK TOP	LEFT-BACK BOTTOM	CENTER	RIGHT-FRONT TOP	RIGHT-FRONT BOTTOM
Density lbs/ft^3	4.8	4.8	4.8	4.7	4.6
Compressive Strength, psi	86	96	85	84	87

DC-113	2 grams
Freon 11	16
C-16	1
Trichloroethylene	32

The exotherm decreased to 128°C from 150°-160°C normally obtained from lab quantities. However, the density also decreased to 1.7 lbs./ft.^{3} due to the trichloroethylene acting as pneumatogen.

The formulation was scaled to pound quantities for large-pour purposes; however, the Freon level was reduced one-half to compensate for the pneumatogen effect of the trichloroethylene.

The foam split and was not tested. It appears that the excessive exotherm generated in large-scale pours causes slight fissure formation, though not detrimental to density or strength properties.

Machine Processing

As an integral part of the NASA foam program, machine processing of the foam system giving 4 lbs./ft.^{3} density was studied in the L-50 Stafoamer. The formulation was prepared in two parts as follows:

Part I		Part II
SP-560	12 lbs.	Mondur MR
CP-260	18	
Freon 11	5 (slight excess)	
DC-113	0.6	
C-16	0.3	

Upon mixing part I, an undetermined amount of Freon was lost through evaporation at the time of its incorporation. However, process development continued regardless of Freon loss, to determine handling characteristics.

After calibration of the resin mixture and pneumatogen pumps, five pours were made into containers of varying volume as summarized in Table 40. As seen in Table 40, all densities were higher than the 4 lbs./ft.^{3} range. However, due to the aforementioned loss of pneumatogen, the density data were not unexpected.

No fissures or cracks were noted when the foams were cut. Very little shrinkage was observed, although some "undercutting" was observed. Undercutting is caused by initiation of foam rise before the shot is complete and is the result of the foam machine being incapable of large, fast deliveries. From the data obtained from the machine pour experiments, it appears a machine larger than the L-50 Stafoamer would be required for large pours.

c. Heterogeneous foams. It should be possible to obtain a foam of superior strength characteristics with a heterogeneous mixture of two incompatible foams of different densities. The resulting composite foam should have a density intermediate between that of the two parts, and should have strength characteristics which, in the ideal case, approach that of the most dense part. The degree to which the strength approaches the ideal case will depend largely upon the special arrangement of the component foam structures which in turn depend upon the method of mixing.

Initial efforts at heterogeneous foaming utilized two parts of identical polyol-isocyanate composition, but with one part being void of pneumatogen and foaming agent. The objective was to find an efficient method of blending the two parts in the manner desired. We found that the compatibility of the two parts was such that the pneumatogen quickly diffused from one into the other, resulting in a homogeneous, rather than heterogeneous, foam.

A significant improvement was made in obtaining a heterogeneous system by mixing togethertwo foam formulations wherein the polyol in formulation #1 was not compatible with the isocyanate in formulation #2. Freon pneumatogen was added to formulation #1 only.

TABLE 40

MACHINE PROCESSED FOAM

Designation	MF-1	MF-2	MF-3	MF-4	MF-5
Container Size, inches	6X8X8	6X8X8	17.5X23.5X15.5	7X12X16	8 1/2X11X15
Density, lbs/ft^3	4.8	4.9	4.9	5.2	5.0
Compressive Strength, psi	110	121	123	118	119

FORMULATION #1

SP-560	(Hexafunctional polyether)
DC-113	
Freon, 11	
Mondur TD-80	(Tolylene diisocyanate)

FORMULATION #2

LS-490	(Hexafunctional polyether)
DC-113	
PAPI	(Trifunctional isocyanate)

Mixing was accomplished by simply pouring the two individually blended formulations together into a cardboard box. The foam rise time for formulation #1 was about five minutes. During this time, the high density formulation was effectively dispersed in the expanding low density foam (e.g., the outlines of the high density areas were clearly defined in every portion of the composite structure).

The preliminary work on heterogeneous foam progressed to the point where a method of preparation was established. Our first experimental products showed a slight improvement in strength ($psi/d^2 = 5.6$) compared with the average commercial rigid urethane foam.

It was felt, however, that heterogeneous foams would impose limitations on the application of these materials due to the directional nature of their strength and insulation properties. Accordingly, the remaining time was devoted to optimizing and developing our preferred system.

2. Prepolymer Based Rigid Foams

The prepolymer method of rigid foam formulation was investigated to evaluate its effect on compressive strength compared to the one-shot method.

Initially, prepolymers were prepared from the following systems: LS-490 (sorbitol-propylene oxide) /TDI, LS-490/ Mondur MR, CP-260 (tris hydroxypropylene glycerine)/TDI, and Voranol RS-375 (sucrose-propylene oxide)/TDI.

Two prepolymers were prepared from 100 parts of LS-490 added to 320 parts of TDI. In the first, no external heat was applied during prepolymer preparation; as a result, the reaction temperature attained a maximum of only 40°C. Mild heat was applied to the second; reaction temperature reached, and maintained, 100°C for one hour.

Based on the two above prepolymers, three foams (Nos. 72.0, 72.1, and 72.2), were formulated utilizing Quadrol [tetrafunctional N,N,N',N', tetrakis (2-hydroxy propyl)-ethylene diamine] as the crosslinking resin. All three foams had extremely fine cell structures. As seen in Table 41, No. 72.2 prepared from the second prepolymer, showed a significant improvement in strength characteristics. The compressive strength, 53 psi at 2.9 lbs./ft.^{3} density, is the highest obtained at this density to date. From these results, it appears the reaction temperature is very important (40°C vs. 100°C).

Nos. 72.0 and 72.1, prepared from the first prepolymer, varied in density and strength significantly. Foam No. 72.0 had a density of 2.5 lbs./ft.^{3} and evaluation factor of 4.33. The results compare favorably with foams obtained from the one-shot method. Foam No. 72.1, containing double the Quadrol content of 72.0, was of lower density (1.7 lbs./ft.^{3}) and showed excellent compressive strength (28 psi) and high psi/d^2 factor (8.9).

