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FOAMED PLASTICS

Proceedings of a Conference
April 22-23, 1963
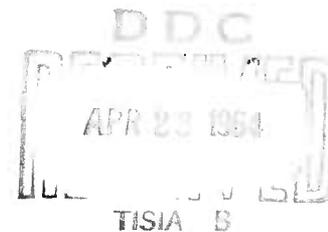
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FOAMED PLASTICS

Proceedings of a Conference

Statler-Hilton Hotel
Boston, Massachusetts
April 22-23, 1963

Sponsored by

U.S. ARMY NATICK LABORATORIES

and

COMMITTEE ON FOAMED PLASTICS
Advisory Board on Military Personnel Supplies
Division of Engineering and Industrial Research
National Academy of Sciences—National Research Council

Edited by

Frank R. Fisher

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James H. Saunders
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Mobay Chemical Company

FOREWORD

There has long existed a need for a forum where programs, problems, applications, and ideas relative to foamed plastics could be discussed by experts working directly in this and related fields. This Conference, the first to be conducted on such a broad and nationwide scale, has been organized and designed to satisfy this requirement. The Committee on Foamed Plastics of the Advisory Board on Military Personnel Supplies, National Academy of Sciences—National Research Council, and the U.S. Army Natick Laboratories, Natick, Massachusetts, are pleased to sponsor such a meeting.

This publication covers the Conference introductory remarks session; the papers given during the three technical sessions: Chemistry and Physics of Foams, Foam-Making Processes, and Foamed Plastics Applications and Requirements; and talks given during the evening program.

About ten years ago, foamed plastic, emerging from industrial laboratories as a new product, was widely regarded as an interesting material because of its method of manufacture and unusual physical properties. Today, these foams are useful materials--used in many military, industrial, commercial, and consumer applications. Foams are now being used for insulation, cushioning, noise and vibration abatement, packaging, flotation, electronic potting, energy absorption, in lightweight structures, and in many new applications.

This meeting was most helpful in providing the free exchange of ideas which will accelerate progress in the foamed plastics field. It is expected that the papers presented here will be more useful in conveying information and future requirements to the chemist, scientist, and businessman in the joint industry-military community.

John A. Lacz
General Chairman of Conference

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INTRODUCTION

General Chairman of Conference
John Lacz

On behalf of the National Academy of Sciences—National Research Council, Advisory Board on Military Personnel Supplies, Committee on Foamed Plastics, and the U.S. Army Natick Laboratories, I welcome you to the Conference on Foamed Plastics.

The purpose of this gathering is to broaden our knowledge of and interest in this relatively new, but extremely important, material. The three-session technical program covers the more important aspects of foamed plastics. We believe that this Conference will stimulate and encourage the establishment and maintenance of valuable liaison among the researchers, developers, suppliers, and users in government, industry, and academic institutions.

Honorary Chairman of Conference
Arthur W. Sloan

This Conference, sponsored by the Committee on Foamed Plastics of the Advisory Board on Military Personnel Supplies, National Academy of Sciences—National Research Council, and the U.S. Army Natick Laboratories is divided into three technical sessions: Chemistry and Physics of Foams; Foam-Making Processes; and Foamed Plastics Applications and Requirements.

The first session, chaired by Dr. James H. Saunders, Director of Research, Mobay Chemical Company, deals with some of the basic and applied research work now being conducted. During this session, we will hear papers on foam chemistry and physical and chemical properties of foam materials. The next session covers current and state-of-the-art foam-making processes. Of particular interest are the last two papers which cover advanced techniques for foaming under the difficult environmental conditions experienced in the field and in a vacuum. Dr. Kurt C. Frisch, Director of Polymer Research, Wyandotte Chemical, is the session chairman.

Session three is "hardware" oriented inasmuch as the papers deal with applications and requirements. We will hear talks by representatives of the three services in which we hope they will discuss future military foam material requirements. Another paper given by an architect covers foam applications in the housing and construction field. The last presentation, which

covers an area which is of keen interest to many, is on the flammability investigations conducted by the Bureau of Mines. Mr. John Lacz, of the Research Development Activity of Atlantic Research Corporation, will chair this session.

I am sure that we will all benefit from the papers presented here during the next two days.

Before concluding my remarks, I would like to bring to your attention the evening program which covers a 6:30 p.m. reception, courtesy of Atlantic Research Corporation, and a banquet at 7:15 p.m., after which we will have a talk by Professor Stephen C. A. Paraskevopoulos, of the Architectural Research Laboratory, University of Michigan, on "Foamed Plastics and Housing in Underdeveloped Countries," followed by a talk and a 20-minute movie on Plastic Structure Research or the "Building-In-Barrels" development.

SESSION NO. 1

CHEMISTRY AND PHYSICS OF FOAMS

Dr. James H. Saunders, Chairman
Mobay Chemical Company
Pittsburgh, Pennsylvania

MECHANICS OF FOAMED ELASTIC MATERIALS

A. N. Gent and A. G. Thomas

Introduction

The widespread use of foamed elastic materials makes an understanding
of the mechanics of deformation and failure highly desirable. Recently, theo-
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those of the constituent material.[1,2] A simple model structure is assumed,
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compared with experimental measurements on natural rubber foams covering
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behavior of closed-cell foams is described in the section on Small Deformations
of a Closed-Cell Foam.

Under deformations varying with time, open-cell foams will dissipate
energy by a viscous mechanism as air flows through the network of threads.
A treatment of the visco-elastic behavior on this basis by Kosten and Zwikker[3]
is also discussed.

Then the resistance of a network of threads to tearing and to tensile
rupture is considered. Experimental measurements on rubber foams are
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Load-Deformation Relations[1]

General Character

Load-deformation relations for a rubber foam of relatively low density
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theoretical relation between Young's modulus and the density is derived below
for a simple model of an elastic foam. In compression the load-deformation
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Fig. 1. Load-deformation relations in simple extension and compression for a natural rubber foam having a volume fraction of rubber of 0.125.
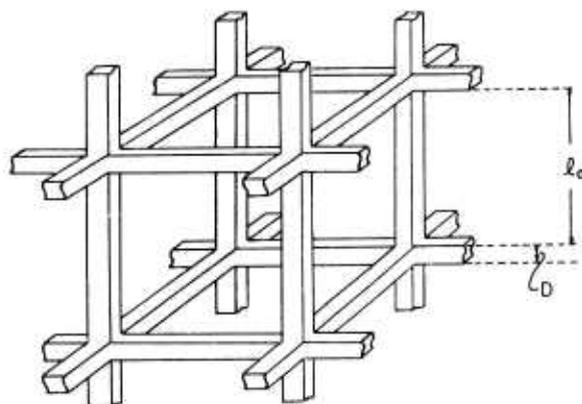
Fig. 2. A simple model of a foamed material.

Theoretical Treatment for Small Deformations

An extremely simple model of a foamed material is shown in Fig. 2. It consists of thin threads of unstrained length, 1_o, and cross-sectional area, D^2, joined together to form a cubical lattice. The intersections, consisting of cubical regions of volume D^3, are assumed to be substantially undeformable. A fractional extension of the foam by an amount e' parallel to one set of threads is therefore associated with a larger extension, e, of the threads themselves, given by $(1 + \beta)e'$ where $\beta = D/1_o$. The threads occupy a fractional area, $\beta^2/(1 + \beta)^2$, for any cross-section perpendicular to one set of threads. Young's modulus, Y_f, for this simple model, under a small strain parallel to one set of threads, will therefore be given by the product of three terms: the modulus of the solid material, Y; the strain-magnification factor, $(1 + \beta)$; and the factor representing the true load-bearing area. Hence,

$$Y_f = Y\beta^2/(1 + \beta). \qquad (1)$$

The density of this model structure is readily evaluated by considering a cube of side $D + 1_o$ centered on one intersection. Expressed as the fractional volume, ν_r, occupied by the solid material, it is

$$\nu_r = (3\beta^2 + \beta^3)/(1 + \beta)^3. \qquad (2)$$

The parameter β describing the model is thus a direct measure of the foam density. The relation between them, Equation 2, is presented graphically in Fig. 3.

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Although these relations for Young's modulus and density have been derived for a particularly simple model, they retain the same general forms when somewhat more realistic models are considered. For example, when a system of n randomly-disposed threads enter each intersection, and these are approximated by spheres of surface area nD^2, the density of the foam is found to be given by the same relation (Equation 2). When a general deformation of such a structure is considered,[1] Young's modulus is obtained as

$$Y_f = Y\beta^2/2(1 + \beta) \qquad (3)$$

differing from the former result only by a factor of $1/2$.

Poisson's ratio for the simple model is zero, since the threads lying perpendicular to the direction of the deformation are not deformed. For the model with randomly-disposed threads, it takes the value $1/4$, independent of the density.
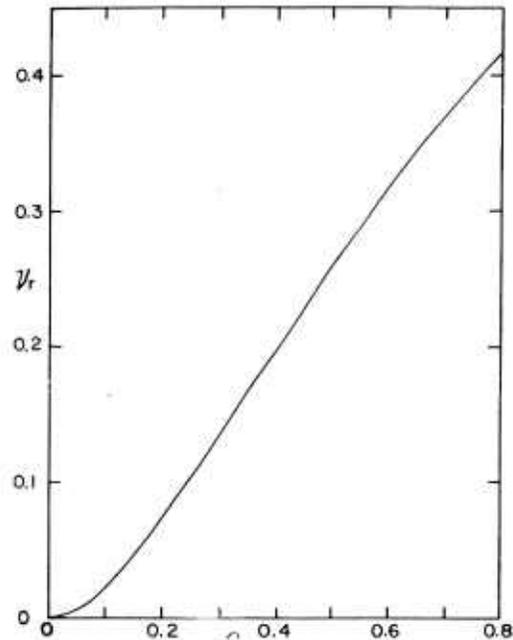
Fig. 3. Relation between the foam density, ν_r, and the parameter β.

Theoretical Treatment for Simple Compression

The compression is assumed to be directed parallel to one set of threads (Fig. 2) and to take place by buckling of the threads. The force F on each thread will then be governed by the bending moments developed. Thus, from dimensional considerations,

$$F = YAK^2 f(e)/l_o^2$$

where AK^2 is the moment of inertia of the thread cross-section and $f(e)$ is an unknown function of the fractional approach, e, of the thread ends. For threads of similar cross-section, $AK^2 = mD^4$, where m is a constant. The number of threads per unit cross-sectional area of the foam is $(l_o + D)^{-2}$. The average compressive stress is therefore given by

$$t = F/(l_o + D)^2 = Y \beta^4 f(e)/(1 + \beta)^2 \qquad (4)$$

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on substituting β for $D/1_o$ and absorbing the constant m in f(e). As before, the fractional compression, e', of the foam is given by

$$e = e'(1 + \beta). \tag{5}$$

Equations 4 and 5 give the relation between the compressive stress, t, and the compressive strain, e', in terms of the foam parameter β, and thus in terms of the density of the foam (by Equation 2). The relation contains an unknown function, f(e). This function should, however, be independent of Y and ν_r and so, in principle, should be determinable from a single compression curve at a particular value of ν_r.

A contribution to the total deformation will be made by simple compression of the threads, by an amount t/Y_f. For small deformations it may be assumed additional to that arising from buckling of the threads. It will be small, in any case, for foams of low density.

Foams of Low Density

At low foam densities, ν_r is approximately given by $3\beta^2$ (Equation 2) and the over-all deformation, e', approaches that of the threads themselves, e. The compressive stress at a given degree of compression is therefore predicted by Equation 4 to be proportional to ν_r^2, at low foam densities. In contrast, Young's modulus is predicted by Equation 3 to be directly proportional to ν_r. This has interesting consequences when materials of different Young's modulus are employed in foam manufacture. If a polyurethane material, for example, is assumed to have a modulus four times that of a typical vulcanized rubber, a similar resistance to compression will be obtained in a polyurethane foam of only one-half the density of a rubber foam. The resistance to extension, however, will be about twice as large as for the denser rubber foam. These predictions are in fair accord with the behavior of the two types of foam.

Experimental Measurements at Small Extensions

Values of Young's modulus have been determined on natural rubber foams prepared from latex, having densities ranging from 0.09 to 0.57 g/cm^3. The moduli were calculated from the substantially linear load-extension relations in simple extension. A value of Young's modulus was also determined for a sheet of solid rubber prepared from the same compound, to characterize the material of which the foams consisted.

In Fig. 4, the ratio Y_f/Y of Young's modulus for the foam to that of the solid rubber is plotted against the volume fraction of rubber in the foam, calculated from the measured density. The theoretical relation given in Equations 2 and 3 is represented by the full curve of Fig. 4 and is seen to describe the experimental results quite successfully.

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Measurements were also made of the lateral contractions when small extensions, of the order of 10 per cent, were imposed. Values of Poisson's ratio determined in this way were found to average 0.33 for all the foams, no systematic trend with foam density being apparent. A similar value, 0.36, has been reported for a polyurethane foam.[5] These values are in reasonable accord with the theoretically-predicted value of 0.25.

Fig. 4. Experimental relation between Young's modulus, Y_f, of the rubber foam, relative to that of the solid rubber, Y, and the volume fraction, ν_r, of rubber in the foam. Full curve: theoretical relation given by Equations 2 and 3. Broken curve: limiting form of theoretical relation for low densities.

Experimental Measurements in Compression

Measurements have been made of the load-deformation relations in compression for the same natural rubber foams. For six of the lightest foams $(\nu_r < 0.2)$, corresponding values of f(e) and e were calculated by means of Equations 4 and 5. They are shown in Fig. 5 as a composite curve, the six relations being similar.

The relation obtained for f(e) is of the general form expected for a buckling process. It does not show as abrupt a decrease in slope as a simple strut would show at the point of collapse; this is presumably due, at least in part, to the wide distribution of thread dimensions in the foams examined. A more regular structure, such as that which appears to exist in polyurethane foams, might be expected to yield a relation for f(e) more closely resembling the ideal buckling form. The load-deformation relations for polyurethane foams do in fact appear to be of this kind,[6] although they also show rather marked irreversibility which precludes a detailed analysis.

Fig. 5. Experimental relation between f(e) and e, obtained from the load-compression relations for six low-density natural rubber foams.

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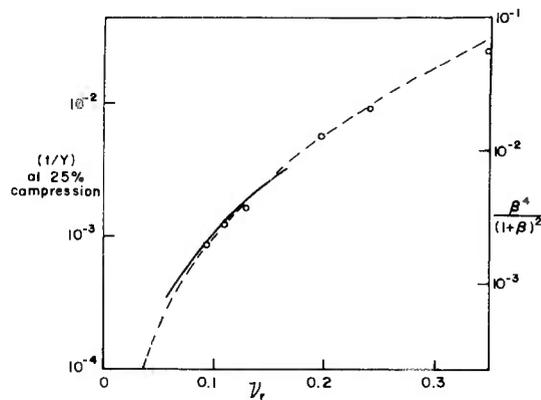
Fig. 6. Experimental relation between compressive stress, t, at 25% compression, relative to Young's modulus, Y, of the solid rubber, and the volume fraction, ν_r, of rubber in the foam. Full curve: experimental results of Talalay.[7] Broken curve: calculated relation between $\beta^4/(1 + \beta)^2$ and ν_r.

The resistance to compression depends strongly on the foam density. In Fig. 6, the compressive stress at 25 per cent compression is plotted on a logarithmic scale against the volume fraction of rubber in the foam. The broken curve of Fig. 6 represents the variation of the factor $\beta^4/(1 + \beta)^2$ with ν_r, calculated from Equation 2. It is multiplied by a constant factor (0.44) corresponding approximately to the value of f(e) at this compression, and is seen to describe the experimental measurements closely. The full curve of Fig. 6 represents the measurements reported by Talalay,[7] referred to a value of Young's modulus, Y, chosen to bring them into agreement with the present measurements. They are also seen to vary with the foam density in substantially the manner predicted by the theory (Equation 4). The value employed for Y was 32 kg/cm^2, somewhat higher than that found for the present vulcanizate, 26.4 kg/cm^2. It may be inferred that Talalay's foams were somewhat more tightly crosslinked.

The theoretical dependence of the compression stiffness on the foam density is thus seen to be substantiated by experiment for a wide range of densities. The values of Young's modulus have also been shown to be quantitatively predicted by the theory. It appears, therefore, that the basic concepts put forward for the structure and mode of deformation of elastic foams are correct.

Small Deformations of a Closed-Cell Foam

A closed-cell foam may be considered as a three-phase system: the matrix itself, the enclosed gas phase, and the surrounding atmosphere. We assume that the elastic behavior of the matrix is substantially the same as for an open-cell foam of the same density, and consider the additional contributions to the strain energy for small deformations due to the two gas phases. The calculations are given in the Appendix. It is shown there that

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Young's modulus, Y_f', and Poisson's ratio, σ', for the closed-cell foam are given by

$$Y_f' = \frac{2[5K + (p_e - p_o) + \frac{3p_o}{2(1 - \nu_r)}] \; [4K - (p_e - p_o)]}{[8K + (p_e - p_o) + \frac{2p_o}{(1 - \nu_r)}]} \qquad (6)$$

and

$$\sigma' = \frac{[2K + (p_e - p_o) + \frac{p_o}{(1 - \nu_r)}]}{[8K + (p_e - p_o) + \frac{2p_o}{(1 - \nu_r)}]} \qquad (7)$$

where 5K is the value of Young's modulus for the corresponding open-cell foam, given by Equation 3 as $Y \beta^2/2(1 + \beta)$. p_e and p_o are the pressures of the external atmosphere and the confined gas, the latter being measured when the matrix is totally unstrained.

If these pressures are equal ($p_o = p_e = p$, say), Y_f' and σ' become

$$Y_f' = 2K[10K (1 - \nu_r) + 3p] / [4K (1 - \nu_r) + p],$$

$$\sigma' = 1/2 [2K (1 - \nu_r) + p] / [4K (1 - \nu_r) + p].$$

When the foam modulus 5K is much greater than p, Y_f' and σ' have the same values as for a corresponding open-cell foam, 5K and 1/4. When p is much greater than the foam modulus, they become equal to 6K and 1/2. The effects of the closed-cell structure are thus predicted to be comparatively small in this case; for a soft closed-cell foam Young's modulus is at most 20 per cent higher than for the equivalent open-cell foam.

The present calculations are restricted to deformations involving small volume changes. Under large compressions the behavior may be altered more substantially.

Visco-Elastic Behavior of Foams

Under deformations varying with time, energy is dissipated in open-cell foams by a viscous mechanism as air flows through the pores, as well as by the mechanical hysteresis of the constituent material. The former contribution may be quite substantial.[3,8] It has been treated by Kosten and

Zwikker[3] using a simple model in which the pores are represented by a capillary tube connnecting the foam "interior" to the external atmosphere. They have shown that the main features of the visco-elastic behavior of a rubber foam over a range of deformation frequencies are also exhibited by the model.

At low frequencies the air flow is slow and the viscous damping is correspondingly small. As the deformation frequency increases, the damping rises due to the increased rate of flow through the pores. However, the viscous resistance increasingly constrains the air within the foam, where it undergoes volume changes in phase with the deformation. Consequently, at higher deformation frequencies the amount of air passing through the pores diminishes and the viscous damping decreases again. The stiffness of the foam increases continuously, from an initial value given by the stiffness of the foam matrix alone to an upper limit given by the resistance to deformation of the matrix and the contained air together. The upper limit will therefore be related to the stiffness of an equivalent closed-cell foam, considered in the preceding section.

The maximum damping is predicted by the theory[3] to be primarily dependent on the density, i.e., the volume fraction, ν_r, occupied by the constituent material, and on the stiffness of the foam. It increases as both ν_r and the foam stiffness decrease. The frequency w_o at which the damping has a maximum value is predicted to depend primarily on the size of the pores, increasing approximately in proportion to the square of the pore diameter. Measurements were reported for one foam, described as having very narrow pores. The value of ν_r was 0.3. The experimentally determined value for w_o was about 11 cps, and the corresponding damping, expressed as the phase angle between force and deformation, was 20°. In contrast, the phase angle at very low frequencies, when the air damping would be negligible, was only about 2°.

The foam stiffness increased by a factor of about 2 over the entire range of deformation frequencies. This change is larger than the relation given in the preceding section would predict. The discrepancy is probably due, at least in part, to the non-isothermal nature of the deformations at high frequencies.