Attempts to obtain prepolymers from LS-490/Mondur MR and Voranol RS-375/TDI systems were unsuccessful. The prepolymer reactions were characterized by rapid temperature rise resulting in solidification. Efforts to obtain prepolymers from these systems were discontinued.

TABLE 41

PREPOLYMER BASED RIGID FOAMS

	1		2	3		4
Prepolymer Ratio	LS-490/TDI 100/320		LS-490/TDI 100/320	CP-260/TDI 100/320		CP-260-TDI 100/410
Reaction Conditions	1 hr. @ 40°C		1 hr. @ 100°C	1 hr. @ 100°C		1 hr. @ 85°C ±5°C
Foam	72.0	72.1	72.2	72.3*	72.4**	72.5
Prepolymer	100 (1)	100 (1)	100 (2)	100 (3)	100 (3)	95.4 (4)
Quadrol	23	46	46	52	52	
Freon 11	16	16	16	10	10	12
L -520	0.5	0.5	0.5	0.7	0.7	
RS-375						100
DC-113						0.6
C-16						0.6
Density, lbs/ft^3	2.587	1.780	2.965			7.0
Strength, psi	29	28.1	53.6			178
Constant, psi/d^2	4.33	8.87	6.10			3.68

*Quadrol added last; difficult to mix.

**Prepolymer added last; foamed in blender

(1) Prepolymer 1
(2) Prepolymer 2
(3) Prepolymer 3
(4) Prepolymer 4

Two prepolymers were prepared from the CP-260/TDI system. The first consisted of 100 parts of CP-260 added to 320 parts of TDI. Two foams were prepared from the prepolymer, utilizing Quadrol as the crosslinking resin. Poor mixing was encountered in the first foam due to the high viscosity of Quadrol. The resultant foam was non-uniform and unsatisfactory for evaluation. In the second foam, Freon 11 was added to Quadrol in an attempt to decrease the viscosity and the prepolymer added to the mixture. Mixing was satisfactory; however, the reaction was extremely fast, and the formulation foamed in the blender. Work on this system was discontinued.

The second prepolymer consisted of 100 parts of CP-260 and 410 parts TDI. A foam, No. 72.5, was prepared based on this prepolymer utilizing Voranol RS-375 (octa-functional sucrose-propylene oxide) as the crosslinking resin. As seen in Table 41, no significant improvement in strength was realized. The evaluation factor (psi/d^2), 3.68, approaches that normally associated with this density.

It appeared that a significant increase in compressive strength was gained from the prepolymer approach of foam preparation in the desired higher density range (4 lbs./ft.^{3}). Also, some improvement in strength characteristics was obtained in the lower density range (2-3 lbs./ft.^{3}), as evidenced by high strength-to-density ratios.

The formulation giving the highest strength was Freon-blown and based on LS-490/TDI prepolymer (100 parts/320 parts), utilizing Quadrol as the crosslinking resin. Since the density was slightly low (goal - 4.0 lbs./ft.^{3}), the Freon level was adjusted in an attempt to increase the density. This formulation, designated No. 75.4 and shown in Table 42, had a density of 4.2 lbs./ft.^{3} and a compressive strength of 112 psi. This was the highest strength obtained at this density. A major drawback of this formulation, however, is the fast foam time. The formulation was stirred for 18 seconds and poured. Within one minute, foaming was complete. Obviously, this fast foam time would limit the utility of this system.

The high reactivity of the formulation is believed due to the amine-base characteristic of Quadrol [N,N,N',N',-Tetrakis(2-hydroxypropyl)ethylenediamine], which serves as catalyst. Further investigation was conducted in an attempt to increase the foam time by replacing Quadrol as

TABLE 42

PREPOLYMER BASED RIGID FOAMS - TDI

				Prepolymer No. 1		Prepolymer No. 2			
		Prepolymer Ratio, gms		LS-490/TDI 100/320		SP-760/TDI 100/320			
		Reaction Conditions		1 hour at 100°C		1 hour at 100°C			
Foam No.	75.4	75.6*	75.7	75.8	75.9	77.1	77.2	77.3	77.4
Prepolymer	200 gms(1)	100(2)	100(2)	100(2)	100(1)	100(1)	100(1)	100(1)	100(1)
Quadrol	92	46						10	23
Freon 11	20	10	10	10	10	10	10	10	10
L-520	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
SP-760			110	110	110				
N,N-Dimethyl-piperazine				1	2				
UI-800						46			
RS-350							108		
PeP 550								66	41
**Reaction Time. min	1		15***	15	9	0.5	15***	30	6
Density, lbs/ft^3	4.2		7.01	9.7	7.0	4.4	7.5	6.15	5.2
Strength, psi	112		164	272	171	104	177	142	116
psi/d^2	6.2		3.19	2.87	3.45	5.36	3.17	3.75	4.3

(1) Prepolymer No.1
(2) Prepolymer No.2

* Foam set up in blender.
** Time elapsed from initiation of stirring to non-tacky surface.
*** Placed in 75°C oven at 10 minutes.

the crosslinking resin with other polyols. Other polyols evaluated were: UI-800 (similar to Quadrol, but lower viscosity), Voranol RS-350 (octafunctional, sucrose-propylene oxide), SP-760 (hexafunctional, sorbitol-propylene oxide), and blends of Pluracol PeP 550 and Quadrol. (PeP 550 is a tetrafunctional aliphatic polyether.) Formulations and data are shown in Table 42.

As shown in Table 42, RS-350, SP-760, and PeP 550/Quadrol, decreased the reaction rate considerably. However, UI-800, which is amine-based, was exceedingly fast.

In a further attempt to decrease the reaction rate, it was felt that preparing a prepolymer based on Quadrol (rather than LS-490), and reacting the prepolymer with LS-490 in the same ratios as the best formulation should slow the foaming. However, attempts to prepare the prepolymer were unsuccessful, resulting in solidification.