Rupture Properties of Foams[2]

General Observations

The tensile strength of rubber foams is surprisingly low, being of the order of one-hundredth of that for the bulk rubber when the volume fraction of rubber in the foam is 10 per cent. As the breaking load is approached, some of the threads of which the foam is comprised can be seen (and sometimes heard) to break, particularly in the neighborhood of flaws in the foam structure. This suggests that tensile failure is due to the growth of flaws by catastrophic tearing.

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In the present section the tearing energy for the simple model structure shown in Fig. 2 is calculated, and the work required to cause tensile failure is deduced from it. Some experimental measurements of tearing energy and breaking energy are then compared with the theoretical predictions.

Calculation of Tearing Energy

A convenient measure of the resistance to tearing is provided by the tearing energy, T_f, defined as the amount of work required to advance a tear by unit distance in a specimen of unit thickness. For the simple tear test-piece shown in Fig. 7, it is given approximately by[9,10]

$$T_f = 2F/t$$

where F is the applied force required to propagate the tear and t is the test-piece thickness.

Fig. 7.   Tear test-piece.

The minimum value of T_f is given by the energy required to break all the threads crossing a plane of unit area. The number of such threads, for a plane parallel to one set of threads, is $(1_o + D)^{-2}$ for the simple model structure shown in Fig. 2. The work required to break each thread is $1_o D^2 E_r$, where E_r is the breaking energy per unit volume of the bulk material. Thus,

$$T_f = E_r 1_o \beta^2 / (1 + \beta)^2 \tag{8}$$

where $\beta = D/1_o$. At low foam densities, when β is small in comparison with unity, Equation 8 may be approximated by

$$T_f = 1/3 \nu_r E_r 1_o . \tag{9}$$

The quantity 1_o in Equation 9 may be considered as the effective "width" of the tear tip, assumed here to have the minimum possible value; i.e., one thread length. If tearing proceeds on a wider front, involving a greater number of threads, a corresponding multiple of 1_o will be required in Equation 9.

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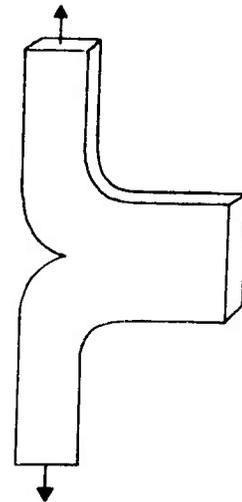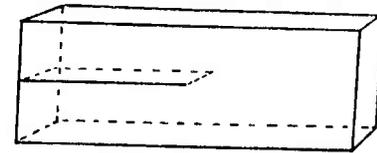
Calculation of Breaking Energy in Simple Extension

It is assumed that tensile rupture occurs by catastrophic tearing from a flaw in one of the test-piece surfaces. The energy, T, available for tearing at the tip of such a flaw is given by[9]

$$T = 2KLE'$$

where K is a numerical constant having a value of about 2, L is the depth of the flaw, and E' is the energy stored in the bulk of the specimen, per unit volume. Rupture occurs when T attains the value T_f required to maintain tearing. The corresponding energy, E_f', stored in unit volume of the specimen, i.e., the breaking energy for the foam in simple extension, is therefore given by

$$E_f' = T_f/4L . \tag{10}$$

Experimental Measurements of Tearing Energy

Characteristic tearing energies, T_f, have been determined for a series of natural rubber foams covering a wide range of density, using the form of test-piece shown in Fig. 7. They are plotted in Fig. 8 against the volume fraction of rubber in the foam. The experimental results are seen to be in satisfactory accord with a linear relation, as predicted by Equation 9. The breaking energy, E_r, of the rubber matrix, 4.0×10^8 ergs/cm^3, was determined from tensile measurements on a cast latex sheet prepared with the same mix formulation. From the slope of the linear relation of Fig. 8, a value for l_o is then obtained of 1.0 mm, by means of Equation 9.

The average pore diameters for this series of foams were obtained by microscopic examination. They were found to range from 0.2 to 0.4 mm. Thus the effective width of the tear is of the same order as, but about three times larger than, the average pore diameter. This does not seem unreasonable. For a random arrangement of pores, the tear width would be expected to be larger than the average pore diameter. Imperfections in the foam will lead to local

Fig. 8. Experimental relation between tearing energy, T_f, and the volume fraction, ν_r, of rubber in the foam.

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deviations of the tear from a linear path also, and hence give rise to a correspondingly large tear width.

Some tearing was found to occur at the tip of the initial razor cut for values of the applied force only about one-half of those necessary for steady propagation of the tear. It appears, therefore, that the tearing energy for <u>initiation</u> of a tear in a rubber foam may be calculated by means of the simple theory outlined above, on the assumption that the tear tip width is about twice the average pore diameter. The energy for steady tearing is about twice as large, probably due to deviations from a linear path.

The theory predicts that the tearing energy is directly proportional to the average thread length. The range in pore size was relatively small for the foams for which the tearing energies are plotted in Fig. 8. However, a general tendency was evident for the foams with larger pores to be stronger. Another foam, having relatively small pores of only 0.13 mm average diameter, was also examined and found to be particularly weak in tearing, with a tearing energy of only one-half of that for other foams of similar density. The prediction appears, therefore, to be correct.

Experimental Measurements of Breaking Energy

Measurements were made of the tensile strength and the elongation at break of dumb-bell shaped test-pieces of the same foams. The breaking energies, E_f', were calculated from them on the assumption that a linear relation exists between the applied load and the corresponding extension. Approximately linear relations are observed experimentally. Values of the depth of flaw from which fracture occurred were then calculated by means of Equation 10 using the measured values of the tearing energy, T_f, and breaking energy, E_f'. They were found to be in reasonable agreement with the largest pore diameters observed in representative cross-sections of the same foams; both quantities varied from about 0.4 mm to 3 mm over the range of foams. The numerical agreement suggests that tensile failure occurs by catastrophic tearing from a flaw of the order of the largest pore diameter in length. In this way the relatively low tensile strength of foams is acounted for.

Conclusions

The theoretical model used is a very idealized representation of an actual foam, which is far from homogeneous, the threads and the interstices having a wide range of shapes and sizes. Such variations cannot easily be taken account of in a theory, and no attempt has been made to do so. In view of this, the agreement obtained with theory for the Young's modulus of materials of different density (Fig. 4) is very satisfactory, particularly as no arbitrary constants are involved.

The general shape of the load-compression curve has been attributed to buckling of the threads, and is probably affected markedly by the detailed structure of the foam. A suitable average is provided by the arbitrary function f(e), which has been determined experimentally for a series of natural rubber foams. The theory unequivocally gives the variation of compression stiffness with density, and good agreement is obtained with experiment in this case also over a wide range of stiffness (Fig. 6). The basic features of the deformation of elastic foams thus appear to be present in the proposed model.

Relations have been derived for the Young's modulus and Poisson's ratio of a closed-cell foam by an extension of the previous treatment. Experimental verification has not yet been attempted.

Kosten and Zwikker have shown that a simple model of the damping effect of air flow through the pores provides a satisfactory description of the visco-elastic behavior of foams under vibratory conditions. The main predictions of their treatment have been described. They conclude that substantial damping will be obtained with soft, low density foams at deformation frequencies depending primarily on the pore size.

The tear strength and tensile breaking energy have also been deduced for the simple model of a network of threads. The quantitative agreement with experiment is satisfactory for foams of a wide range of density when the tear tip width is assumed, not unreasonably, to vary from two to four times the average pore diameter as the tip changes from a razor cut to a rough tear. The measured breaking energies are in good agreement with those calculated on the assumption that tensile failure occurs by tearing at the tip of the largest pore. The theory suggests that the maximum tensile strength and work-to-break will be obtained when the pore structure is perfectly uniform, no abnormally large pores being present, while the tear resistance will increase approximately in proportion to the pore size.

Acknowledgement

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APPENDIX

SMALL DEFORMATIONS OF A CLOSED-CELL ELASTIC FOAM

Strain Energy Function

The strain energy for a network of randomly-directed threads has been obtained previously[1] in the form

$$W = K[3 \, \Sigma e_1^2 + 2\Sigma e_1 e_2] \tag{11}$$

where e_1, e_2, e_3 are the principal extensions, $K = \beta^2/10 \, (1 + \beta)$, and β is a structural parameter directly related to the foam density, by Equation 2. We assume that the matrix of a closed-cell foam will contribute a term of this form to the strain energy also, and we shall now consider the additional contributions to the strain energy when the foam contains an ideal gas, initially at a pressure p_o, and is surrounded by a gaseous atmosphere of pressure p_e.

If unit volume of the foam increases in volume by an amount ΔV as a result of the deformation, the work done by the confined gas, initially of volume $(1 - \nu_r)$, is

$$W_1 = \int_{1-\nu_r}^{1-\nu_r + \Delta V} p \, dV. \tag{12}$$

Under isothermal conditions, $pV = p_o \, (1-\nu_r)$. Substituting for p in Equation 12, and integrating,

$$W_1 = p_o \, (1-\nu_r)\ln\left(1 + \frac{\Delta V}{(1-\nu_r)}\right) . \tag{13}$$

The work done against the surrounding atmosphere is

$$W_2 = p_e \, \Delta V .$$

The net increase in stored energy due to the presence of the two gas phases is therefore given by

$$\Delta W = W_1 - W_2 = (p_e - p_o)\Delta V + \frac{1}{2} \, p_o \, \frac{(\Delta V)^2}{(1-\nu_r)}$$

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after expanding the logarithm in Equation 13, retaining only the first two terms. Putting ΔV and $(\Delta V)^2$ in terms of the principal extensions, and neglecting terms of order e^3 and above,

$$\Delta W = (p_e - p_o) \Sigma e_1 + \frac{1}{2} \frac{p_o}{(1 - \nu_r)} \Sigma e_1^2 + (p_e - p_o + \frac{p_o}{(1 - \nu_r)}) \Sigma e_1 e_2 \ . \tag{14}$$

The total strain energy of the closed-cell foam is therefore obtained from Equations 11 and 14 as

$$W' = A \Sigma e_1^2 + B \Sigma e_1 e_2 + C \Sigma e_1 \tag{15}$$

where

$$A = 3K + \frac{p_o}{2(1 - \nu_r)}$$

$$B = 2K + (p_e - p_o) + \frac{p_o}{(1 - \nu_r)}$$

$$C = p_e - p_o \ . \tag{16}$$

Unstressed State

The minimum strain energy for the system, which defines the unstressed state, is not given by $e_1 = e_2 = e_3 = 0$ when the confined gas is at a different pressure from that of the surrounding atmosphere. The unstressed state is defined by the relation

$$\partial W' / \partial e_o = 0$$

when e_1, e_2, e_3 are put equal to e_o in Equation 15. This yields

$$e_o = -C / 2(A + B).$$

Thus, the dilation of the foam from its "initial" state when the matrix is unstressed $(p_o = p_e)$ is given by

$$e_o = (p_o - p_e)/2 \left[5K + (p_e - p_o) + \frac{3 p_o}{2(1 - \nu_r)} \right]$$

in the absence of applied stresses.

By considering extensions relative to the unstressed state, i.e., by substituting $e_1' = e_1 - e_o$, etc. in Equation 15, the form of the stored energy

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function and the values of the constants A and B are found to be unchanged to a first approximation. (The term $C\Sigma e_1$ disappears.) The load-deformation relations for the unstressed foam may thus be calculated from the strain energy function given in Equation 15, provided p_o and ν_r are given their values in the "initial" state and the stresses are referred to this state also.

Simple extension

The tensile stress, t_1, per unit area in the initial state ($p_o = p_e$) is given by

$$t_1 = \partial W'/\partial e_1$$

and $t_2 = t_3 = 0$. Putting $e_2 = e_3$ in Equation 15, we obtain

$$t_1 = 2Ae_1 + 2Be_2,$$

and $\quad\quad\quad e_2/e_1 \quad -B/(2A + B).$

Young's modulus, Y_f', and Poisson's ratio, σ', are therefore given by

$$Y_f' = 2A - \frac{2B^2}{(2A+B)},$$

$$\sigma' = B/(2A+B).$$

On substituting for A and B from Equation 16 the relations 6 and 7 given in the text are obtained.

CHEMISTRY OF URETHANE FOAM FORMATION

J. H. Saunders

Introduction

The chemistry of urethane foam formation was reviewed in 1960[4,15] and again in 1961.[16] This summary will include only those points from earlier reviews which appear essential to the presentation of a clear, yet concise, picture of foam formation. For additional details of those phases which have already been reported, the reader is referred to those earlier reviews. Emphasis here is placed on some newer developments and thoughts, particularly in the areas of cell size control and the reactions which occur after the polymerizing system has passed the gel point.

Urethane foams of the rigid type were developed in Germany prior to 1945 and reported by O. Bayer in 1947.[2] This type of foam sparked the principle interest in isocyanates and polyurethanes in the period of 1945 - 1952. Further research in the laboratories of Farbenfabriken Bayer led to the development of a flexible urethane foam system which was announced in 1952 by Höchtlen.[11] It was the development of this system which insured the commercial success of the polyurethane industry.

An understanding of the formation of these urethane foams, both rigid and flexible, involves consideration of the organic chemistry of the reactions leading to gas formation and molecular growth, the colloid chemistry of nucleation and bubble stability, and the rheology of the polymer system as it cures. Each of these aspects will be considered.

The Organic Chemistry of Foam Formation

The reactive ingredients of a foam system usually include an isocyanate and a hydroxyl-terminated resin. In addition, flexible foam systems and a few rigid foam systems include water as a source of gas for blowing. The reaction with a hydroxyl compound produces a urethane:

$$RNCO + R'OH \longrightarrow RNH\overset{O}{\overset{\|}{C}}OR' \tag{1}$$

while that with water produces a urea, via an amine intermediate, and carbon dioxide:

$$RNCO + H_2O \longrightarrow (RNHCOOH) \longrightarrow RNH_2 + CO_2, \qquad (2)$$

$$RNCO - RNH_2 \longrightarrow RNHCONHR. \qquad (3)$$
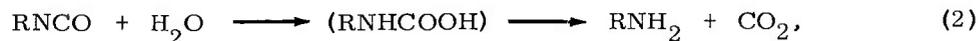
In uncatalyzed systems, the reaction with the amine is relatively quite fast, so much so that mixing an isocyanate with a large excess of water gives a high yield of the disubstituted urea. The rate of the isocyanate reaction with water is close to that with primary and secondary alcohols in uncatalyzed systems. Although the water reaction is somewhat more complicated than these equations indicate, the foam density is very near that calculated assuming Equations 2 and 3 to be correct, at least in some systems. [14]

The isocyanate may also react with the urea and with the urethane, to give a biuret and an allophanate, respectively:

$$RNCO + RNH\overset{\overset{\displaystyle O}{\|}}{C}NHR \longrightarrow R\underset{\underset{\displaystyle CONHR}{|}}{N}\overset{\overset{\displaystyle O}{\|}}{C}NHR \qquad \text{biuret} \qquad (4)$$

$$RNCO + RNH\overset{\overset{\displaystyle O}{\|}}{C}OR' \longrightarrow R\underset{\underset{\displaystyle CONHR}{|}}{N}\overset{\overset{\displaystyle O}{\|}}{C}OR' \qquad \text{allophanate} \qquad (5)$$

These last two reactions are much slower than the reactions with alcohols and water, and may be reversed slowly by heating to temperatures of approximately 110-130°C, and faster at higher temperatures.

Most rigid foam systems are blown with an inert, low-boiling liquid such as monofluorotrichloromethane. The heat of reaction between isocyanate and resin provides the energy required to vaporize the blowing agents. Some foam systems use a combination of water and inert blowing agent to provide a useful control of properties.

The isocyanate used in producing flexible foams is usually an 80:20 mixture of 2,4- and 2,6-tolylene diisocyanate. The same isocyanate is used for some rigid foams, and an undistilled grade of diphenylmethane diisocyanate is now being used for many rigid foams. In any case, the diisocyanate reacts with the functional groups in the resin, insuring that the resin is built into the final polymer molecules. In water blown systems the isocyanate also reacts with the water, thus providing the gas for foaming. The stoichiometry of the system is such that in the latter stages of polymerization the polymer end groups are largely the very reactive isocyanate group. This high reactivity helps greatly in insuring that a maximum number of chain ends will be joined to other chain ends, thus providing a relatively close approach to a theoretical network structure.

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A slightly branched resin is normally used for flexible foams, and a more highly branched one for rigid foam. The chemistry of foam formation is similar in either case, except that the rigid foam is much more cross linked than the flexible.

In addition to the major reactants, a foam system usually contains one or more catalysts which have a major effect on the chemistry of the system. The catalyst serves to drive the reactions at such rates that the foam rises and cures fast enough to prevent collapse of the foam. In any foam system several different reactions are involved, for example, those of the isocyanate groups in the 2- and 4-positions of tolylene diisocyanate, so the catalyst type and concentration must be carefully chosen to provide a suitable balance of reactions. The gas evolution and the polymer growth must be matched so that the gas is trapped efficiently and the polymer has the right strength at the end of the gas evolution to maintain its volume without collapse or gross shrinkage. The significant aspects of the development of polymer strength will be discussed in a later section.

The catalysts most commonly used are tertiary amines and tin compounds such as stannous octoate, stannous oleate, dibutyltin dioctoate, and dibutyl-tin dilaurate. Acidic impurities, especially in the newer undistilled polyisocyanates, may neutralize a portion of the catalyst, thus reducing the catalytic effect slightly.

Two types of processes are generally used for producing foam. In the "one-shot" process for rigid or flexible foam the isocyanate and resin are mixed simultaneously, along with suitable catalysts, stabilizers, cell size control agents, and water or additional blowing agent if desired. The reactions begin immediately, with foam rise starting about ten seconds after mixing and being complete within one or two minutes. The foam continues to cure for several hours to a day. The reactions involved are the same as in the pre-polymer method, but may be more readily illustrated in the description of that process as indicated below.

The second general type of process for flexible foam is the "prepolymer" process. In this method the reaction with the resin is completed first:

$$2\ R(NCO)_2 + HO \frown OH \longrightarrow OCN\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}O \frown O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-}NCO.$$
$$\text{"Prepolymer"} \qquad (8)$$
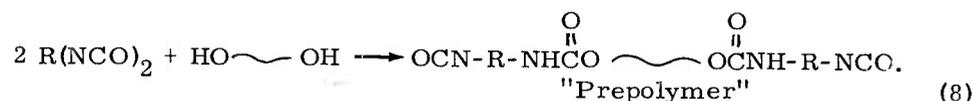
The prepolymer may later be foamed by reaction with water, with simultaneous growth of molecular structure:

$$n\ OCN\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}O \frown O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-}NCO + n\ H_2O \longrightarrow$$

$$\left[-NH\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}O \frown O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R - \right]_n + n\ CO_2. \qquad (9)$$
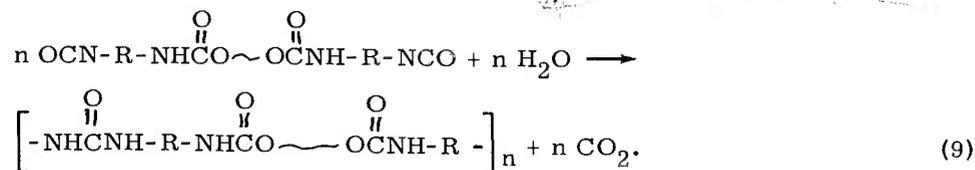
An inert blowing agent may also be used in small amounts to augment the foaming.

For low density water-blown foams, the molecular ratio of diisocyanate to resin is usually higher than 2:1, so that much more urea structure is built into the polymer chain:

$$\left[-(NHCNH-R-)_x NHCO \sim\!\!\sim\!\!\sim OCNH-R- \right]_n$$
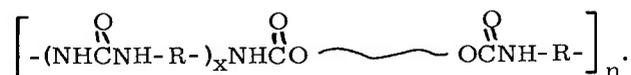
Cross linking is most successfully introduced into the polymer by the use of branched resins, so that an idealized structure may be illustrated by the following formula when a trifunctional resin is used:

$$\left[\sim (NHCNH-R-)_x \; NHCO \sim\!\!\curvearrowright\!\!\sim OCNH-R \quad \sim \atop \qquad\qquad\qquad OCHN-(R-NHCNH)_y \sim \right]_m$$
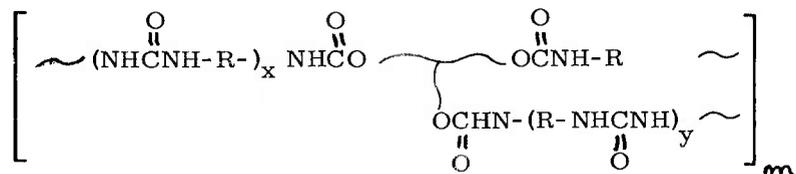
The average weight for each such unit, i.e., average weight per branch point, has been shown to be in the order for 400-700 for "rigid" foams and 2500-20,000 or more for "flexible" foams.[3] "Semi-flexible" and "semi-rigid" foams bridge the gap from about 2500 to 700 weight per branch point.