A prepolymer of SP-760 and TDI (100 parts/320 parts) was prepared by pouring all of the TDI into the SP-760 and allowing the materials to react at 100°C for one hour. SP-760 is hexafunctional and similar to LS-490. An attempt to prepare a foam utilizing Quadrol as the crosslinking resin was unsuccessful; the reaction rate was extremely fast--in fact, the foam set up in the blendor. Quadrol was replaced with SP-760 in the foam formulation; however, the system was then exceedingly slow. Two formulations, Nos. 75.8 and 75.9, were prepared utilizing N,N,-dimethylpiperazine as catalyst (1 and 2 cc). The addition of catalyst increased the foaming rage. However, as seen in Table 42, strength results were no higher than normally obtained from the one-shot method.

Additional prepolymers were prepared utilizing Mondur MR as the isocyanate. Polyols evaluated were CP-260 (10 parts CP-260/300 parts MR), LS-490 (27 parts/320 parts MR), and LK-380 (30 parts/300 parts MR).

Previous attempts to prepare prepolymers based on Mondur MR were unsuccessful, generally resulting in polymerization and solidification. The solidification was felt to be caused by the two-plus functionality level resulting in crosslinking upon reacting with polyols. It was found that the addition of small amounts of catalyst to the prepolymer during preparation facilitated the formation of chain lengths (prepolymer) and resulted in decreased rate of crosslink formation.

Foam formulations based on Mondur MR-prepolymers and strength-density data are shown in Table 43. As can be seen in the table, no significant improvement in strength was realized, based on the evaluation constant, psi/d^2. This approach will not be investigated further.

Several attempts were investigated in attempts to decrease the reaction rate as follows.

1. Increased Polyol Content

It was felt that an increase in polyol content in the prepolymer should, by virtue of decreased available TDI, decrease the relative reactivity of the isocyanate in its subsequent reaction with Quadrol. The ratio of polyol (LS-490) to TDI in the prepolymer giving the highest strength is 100/320. Consequently, a prepolymer was prepared containing 120 grams LS-490 and 320 grams TDI. The prepolymer was prepared by pouring all of the TDI into the LS-490 and allowing the materials to react for one hour at 100°C. Attempts to prepare prepolymers of higher polyol content were unsuccessful, resulting in solidification during preparation.

Foam formulations based on this prepolymer and strength-density data are shown in Table 44. Foam No. 77.7 is similar to the best foam formulation (Ref. No. 75.4) with an adjustment in Quadrol content based on free TDI present. As seen in the table, Foam No. 77.7 showed a marked decrease in foam strength and increased reaction rate.

Foam No. 77.8 utilized a blend of Quadrol and PeP 550 as crosslinking resins (Ref. MPR No. 10, Formulation No. 77.4). In this case, decreased reaction rate and foam strength occurred.

It appeared that increasing the polyol content in the prepolymer blend was not completely successful in decreasing the reaction rate without also decreasing foam strength. Therefore, this approach was discontinued.

TABLE 43

PREPOLYMER BASED RIGID FOAMS - MONDUR MR

Prepolymer No. 3	Prepolymer No. 4	Prepolymer No. 5
Mondur MR-300 parts	Mondur MR-320 parts	Mondur MR-300 parts
CP-260- 10	LS-490- 27	LK-380- 30
C-16- 2	Stannous Oleate- 2 drops	Stannous Oleate- 3 drops

Foam No.	76.0	76.1	76.2	76.3	76.4
Prepolymer	150 gms(3)	115(3)	125(4)	100(5)	100(5)
RS-350	167	127	124		
Freon 11	15	13	15	10	15
DC-113	7	6	5	5	5
C-16		2	1	2	2
PeP 650				72	72
Freon 113					5
Density, lbs/ft^3	22.5	15.5	15.0	6.6	3.6
Strength, psi	795	425	345	118	45
psi/d^2	1.56	1.78	1.54	2.7	3.45

(3) Prepolymer No. 3

(4) Prepolymer No. 4

(5) Prepolymer No. 5

TABLE 44

PREPOLYMER BASED RIGID FOAMS-INCREASED POLYOL

Prepolymer

Prepolymer	LS-490/TDI
Ratio, gms	120/320
Reaction Conditions	1 hr. @ 100°C

FOAM NO.	77.7	77.8
Prepolymer	100 grams	100 grams
Quadrol	45	23
L-520	0.5	0.5
Freon 11	10	10
PeP 550		41
Rise time, min	0.5	9.0
Density, lbs/ft.^{3}	4.3	4.7
Compressive strength, psi	87	101.5

2. LS-490/Quadrol Prepolymers

In a further attempt to decrease the foam rise time of the prepolymer-based foam, the concept of utilizing a blend of LS-490/Quadrol in the preparation of the prepolymer was investigated.

A blend of LS-490 and Quadrol was prepared in which the polyol ratio was equivalent to that in the original formulation. In this case, it is 24/46 or multiples thereof (LS-490/Quadrol, respectively). A portion of this blend (8.5 gm) was added to 76 gm TDI (amount of TDI in foam system) and allowed to react for one hour at 75°-80°C. Since the percentage of polyol in the new prepolymer is only 10%, it was felt the great excess of TDI should decrease the reaction rate. In the foam preparation sufficient polyol blend is added to the prepolymer to obtain a polyol-TDI level equivalent to that in the original system (24/46/76, LS-490/Quadrol/TDI). However, no change in foam rise time was noted (1 min. 15 sec.); consequently, this approach was discontinued.

3. Catalysis Investigation

Further attempts to decrease the reaction rate between free TDI present in the prepolymer and Quadrol through the use of catalytic agents were conducted. Evaluated as reaction inhibitors were ferric acetylacetonate, p-nitrobenzoyl chloride, acetic acid, and hydrochloric acid. Additionally, blends of Quadrol-PeP 500 as crosslinking resins were studied.

The formulations, foam rise times, and strength-density results are shown in Table 45. All attempts were unsuccessful. In fact, most foams started to rise in the blendor. As seen in the table, very fast foaming occurred. Since this approach held no promise, it was discontinued.