Branching in the polymer may also be developed by forcing allophanate or biuret formation by the use of appropriate catalysts or by heating. Such branch points are not preferred because of their limited thermal stability.

A hybrid method, the "partial prepolymer" process, is also widely used for rigid foam. In this process a part of the resin is mixed with all of the isocyanate to give a prepolymer containing a large excess of unreacted isocyanate. This prepolymer is then foamed by reaction with the remainder of the resin, which may contain the blowing agent, catalyst, and silicone oil.

The reactions indicated above will occur as long as the reactant groups are sufficiently mobile to collide with each other with reasonable frequency. Toward the end of the foam formation, after the polymerization has passed the gel point, however, chain ends will be relatively immobile, so that the rate of collision of end groups with a reactive site will become progressively slower. One may expect the time to come when diffusion of water molecules, present as an excess in the foam system or from the atmosphere, will provide an opportunity for the few remaining isocyanate end groups to react. In this case some will doubtless be converted to amine end groups and will not have the opportunity to collide with an isocyanate group. Thus one should expect the foam to contain some terminal amine groups. Furthermore, especially in TDI foam systems, because of the slow rate of reaction of isocyanate and

amine groups when each is shielded by an <u>ortho</u> methyl group,[1,5] compared to the isocyanate-water reaction, the water reaction may be preferred at similar effective concentrations of water and amine end groups.

The Final Cure of Urethane Foams

In previous reviews[15,16] the cure of foams was considered, with special emphasis on the development of final properties in flexible foams. It was shown that compression set is one of the slowest properties to reach its ultimate value, and it was proposed that this behavior was related to the slow reaction of isocyanate groups on polymer chain ends, after chain ends were relatively immobilized by gelation of the polymer. This consideration of reactions occurring after gelation has been extended recently to include more highly cross-linked systems typical of rigid foams.

Using Flory's equations for calculation of the per cent reaction required to reach the gel point,[8] Darr and co-workers[6] calculated the per cent reaction at the gel point for polyurethane systems as related to the functionality of the isocyanate and of the resin. Their results are shown in Table 1.

TABLE 1

Calculated Degree of Reaction at the Gel Point

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

It can readily be seen that even in a flexible foam system, utilizing in most cases a difunctional isocyanate and a trifunctional resin, a considerable percentage of the reaction must occur after the gel point has been reached. It is reasonable to believe that the most important contribution of an oven cure is that the elevated temperature increases the mobility of chain ends (chain segments free at one end, anchored at the other) to increase the probability of collision with another reactive chain end.

In a rigid foam system, which utilizes isocyanates having a functionality of 2 to 3, and resins with average functionality of at least four, a very high percentage of the reaction must occur after the gel point. Especially in rigid foams the efficiency of mixing of ingredients is thus of great importance. Since no mixing can occur after the gel point has been reached, the development of a uniform network structure, with few loose ends, requires that nearly perfect mixing must be achieved before about 14 per cent reaction occurs in the extreme case of the trifunctional isocyanate and octafunctional resin.

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The importance of mixing and the difficulty of achieving efficient reaction in a highly cross-linked system has been illustrated in different ways. For example, Darr and co-workers[6] prepared solid polymers analogous to rigid foams without the blowing agent, using a variety of polyols and isocyanates. The relation between temperature and modulus, as indicated by Vicat softening behavior (adaptation of ASTM D1525-58T), gave some insight into the efficiency of the network structure. Data obtained with a hexafunctional sorbitol-derived polyol and several isocyanates are shown in Fig. 1. The comparison of the polymer from hexamethylene diisocyanate (HDI) with that from 80:20-tolylene diisocyanate (TDI) is of interest in this connection. As expected, the polymer from the aliphatic diisocyanate exhibited a lower glass transition region and showed lower modulus in the initial portion of the rubbery region. However, the rubbery modulus of the polymer from HDI rose above that of the polymer from TDI as the temperature was increased. Since this increase in modulus is usually associated with the cross-links in a polymer structure, this behavior suggests that the polymer from HDI had a greater efficiency of cross-linking than that from TDI, even though the functionalities of reactants was exactly the same in each polymer. It appears reasonable to attribute this to the greater flexibility and hence mobility of the polymer ends terminated with HDI, compared to those terminated with TDI.
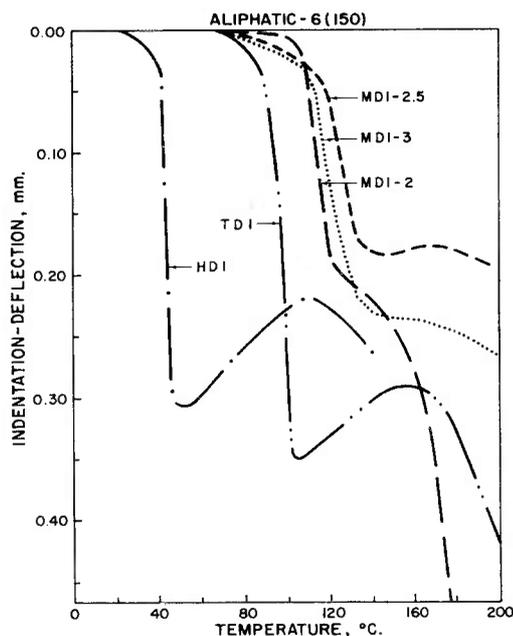
Fig. 1. Vicat softening of solid urethane polymers, analogous to rigid foams, derived from aliphatic based resins.

Of even more practical importance was the comparison of polymers from an octafunctional resin and isocyanates of varying functionality. [6] The isocyanates used were HDI, TDI, and undistilled grades of polyphenyl polymethylene polyisocyanates having average functionalities of about two (MDI-2), about 2.5 (MDI-25), and about three (MDI-3). Similar Vicat data on these polymers are shown in Fig. 2. In this case it is seen that the polymer from the reactants having the highest degree of branching (using MDI-3) had lower temperature resistance than that from similar reactants of lower degree of branching (MDI-2). As noted in Table 1, the gel point in this system with MDI-3 was reached at about 14 per cent reaction, while that with MDI-2 was reached at about 38 per cent reaction. Thus it is not surprising that reactions in the most highly branched system were not greatly efficient.

While most foam machines with mechanical agitators give excellent

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mixing with mixing times of approxi-
mately one second, the problem may
be much more severe with spray units
having no mechanical agitators. We
have found it highly desirable to check
the performance of spray equipment
with regard to mixing efficiency.
Changes in mixing with a given rigid
foam system have been found to have
a moderate effect on solvent swell-
ing, mechanical properties, and
flammability.

The degree of cross-linking
and the nearness to perfection of the
network structure (freedom from sol
fraction and from free ends) control
the foam properties to a large ex-
tent.[16] Increasing the degree of
branching of the reactants, at least
up to a point, favors increasing the
degree of cross-linking. Unfor-
tunately at high levels of branching
in the reactants, it seems apparent
that further increases in branching
tend to reduce the degree of perfection
of the network, due to early gelation
and loss of mobility of end groups.
Further studies of reactions occurring after gelation should prove to be very
useful, especially in connection with rigid foam systems.

Fig. 2. Vicat softening of solid ure-
thane polymers, analogous to rigid
foams, derived from heterocyclic
based resins.

Colloid Chemistry of Foam Formation

The preparation of a urethane foam involves the formation of gas bubbles
in a liquid system which is polymerizing, and the growth and stabilization of
these bubbles as the polymer forms and cures. Hence the colloidal aspects
of bubble nucleation, growth, and stability are of prime importance to the
foam chemist.

The formation of a foam proceeds through several stages. In the first,
the blowing agent, whatever it may be, generates a gas in solution in the liquid
phase, with the gas reaching its saturation limit in solution, then becoming
supersaturated, and finally coming out of solution in the form of a bubble.
This formation of a bubble is called "nucleation" and is assisted by the
presence of a second, finely divided phase such as a finely divided gas phase
or solid phase, or an irregular solid surface. Such a second phase which
assists the transport of a blowing agent molecule from solution into the gas

phase is called a "nucleating agent." A familiar example is the "boiling chip" which is added to a distillation to insure a steady, even flow of small gas bubbles during distillation.

When the bubble is first formed it is a sphere surrounded by a relatively thick liquid phase. As more gas is generated by the blowing agent, the new gas may form new bubbles and may also diffuse from the liquid phase into existing bubbles, causing them to become larger. As more bubbles form and as the bubbles grow, the foam volume increases, with the result that the polymerizing liquid phase becomes even thinner. The bubbles lose their spherical shape as the liquid phase becomes thinner, the bubbles finally assuming a structure bounded by several flat planes or membranes of polymerizing liquid. Where membranes join each other, a rib or stalk is seen which is thick compared to the membranes.[14] Such a sequence has been presented by deVries[7] for foaming systems in general, and has been confirmed by movies of urethane foam systems.[16] A magnified cross-section of a rigid polyester urethane foam is shown in Fig. 3,[15] where the straight ribs
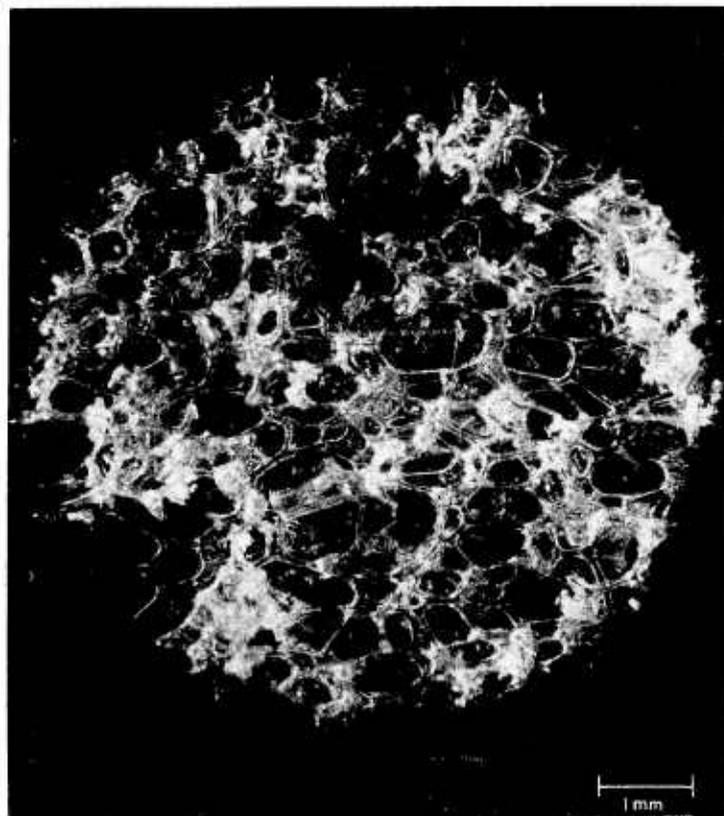
Fig. 3. Photomicrograph of rigid polyester-urethane foam.

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and five- and six-sided cells may readily be seen. Thus in the final foam most of the polymer is in the ribs, relatively little in the membranes. Other types of urethane foams have a similar appearance.[16]

The different stages of bubble formation and growth were considered in detail in previous reviews[15,16] and will be mentioned only briefly here. New emphasis will be placed, however, on those factors which may help provide a very fine cell size. The following sections explain, at least to some degree, the roll of the components in a foam system--components other than the reactants and catalysts, e.g., the surface tension depressants (silicone oils or emulsifiers) and cell size regulating agents.

Bubble Nucleation

The first key to the preparation of a foam is the formation of a gas bubble in the liquid system. The gas may be carbon dioxide, generated by the reaction of isocyanate and water. In some cases the gas may be the vapor state of a low boiling liquid which was initially dissolved in the reactants. In any case, the gas must come out of solution, quickly forming a tremendous number of tiny bubbles in the liquid mass. These bubbles must be stabilized while the liquid medium polymerizes, i.e., while viscosity is increasing very rapidly.

The process of forming bubbles in a gas-liquid solution is often called nucleation. A very enlightening description by LaMer[12] of the nucleation of sulfur solutions may be applied to the nucleation of other materials such as gases. Fig. 4 shows the general relationships which may be expected.

NUCLEATION AND CELL GROWTH

LEGEND
CLS : Critical Limiting Supersaturation
RSN : Rapid Self-Nucleation partial relief of supersaturation
GBD : Growth By Diffusion
S : Saturation
Cr_n : Nucleation

Fig. 4 may be applied to urethane foam as follows[15,16] assuming first that no added nucleating agent is present. In the time interval of Zone I, the gas concentration in solution exceeds the equilibrium saturation concentration (the solution becomes super saturated) and, with rapid gas generation, reaches the concentration where self nucleation begins. Sufficiently rapid gas generation may be achieved by catalysis of the isocyanate-water reaction, or by a sharp increase in the vapor pressure of an added low-boiling
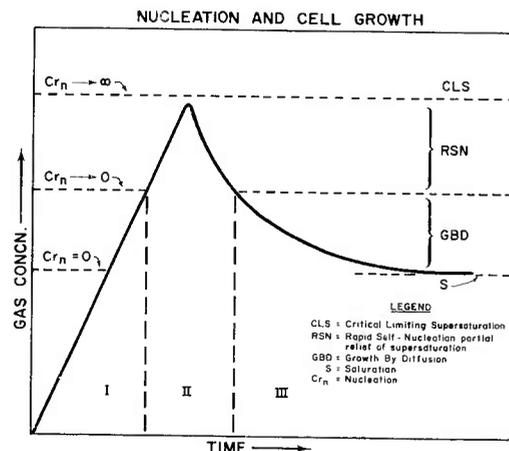
Fig. 4. Relation between changes in gas concentration in solution and nucleation and growth of foam cells.

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solvent, the increase being due to an increase in the temperature of the system. Such an increase in temperature is a rapid result of the catalyzed isocyanate-hydroxyl reaction in one-shot systems.

Self nucleation will occur (Zone II) as long as the gas concentration is in the indicated range. As soon as nucleation relieves the gas concentration sufficiently, no more bubbles are formed, but the concentration of gas in solution is further reduced by diffusion into the bubbles which already exist (Zone III). Finally, no more gas is generated and the equilibrium saturation concentration of gas in solution is reached. From this time on, bubbles can grow only by diffusion of gas from small bubbles into larger bubbles, by coalescence, or because of exothermic expansion of the gas in the bubbles.

The beginning of Zone II corresponds approximately to the development of a creamy appearance in the reaction mixture. Thus the time interval of Zone I is approximately the time often called the "cream time" of a foam system. This interval may be approximately ten seconds.

Thus far the duration of Zone II has not been clearly established, but may be assumed to be less than the time required to reach maximum foam volume ("rise time"), hence must be less than approximately 60-120 seconds for most systems. A reasonable approximation might be closer to 10-50 seconds. The time interval of Zone III should be terminated approximately when the foam rise is completed.

In most foam systems added nucleating agents may be present. It is possible that finely dispersed silicone oils, especially the dimethyl siloxane type, may serve as nucleating agents. In the presence of nucleating agents, one would expect a behavior similar to that described above except that bubble formation would occur at lower gas concentrations than in the absence of nucleating agents. The function of a silicone oil as a nucleating agent would explain the well-known relation in polyether prepolymer foam systems: an increase in silicone oil concentration favors fine cells. Fine cells would be the result of faster nucleation and continued nucleation at relatively low degrees of super saturation, so that more cells were formed.

Dissolved gases in the reactants should be expected to influence foaming. Thus if dissolved gases were sufficient to have the reactants near saturation before the foaming reactions begin, one might expect faster nucleation and finer cells. Several related observations are well known to the industry. For example, feeding limited amounts of air into the mix head of the foam machine aids in producing fine cells. Similarly, using a large orifice opening on the mix head, thus reducing pressure in the mix head and probably increasing air leakage into the mix head, favors fine cells.[15] Complete degassing of all reactants generally results in difficulty in foaming, and especially in obtaining fine cell size.[15]

It has been observed that strong catalysts for the isocyanate-water reaction in flexible foam systems often favor fine cell structure.[15,16] This

behavior may be explained if one considers in more detail the nucleation process. Reference to Fig. 5 may illustrate some of the aspects of fine cell formation.

Fig. 5. Schematic diagram of a liquid system containing a nucleating agent, gas molecules in solution, and a gas bubble.

A urethane foam system in its first few seconds of existence may consist of a liquid phase with gas dissolved in the liquid, with nucleating agents dispersed in the liquid, and with more gas continually being generated as the polymerization develops. In some microscopic volume, the concentration of gas reaches the level at which nucleation can occur, and a bubble forms. Other bubbles will be formed similarly, with varying distances separating the bubbles. Obviously, to have a fine cell foam the distance between the bubbles in this first stage of foaming should be as short as possible. Several factors may be expected to influence this distance, and hence the final cell size.

The process of forming a bubble immediately reduces the gas concentration in solution adjacent to the bubble, doubtless below the level at which nucleation can occur. These gas molecules can diffuse into the bubble, causing it to grow, and favoring large cell size. At the same time, new gas is being generated, which can bring the concentration of gas in solution again into the range where nucleation can occur. The required concentration will be lower if an efficient nucleating agent is present. The problem of cell size thus depends upon a balance of gas molecules diffusing through the liquid into existing bubbles, or diffusing through the liquid to a nucleating agent, the rate of generation of new gas molecules in the liquid phase, and the concentration and effectiveness of the nucleating agent.

An ideal system designed to give fine cells thus might consist of a liquid system permitting rapid diffusion of blowing agent molecules through the liquid, a foam stabilizer which will form a stabilizing layer around each bubble and which also will reduce the rate of diffusion of gas from the liquid into the bubble, very rapid generation of blowing agent molecules to maintain the concentration in the range need for nucleation, and a high concentration of efficient nucleating agents.

The strong catalyst for the isocyanate-water reaction obviously helps fulfill the need for rapid generation of gas. The requirement for a nucleating agent explains the beneficial role of finely divided solids or finely dispersed air. It is interesting to note that a flexible foam having a cell count of one hundred cells per linear inch has one million cells per cubic inch, and so
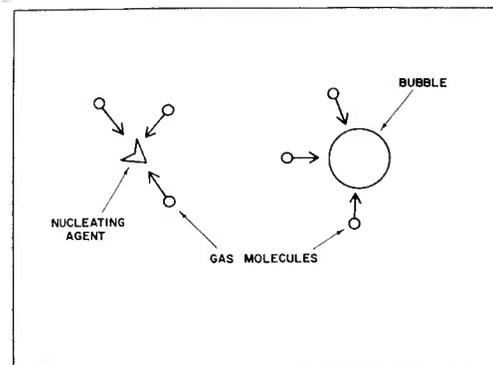
should have one million effective nuclei per cubic inch of foam or about three million per cubic centimeter of liquid foaming mixture! Naturally, not all nuclei will be effective, so one should have several times this many present if such a fine cell foam is desired. While one can easily add this many particles of a finely divided silica, the selection of the optimum particle shape and size for effective nucleation and the proper dispersion may not be easily achieved.

Hansen[10] has presented data in support of a similar role of nucleation in the extrusion of polyolefin foams. He obtained the finest cell size when the polyolefin contained finely dispersed blowing agent which was still decomposing outside the extruder die, and thus acting as nuclei for all formation. Under conditions with no blowing agent still decomposing and providing nuclei, the average cell struction was considerably coarser.

Bubble Stability

The formation of a bubble in a foam system is only one step along the road to successful foam production. The next step is that the bubbles must be stabilized so the foam will not collapse. The principal factors relating to bubble stability have been reviewed in detail,[15,16] and the main points need be summarized only briefly here.

To disperse a given volume of gas in a unit volume of liquid, one must increase the free energy of the system by an amount of energy (ΔF) as indicated by the equation

$$\Delta F = \gamma A = \Delta F = \gamma A$$

where γ is the surface tension and A is the total interfacial area. Therefore in a liquid foam system there is always a tendency to reduce the interfacial area. This relation means that a greater increase in free energy of the system will be required to produce fine cells than to produce large cells. It also means that coalescence of cells and foam collapse will be favored energetically unless prevented, i.e., curing of the foam before collapse can occur. It is also apparent that lowering the surface tension of the liquid, e.g., by the addition of silicone oil, will reduce the free energy increase associated with the dispersion of gas and will aid in the development of fine cells, which correspond to a large value for A.