POLYESTER FOAM

Most of the experimental foams under this contract were prepared from polyether materials, rather than polyesters, because a greater selection of commercially

TABLE 45

PREPOLYMER BASED RIGID FOAMS, CATALYST INVESTIGATION

Prepolymer Ratio LS-490/TDI
100/320

Reaction Conditions 1 hr. @ 100°C

FOAM NO.	80.0	80.1	80.2	80.4	80.5	80.6	80.7	80.8
Prepolymer	100 gm	100	100	100	100	100	100	100
Quadrol	46	46	46	46	37	37	46	46
L-520	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Freon 11	10	10	10	10	10	8	10	10
Ferric Acetylacetonate	0.5							
p-nitrobenzoyl-chloride		0.5	2				1(7)	
Acetic acid				4.6(7)				
Hydrochloric acid								1(7)
PeP 550					16	16		
Rise time, min.	1(1)	1(2)	0.75(3)	0.75(4)	2	1.3	0.25(5)	1(6)
Density, $lbs/ft.^3$	4.27	4.19	3.94	3.7	3.1	4.9	3.5	2.9
Compressive strength, psi	103.5	91	86.5	38	82	129	77	59

(1) Started to rise in blendor at 20 seconds
(2) Started to rise in blendor at 18 seconds
(3) Started to rise in blendor at 12 seconds
(4) Started to rise in blendor at 12 seconds
(5) Started to rise in blendor at 5 seconds
(6) Started to rise in blendor at 15 seconds
(7) Added to Quadrol prior to foam preparation

available polyethers exist. Also, since they are cheaper, there is an abundance of technical information concerning the use of polyethers in rigid urethane foams. However, preliminary experiments with two polyester materials recommended by Mobay Chemical Company for high-strength rigid urethane foam were conducted. Mondur MR (diphenyl methane diisocyanate) was chosen to complete the urethane reaction, since we have found this to be the best isocyanate material for high-strength foam. The polyesters are identified by trade name only. They are Multron R-2 --a highly viscous, light yellow liquid with Hydroxyl and Acid numbers of 415 and 9.0, respectively; and Multron R-4 --also a highly viscous, yellow-brown liquid, with lower Hydroxyl and Acid numbers of 290 and 4.0, respectively.

Water and Freon 11 were selected as blowing agents for the initial polyester evaluation. It was necessary to heat both polyesters to about 60°C to obtain homogeneous blends with water and the foam stabilizer. After the isocyanate was added, excessive stirring was required to obtain a homogeneous blend of the reactants. We were able to prepare a high-strength rigid foam using Multron R-4 with water as the blowing agent. A compressive strength of 34 psi was recorded at 2.2 lbs./ft.^{3} foam density, which represents a 30-40% improvement over other experimental foams at this density.

Multron R-4 has a relatively low Hydroxyl number of 290 for rigid foam applications. The freshly prepared foam was quite flexible, but became rigid during the overnight cure at 75°C. An attempt was made to improve the rigidity of the foam by adding 30% Multron R-2 (Hydroxyl No. = 415). A series of polyester foams were prepared using varying amounts of water as the blowing agent. The composition and properties of these foams are given below.

Water (gms)	R-4 (gms)	R-2 (gms)	DC-113 (gms)	Mondur MR (gms)	Density lbs./ft.^{3})	Compressive Strength (psi)	psi (lbs/ft.^{3})^2
3.3	115	50	5	195	3.5	6.7	5.5
6.6	115	50	5	241	2.6	43	6.4
9	105	45	4.5	258	1.7	21	6.8

The strengths of these polyester foams are significantly higher than the experimental polyether foams, although the high viscosity of the Multron resins makes it more difficult to obtain efficient mixing during the short mixing interval.

Similar work currently under investigation for another agency has shown that solutions of resin and solvent result in lower viscosities and easier processing and foam preparation.

As shown in Table 46, two polyester-based foams were prepared. Solutions of resin and toluene were prepared initially, and no difficulties in mixing were encountered.

Foam No. 77.5 was still tacky after 30 minutes; therefore, the foam eas placed in the oven. However, this resulted in collapsed foam; consequently, no sample was available. Foam No. 77.6 utilized UI-800 (similar to Quadrol) as a crosslinking resin, and a satisfactory foam was obtained, although fissures were present. The use of polyester-based polyols appeared to present many handling problems and, based on limited data, no significant improvement in strength properties. It was decided to discontinue further effort along these lines.

Sol-Gel Analysis

Our initial approach to this project involved the evaluation of polyol and isocyanate materials in the form of dense polymers, and the selection of promising systems for investigation in rigid foam formulations. We have described the numerous high-strength urethane polymers which were obtained from this dense-polymer work, together with the surprising fact that foam strength is obviously independent of the strength (modulus) of the corresponding dense polymer. We thought that perhaps the chemical reaction between polymer and isocyanate might be influenced by the foaming process, causing the type and extent of polymerization (crosslinking) in the foam to be different from that in the dense polymer.

A series of experiments were conducted to investigate this possibility. We selected representative samples of dense polymer castings, and rigid urethane

TABLE 46

POLYESTER BASED RIGID FOAMS

Foam No.	77.5*	77.6**
Multron R-4	120 gms	96
UI-800		24
Mondur MR	125	155
Water	3	3
DC-113	6	6
Toluene	50	50
Density, lbs/ft^3		2.5
Strength, psi		10.5
psi/d^2		1.7

*Foam cracked, unsuitable for testing.

**Foam full of fissures.

Note: R-4 and Toluene were premixed to decrease viscosity of R-4.

foams cured under different conditions. The sol/gel ratio was determined for each sample. Sol/gel ratio provides a measure of the degree of crosslinking present in branched polymers. The test materials were first cut into small pieces, dried, then accurately weighed into small bottles. Methyl ethyl ketone (50 ml) was added, and the bottles were capped. The samples stood overnight in contact with the solvent. Then the solvent was removed, and the samples were dried for 24 hrs. at 80°C (or until constant weight was achieved). The samples were then re-weighed. The sol is that non-crosslinked portion of each sample which was extracted by the solvent. The gel is the insoluble portion of each sample. In addition to being insoluble, a highly crosslinked polymer will also have a low swelling index (little solvent uptake).

The results of the sol/gel tests are given in Table 47. Sol/gel data showed that the foams were as well crosslinked as the dense polymer castings. A high degree of crosslinking was evident in both cases from the low sol (sol/gel $< 8\%$) and the visually observed low swelling. The sol/gel ratios for the foams indicated that only a minimum cure time (overnight at 75°C) was required for optimum crosslinking as indicated by lowest sol content. Longer cure times or higher temperature are not beneficial, and may be detrimental if the temperature is sufficiently high to cause degradation.

It was interesting to note that the uncatalyzed foams showed more crosslinking than similar foams containing C-16 catalyst under identical curing conditions.

In the work reported above, the swelling index of the gel portion was not determined. The swelling index of the crosslinked material is the volume ratio of the gel in the swollen state to the unswollen condition and is a further indication of the degree of crosslinking. Sol-gel and swelling index analyses were conducted on solid castings and foams prepared from LK-380/TDI and SP-560/CP-260/Mondur MR systems. The results are shown in Table 48.

The results indicate that, in both systems, the dense castings may be more crosslinked than their respective foams. The high ratio of gel to sol observed in the dense bodies, compared with the foams, indicates a greater degree of crosslinking has been attained in the solid casting. This was not entirely in line with the results earlier obtained and reported (Ref. MPR No. 7). However,

TABLE 47

SOL-GEL ANALYSIS IN METHYL ETHYL KETONE

	Dense Polymers				Foams					
Sample No.	#33	#126	#137	#140	53.2	53.3	53.4	53.5	54.0	55.0
Wt. Sol (gms)	0.0213	0.0109	0.0214	0.0211	0.0010	0.0022	0.0032	0.0123	0.0212	0.0182
Wt. Gel (gms)	0.4033	0.4126	0.3782	0.4088	0.3151	0.3162	0.3185	0.3208	0.2972	0.2940
Sol/Gel %	5.3	2.6	5.7	5.2	0.32	0.70	1.00	3.87	7.16	6.18
Cure	Overnight				O'night	3 days	4 hrs.	No	Overnight	
Conditions	@ 75°C	@ 75°C	@ 75°C	@ 75°C	@ 75°C	@125°C	@125°C	Cure	@ 75°C	@175°C

Dense Polymer Compositions

#33 Mondur MR - RS-375
#126 TD-80 - CP-260
#137 Mondur MR - LK-380
#140 TD-80 - CP-260

Foam Compositions

All samples TD-80 - LK-380
53 series - no catalyst
54.0 & 55.0 - C-16 catalyst

TABLE 48

SOL-GEL AND SWELL INDEX ANALYSIS IN DI-METHYL FORMAMIDE

	LK-380/TDI	LK-380/TDI	SP-560/CP-260/ Mondur MR	SP-560/CP-260/ Mondur MR
	Foam	Solid	Foam	Solid
Designation No.	30.3	56	8.21	None
Trial No. 1				
Sol-Gel	1:43	1:153	1:51	All gel
Swell Index	1.034	1.296	1.029	1.078
Trial No. 2*				
Sol-Gel	1:57	1:112	1:70	All gel
Swell Index	1.006	1.243	1.010	1.106

*In trial No. 2, foam samples were more finely divided than No. 1

as noted above, methyl ethyl ketone (MEK) was the solvent used. In the latter work, dimethyl formamide (DMF) served as solvent. It is possible the DMF is more efficient than MEK in separating the sol and gel; hence, the difference in results.

Both dense bodies appear to be highly crosslinked, although the SP-560/CP-260/Mondur MR had virtually no sol present, which indicates an extremely high degree of crosslinking.

The results indicate the two foam systems are crosslinked to approximately the same degree as evidenced by equivalent sol/gel ratios.

Mechanical Foams

Mathematical analyses indicated that the strength of a foam system is a function of its density. If we take a block of high-density material, i.e., 10 lbs./ft.^{3}, and mechanically take away half of the material, an apparent density of half the original value would be obtained. Since the original strength of the material is determined by the original density, the resultant strength should be intermediate between the original value and that expected from material of the final apparent density.

A square mold, cored in the center, was fabricated in which the outer frame enclosed a 4-inch cube, and the inner frame occupied 4" x 3" x 3". Thus, material foamed in place would possess outer dimensions 4" x 4" x 4" and 1" wall thickness. Theoretically, if a 10 lbs./ft.^{3} density foam were placed in the walls, the overall apparent density would be 4.35 lbs./ft.^{3}. In practice, a formulation calculated to give 10 lbs./ft.^{3} density was cast into the mold. However, the actual density was 18.5 lbs./ft.^{3}, and the apparent density was 8.09 lbs./ft.^{3}. It was felt the reason for the high density was that the confined space of the mold prevented the necessary expansion to the 10 lbs./ft.^{3} density level.

The strength property for the apparent 8.09 lbs./ft.^{3} density foam was excellent. A compressive strength of 396 psi was obtained. This is much higher than normally obtained at this density level (250 psi).

Further along these lines, a foam 7" x 7" x 7" was cast at a density of 6.43 lbs./ft.^{3}. A core, 3" x 3" x 7", was removed leaving 2" walls. The resultant apparent density was 5.15 lbs./ft.^{3}; compressive strength was 104 psi. This was not as high as expected. Two inches were removed from each wall, giving an apparent density of 2.52 lbs/ft.^{3} and compressive strength of 79 psi. This strength level is excellent and is more in line with the expected improvement in strength at the intermediate level.

Ping Pong Ball Foams

Work was conducted on the use of light-weight, hollow plastic spheres in rigid urethane foams to produce a 4 lb./ft.^{3} composite cellular structure having improved strength.

The theory behind this method for improving foam strength involves the relationship between foam density and foam strength ($psi/d^2 = 4.25$) derived from our experimental foam data within the density range of 2 - 20 lbs./ft.^{3}. In other words, doubling foam density produces a fourfold increase in compressive strength.