A major factor affecting bubble stability is the drainage of the liquid in the bubble wall, due to both capillary action and gravity. This drainage thins the wall, thus favoring rupture. The principal factor which retards drainage is the increase in viscosity of the liquid, due to the polymerization reactions.

It is thus apparent that an attempt to prepare too fine cells may lead to collapse because rupture is more likely to occur in very thin cell walls.

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What may be even more important is that in very fine cells the ribs of the cells are very thin and may not be strong enough to stop the rupture which has started in a membrane. Thus the rupture will continue indefinitely and the foam will collapse.

An ideal situation for the preparation of open celled flexible foams is one in which the cell membranes do thin and rupture, then flow back into the stalks, leaving completely open cells. This rupture must occur late enough, however, so that polymerization has made the stalks strong enough to stop the rupture, thus avoiding splits or collapse.

The opening of the cells in certain flexible foams has been found to occur to a large extent just as the foam reached its maximum height. [15,16] The following sequence of events was suggested as a suitable hypothesis. It was suggested that the membranes of the cells at this time had reached a state of high viscosity, but still had very low elasticity. The high viscosity did not permit the membrane to flow fast enough to expand and relieve the pressure of the gas which was still being generated. At the same time, the elasticity was too low to permit reversible stretching of the membranes. The combination of failure of the cell to expand, a steadily increasing gas pressure, and low mechanical strength of the thin membrane resulted in rupture of the membrane, i.e., an opening of the cells.

If at this time of maximum gas evolution the membrane ruptured and the stalk or rib of the cell did not have sufficient mechanical strength to stop the rupture, then the rupture would spread. If the rupture stopped within several inches, one had a "split" or a "void" in the foam. If the rupture did not stop, the foam collapsed. The rib would be expected to rupture if the cells were so small that the rib was little thicker than the membrane, or if the polymer cure had not progressed far enough for the rib to have the strength to stop the rupture. The two effects would be expected to be interrelated.

On the other hand, if at the time of maximum gas evolution the cell membranes did not rupture, one had closed cells, and when the foam cooled, the cells of a flexible foam would contract due to the reduced internal pressure of the cooling gas. Failure of the membranes to rupture could be expected to result from too low a viscosity, so that the membrane could flow as the gas volume increased, thus relieving pressure as it developed. Failure to rupture could also be expected to occur if the membrane were so elastic that it could stretch reversibly to accommodate the last increase in gas volume. In the former case the polymer cure would not have progressed far enough at the time of maximum gas evolution, and in the latter case the cure would have progressed too far.

This hypothesis concerning the natural opening of the cell walls was shown to be in agreement with many observations of flexible foam systems. [15,16]

In most rigid foams closed cells are desired. In these cases the system is so balanced that the cell membranes do not rupture at the peak or gas evolution, very likely because of the presence of adequate elasticity to permit stretching without rupture.

In rigid foams a new problem is introduced by the closed cell character. The polymer must develop adequate strength to maintain its shape before the gas in the cells is cooled or shrinkage will occur because of contraction of the gas on cooling. Furthermore, in carbon dioxide blown foams, the carbon dioxide can diffuse out of the cells faster than air can diffuse in,[9] thus reducing the pressure in the cells still further. This loss of pressure due to diffusion can cause a very slow shrinkage of the foam. For these reasons, a highly cross linked structure is needed to provide adequate strength in the cell membranes to resist shrinkage, giving dimensionally stable rigid foams. An added advantage of the fluorocarbon-blown rigid foams is the extremely slow rate of fluorocarbon diffusion out of the foam and hence less likelihood of foam shrinkage.

Acknowledgement

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URETHANE FOAM PROPERTIES RELATED TO
THE FUNDAMENTAL POLYMER MOLECULAR STRUCTURE

R. D. Whitman, J. A. Faucher, and F. P. Reding

Introduction

Several publications have appeared in recent years concerning structure-property relationships in urethane polymers of the general type used in foam applications.[1,2,3,4,5] From these publications it is evident that urethane foam properties can be attributed to two factors: (1) the cell structure, and (2) the base polymer properties. This study was conducted specifically to determine how foam properties are influenced by the molecular structure of the polymer rather than the cell structure.

In this investigation the urethane polymers were prepared from exactly the same formulations of reactants used to make urethane foam, i.e., polyether triols, tolylene diisocyanate, water, surfactant, and catalysts. Structure-property relationships were established by changing the polymer molecular structure and observing the effect on the physical behavior. The polymer molecular structure was changed by varying the reactant ratios and the molecular weight of the polyol. In these studies the isocyanate structure was not changed; 80/20 2,4/2,6-tolylene diisocyanate was used in every case. The influence of the isocyanate structure on polymer properties has been investigated elsewhere.[4,6,7,8]

The urethane foams were compression molded into plaque-form in order to eliminate the cell structure. This greatly improved the accuracy of the physical testing of these materials since variations which usually occur in the cell structure were eliminated. The polymers were cured at a high temperature to force the reactions to completion as nearly as possible. Since the polymers in foam are usually cured under very mild conditions, they are most likely inferior to the molded polymers with respect to mechanical properties.

Experimental

Materials

Polyols. The polyols used for polymer preparation were resin grade oxypropylene triols (Union Carbide Corp. "Niax" Triols) with molecular weights of 265, 425, 700, 980, 1550, 2400, 3000, 4330, and 5200.

Tolylene Diisocyanate (TDI). A commercial grade of tolylene diisocyanate, an 80/20 mixture of 2,4/2,6-tolylene diisocyanate (Mobay Chemical Co.), was used in the production of all polymer samples.

Catalysts. The reaction leading to polymer formation were catalyzed with conventional urethane flexible foam catalysts such as stannous octoate (Metal and Thermit Corp.), N-methylmorpholine (Union Carbide Corp.), and N,N,N',N' tetramethyl-1,3-butane-diamine (Union Carbide Corp.).

Surfactant. Silicone oil L-520 (Union Carbide Corp.) was used as the surfactant.

Preparation of Polymers

Two types of polymers were prepared: (1) the reaction products of polyols, tolylene diisocyanate, and water, and (2) the products of polyols and tolylene diisocyanate without the addition of water. The former polymer is representative of those constituting urethane flexible foam.

Molded urethane polymer plaques were prepared by mixing the reactants, allowing the foam to rise in cases where water was included in the formulation, and immediately compression molding the mixture while in a semi-gelled state. The polymers were molded in a closed mold at 150°C with a pressure of 2,000 pounds per square inch. The molded samples had densities ranging from 1.0 to 1.3 grams/cc. Extended cure at a high temperature was used to optimize the polymer properties. In most cases equilibrium cure was achieved with a 2-hour cure at 150°C. The polymer samples made with water were cured in an air oven, and the polymers made without water were cured under vacuum.

Test Methods

In order to determine the relationships between polymer properties and molecular structure, it was necessary to investigate polymer mechanical properties such as the stiffness modulus, tensile strength, elongation, and mechanical loss; and physical properties such as glass transitions.

An Instron tester was used for determining the tensile properties. The tensile specimens were die-cut from the molded plaques with a dumbell-shaped cutter which provided a 0.25 x 1.0 inch test specimen. The stiffness measurements were made at a crosshead speed of 0.1 in./min. and the tensile strength and ultimate elongation tests were performed at 1.0 in./min. The stiffness was calculated as the ratio of stress to strain at a 1 per cent elongation based on jaw separation. The ultimate elongation was determined by the increase in the distance between bench-marks which were made on the specimen before testing. The tensile strength was calculated as the maximum stress attained before specimen failure.

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Both an Instron tester and recording torsion pendulum were used for measurements of polymer mechanical loss. The Instron method consisted of stretching the specimen to a 50 per cent elongation at a 1.0 in./min. crosshead speed and then immediately reversing the crosshead to relax the specimen at the same rate. Mechanical loss was then calculated from the stress-strain hysteresis curve as shown in Fig. 1. A recording torsion pendulum similar to the one described by Nielsen[9] was used to measure dynamic mechanical loss in the polymer samples. In this device the oscillating motions of an inertia wheel are damped by the mechanical loss in the test specimen. The frequency of inertia wheel oscillations was about 1 cycle per second. A typical damping curve and the equation of the mechanical loss coefficient, Q^{-1}, are shown in Fig. 2. The values of the loss coefficient, Q^{-1}, usually ranged from 0.01 to 0.5, but the polymer was considered to be fairly lossy or non-elastic if Q^{-1} exceeded 0.05.
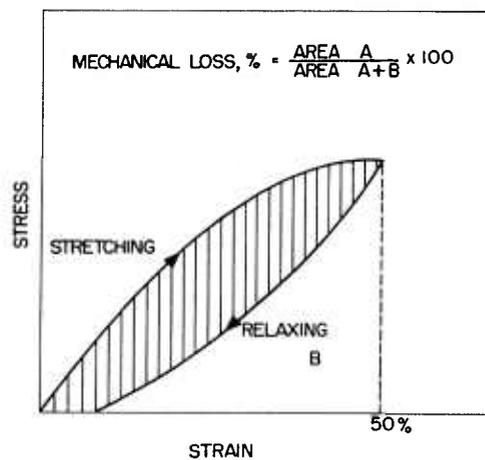
Fig. 1. Method of determining mechanical loss from stress-strain hysteresis curve.
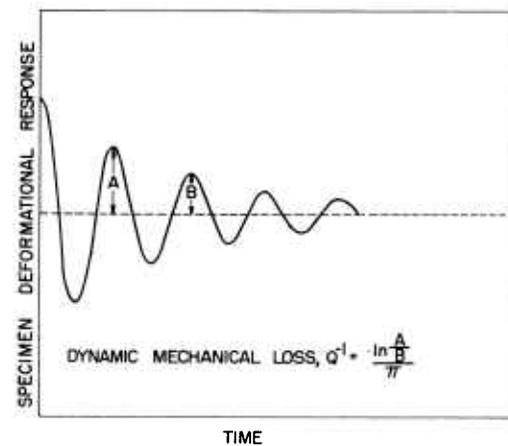
Fig. 2. Dynamic mechanical loss described by a torsion pendulum damping curve.

Both the Instron tester and the torsion pendulum were equipped with a temperature-control device which made it possible to make measurements of the tensile properties and mechanical loss from -180° to 250°C. This equipment provided a means for investigating the temperature dependency of the polymer properties.

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Results and Discussion

Polymer Structure

The urethane polymers were produced by reacting three basic ingrediets: (1) oxypropylene triols, (2) tolylene diisocyanate, and (3) water. Polymer formation proceeds through two general reactions:

$$-NCO + -OH \longrightarrow \underset{\displaystyle -N-C-O-}{\overset{\displaystyle H \;\; O}{}} \, , \tag{1}$$

$$2\,(-NCO) + HOH \xrightarrow{\;-CO_2\;} \underset{\displaystyle -N-C-N-}{\overset{\displaystyle H \;\; O \;\; H}{}} \, . \tag{2}$$
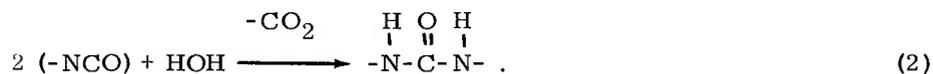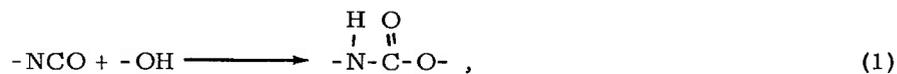
Reaction 1 produces the urethane group and Reaction 2 leads to disubstituted ureas. The former reaction occurs in one step and the latter reaction possibly proceeds through several intermediates. The products of both of these reactions contain active hydrogens that can be further reacted with isocyanate as follows:

$$-NCO + \underset{\displaystyle -N-C-O-}{\overset{\displaystyle H \;\; O}{}} \longrightarrow -\underset{\substack{C=O\\ | \\ N-H \\ |}}{\overset{\displaystyle O}{N-C-O-}} \, , \tag{3}$$

$$-NCO + \underset{\displaystyle -N-C-N-}{\overset{\displaystyle H \;\; O \;\; H}{}} \longrightarrow -\underset{\substack{C=O\\ \backslash \\ N-H \\ |}}{\overset{\displaystyle H \;\; O}{N-C-N-}} \, . \tag{4}$$
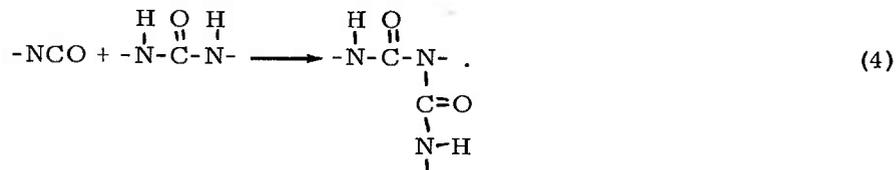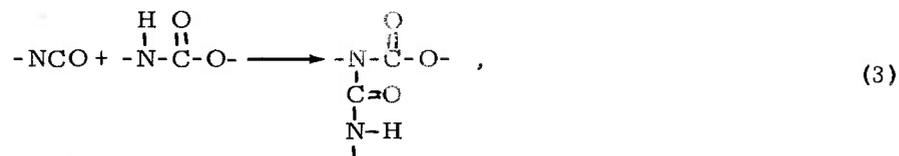
The products of the secondary Reactions 3 and 4 are allophanates and biurets, respectively.

Assuming that Reactions 1 and 2 predominate, the polymer molecular structure can be described by the schematic diagram of Fig. 3. In order to simplify the schematic the aromatic portion of the isocyanate is not shown.

If the urethane polymer is made without water, the polymerization process involves essentially only Reaction 1. The molecular structure of this polymer is shown in Fig. 4.

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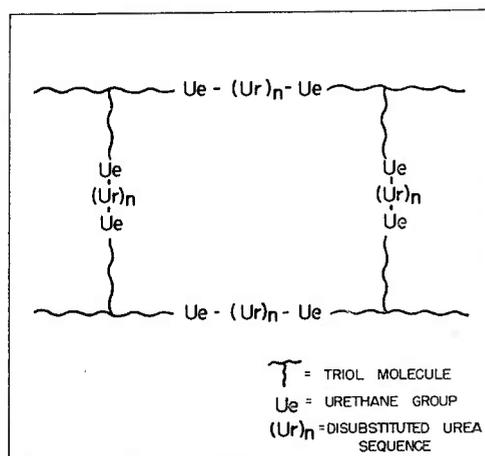
Fig. 3. Schematic diagram of urethane polymers made with water.
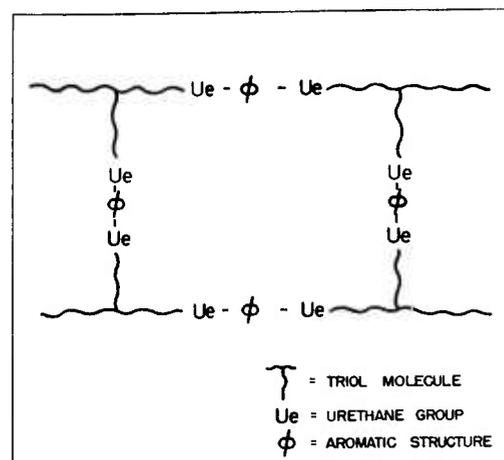
Fig. 4. Schematic diagram of urethane polymers made without water.

The primary cross-link density of the urethane polymer is determined by the molecular weight and functionality of the polyol (in this case triol). The average urea sequence length is proportional to the triol molecular weight and the amount of water used.

Polymer-Properties

Glass Transition, T_g. The glass transition phenomenon is associated with long range molecular motions in the amorphous regions of a polymer. Such motions in these regions are "frozen" at temperatures below the glass transition temperature, T_g, and the amorphous regions in the polymer are rigid and glass-like. At temperatures above T_g, the amorphous polymer is very flexible and rubber-like. T_g is a function of the flexibility of the polymer chain segments; an increase in chain flexibility lowers T_g and conversely a decrease in chain flexibility raises T_g. The physical state of a polymer, therefore, is determined not only by temperature but also by the characteristic molecular structure.

Measurements of stiffness and mechanical loss at different temperatures were used to establish the glass transitions of the urethane polymers. Fig. 5 describes how T_g was obtained from the stiffness-temperature and loss temperature curves. Although the transition behavior is characterized by a rather broad temperature range, the T_g is defined as the inflection point of the stiffness temperature curve and the maximum of mechanical loss of the loss-temperature relationship.

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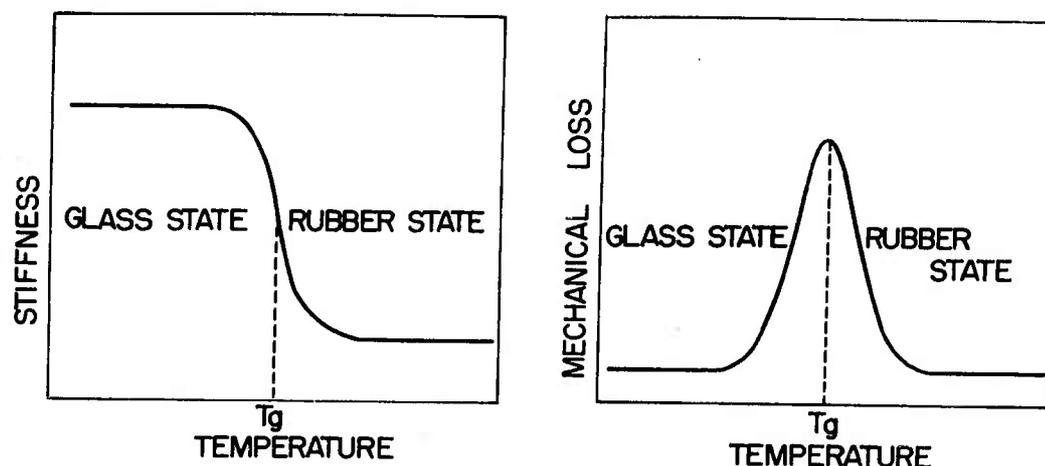
Fig. 5. Determination of Tg from stiffness-temperature
and loss-temperature curves.

The transitions of urethane polymers are represented by fairly high
amplitude loss peaks in loss-temperature curves indicative of the amorphous
nature of these polymers. The absence of crystalline melting behavior is
further evidence that the polymers are almost completely amorphous. Fig. 6
shows the loss-temperature curve of a polymer made from a 3,000 molecular
weight triol. This polymer was prepared with water and is, therefore, repre-
sentative of polymers in urethane flexible foam. The Tg of this material is
about -45°C.

Fig. 7 shows the relationship between Tg and the molecular weight of
the base-triol in polyurethanes prepared without water. Molecular weight is
expressed in terms of the hydroxyl number of the triol. The triol molecular
weight can be calculated from the hydroxyl number (assuming an average
functionality of 3) using the following equation:

$$\text{triol molecular weight} = \frac{168,000}{\text{hydroxyl number}}$$

As expected, Tg increases as the hydroxyl number increases. Extrapolation
of the glass transitions gives a Tg of -70°C for a polymer based on a triol of
infinite molecular weight (zero hydroxyl number) which is, in essence, poly-
(propylene oxide). This is in good agreement with the Tg of -62° to -65°C
for poly(propylene oxide) determined experimentally by Read.[10]

The urethane polymer glass transition behavior appears to result from
motions of the oxypropylene sequences located between fairly rigid urethane

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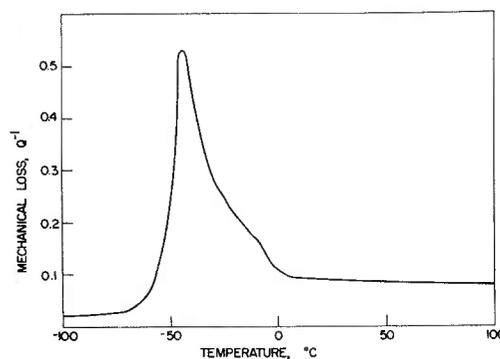
Fig. 6. Loss-temperature curve of a urethane polymer made from a 3,000 molecular weight oxypropylene-triol, TDI and water (4 parts in 100 parts triol).
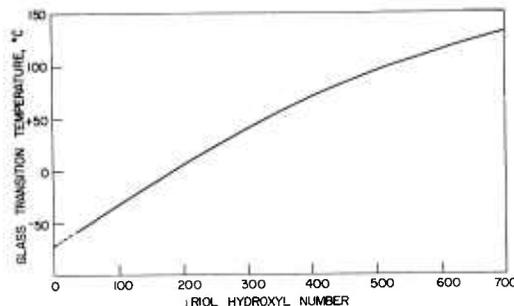
Fig. 7. Urethane polymer Tg as a function of the oxypropylene-triol hydroxyl number (polymers made without water).
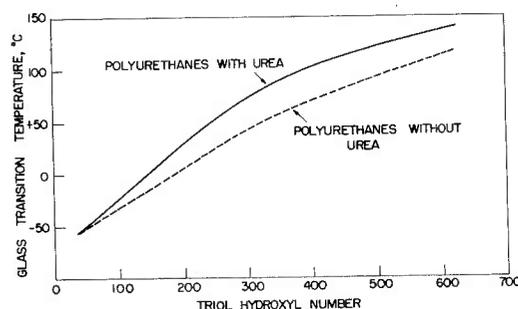
Fig. 8. Effect of urea structures on the Tg of urethane polymers of various oxypropylene-triols.

(and urea where water is used) structures. Reduction of the oxypropylene chain length has the net result of adding restrictions to the chain flexibility which causes an increase in Tg.

Disubstituted urea structures in polyurethanes which are produced by adding water, and the necessary iso-cyanate for the water, to the base formulation have some influence on Tg as seen in Fig. 8. These polymers were made from formulations in which the triol molecular weight was varied but the amount of water (4 parts in 100 parts triol) was held constant. Although the Tg of polymers made from high molecular weight triols is unaffected by the ureas, an increase in the Tg of low molecular weight triol polymers does occur. This phenomenon probably does not relate to molecular motions of the ureas since these structures are certainly rigid throughout the whole temperature range of the measurements. The hydrogen bonding associated with the highly polar urea is probably responsible for the observed increase in Tg.

Stiffness. The stiffness or rigidity of the urethane polymer is greatly dependent upon temperature which determines the polymer physical state. The general relationship between stiffness and temperature was demonstrated in Fig. 5. At temperatures below Tg the polymer is a glass-like material and has a very high stiffness. This high stiffness is due to the rigidity of the polymer backbone chains. As the temperature is raised above Tg, the chains become more flexible and the stiffness greatly decreases.

The oxypropylene block sequences have previously been described as the flexible parts of the urethane polymers

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responsible for the glass transition behavior. Fig. 9 shows the effect of this polymer chain flexibility on the room temperature stiffness of polyurethanes prepared from triols of various molecular weights. These polymers were made without water and hence do not contain disubstituted ureas. As the triol molecular weight is lowered (increasing hydroxyl number), the polymer stiffness increases proportionally until the triol molecular weight is low enough to raise the polymer Tg above room temperature. At this point a very sharp rise in stiffness is observed. All of the polymers with glass transitions above room temperature show nearly the same stiffness, around 200,000 pounds per square inch, which is characteristic of the glassy state.

Fig. 9. Room-temperature stiffness of urethane polymers as a function of the hydroxyl number of the oxypropylene-triol (polymers made without water).

Polyurethanes prepared with water differ greatly from the polyurethanes made without water in their stiffness behavior at temperatures above Tg. These differences are due to the presence of disubstituted ureas, the major products of the water/isocyanate reactions. Hydrogen bonding between the urea sequences makes these structures very efficient in rigidifying the polymer molecular structure at temperatures above Tg where the chain segments are very flexible.

The relationship between the room temperature stiffness of polyols based on a 3,000 molecular weight triol and the amount of urea in the polymer is shown in Fig. 10. The urea content was varied over a wide range by using different amounts of water in the base polymer formulation. The increase in stiffness is attributed very simply to the greater weight per cent of the rigidifying urea.

The stiffness of the urethane polymer at temperatures below Tg does not appear to be further increased by the addition of urea. In the glassy state the polymer chains are quite rigid and the extra rigidifying action of the ureas is of little consequence. Fig. 11 illustrates the effects of the ureas on the room temperature stiffness of polyurethanes based on triols of different molecular weights. At a low triol molecular weight (high triol hydroxyl number) where the polyurethane Tg is well above room temperature, the stiffness of the urea-containing polymers does not differ greatly from the polymers

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Fig. 11. Room-temperature stiffness
of urethane polymers vs. hydroxyl
number of the oxypropylene-triol
(polymers made with water).

Fig. 10. Relationship between the
room-temperature stiffness of
urethane polymers based on a
3,000 molecular weight
oxypropylene-triol and the urea
concentration.

without the ureas. As the triol molecular weight is raised (triol hydroxyl
number is lowered), an abrupt decrease in stiffness occurs at different triol
molecular weights in the two types of polymers. The transition in stiffness
occurs at a higher triol molecular weight in the urea-containing polymers
because of the increase in the Tg due to the ureas (see Fig. 8). As the triol
molecular weight is further increased, the polymer Tg is displaced below
room temperature and a slight increase in stiffness follows.

The increase in stiffness of urea-containing polymers which results from
increasing the triol molecular weight without changing the amount of water and,
therefore, the weight per cent urea structure in the formulation can be attrib-
uted to the length of the urea sequences. Raising the triol molecular weight
while maintaining a constant weight ratio of water increases the length of the
disubstituted urea sequences between polyol molecules. Probably more effi-
cient hydrogen bonding is possible in these longer sequences. It is recalled
from Fig. 7 that the stiffness of polymers without the ureas decreases as the
triol molecular weight is raised. With water, however, the reverse is true.

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Tensile Strength and Elongation. The polymer physical state greatly influences the ultimate tensile properties, the tensile strength and elongation, as well as stiffness. In the rubbery state the polymers are characterized by fairly high elongations and relatively low tensile strengths. The tensile strength of these materials is very dependent on the concentration of the disubstituted ureas. Moreover, the increase in tensile strength which is produced by the ureas is of the same order as the stiffness increase which was previously discussed. This is shown in Table 1.

TABLE 1

Effect of Urea on the Tensile Properties of
Polyurethanes Made From 3,000 Molecular Weight Triols

	Stiffness, psi	Tensile, psi
Polyurethanes without urea	300	120
Polyurethanes with 9 wt. per cent urea	8,200	1,800

The elongation of polymers in the rubber state appears to be related more to the primary cross-link density than any other one factor. Increasing the molecular weight of the triol lowers the primary cross-link density and the elongation is raised as illustrated in Fig. 12. The urea-containing polymers exhibit elongations similar to those of the polymers without urea.

In the glassy state the urethane polymers are fairly brittle with high tensile strengths and low elongations. Table 2 reveals these trends in polymers prepared from 265 and 425 molecular weight triols. The glass transitions of both polymers are well above room temperature and the tensile properties are, therefore, typical of glass-like materials. The addition of urea to the polymers in the glassy state does not appear to increase the tensile strength or the elongation to an appreciable extent.

Mechanical Loss. The loss temperature curve (Fig. 6) of the urea-containing urethane polymer based on a 3,000 molecular weight triol suggests that this material is
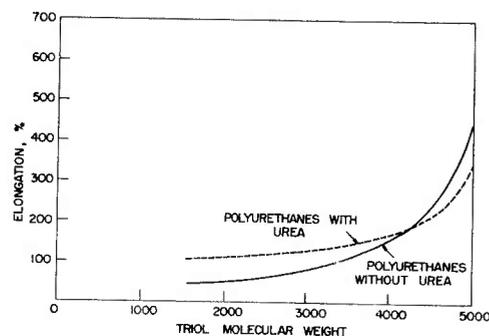
Fig. 12. Effect of triol molecular weight on the elongation of urethane polymers.

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TABLE 2

Brittle Behavior of Polyurethanes
Based on Low Molecular Weight Triols

Triol Molecular Weight	Polyurethane Tensile Properties	
	Tensile Strength, psi	Elongation %
265	10,000	6.5
425	6,800	8

fairly non-elastic. The level of loss above the Tg of this polymer is quite high when compared to the behavior of most other polymeric materials. The elastic properties of the urethanes appear to be fundamentally related to the disubstituted urea structures and the hydrogen bonding associated with them.

Fig. 13 compares the loss behavior above the Tg of the two types of urethane polymers, those with urea and those without urea. Both of these polymers were made from 3,000 molecular weight triols, and the polymer with urea was formulated with 4 parts water in 100 parts polyol which produces about 9 weight per cent urea in the final polymer.

The relationship between mechanical loss and the urea content is shown in Fig. 14. All of the polymers contained in this figure were prepared from a
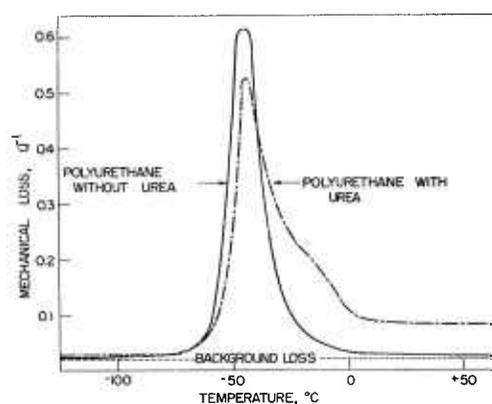
Fig. 13. Effect of urea on the loss-
temperature behavior of urethane
polymers based on a 3,000 mo-
lecular weight oxypropylene-triol.
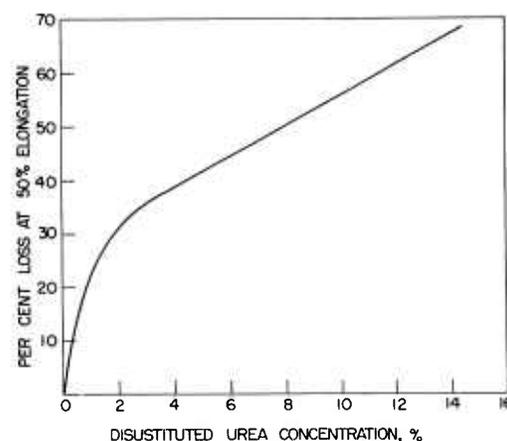
Fig. 14. Relationship between per
cent hysteresis loss and the urea
content of urethane polymers made
from a 3,000 molecular weight
oxypropylene-triol.

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3,000 molecular weight triol and the urea content was varied by the addition of water, and isocyanate necessary to react with the water, to the base poly-mer formulation.

Mechanical loss above Tg in urethane polymers made with water is believed to result mostly from the breaking of hydrogen bonds when the polymer is strained.[4] Since a major part of the polymer strength is derived from the hydrogen bonding, a marked decrease in the strength results when the bonds are disrupted. Moreover, if the polymer is maintained in a strained condition for a long period of time the hydrogen bonds continue to break and the polymer "creeps," as evidenced by a stress relaxation. If the polymer is relaxed and especially if it is heated while it is relaxed, the hydrogen bonds will be re-established and the strength recovers. Although most polymers are subject to creep-behavior because of factors such as chain slippage the urethanes appear to be poorer than most in this respect because of the hydrogen bonding phenomena. The loss properties of the urethanes used in flexible foam can be improved considerably by making the polymer without the water which is responsible for the ureas, but the reduction in strength would be intolerable.

Foam Properties Related to Polymer Properties

Load-Bearing. The load-bearing properties of urethane foams are basically determined by the stiffness of the urethane polymer. The urethane polymer glass transition is important in the production of the various types of foams, e.g., rigids, semi-rigids, and flexibles. A foam comprised of a polymer with a Tg well above room temperature is very rigid. Conversely, if the polymer Tg is well below room temperature, the foam is a flexible type. Semi-flexible foams are produced from polymers with glass transitions in the immediate vicinity of room temperature.

The stiffness of polymers with glass transitions well below room temperature is derived mostly from hydrogen bonding. Polymers of this type are used mostly for flexible foam applications and must have this hydrogen bonding in order to provide these foams with the required strength. Since the urethane polymers used in rigid foam applications have glass transitions above room temperature, they are very rigid and do not require the hydrogen bonding from the ureas. For this reason water is not usually required in rigid-foam formulations. Although rigid foams are generally not produced from the same type of polyols used in flexible foams, the resulting polymer always has a Tg above room temperature.

A comparison of the trends in foam properties with the trends observed in the properties of the molded urethane polymers suggests that the polymers are not the same even though they are based on the same ingredients. These differences are believed to result from the manner in which the two products are reacted or "cured." For example, the foams based on triols with molecular weights above 3,000 generally exhibit poor load-bearing properties;

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whereas, the molded polymers of these same ingredients have a very high stiffness. The molded polymers were cured much more rigorously than the foams and for this reason are more completely reacted. This indicates that the potential properties of the polymer are never fully realized in foams because of insufficient cure. The cure problem is most apparent in foams made from high molecular weight polyols.

Tensile Strength and Elongation. Foam tensile strength and elongation properties result from these same properties of the polymer. Hydrogen bonding has a great bearing on the tensile strength in flexible foams similar to the affect on stiffness. Of course, in rigid foams the forces of hydrogen bonding have very little effect on the tensile strength or stiffness. Although hydrogen bonding tends to increase the elongation somewhat in flexible foams, the elongation seems to relate more to the polymer primary cross-link density.

The extent of cure of the flexible urethane foams has a very large effect on the elongation properties. If the cure is relatively incomplete, unreacted chain ends are left in the polymer. As a result, chain slippage is increased. This phenomenon probably accounts for the unusually high elongations which are observed in foams based on triols of molecular weights higher than 3,000. The elongations of these foams could very likely be reduced by extending the cure to complete the reactions.

Flex Fatigue. Mechanical loss in the urethane polymer is responsible for flex fatigue in urethane foam. A high-loss behavior is inherent in the urethane polymers made with water because of the actions of hydrogen bonding, and, therefore, flex fatigue is observed in all foams made from polymers of this type.

In flexible urethane foams, flex fatigue and the load-bearing properties are directly related to the amount of water used in their preparation. Improvements in flex fatigue obtained through a reduction in the amount of water used are more than offset by the decrease in load-bearing properties.

Although flex fatigue in urethane flexible foams will very likely never be eliminated completely, it can certainly be minimized to a tolerable level. Fortunately, flex fatigue as experience in most urethane flexible foam applications is not a severe problem since these materials generally outwear most competitive products. This can be attributed to the fact that the loss in load-bearing properties caused by the breaking of hydrogen bonds during flexing is recoverable to a great extent through re-establishment of these bonds. Since most usages of flexible foam involve cyclic compression and relaxation, the relaxation periods offer an opportunity for the hydrogen bonds to reform.

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INSULATION PROPERTIES OF FLUOROCARBON
EXPANDED RIGID URETHANE FOAM

R. E. Knox

Introduction

The development, use, and acceptance of urethane foam for numerous end uses has been extremely rapid with continued future growth expected. In one decade, urethane foam has evolved from a laboratory curiosity to an item of commerce, with consumption now in excess of 100 MM lb/year.[1] To date, the major outlet for urethane foam has been for flexible applications. Recently, however, the use of rigid urethane foam has started to increase, and its consumption could well equal that of resilient foam by the end of the decade with a total market in excess of 500 MM lb/year.

Rapid growth of rigid urethane foam is expected to materialize because of its remarkable combination of physical properties and the relative ease by which resilient foam processing technology, already well advanced, can be applied to rigid urethane foam. Being fluid, rigid urethane foam systems can be casted, poured-in-place, or sprayed. Equipment and techniques quite similar to those employed with resilient urethane foam are being used today to manufacture rigid foam at high output rates. Rigid urethane foam cures without the need of external heat to yield a dimensionally stable product. This product has high strength at low density and is resistant to many chemicals and to moisture pick-up. It has good adhesion properties and can be produced over a wide range of densities in fire resistant form. Typical physical properties of rigid urethane foam are given in Table 1.

In addition to the above features, rigid urethane foam possesses another outstanding property--it has extremely low heat transmission rates when produced with fluorinated hydrocarbon expanding agents such as trichloromonofluoromethane (Fluorocarbon 11)* and dichlorodifluoromethane (Fluorocarbon 12).** This particular property is the subject of this paper. Data for fluorocarbon expanded foam will be presented showing (1) its insulation performance relative to other insulating media under simulated in-use conditions, (2) its heat transmission rate as a function of temperature and age, and (3) the effect of foam structure on its heat transmission rate.

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*Available as "FREON 11", registered trademark of E. I. du Pont de Nemours & Co.
**Available as "FREON 12", registered trademark of E. I. du Pont de Nemours & Co.

TABLE 1

Typical Physical Properties of Fluorocarbon 11 Expanded Polyether Rigid Urethane Foam

Density, lb/ft^3	1.8 - 2.2
Tensile Strength, psi at break	44
Compressive Strength, psi at yield	41
Closed Cells, % of foam volume	91
Moisture Vapor Transmission, perm. in. (at $100^{O}F$, 100% R.H.)	2.5
Water Absorption, lb/ft^2 (Water Immersion 8' head for 7 days at R.T.)	0.05
Dimensional Stability, % Linear Change	
14 days at $-15^{O}F$	<-0.5
14 days at $100^{O}F$, 100% R.H.	< 2
14 days at $200^{O}F$	< 1
*Thermal Conductivity ("k" Factor), (Btu)/(hr) (ft^2) $(^{O}F/in.)$ at $75^{O}F$ mean temperature	0.11 - 0.13
Service Temperature, Upper Limit, ^{O}F	225
Lower Limit, ^{O}F	-300

*Determined on unaged foam sample.

"k" Factor of Fluorocarbon Expanded Rigid Urethane Foam

The insulation industry traditionally has used the term "k" factor, usually expressed as $(Btu)/(hr)(ft^2)(^{O}F/in.)$, to characterize the insulation performance of a material. That rigid urethane foam is a superior insulating material is evident from Table 2 which compares its heat transmission rate to that of other common insulating materials. The low "k" factor results from encapsulation of high molecular weight fluorocarbon gases in urethane foam polymer. The relationship between molecular weight and thermal conductivity of several gases is shown in Fig. 1. Although this relationship has long been known, high molecular weight gases have not been widely utilized until recently because of the difficulty of efficiently containing the gas for insulation applications. Rigid urethane foam technology has been developed to the point that this problem no longer exists.

TABLE 2

Typical "k"* Factor for Commercial Insulation Materials

	"k" Factor at 75°F
Powdered Gypsum	0.50
Glass Foam	0.40
Sawdust	0.36
Rock Wool	0.32
Cork	0.28
Polystyrene Foam	0.26
Hair Felt	0.25
Glass Fiber	0.23
Urethane Foam, CO_2 expanded	0.23
Urethane Foam, Fluorocarbon 11 expanded	0.12

*"k" = $(Btu)/(hr) (ft^2) (°F/in.)$
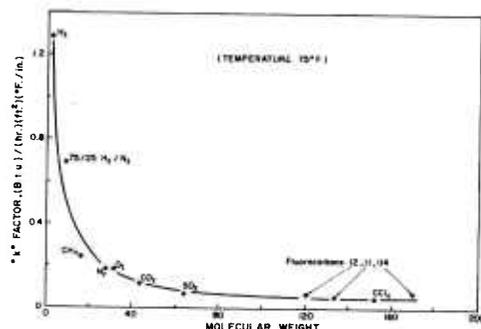
Fig. 1. Thermal conductivity of gases as a function of molecular weight.

It is now common practice to employ fluorocarbon gases such as Fluorocarbon 11 for the dual purpose of generating the foam and reducing the foams' thermal conductivity. Urethane foam polymer is relatively impermeable to fluorocarbon gas and, as a result, gas retention is excellent.

Relative Insulating Effectiveness
of Fluorocarbon Expanded
Rigid Urethane Foam

A "k" factor value, though useful in assessing a material's thermal insulation properties, cannot quantitatively predict the performance of a material in actual service because the test does not simulate well the many environmental conditions which can be encountered. For example, "k" factors are run very often at a mean temperature of 75°F where the cold side is maintained at 32°F and the hot side at 118°F. Very seldom is an insulating material used at these particular temperature conditions. Also, when a foamed material is tested for "k" factor, a relatively thin specimen is used, while in actual service the foam either has a dense skin on its outer surface or is integrally adhered to common facing materials. It was felt that a simulated in-use test would give more practical and meaningful data than data obtained by conventional "k" factor determinations. A simple but reproducible test was devised which enabled comparisons to be made of the relative thermal insulation resistance of a number of media under a wide variety of exposure conditions.

Test Principle for Determining Relative
Insulating Effectiveness

Insulating effectiveness was determined by measuring the evaporation rate of a constant boiling liquid under equilibrium conditions from containers completely insulated with the various test media. By running several different insulating media simultaneously under controlled environmental conditions, a direct comparison could be made of their relative insulating effectiveness.