According to this theory, it should be possible to take a 4" x 4" x 4" cube of 10 lb./ft.^{3} rigid urethane foam, prepared from any of our experimental foam formulations, and drill sixteen regularly spaced, 7/8" diameter holes in one dimension of the cube, thereby producing a 4 lb./ft.^{3} "foam" having a compressive strength of 170 psi (see Figure 14). This would represent a 150% improvement in foam strength. Starting with a 16 lb./ft.^{3} rigid foam (1088 psi compressive strength) and removing 75% of the mass by drilling regularly spaced holes should theoretically produce a 4 lb./ft.^{3} "foam" with a compressive strength of 272 psi.

Accordingly, the purpose of our experimental work with hollow spheres was to develop a high-density (10 - 15 lb./ft.^{3}), rigid urethane foam formulation which can be applied as a thick coating to light-weight (0.5 lbs./ft.^{3}) spheres and then deactivated by freezing. The cold, free-flowing, coated spheres could then be poured into a mold or other cavity where they would assume a random, close-packed configuration. As the spheres warm up to room temperature, the viscous coating should foam and fill

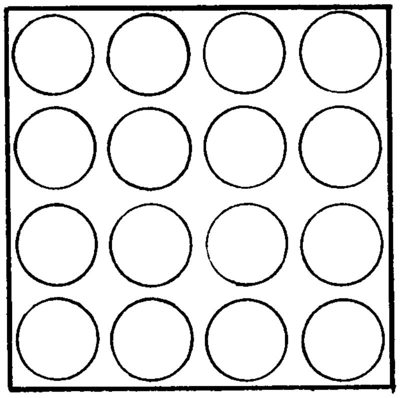
Figure 14. Theoretical Method for Producing a Four lb./ft.^{3} Urethane Foam with a Compressive Strength of 170 psi

1. Start with a 4" x 4" x 4" block of experimental rigid urethane foam of 10 lbs./ft.^{3} density, where

$$\frac{\text{psi}}{d^2} = 4.25$$

$$\text{psi} = (10)^2(4.25) = 425$$

2. Drill sixteen regularly spaced, 7/8" diameter holes in one dimension of the block as illustrated -



$$\begin{aligned} \text{Volume of each hole (V)} &= \pi r^2 h \\ &= (3.1416)(0.4375)^2(4) \\ &= 2.405 \text{ cu. in.} \\ 16 \text{ (holes) x } 2.405 &= 38.4 \text{ cu. in.} \end{aligned}$$

$$\begin{aligned} \text{Ratio of holes to foam} &= \frac{38.4}{64} \ (60\%) \\ \text{"Foam" density} &= (10)(0.40) = 4 \text{ lb./ft.}^3 \end{aligned}$$

3. Calculation of compressive strength in a direction parallel to the axes of the holes -

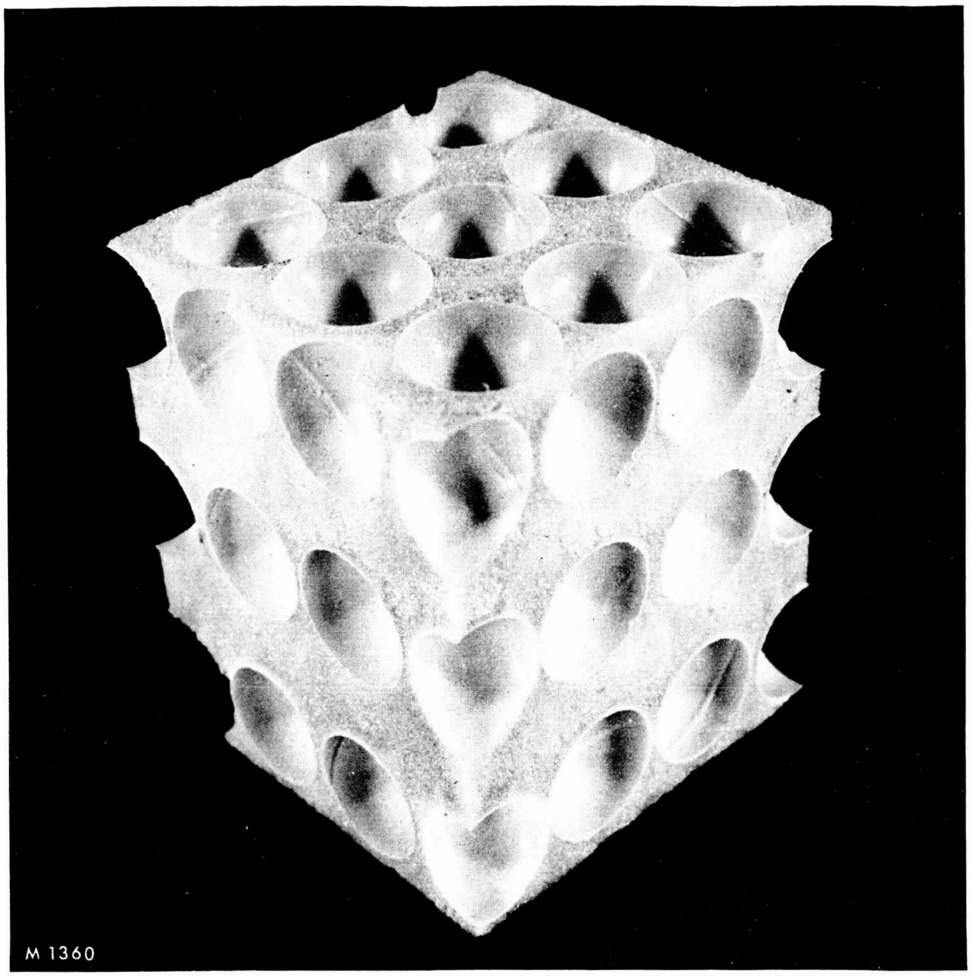
$$\begin{aligned} \text{Surface Area of each hole (A)} &= \pi r^2 \\ &= (3.1416)(0.4375)^2 \\ &= 0.6013 \text{ sq. in.} \\ 16 \text{ (holes) x } 0.6013 &= 9.621 \text{ sq. in.} \\ 16.00 - 9.62 &= 6.38 \text{ sq. in. of} \\ &\quad (10 \text{ lb./ft.}^3) \text{ test surface} \end{aligned}$$

$$\begin{aligned} \text{Compressive Strength} &= (425)\left(\frac{6.38}{16}\right) \\ (4 \text{ lb./ft.}^3 \text{ "foam"}) & \\ &= 170 \text{ psi} \end{aligned}$$

the regularly spaced voids (approximately 30% of the total volume) with high-density, high-strength urethane foam.