Equipment Used

A dimensioned view of the insulated evaporation tube assembly used for this study is shown in Fig. 2. The cylindrical shape of the evaporation tube was chosen to assure a constant insulation thickness and to simplify heat transfer calculations. The insulation thickness used for all experiments was 1.8". The tubes were made of copper which has a heat transmission rate over 100 times that of the insulating media being tested. Any heat transmitted through the insulation above the liquid level was transferred immediately by the copper to the liquid, and as a result, the liquid evaporation rate became largely independent of the liquid level in the tube. This simplified the procedure since it eliminated the need to maintain a constant liquid level within the evaporation tube.

The tube was equipped with an insulated but loose fitting plug. This facilitated filling, prevented pressure buildup by providing a narrow path for venting the vaporizing liquid, and minimized heat flow via a large uninsulated opening.

In most tests the insulated evaporation tubes were covered with a "MYLAR"* film. This film served as an effective vapor barrier but which could be removed in order to study the effect of moisture and free convection on the insulating efficiency of the test media. Provisions also were made for determining the effect of air flow across the insulated surfaces on the relative insulating effectiveness of the various test media.

The procedure used is similar to those employed for cryogenic investigations[2] with the following major difference. The Elastomers

Fig. 2. Cross section of evaporation tube.

REMOVABLE INSULATED PLUG (VAPOR FROM TUBE ESCAPES AROUND PLUG'S PERIPHERY)

INSULATION (1.8" THICK)

2" DIAMETER x 20" LONG COPPER TUBE (.0625" WALL THICKNESS)

CONSTANT BOILING LIQUID

REMOVABLE MYLAR® BARRIER

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*du Pont trademark for its polyester film.

Laboratory procedure determines the equilibrium evaporation rate by direct weight measurement of the entire tube assembly, whereas in cryogenics experimentation the evaporation rate is determined by passing the vapor through a wet test meter. Provisions must be made in the cyrogenic procedure to prevent vapor condensation in the lines leading to the meter. The procedure to be reported on here is simpler, less expensive, and yields more rapid results without apparent sacrifice in accuracy. While errors in the procedure can occur (e. g. , very small return heat flow through a non-insulated pathway, minor external temperature fluctuations), they will be small and will cancel out since all media are tested concurrently.

Materials Used

Table 3 lists the constant boiling liquids used for test purposes with their pertinent physical properties. The choice of liquid was made on the basis of boiling point, availability, low toxicity, and non-flammability.

TABLE 3

Constant Boiling Liquids

Name	Molecular Weight	Boiling Pt. , $^{\circ}$F at 1 atm	Thermal Conductivity of Vapor at 86°F Btu/hr ft^2 $^{\circ}$F - in.	Ht. of Vap. , at B.P. , Btu/lb
Fluorocarbon 11 (CCl_3F)[1]	137.38	74.8	0.058	78.31
Fluorocarbon 114 ($CClF_2CClF_2$)[2]	170.93	38.4	0.078	59.00
Fluorocarbon 12 (CCl_2F_2)[3]	120.93	-21.6	0.067	71.04
Fluorocarbon 22 ($CHClF_2$)[4]	86.48	-41.4	0.081	100.66
Fluorocarbon 13Bl ($CBrF_3$)[5]	148.9	-72.0	-	51.08
Fluorocarbon 13 ($CClF_3$)[6]	104.47	-114.6	-	63.85
N_2	28.0	-320.0	-	85.00

(1) FREON 11, (2) FREON 114, (3) FREON 12, (4) FREON 22, (5) FREON 13Bl, (6) FREON 13, E. I. du Pont de Nemours & Co.

The insulating media tested included commercially available fluorocarbon expanded rigid urethane foam, ground cork, vermiculite, several grades of commercially available glass fiber, and polystyrene foam (see Table 4).

TABLE 4

Insulating Media Used for Relative Insulating Effectiveness Evaluation

Media	Density, lb/ft^3
Polyether Urethane Foam, Fluorocarbon 11 expanded (cast in place)	2.0
Glass Fiber, purchased	
(a) standard pipe type	7.0
(b) blanket type	1.0
(c) semi-rigid board type	6.0
Ground Cork, purchased, bulk	10.0
Polystyrene Foam, purchased	2.0
Vermiculite, purchased, bulk	12.0

Test Conditions

Many different experimental hot and cold side temperature conditions were used. The cold side temperature was varied by substituting liquids of different boiling point in the evaporation tube, while the hot side (outside of tube) was maintained at room temperature or varied by placing the evaporation tube in a temperature controlled oven or cold box. Over an experimentation period of several months, the hot side temperature was varied from 230° to $-60^\circ F$ and the cold side from 75° to $-320^\circ F$. Also, during the experimentation period, frequent reruns at specific temperatures were made to determine the effect of aging and temperature extremes on maintenance of insulation properties. Many of the test conditions used approximated temperatures associated with home and commercial appliances, cold storage, reefer trucks, and building insulation. For example, a home refrigerator was simulated by using an external (hot) temperature of $78^\circ F$ and an inside (cold) temperature of $38^\circ F$, while a refrigerated meat truck was simulated by using either external (hot side) temperatures of 78° and $120^\circ F$, and an inside (cold side) temperature of $-21.6^\circ F$.

Experimental Procedure

Each insulated tube of known tare weight was filled with a given quantity of liquid. After sufficient time elapsed for equilibration, each tube was re-standardized by adding additional liquid. Then the experiment was commenced. Rate of weight loss of constant boiling liquid was determined by weighing each tube periodically. The test was terminated when less than five per cent of the liquid remained. Since most of the liquids used were low boiling, i.e., less than room temperature, and were normally received in pressurized cylinders, it was necessary to cool them below their boiling point before transferring to the insulated tube.

Data Analysis

Equilibrium evaporation rates were determined by plotting the weight of liquid remaining versus time. As an example, typical evaporation rate plots are shown in Fig. 3 for the various insulating media in which an external temperature of $118^{\circ}F$ and an internal temperature of $-21.6^{\circ}F$ was used. Significantly, weight loss is linear with time verifying that by this technique evaporation rate is independent of liquid depth in the tube. Also, under these test conditions, it will be noted that the evaporation rate increases in the following order: urethane foam, glass fiber, polystyrene foam, and vermiculite.

The rate of heat transfer through the various insulating media may be determined by the following equation:

$$\text{rate of heat transfer (Btu/hr)} = \frac{\text{evaporation rate, g/hr x heat of vaporization Btu/lb}}{453.6 \text{ g/lb}} .$$
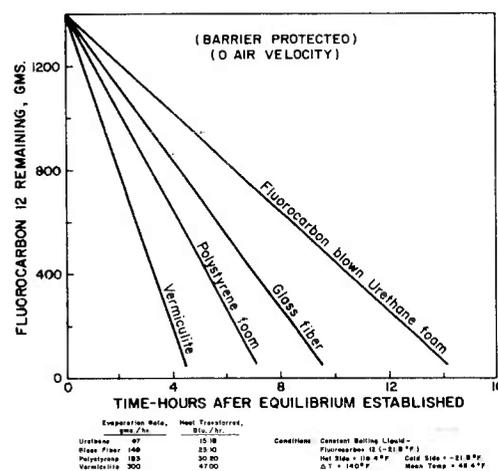
Fig. 3. Typical evaporation experiment.

By knowing the heat transfer rate that occurs with each insulation under the various simulated service conditions, it is an easy matter to calculate the relative insulation effectiveness of any two materials. For example, it can be determined, by applying the above equation to the data in Fig. 3, that the rate of heat transfer for polystyrene foam is 30.2 Btu/hr and for rigid urethane foam 15.18 Btu/hr. Thus, for non-curved surfaces, one inch of rigid urethane foam gives insulation performance equivalent to 2 inches of polystyrene foam.

Fig. 4 shows the relative insulating effectiveness of urethane foam compared to other insulating media

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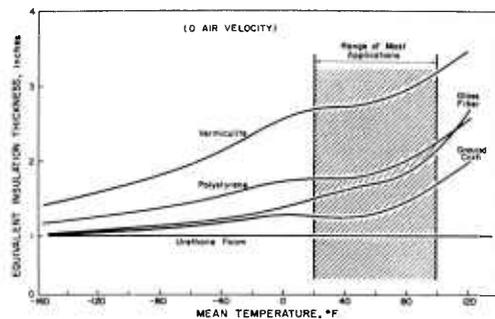
Fig. 4. Equivalent insulation thick-
ness of various media.
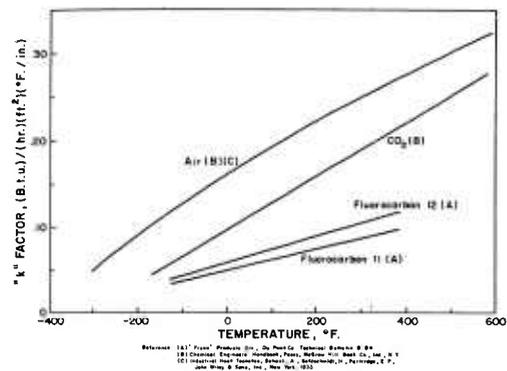
Fig. 5. Thermal conductivity of
gases at various temperatures.

over a wide range of mean tempera-
tures. In this work all media tested
were vapor barrier protected with
MYLAR film. Of particular interest are the following points: (1) fluorocarbon
expanded urethane foam is superior to all media tested; (2) fluorocarbon ex-
panded urethane foam's relative insulating effectiveness advantage over other
media decreases with decreasing mean temperature. This latter point is to
be expected since all insulating media will be equivalent at or near absolute
zero. This is best shown by referring to Fig. 5 which shows the variation of
thermal conductance of various gases as a function of temperature. As the
temperature decreases, all values decrease. However, the slopes for the
higher conductivity gases are greater, resulting in greater decrease in ther-
mal conductance with decreasing temperature. Thus, the relative insulating
effectiveness of urethane foam compared to other media should be expected
to and, in fact, does decrease with decreasing mean temperature. Referring
to Fig. 4, the cross-hatched area represents the temperature range for the
major actual and anticipated volume outlets for insulating media. Table 5
lists the hot, cold, and mean temperature conditions for several commercial
insulation applications. As indicated in Fig. 4, the outlets listed in Table 5
fall well within the region wherein fluorocarbon expanded urethane foam enjoys
its greatest relative insulating effectiveness advantage over other insulating
media.

In some cases, evaporation tests were run with the vapor barrier
(MYLAR) protection removed from the test insulating media. Urethane foam
gave equivalent insulation with and without barrier protection. However, this
was not true with the other insulating media as is shown in Fig. 6. The in-
creased rate of heat transmission for unprotected glass fiber, polystyrene
foam, and cork is believed due to the increased convection currents set up
within these other media which do not have a tight or as small a closed cell
network as does urethane foam. Also, the data in Fig. 6 show that with the

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TABLE 5

Service Temperatures for Various Insulation Applications

	Temperatures, ^{O}F		
Service	Hot	Cold	Average
Home Refrigerator	80	38	59
Home Freezers	80	-20	30
Reefer (refrigerator) Trucks			
Vegetable Service	120	40	80
Meats	120	-20	50
Building Insulation			
Summer	120	80	100
Winter, south	80	38	59
north	80	-20	30
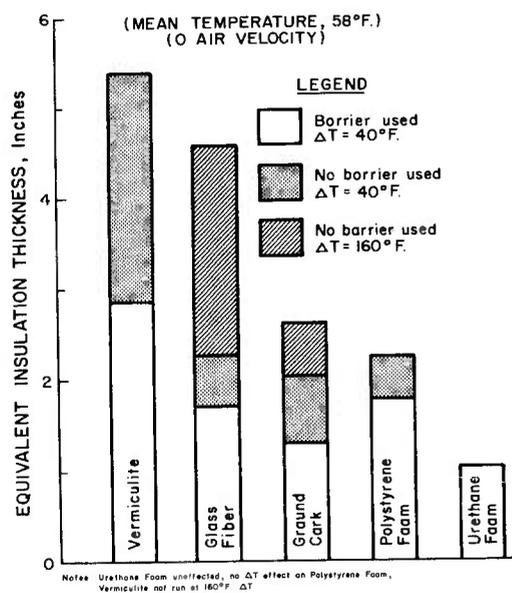
Fig. 6. Factors influencing insulating effectiveness.

porous media heat transmission increased with increased ΔT, i.e., the temperature difference between the hot and cold sides. This tends to support the theory that convection currents are responsible for the increased thermal conductance of porous materials.

To demonstrate the influence that increased convection currents can have on heat transfer, relative insulation effectiveness was determined with air flowing across the faces of urethane foam and glass fiber insulated tubes. The results are shown in Fig. 7. Urethane foam, because of its small but individual cell nature, is unaffected by air flow whether unprotected or not, while the porous medium shows increased rates of heat transfer with air flow across the tube. While the air flow was arbitrarily chosen (500 ft/min. = 6 mph) it does show the pronounced effect which winds can have on an insulated building or refrigerated truck.

For optimum insulation performance, moisture pick-up must be kept to a minimum. Moisture pick-up not only adversely affects heat transmission rates[3] but also, in the case of refrigerated trucks, decreases payload weight, necessitating periodic moisture removal from porous insulating media.[4] Although heat transmission rates were not studied over a long period of time with the refrigerant in the tube, Table 6 shows unprotected urethane foam picked up negligible moisture. The other insulating material tested showed a weight gain indicating moisture pick-up even in this short period of time.

Moisture penetration into insulating media can be markedly decreased by vapor barrier protection. However, the difficulties encountered in hermetically sealing porous insulating media are obvious. Urethane foam has inherent hermetic sealing properties. For pour-in-place, spray, or laminated construction, only the exposed urethane foam surface need be vapor barrier protected. In applications where rigid urethane foam is enclosed in porous media, e.g., brick or cement blocks, the foam for optimum performance should be protected with a moisture vapor barrier.

Since the insulating qualities of urethane foam are due to encapsulation and containment of fluorocarbon gas, aging effects on urethane foam are of prime importance. Urethane foam exhibits excellent resistance to aging even
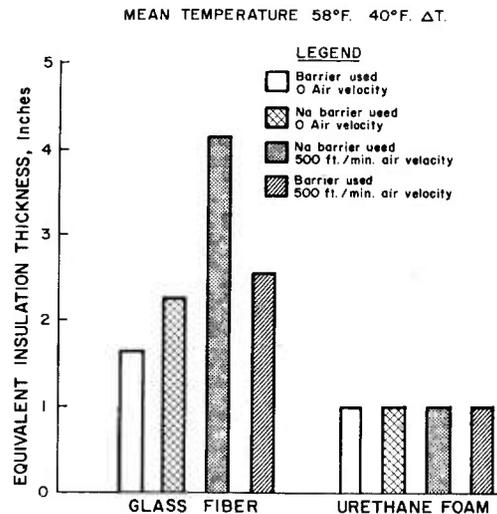
Fig. 7. Effect of air velocity on relative effectiveness of insulating media.

TABLE 6

Effect of Insulation Type on Moisture Pickup

(Cold side maintained at -21.6°F; Hot side maintained at 78°F)

Material*	Cumulative Insulation Weight Gain, g		
	24 hrs	48 hrs	72 hrs
Closed Cell (urethane foam)	0	0	0
Porous Media (Glass fiber)	22	39	46

*No barrier protection, 0 air velocity.

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though the material is subjected to wide variations in temperature. The evaporation rates determined on the urethane foam insulated tube over a 200 day period are shown in Table 7. There is essentially no change in insulating efficiency. This indicates little aging (little or no loss of fluorocarbon gas) or change of foam gas composition occurred even though the material was exposed to temperatures as high as 220°F and as low as -320°F between the tests given in Table 7.

TABLE 7

Effect of Aging on Evaporation Rate of Fluorocarbon Expanded Urethane Foam

Aging Conditions: Hot Side   78°F
Cold Side   -21.6°F (Fluorocarbon 12)

Foam Age, days	Fluorocarbon 12 Evaporation Rate, g/hr
5	68
25	69
100	67
200	69

Effect of Mean Temperature on Thermal Conductivity of Urethane Foam

The experiments just described are effective for gauging in-use performance of insulating media. For design purposes, however, it is desirable to know the effects of changing mean temperature on the heat transmission rate of urethane foam.

The standard ASTM method of doing this is to measure the rate of heat flow through a test specimen under steady state conditions. The measurement is made under static conditions by heating electrically one side of the specimen and maintaining the other side at a constant, but lower, temperature. When steady state conditions are reached, the measured heat output rate is equal to the heat transfer rate through the sample. Heat losses through the edge of the specimen can be compensated for by the use of a guarded hot plate.[5]

As stated earlier, "k" factor determinations are usually made at a mean temperature of 75°F. Knowing the "k" factor value at 75°F, it has been traditional to assume that it would decrease linearly with decreasing temperature to be essentially zero at temperatures approaching absolute zero. Recently,

there has been increasing evidence that this linear relationship does not hold for fluorocarbon expanded rigid urethane foam.[6] Consequently, guarded hot plate. equipment of high precision was used to determine the effect of mean temperature on thermal conductivity. Fluorocarbon expanded rigid urethane foam of 2.0 lb/ft^3 density was supplied by the Elastomers Laboratory to R.M. Lander of the University of Minnesota who performed this work. The data obtained are shown in Fig. 8. It can be seen that "k" factor does not decrease linearly between +45° and -40°F. Rather, in this region a slight increase in heat transmission rate occurs. Above +45° and below -40°F mean temperature, the "k" factor decreases linearly with

Fig. 8. Thermal conductivity vs. mean temperature fluorocarbon expanded rigid urethane foam.

decreasing mean temperature. This non-linearity in the "k" factor-mean temperature curve has little significance from a practical standpoint as the evaporation tube experiment has shown. Also, it will be noted that the "k" factor obtained at the point of maximum rise (0.14) at -40°F is still well below that obtained with other typical insulation media.

It is interesting to speculate as to the cause of this "k" factor rise. The most plausible theory to explain this phenomenon is fluorocarbon gas condensation leading to:

1. Decreased pressure in the foam cell which results in increased heat transfer by convection due to increased mean free path.

2. Increased heat transfer due to convection currents resulting from reboiling of condensed fluorocarbon liquid.

3. Saturation of foam cell's surface with liquid fluorocarbon resulting in increased heat transfer by conduction.

4. Equilibrium saturation of the foam cell surface with liquid fluorocarbon. In this case the addition of heat to the hot side of the foam cell causes the ejection and transfer of saturated fluorocarbon vapor to the cold side with subsequent fluorocarbon condensation. Abnormal quantities of heat are then transferred due to the release of latent heat during condensation of fluorocarbon gas.

Gas chromatographic measurements on unaged fluorocarbon expanded urethane foam has shown that there is essentially no net change in the total weight of material in the foam cell at any temperature.[7] However, the

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molar concentration of the gas phase does change with changing temperature, with a higher per cent of non-condensibles resulting as temperature is decreased. This is good evidence of fluorocarbon condensation which would be expected since the boiling point of Fluorocarbon 11, for example, is $74.8^{\circ}F$ at 1 atm. It has also been shown[7] that the total pressure in a foam cell which has been expanded with Fluorocarbon 11 is approximately 0.8 atm at $74.8^{\circ}F$. The condensing temperature of Fluorocarbon 11 at this pressure is approximately $50^{\circ}F$. Increased heat transmission rates as the temperature is lowered from $50^{\circ}F$ would then be expected to result due to Fluorocarbon 11 condensation. The experimental measurements shown in Fig. 8 are good confirmation of this theory.

The non-linearity of the "k" factor versus mean temperature curve is not wholly restricted to fluorocarbon expanded urethane foam. Departures from linearity have been shown for other media in which the voids contained CO_2.[8] It should be restated, however, that even though fluorocarbon expanded urethane foam shows decreased insulation resistance from $+45^{\circ}$ to $-45^{\circ}F$, this material is still superior to other commercially available materials at comparable economics. In addition, for the majority of applications envisioned for rigid urethane foam (see Table 5), the non-linearity of the "k" factor versus mean temperature curve is primarily of academic interest.

Effect of Aging on Insulation Performance of Fluorocarbon Expanded Rigid Urethane Foam

Typical aging effects as determined by "k" factor measurements on cut fluorocarbon expanded rigid urethane foam (1/2" thick) are shown in Fig. 9. Aging occurs in two stages termed primary and secondary aging. Primary aging is due to air diffusion into the foam cells. Cut, unprotected urethane foam polymer is relatively permeable to air, thus air will enter the foam cells until essentially equilibrium conditions are established. With the thin specimens used for "k" factor determination, this usually occurs in within 80 to 100 days at room temperature. At completion of primary aging, the "k" factor value is generally increased 30 to 35 per cent. Thus, the lower the "k" factor value of the foam as originally made, the lower will be the value at completion of primary aging. Since this value is commonly assumed as the equilibrium "k" factor of exposed urethane foam, it points out the need for as low an initial "k" factor value as possible. Secondary or long term aging occurs slowly and is due to gradual gaseous fluorocarbon loss from the foam cells. Urethane foam polymer is relatively impermeable to fluorocarbon gases,[9] thus, complete loss of fluorocarbon gas will occur only after many years aging. Data published on urethane foam aging characteristics[10] have shown essentially no change in the secondary aging curve after 500 days continuous exposure.

Experiments have shown that the "k" factor of uncut or barrier protected fluorocarbon expanded rigid urethane foam does not change significantly even when aged for as long as 720 days at $75^{\circ}F$ and 50 per cent

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Relative Humidity. This would be expected since primary aging due to air diffusion has been prevented. The general tendency of the urethane foam industry to assume equilibrium "k" factor values of the order of 0.16 to 0.17 is unrealistically high on the basis of the data contained in this paper. Rather when it is remembered that insulating quality urethane foam should be encased in an impermeable covering, it is reasonable to assume the "k" factor obtained originally will closely approximate the long term "k" factor value.
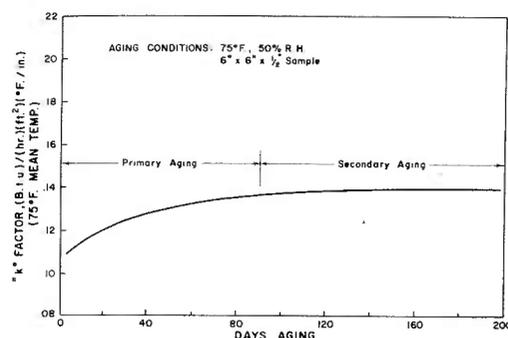
Fig. 9. Aging of cut surface fluorocarbon expanded rigid urethane foam.

Effect of Foam Variables on Insulation Resistance

It is important to obtain as low an initial "k" value as possible in order to fully utilize urethane foam's insulation capabilities. Several foam physical variables have been identified which have an influence on heat transmission rate. These include closed cell content, cell size, foam density, and type and amount of gas entrapped.

The effect of closed cell content on "k" factor is shown in Fig. 10. As would be expected, the higher the closed cell content, the lower the "k" factor because of the greater quantity of gas per unit volume which is trapped. The effect of cell size is shown in Fig. 11. This figure shows that "k" factor
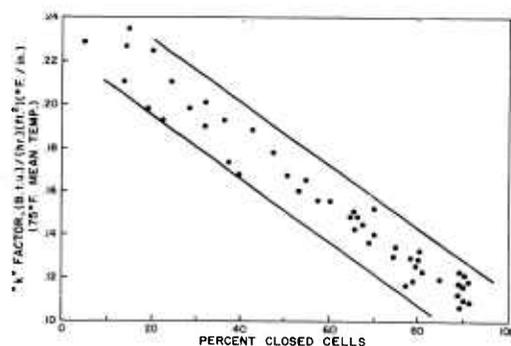
Fig. 10. Effect of closed cells on "k" factor of fluorocarbon expanded rigid urethane foam.
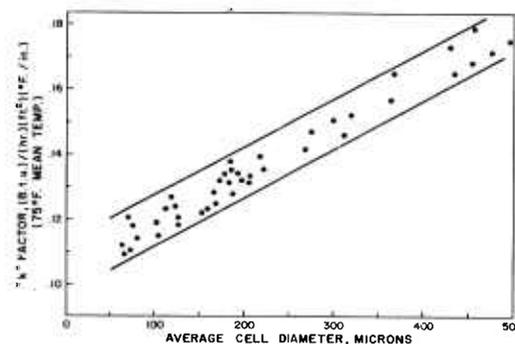
Fig. 11. Effect of cell size on "k" factor of fluorocarbon expanded urethane foam.

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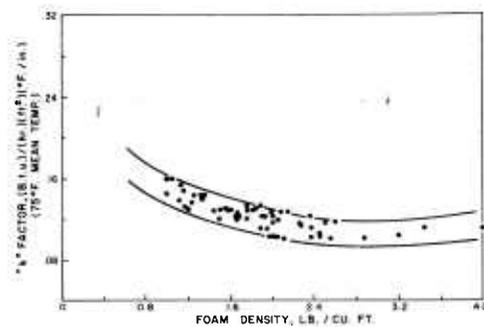
Fig. 12. "k" factor-density relation-
ship, fluorocarbon expanded rigid
urethane foam.

decreases as the cell size decreases because there are more heat flow barriers per unit thickness, thus less heat transfer due to convection. Urethane foam has low heat transmission rates over a wide range of densities as shown in Fig. 12. The spread in the data presented is due to variation in cell size, closed cell content, polymer species, etc. Future improvements in processing techniques can be expected to lower but not change the shape of the "k" factor density curve shown. The gradual increase in "k" factor as the density is decreased is not restricted to urethane foam, rather occurs in all media (but not necessarily at the same density) due to increased heat transfer by radiation as the density decreases.[11] Even though the thermal conductance of fluorocarbon expanded urethane foam increases gradually with decreasing density, "k" factor values as low as 0.13 (Btu)/(hr)(ft^2)(^{O}F/in.) at 1.2 lb/ft^3 densities have been obtained. This does not imply, however, that this is the minimum obtainable "k" factor value at this density since, as shown in Fig. 5, the thermal conductance of gaseous Fluorocarbon 11 at 75°F mean temperature is approximately 0.06 (Btu)/(hr) (ft^2)(^{O}F/in.). While increased heat transfer due to radiation as the density is decreased will prevent this low value from being obtained, it may be approached more closely in the future as techniques develop for increasing the number of closed cells and decreasing the average cell size.

Summary

A test method has been devised and described for determining the relative insulating effectiveness of various insulating media under simulated in-use conditions. Heat transmission rates were determined for urethane foam over a wide range of mean temperatures. Certain foam variables were identified which have an influence on initial and aged "k" factor values.

Conclusions

The evaluation of several insulating media under simulated in-use conditions has demonstrated the superiority of fluorocarbon expanded urethane foam. The proven insulation excellence of fluorocarbon expanded urethane foam when combined with its other outstanding physical properties such as low density, low moisture pick-up, high strength, etc., more than justifies the choice of this material for both insulation and combination structural-insulation applications.

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When fluorocarbon expanded rigid urethane foam is properly formulated and applied, good long term performance may be expected from this unique and unusually effective insulating material.

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DESIGN OF POLYETHER BASED RIGID FOAMS

J. T. Willett and E. J. Robertson

Since their commercial introduction in 1956, the polyether polyols for use in rigid urethane foams have increased to encompass a large number and variety of materials. Because polyethers are generally propylene oxide adducts of polyhydric alcohols, the functionality of the currently available products can range from three when glycerine is the base up to eight with sucrose. There are also the propylene oxide adducts of diamines and tri- amines or other organic structures. Table 1 lists the commercially avail- able polyether polyols and suppliers. For flame retardance, products have been developed which contain either halogents, phosphorus, or their com- binations. However, the development of these molecules is so recent that their structures have not been highly publicized by the companies which produce them. The trend, however, is towards reactive flame retardant compounds as opposed to the additive type.

TABLE 1

Commercially Available Polyethers and Suppliers

Functionality	Propylene Oxide Adduct of	
Triols	Glycerine, trimethylolpropane, and hexane-triol	
Tetrols	Pentaerythritol, alpha-methyl glucoside, and Ethylene diamine	
Hexol	Sorbitol	
Octols	Sucrose	
Allied Chemicals	Jefferson Chemicals	Witco Chemicals
Atlas Chemicals	Olin Mathieson	Wyandotte Chemicals
Dow Chemicals	Union Carbide	

The other major component of rigid foams is the isocyanate. The most accepted product in this country has been the 80/20 2,4/2,6 isomer of tolylene diisocyanate which is used in most quasi-prepolymer systems. The demand for less handling and one-shot systems has led to the rise of the crude mate- rials, namely, 85 per cent tolylene diisocyanate, 4,4'diphenylmethane

diisocyanate, and polymethylene polyphenyl-isocyanate. The popularity of these crude products has increased because of their lower reactivity and less tendency to scorch, their ability to improve dimensional stability and to enhance flame retardance, and their lower cost. Also the crude isocyanates are generally less volatile and therefore not as irritating to the eyes, and respiratory tract. The isocyanates and their suppliers are listed in Table 2.

TABLE 2

Isocyanates and Suppliers

Tolylene diisocyanate 80/20 2,4/2,6 isomer
4,4'diphenylmethane diisocyanate, Mondur MR, and Hylene MCC
Polymethylenepolyphenylisocyanate - PAPI
Crude 80/20 tolylene diisocyanate - Nacconate 4040

Allied Chemicals	E. I. du Pont de Nemours
Carwin Chemicals	Mobay Chemicals

To aid in the dispersion of the materials, surfactants or surface active agents are essential to the foam system. These agents are also effective in controlling cell size and closed cell content. The basic types are organo-silicones.

For catalysis of the systems, two types of compounds are used either alone or in combination. These are tertiary amines such as 2,2,2-bicyclo-octane (Dabco), 1,2,4-trimethylpiperazine, tetramethylbutane diamine, and tetramethyl guanidine or organo-tin compounds such as dibutyltin dilaurate or dibutyltin diacetate.

In their early development the foams were expanded by carbon dioxide generated in the reaction between water and the isocyanate. Later developments revealed that halogenated fluorocarbons performed well as blowing agents and greatly improved thermal insulation. [1]

How and in what order these components are combined is also important. Two basic methods of foam preparation are considered commercially feasible for rigid polyether urethane foam production. These two methods are:

1. Quasi-prepolymer preparation, and
2. One-shot preparation.

Each method is unique and has its own set of problems. The prepolymer method, for example, was plagued by viscosity. Unlike the flexible polyols

which are low viscosity materials, the rigid polyols are of much higher viscosities, as high as 100,000 cps at 25°C. This presented a problem of pumping in available equipment so a method of reducing viscosity was devised. This meant the preparation of a quasi- or semi-prepolymer by reacting the polyol with enough isocyanate to produce NCO terminated polymers and enough excess isocyanate to reduce the viscosity to 5000 cps or less. This method had the advantage over prepolymers by reducing viscosity and over one-shots by reducing exotherm to prevent scorch. This reaction also favors the urethane linkage and means the allophonate and biuret linkages which are most susceptible to accelerated aging[2] are not formed or at least minimized. The quasi-prepolymer is then reacted with a cross-linking agent which contains the surfactant, the catalyst, the blowing agent, and enough polyol to reduce the NCO/OH ratio from 4/1 to 1.05/1. In some cases, particularly to ensure polyol stability, the surfactant is added to the quasi-prepolymer.

The quasi-prepolymer had just settled into use when the demands of industry moved on and set its sights on the one-shot method. This method of preparation is desirable both economically and in simplicity. In the one-shot technique, polymer formation and foaming take place simultaneously. However, many problems had to be and are still in the process of being solved. The first problem needing a solution was scorch. Since the heat of reaction is sufficient to cause scorching in the foam and since the foam is an excellent insulator, a means of heat dissipation was considered a major problem. Because of this problem some method was sought to reduce the exotherm. Tolylene diisocyanate was replaced by crude tolylene diisocyante which reduced the exotherm below the scorch level. However, this brought about other problems--one being friability and from here we proceeded to the crude MDI or polymethylene isocyanates. In these materials an answer seems to have been found, i.e., foams are produced with no scorch, reduced friability, and increased flame retardance.

Now that we have seen the two main means of foam preparation it behooves us to examine more closely the components of a formulation and the characteristics each will impart to the final rigid polyether urethane foam.

Since the polyether polyol can result in foams ranging from flexible to rigid, we must limit the equivalent weight range of the polyol. The most useful range has been an equivalent weight between 75 and 150. As can be seen in Table 3, the equivalent weight will affect the compression strength of any foam system.[3] In general as equivalent weight decreases, compression strength increases. Table 3 shows a polyether polyol series made into rigid foams by the quasi-prepolymer method. This series is a propylene oxide adduct of sucrose in which the equivalent weight of the polyol has been varied. The effect of the variation is noticeable primarily in the strength properties. By decreasing the equivalent weight, the compression strength increases in each foam. Although not as dramatic, the effect of varying the equivalent weight is also noticeable in the tensile strength. A more gradual trend to a stronger tensile is noticed with an increase in equivalent weight.

TABLE 3

Strength Properties vs. Equivalent Weight
in Sucrose Polyether Rigid Foams

OH no.	450	410	375	350
Equivalent weight	127	137	150	160
Component A				
Sucrose polyether[a]	127.0	137.0	150.0	160.0
Trichlorofluoromethane	40.5	42.0	46.9	50.0
Dabco catalyst[b]	0.81	0.84	0.88	0.91
Silicone DC-113 or DC-199[c]	0.81	0.84	0.88	0.91
Component B				
Quasi-prepolymer				
(29.4% excess NCO)	143.0	143.0	143.0	143.0
Density, pcf	2.1	2.1	2.1	2.1
Compression strength, psi	55	45	40	40
Tensile strength, psi	34	35	35	40

[a]Voranol polyethers, Dow

[b]Houdry Process

[c]Dow Corning

Another means of controlling strength properties is the polyether polyol functionality. Table 4 shows this effect in a series of foams prepared from polyether polyols of approximately the same hydroxyl number but differing in functionality. The decrease in tensile strength as the functionality is increased is self-evident. However, the expected increase in compression strength is not as noticeable. A possible explanation of this paradox is suggested by the results of the study of Darr, Gemeinhardt, and Saunders.[4] They show evidence that there is an incomplete chemical reaction in resins whose functionality is six or greater and that the tetra-functional resin equivalent to the one used in this foam was the most completely reacted. The relationship between the foam properties and polyether polyol properties is important to know because it affords a means of controlling the foam properties at a minimum cost. For example, to get stronger foam we could increase the equivalent weight which in turn would increase the cost by requiring an increase in the amount of iso-cyanate needed. We also know that a higher polyether polyol functionality will improve strength properties. Therefore, we are able to use the same equiva-lent weight, thus holding cost at the same level. It should be feasible to reduce the cost of a foam system by the same reasoning. Therefore, we see before us the possibility of controlling the strength and cost of foams by the proper com-bination of equivalent weight and functionality in the polyether polyol. However, using polyols with very low equivalent weights tends to increase brittleness and friability.

TABLE 4

Strength Properties vs. Functionality

OH no.	450	490	450
Functionality	4	6	8
Polyol type	pentaerythritol	sorbitol	sucrose
Component A			
Polyether	65.0	73.4	88.9
Trichlorofluoromethane	27.0	35.9	28.4
Dabco[a]	0.5	0.8	0.6
Stannous octoate	0.1	--	--
Silicone DC-113 or 199[b]	0.5	1.1	0.6
Component B			
Quasi-prepolymer	100.0	100.0	100.0
Density, pcf	1.9	1.9	2.1
Compression strength, psi	32.0	29.8	55.0
Tensile strength, psi	60.0	46.9	34.0

[a]Houdry Process

[b]Dow Corning

The structure of the polyol component also affects foam properties, especially temperature resistance. For example, in polyether systems the use of a polyether having a cyclic structure such as alpha-methyl glucoside usually leads to better temperature resistance than a polyether of equal functionality and equivalent weight based on pentaerythritol. The effects of several of these polyol features, as well as the combined effects of isocyanate and polyol structures, were shown by Darr and co-workers.[4] A correlation was shown between properties of rigid foams and properties of analogous solid polymers made from the same isocyanate and polyols, without the blowing agents. The temperature resistance of the two series of polymers appeared to be the most sensitive measure of the effect of structural changes in either foams or solid polymers, so primary emphasis was placed on this property.

One particular property which has received considerable attention for a number of years is flame resistance. Flame retardant materials can be physical additives such as unreactive organic phosphorus and/or halogen compounds or certain inorganic phosphates or oxides. Typical organic examples are tris(chloroethyl) phosphate or tris(2,3-dibromopropyl) phosphate. Inorganic materials such as antimony oxide or ammonium phosphate are also effective either alone or in combination with the organic materials.[5] Another approach is to incorporate organic halogen or phosphorus compounds which

have active hydrogen atoms which when reacted from an integral part of the polymer structure. An example of this type is Virginia Carolina's Vircol 82 (a phosphorus-containing diol) which is effective in both polyether and polyester based systems. An increasing number of polyether polyols of higher functionality are rapidly becoming available. Wyandotte Chemicals has developed a number of such polyols which are now available in commercial quantities. Tables 5, 6, 7, 8, and 9 show examples of these polyether polyols in three types of foam application, molding, slab, and spray. Still another approach is the use of a flame resistant coating, especially on spray applied foam for outdoor applications, where good low water vapor permeability and good weather protection is desired.

TABLE 5

Self-Extinguishing Molding Formulation

Formulation	
Phosphorus polyether[a] (OH no. 329)	87.5
Sucrose polyether[b] (OH no. 545)	12.5
Fluorocarbon 11	32.5
Tetramethylbutane diamine	2.0
Dibutyltin dilaurate	0.02
Silicone DC-113[c]	2.0
PAPI[d] 1.05/1 NCO/OH ratio	89.5

Mechanical Variables
    Martin Sweets On/Off Mixing Head, 60 lb/min. (nominal rate)

[a]Polyol 216, Wyandotte Chemicals Corporation
[b]Polyol 195, Wyandotte Chemicals Corporation
[c]Dow Corning
[d]Carwin Chemicals

The type of isocyanate used also has an effect on foam properties. For instance, a combination of either tolylene diisocyanate or crude tolylene diisocyanate with an alpha-methyl glucoside polyol produces foams with a high degree of friability. However, by replacing the tolylene diisocyanate with either crude methylene bis(4-phenyliscoyanate) or crude polyphenyl polyisocyanate the friability is greatly reduced. The amount of isocyanate also plays an important part in determining foam properties. An NCO/OH ratio less than one usually results in a foam susceptible to humid aging instability and, in some systems, to shrinkage at room temperature. It has, however, been standard practice to run at an NCO/OH ratio of about 1.05/1. This ratio has been found to be beneficial to the foam in that it gives the best cost/performance ratio.

TABLE 6

Self-Extinguishing Molded Foam Properties

Foaming Characteristics	
Cream, seconds	12
Rise, seconds	77
Tack-free, seconds	77
Properties	
Density	2.0
Compression strength, psi measured perpendicular to foam rise	23.0
"k" factor at 75°F mean temp.	0.107
Flame resistance ASTM D-1692	self-extinguishing

TABLE 7

Self-Extinguishing Slab Foam Formulation

Formulation	
Phosphorus polyether[a] OH no. 450	87.5
Sorbitol polyether[b] OH no. 676	12.5
Silicone DC113[c]	1.5
Fluorocarbon 11	38.5
Tetramethylbutane diamine	1.5
Dibutyltin dilaurate	0.1
PAPI[d] 1.05/1 NCO/OH	121
Mechanical Variables	
Machine UBT-65, 60 mm x 150 mm head	
Low pressure, 2 components	
Pin mixer at 5000 rpm	
Air bled into head, cu ft/min.	0.2
Conveyor speed, ft/min.	10
Conveyor angle, degrees from horizontal	4
Output, lb/min.	70
Slab width, inches	30
Slab height, inches	20
PAPI[d], temp., °F	75
Resin, temp., °F	83

[a]Polyol 204, Wyandotte Chemicals Corporation
[b]Polyol SP 560, Wyandotte Chemicals Corporation
[c]Dow Corning
[d]Carwin Chemicals

TABLE 8

Self-Extinguishing Slab Foam Properties

Foaming Characteristics	
Cream, seconds	10
Rise, seconds	75
Tack-free, seconds	on rise

Properties	
Density, pcf	1.8
Compression strength, psi	
measured parallel to foam rise	26
measured perpendicular to foam rise	21
"k" factor at 75°F mean temp.	
measured perpendicular to foam rise	0.130
Flame resistance, ASTM D-1692	self-extinguishing

TABLE 9

Rigid Spray Foam Formulation

Formulation	
Phosphorus polyether polyol[a] (OH no. 430)	59.1
QUADROL[b] (OH no. 770)	14.8
Silicone DC-113[c]	2.0
Dabco[d]	0.5
Dibutyltin diacetate	0.025
Fluorocarbon 11	35.3

Premix	
Mondur MR[e]/TP 740, 94/6	100

Mechanical - Equipment
  DeVilbiss 51269 External mix spray gun
  Low pressure pumping unit with 2-10 lb/min. output

Properties	
Density, core, pcf	2.0
Compressive strength, psi	26
Tensile strength, psi	41
"k" factor at 75°F mean temp.	0.120
Flammability, ASTM D-1692	self-extinguishing

[a]Polyol 216, Wyandotte Chemicals Corporation
[b]Wyandotte Chemicals Corporation
[c]Dow Corning Corporation
[d]Houdry Process Corporation
[e]Mobay Chemical

The NCO/OH ratio cannot be increased indiscriminantly since too large an isocyanate excess would produce hard brittle foams as well as increase the foam cost.