We investigated commercial sources of hollow spheres of various dimensions, and used ping pong balls in the preliminary experiments. Ping pong balls have a 1.50" diameter, 0.010" wall thickness, and a bulk density of 2.5 lbs./ft.^{3}. They are made of cellulose nitrate - which is proved to be a combustion problem.

Our preliminary experimental work with ping pong balls produced small "foams" such as the one shown in Figure 15. However, a number of problems prohibited making large test specimens. We found, for example, that spontaneous combustion of the cellulose nitrate occureed in "foams" larger than 6" x 6" x 6".



This "foam" was prepared by stacking ping pong balls in a mold, clamping them in place, then casting a 6 lb./ft.^{3} rigid urethane foam formulation into the mold. (Foam Density = 4.9 lbs./ft.^{3})

Figure 15. Ping Pong Ball Foam

V. RECOMMENDATIONS FOR FUTURE WORK

One of the most promising methods for obtaining the desired strength-at-density goals was the preparation of heterogeneous foam systems. Methods such as dispersing high-density, high-strength "strands" throughout a low-density system, the incorporation of "zero"-density fillers in high-density foams to decrease the apparent density with no significant decrease in strength, and mechanically removing material from high-density foams to decrease density should be further studied.

The effect of reinforcement-type fibers on properties other than compressive strength should be investigated further. The boron type fibers, or filaments, offer an extremely high strength-to-density ratio. Their high modulus and strength properties appear to offer promise of obtaining high-strength characteristics from foams-in-place systems. Further, along the lines of reinforcement of foam systems, it is suggested that the incorporation of coupling agents into reinforced foam systems be investigated; coupling agents are frequently used to effect a chemical linkage between filler and polymer.

It is recommended that means be studied to vary the characteristic foam cell structure and to obtain a better distribution of material throughout the cell.

To fully characterize the developed foam system discussed for adaptability to service requirements, it is felt that further research should be conducted to evaluate the foam characteristics over the temperature range of -423°F to +250°F, or even higher, temperatures.

Tests should include, but not necessarily be limited to, compressive, shear, and tensile strength; thermal-conductivity; coefficient of linear thermal expansion; and specific heat.

Since materials of construction used in space vehicle applications often come in contact with fuels and oils, the degree of compatibility between foams and these fluids should be investigated.

Rigid urethane foam is commonly used in composite structures to take advantage of its excellent thermal insulation property and high strength-to-weight ratio. Therefore, it is suggested that foam composites be evaluated as structures. Such properties as load-bearing characteristics, shear strength, thermal conductivity (K factor), and resistance to vibration or damping are envisioned as being of interest.

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Monsanto Research Corporation
Dayton, Ohio

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APPENDIX

LIST OF COMMERCIAL MATERIALS

LIST OF COMMERCIAL ISOCYANATES USED IN THE PREPARATION OF POLYURETHANE FOAMS, WITH PERTINENT TECHNICAL DATA

Chemical Name	Manufacturer	Trade Name	Molecular Weight	Amine Equivalent(1)	Functionality(2)
(Aliphatic Isocyanates)					
Methyl Isocyanate	Ott Chemical Company	- - - - - - - - -	57.0	57	Mono-Functional
Ethyl Isocyanate	" " "	- - - - - - - - -	71.1	71	" "
Octadecyl Isocyanate	Mobay Chemical Company	Mondur O	305	305	" "
Hexamethylene Diisocyanate	" " "	Mondur HX	168	84-85.7	Di-Functional
Hexamethylene Diisocyanate	The Carwin Company	Carwinate 84 H	168	84	" "
(Aromatic Isocyanates)					
Phenyl Isocyanate	Mobay Chemical Company	Mondur P	119	119	Mono-Functional
Phenyl Isocyanate	Ott Chemical Company	- - - - - - - - -	119.1	119	" "
o-Tolyl Isocyanate	" " "	- - - - - - - - -	133.2	133	" "
p-Tolyl Isocyanate	" " "	- - - - - - - - -	133.2	133	" "
o-Chlorophenyl Isocyanate	" " "	- - - - - - - - -	153.6	154	" "
p-Chlorophenyl Isocyanate	" " "	- - - - - - - - -	153.6	154	" "
m-Chlorophenyl Isocyanate	" " "	- - - - - - - - -	153.6	154	" "
2,5-Dichlorophenyl Isocyanate	" " "	- - - - - - - - -	188.1	188	" "
3,4-Dichlorophenyl Isocyanate	" " "	- - - - - - - - -	188.1	188	" "
3,5-Dichlorophenyl Isocyanate	" " "	- - - - - - - - -	188.1	188	" "
m-Phenylene Diisocyanate	" " "	- - - - - - - - -	160.13	80	Di-Functional
2,4-Toluene Diisocyanate	Allied Chemical Company	Nacconate 100	174.2	87	" "
80% 2,4-and 20% 2,6-Toluene Diisocyanate	" " "	Nacconate 80	174.2	87	" "
65% 2,4-and 35% 2,6-Toluene Diisocyanate	" " "	Nacconate 65	174.2	87	" "
80% 2,4-and 20% 2,6-Toluene Diisocyanate	Mobay Chemical Company	Mondur TD-80	174.2	87	" "
p,p'-Diphenylmethane Diisocyanate	" " "	Multrathane M	250.3	126.5	" "
Diphenylmethane 4,4-Diisocyanate	Allied Chemical Company	Nacconate 300	250.3	125	" "
Diphenylmethane Diisocyanate	The Carwin Company	Carwinate 125 M	250.3	125	" "
3,3-Dimethyldiphenylmethane-4,4-Diisocyanate	" " "	Carwinate 137 DM	278	140	" "
Bitolylene Diisocyanate	" " "	Carwinate 136 T	288	145	" "
Dianisidine Diisocyanate	" " "	Carwinate 148 D	328	164	" "
Polyphenylmethane Polyisocyanate	Mobay Chemical Company	Mondur MR	250+	131	Poly-Functional(2.5)
Polymethylene Polyphenylisocyanate	The Carwin Company	P A P I	385	133	Tri-Functional
Triphenylmethane Triisocyanate	Mobay Chemical Company	Mondur TM	1700-1900	580-642	" "
3-Methyl-4,6,4'-Diphenylmethane Triisocyanate	" " "	- - - - - - - - -	317	106	" "

(1) The amine equivalent of an isocyanate equals the molecular weight divided by the isocyanate functionality.

(2) The number of isocyanate (NCO) groups per unit weight of material.

List of Commercial Polyether and Polyester Materials Used in the Preparation of Rigid Polyurethane Foams, with Pertinent Technical Data

Chemical Classification	Manufacturer	Trade Name	Molecular Weight	Hydroxyl (1) Number	Acid (2) Number	Viscosity (Cps)	Functionality (3)
(Polyfunctional Polyethers)							
Sucrose-Propyleneoxide	Dow Chemical Company	Voranol RS-450	- - - -	443	- - - -	300,000	Octa-functional
" "	" " "	" RS-530	800	528	- - - -	2,000,000	" "
" "	" " "	" RS-410	- - - -	410	- - - -	75,000	" "
" "	" " "	" RS-375	- - - -	374	- - - -	35,000	" "
" "	" " "	" RS-350	- - - -	350	- - - -	28,000	" "
Polyoxypropylene Sorbitol	Atlas Chemical Industries	Atpol 2421	- - - -	285	0.5	1,500	Hexa-functional
" "	" " "	" 2414	300	330	0.5	5,000	" "
" "	" " "	" 2571	- - - -	450	0.5	13,000	" "
" "	" " "	" 2410	750	495	0.5	8,500	" "
" "	" " "	" 2568	- - - -	495	0.5	15,000	" "
" "	" " "	" 2498	- - - -	540	0.5	13,000	" "
" "	" " "	" 2566	530	620	0.5	130,000	" "
" "	" " "	" 2406	- - - -	640	0.5	80,000	" "
Sorbitol-Propyleneoxide	Union Carbide Chemicals Company	LS-490	700	490	0.2	18,000	" "
N,N,N¦N¦-Tetrakis (2-hydroxypropyl) Ethylenediamine	Wyandotte Chemicals Corporation	Quadrol	292	776	- - - -	44,000	Penta-functional
Ethylenediamine-Propyleneoxide	Union Carbide Chemicals Company	LA-700	400	700	- - - -	100,000	" "
- - - - - - - - - - - - - - -	" " " "	LA-475	590	480	- - - -	19,000	" "
Methyl Glucoside	Corn Products Sales Company	G-609	194	- - - -	- - - -	- - - -	Tetra-functional
" "	" " " "	HP-460	- - - -	460	0.17	100,000	" "
" "	" " " "	HP-370	- - - -	370	0.16	22,500	" "
Alpha Methyl Glucoside	Wyandotte Chemicals Corporation	Polyol 152	503	446	0.19	- - - -	" "
Aliphatic polyether tetrol	" " "	Pluracol PeP 550	- - - -	450	0.03	1,550	" "
" " "	" " "	Pluracol PeP 650	- - - -	375	0.02	1,150	" "
Propylene Oxide	Witco Chemical Company	Fomrez ET-1500	1500	112	0.06	310	Tri-functional
" "	" " "	Fomrez ET-3000	3000	56	0.07	510	" "
" "	" " "	Fomrez ET-3009	3000	57.5	0.08	500	" "
" "	" " "	Fomrez ET-3500	3500	48	0.08	520	" "
Polyoxypropylene	Allied Chemical Company	Actol 31-56	3000	56	0.2	440	" "
"	" " "	Actol 33-46	3600	46	0.2	540	" "
"	" " "	Actol 32-160	1000	160	0.1	235	" "
Trimethylolpropane	Wyandotte Chemicals Corporation	Pluracol TP 440	- - - -	400	0.03	615	" "
Propyleneoxide-Hexane triol	Union Carbide Chemicals Company	LHT - 28	6000	28	- - - -	1,460	" "
" " "	" " " "	LHT - 34	5000	34	- - - -	1,200	" "
" " "	" " " "	LHT - 42	4000	42	- - - -	720	" "
" " "	" " " "	LHT - 67	2500	67	- - - -	526	" "
" " "	" " " "	LHT - 112	1500	112	- - - -	397	" "
" " "	" " " "	LHT - 240	700	240	- - - -	375	" "
Aromatic based Propylene oxide	" " " "	LK - 380	440	380	0.2	13,000	" "
tris Hydroxypropyl Glycerine	Dow Chemical Company	CP - 260	650	260	- - - -	300	" "
Tri-glyceride of Hydroxyoleic Acid	Baker Castor Oil Company	DB Castor Oil	- - - -	164	2.6	10	" "
Tri-glyceride of Hydroxyoleic Acid	" " " "	Polycin 52	- - - -	340	5.0	10	" "
(Polyfunctional Polyesters)							
Glycol Polyadipate	Rubber Corporation of America	RC Polyester F-101	- - - -	60	1.5	12,000	Poly-functional
Polyester	Mobay Chemical Company	Multron R-2	- - - -	400	6.8-9.0	- - -	" "

(1) Hydroxyl number is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of the material.

(2) Acid number is a value which indicates the amount of free acids present in a substance (expressed as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in a gram of the substance).

(3) The number of active hydroxyl groups per unit weight of the polyether (a polyester).