Another important factor to have an effect on the foam properties is the surfactant. Originally included to aid in the mixing and blending of two somewhat incompatible materials, the surfactants were found to yield other beneficial and more noticeable effects, i.e., control of cell size, gas entrapment, and strength. Many types of surfactants have been tried ranging from nonionic surfactants to the silicones, and the most acceptable seems to be the silicones. Until recently, it had been thought that the silicone copolymers were interchangeable and that only stability was a variable. However, more and more reports have been coming in from the field and our own results corroborate the fact that you should be as selective with the surfactant as you are with the polyol, isocyanate, and catalyst.

The next factor to be considered is the catalysts: usually teritiary amines, organo-tin compounds, or combinations of the two. Working in combination with the surfactant, the catalyst will help to produce the fine closed cell structure necessary for good quality insulation. The tin catalysts are more effective on the urethane reaction and higher amounts speed up all three phases of foaming as indicated by cream, rise, and tack-free time. The amine catalysts do not have as much an influence on the urethane reaction but seem to change the rise and tack-free times and are more effective in cross-linking the foam.

The final component of a polyether rigid urethane foam is the blowing agent. Originally, this was carbon dioxide which was generated when the isocyanate and water reacted. Later developments indicated a better and more economical blowing agent, namely, a material which boiled around 75°F and was inert in respect to the reaction. This material, usually a halogenated hydrocarbon, was economical because it eliminated the need for water which in turn reduced the amount of isocyanate and thus lowered costs. The other effect of the new type blowing agent was an increase in insulating efficiency. A 2 pound per cubic foot carbon dioxide blown foam has a "k" factor of about 0.22 BTU/hr/sq ft/$^\circ$F/ in. compared to a halocarbon blown foam of the same density with a "k" factor of 0.15 BTU/hr/sq ft/$^\circ$F/in. This means that the amount of insulating material can be reduced by almost 50 per cent. Besides reducing "k" factor and cost, the blowing agent regulates density. By varying the amount of blowing agent, the density can be controlled between 1-30 pounds per cubic foot.

The potential of rigid polyether urethane foam has become recognized in many fields. It has advanced farthest in the field of household refrigeration. It is no stranger to those who insulate tanks, trailers, and railway cars. Besides "k" factor the foam has appealed to them because of its load bearing potential, low moisture pick-up, and solvent resistance. Even the military has felt the potential of rigid polyether urethane foams. From the radomes for the Air Force[6] to void-filling for the Navy's submarines it has left its

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mark. Foamed in place foxholes, a water and vermin proof shelter simple to construct and abandonable[7] have been prepared. Spray-foamed above ground shelters made by inflating canvas hemispheres and then spray applying the foam have been examined.[8] The Army has also investigated rigid foam shelters for protecting electronic equipment,[9] for barracks, mess halls, and field hospitals.[10] These are some of the uses envisioned for rigid polyether urethane foam and each use presents its particular set of problems. We have the tools, i.e., the polyethers, the isocyanates, the catalysts, the surfactants, and the blowing agents. We know how to use the tools to solve the problems presented, and daily we discover other ways to put these tools to work. Thus, it can be appreciated that by an adroit choice of polyether and isocyanate, paying close attention to their functionality and equivalent weight, choosing the proper catalyst and surfactant, a rigid polyether urethane foam with almost any combination of properties can be obtained.

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SESSION NO. 2

FOAM-MAKING PROCESSES

Dr. Kurt C. Frisch, Chairman
Wyandotte Chemicals Corporation
Wyandotte, Michigan

RIGID POLYURETHANE FOAM, POURED-IN-PLACE:
A RANGE OF DENSITIES

E. C. Galloway

Introduction

"Pouring-in-place" is the oldest, the most versatile, and, therefore, the most popular technique for the application of rigid urethane foam. This paper, the first in a series concerning various foaming techniques, may serve as a review of current basic practices and an introduction to the newer methods.

Conventional "pouring-in-place" may be defined briefly as a type of molding which involves charging freshly mixed liquid formulation into a cavity where simultaneous polymerization and gas generating reactions occur, filling the cavity with cellular (thermosetting) plastic. The technique is applicable over the entire density scale, from 0.7 to 70 pounds per cubic foot. Usually the mold is retained as the exterior of the finished item.

The "semi-" or "quasi-prepolymer" process is generally used. This involves simply the reaction of polyol and toluene diisocyanate in two stages (Fig. 1). The objective of completing part of the reaction at a stage prior to foaming is to avoid difficulties in handling or product degradation which might arise from generation of all of the heat of reaction at one time. Typically, about 20 per cent of the polyol is added slowly to the entire diisocyanate charge, with agitation and cooling as needed to produce a mixture of capped polyol and unreacted TDI. At the time of foaming, this "quasi-prepolymer" is mixed with the remaining polyol and other components, and the foaming sequence begins.

Fig. 1.

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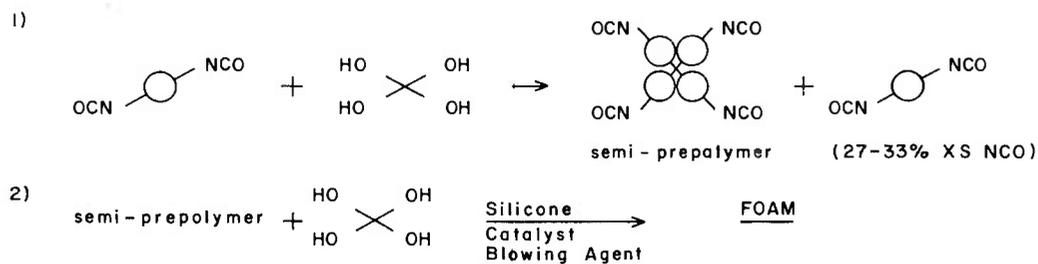
To provide a framework of rigid urethane foam information, a chronology of key developments is presented in Fig. 2. Through these years a vast amount of technology has been accumulated concerning liquid pouring-in-place, and, consequently, this is the technique usually given first consideration for any new use.

1945	Report of German (Bayer) progress, W. W. II.
1946-47	Goodyear, Lockheed programs: light weight military structures - polyester, TDI water (one-shot) systems "foamed-in-place."
1950	du Pont Monsanto: TDI commercially available.
1952	American Latex, Nopco: licensees of Lockheed systems.
1954	du Pont: prepolymer technique.
1957	du Pont, General Motors: use of F-11; Dow: highly functional polyethers commercially available.
1959	Wyandotte: Quadrol spray system; Hooker: F. R. Hetfoam polyester systems; Dow: rigid board stock.
1960	RCA Whirlpool: first major production line - polyether, TDI, F-11; Virginia-Carolina: F. R. polyether systems - Vircol 82.
1961	Allied: Nacconate 4040, modified TDI for one-shot use; du Pont: "Frothing."
1962	Carwin, Mobay: polyaromatic isocyanates for one-shot use.
1963	?

Fig. 2. Rigid polyurethane foam milestones.

The New Development

The following plan is recommended for the development of a new application. Acceptable performance with favorable economics is always

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the objective. If the application has been demonstrated before, explicit instructions will be available (from the supplier) and the matter becomes relatively routine. However, if the application is unique, the phases of development, with considerable overlapping, should be as follows:

1. Consideration of economic limitations; suggestion of a chemical formulation to give the best compromise of (estimated) physical properties and handling characteristics.

2. Determination of needs in proportioning, mixing and dispensing equipment, and mold design; preliminary laboratory test pours to demonstrate feasibility.

3. Prototype preparation to evaluate processing characteristics of the best formulation and intrinsic properties of the item.

4. Maintenance of control during full production.

Throughout the development there is a gradual transfer of responsibility from the supplier (1) through a period of shared effort (2 and 3) to the foam user (4).

Physical Changes

During development it is frequently helpful to consider the foaming sequence in terms of expansion rate and how it is related to temperature and pressure changes (Fig. 3). Not only is useful information developed for candidate formulations, but such a graph provides a point of departure for discussions of equipment and mold requirements. The example used is a quasi-prepolymer polyether system expanded with fluorocarbon-11 to a density of 2 pounds per cubic foot. The mold used was a standard 2-foot square panel with a 2-inch cross section; foam rise was in a 2-foot direction and without restraint (Fig. 4). So that the physical changes (temperature, pressure, and volume) may be compared easily, percentages of change rather than absolute values are plotted against time.

Temperature

Considering temperature first, rise is nearly complete before the maximum temperature is reached. Thus, at 130°F (54.4°C), only 50 per cent of the temperature change, about 90 per cent of the rise, is obtained. This is significant, for example, when considering the possibility of density gradients due to different degrees of thermal expansion within the pour. Even if the temperature near the foam-mold interface reaches only 130°F while 250°F (121.1°C) is exceeded in the center, it is apparent that because the foam is no longer appreciably elastic above 130°F, densities will be within acceptable limits.

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NOPCOFOAM H-602

Panel Dimensions – 2' x 2' x 2"   Maximum Core Temp – 250°F (121.1°C)
Preheat Temp   – 130°F (54.4°C)   Maximum Pressure – 0.17 psig
Component Temp – 76°F (24.4°C)   Maximum Rise   – 26.5"
                                    Core Density   – 1.75 lb/ft³
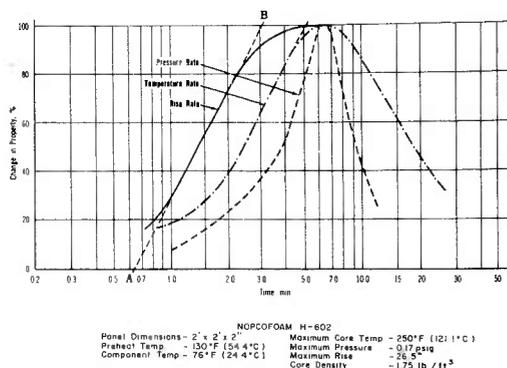
Fig. 3. Pressure, temperature, and rise rate for an unrestrained rise.

APPARATUS FOR PANEL POURING

A. unrestrained mold
B. restrained mold
C. temperature monitoring device
D. pressure gauge
E. finished panel

Fig. 4.

Pressure

Throughout the foaming sequence, work is being done against both the atmosphere and the polymer mass as it continually builds viscosity. Measurements of mold pressure during foaming show that significant pressure increase occurs only after 80-90 per cent of the rise and just before the exotherm reaches its maximum. This is an indication that the polymer matrix no longer has sufficient elasticity to permit easy expansion against the atmosphere and the increase in temperature over the last 15-20 per cent of the range forces fluorocarbon-11 to exert pressure outward against the mold as well as upward against the atmosphere. This increase in outward force is the main source of mold pressure in an unrestrained pour.

Rise Rate

The rate of expansion plotted in this manner yields a straight line segment which can be extrapolated to 0 per cent and 100 per cent of height, providing graphical definition of two useful concepts, Extrapolated Foam Initiation Time (A) and Extrapolated Rise Time (B).*

These two concepts have a direct bearing on the foaming operation. The EFIT gives an indication of the handling time of a system. It is essential to avoid pouring liquid mix on to rising foam, and the theoretical maximum charge must be calculated from handling time and output capability. Thus if a system has an EFIT of 30 seconds and the machine to be used can dispense 20 pounds per minute, it is obvious that the theoretical maximum which can be poured is 10 pounds. By relating this to the finished foam density and the cavity volume, the number of pours to be made for complete fill can be determined.

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*A bulletin describing the test methods is available from the Society of the Plastics Industry.

The ERT measures a critical segment of the mold cycle, that time period during which the foam reactions are actually taking place. If the system under consideration is too reactive, there may be insufficient time to cap and truss the mold, or excessive anisotropy and shearing at the end of the rise may result. If it is too slow, the production time cycle may be extended beyond the practical limit. The ERT provides a useful reference point when altering reactivity of the system.

Analysis of such models plus actual use information for several formulations have led to the following basic recommendations concerning premix (equipment) and postmix (mold environment) requirements.

Equipment Needs

Acceptable repetition of processing characteristics of the system and properties of the foam product demands that component temperatures be replicated to ±2°F (over the range 65-90°F) and proportioning accuracy to ±1 per cent. Also, machine mixing is preferred to minimize variations in physical properties from pour to pour, material wastage, and the work force requirement.

Molds

It is recommended that molds be designed to withstand one psig in an unrestrained pour of cross section more than 2 inches or, more typically, 4 psig in a pour with 10-15 per cent "packing" or overfill. For example, 2-3 psig of mold pressure may be generated by foaming a 2 pound density system in a 2 foot high panel with a 2 inch cross section; so, a mold able to withstand 4 psig provides a safety factor of 100 per cent.

Careful consideration of methods for achieving minimum time cycles is worth-while as this determines the investment needed for molds and handling and storage space required for completed parts. Usually in pouring-in-place, the surface to volume ratio is high and control of the mold temperature is critical. Ideally, for minimum mold cycle time and to prevent foam densification, the rate of temperature increase at the surface should match the exotherm rate in the foam core. This might be achieved by using a heater capable of being programmed. A more practical technique involves preheating the mold and using a material of construction, such as high density urethane foam or plywood, with a sufficiently low heat capacity that loss of heat of reaction is minimized.

Test Pours

The most demanding stage in the development process is that concerned with prototype foaming. This is the "pilot" stage for refinement of

the formulation, equipment and molds, and operating techniques (including training of personnel) prior to advance into commercial production.

Variables associated with the formulation such as catalyst type, expanding agent level, or stoichiometry are better investigated by the supplier rather than the user. However, factors associated with the actual foaming operation such as machine conditions, mold complexity, or mold temperature programing may change with each use. As conditions approach those determined to be optimum in bucket and panel pours, closer correlation between laboratory and prototype (and subsequently production) pours results. Since operating conditions are seldom ideal, extensive prototype study under proposed production conditions is essential.

Production--Maintenance of Control

After several prototypes have been poured successfully and the program has moved into full production, the following check list may be helpful for achieving process control.

1. Check the specific gravity of the resin-fluorocarbon mixture to verify expanding agent content; a hydrometer may be used conveniently.

2. Bring components to the correct equilibrium temperature.

3. Check the proportioning procedure to insure accuracy to ±1 per cent.

4. Obtain a "control cup density."*

5. Measure the mold surface temperature before and after foaming. A final temperature exceeding 130°F (54.4°C) is recommended.

6. Dispense the calculated charge for 10 per cent packing (i.e., a restrained pour) and cap the access port.

7. Take a final control cup density.

Assuming provisions are made for monitoring machine and mold conditions, once the operation is in progress only step "d" need be repeated periodically. The control cup density test is the simplest and most reliable one known for detecting maladjustments in formulation or equipment. It involves measurement of density and visual check of foam initiation and rise times and cell structure. When operating changes are made or when new lots of material are started, the test should be made.

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*The details of this testing technique (Fig. 5) may be obtained from the Society of Plastics Industry.

Density

In successful applications using pouring-in-place, maintaining close control of density is important over the entire range. Density is the chief determinant of cost and the most significant variable affecting mechanical properties. Fig. 6 shows the relationship of density to concentration for the two most commonly used expanding agents, fluorocarbon-11 and carbon dioxide. In the high density range, the system is sensitive to very slight chances in expanding agent level. There is an appreciable decrease in efficiency as more agent is added to reach lower densities until an apparent minimum density is reached at about 1.5 pounds per cubic foot. In the case of fluorocarbon-11, its specific gravity is sufficiently high to offset further decrease in polymer content. When carbon dioxide is used, the water-isocyanate reaction by which it is produced results in an increase in cross-link density and a corresponding more rapid loss of the elasticity necessary for expansion.

It has been demonstrated that a combination of these expanding mechanisms, one physical and the other primarily chemical in type, can be used to extend the useful density range below 1 pound per cubic foot. Fig. 6 indicates that for the particular polyether system used, 1.7 parts of water and 25 parts of fluorocarbon-11 in combination achieves a lower density than either agent alone.

Fig. 5.
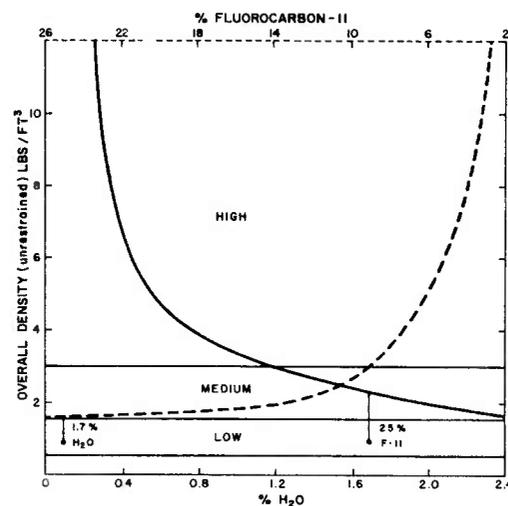
Fig. 6. Density vs. expanding agent concentration.

Applications

The numerous applications for which urethane foam has been successful may be classified into three types according to density: low, medium, and high; up to 1.5 pounds per cubie foot, from 1.5 to 3.0, and above 3.0 pounds per cubic foot respectively. Fig. 7 shows several specific uses where pour-in-place has been suited. The scale on the right indicates the relative volumes of each of the three ranges as estimated for 1968.
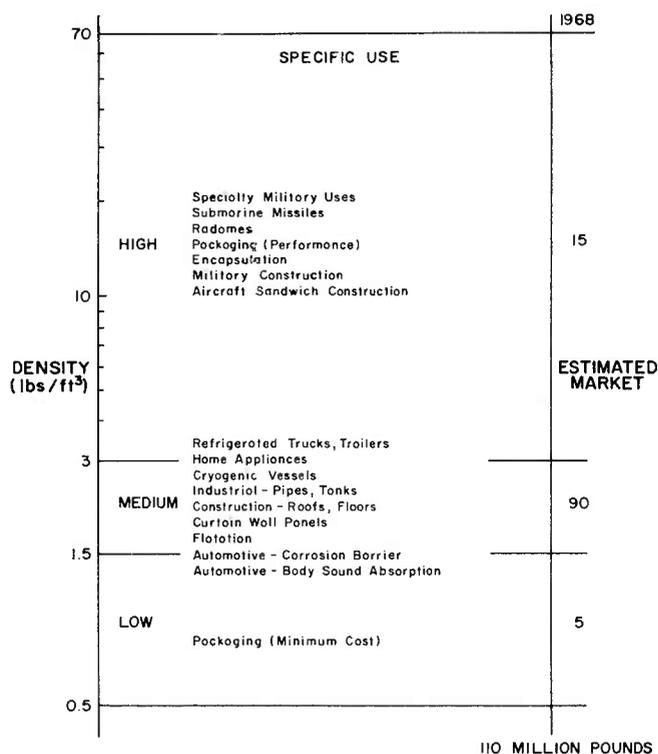
Fig. 7. Pour-in-place applications.

Low Density

Foam in the low density class has one important use: packaging, competing principally against inexpensive loose fill materials. The best example is the Royal McBee Corporation typewriter package (Fig. 8). Cavities on both sides of the typewriter are filled with foam to keep the machine in place and to act as a shock absorbing medium should the cartons receive rough handling during shipment. Foam adheres tenaciously to the carton to form a unitized construction which affords excellent protection at lower cost than any previous design. The combination expanding agent technique was used to achieve an acceptably low density without brittleness, a frequent disadvantage of high
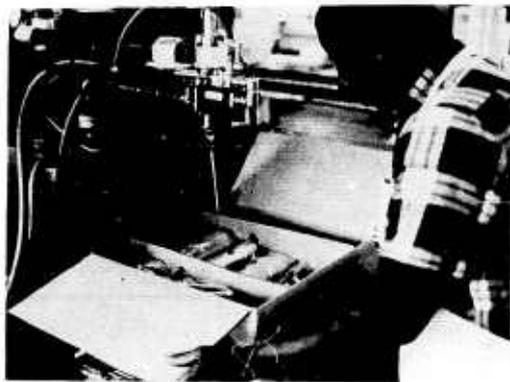
Fig. 8.

water formulations, or inadequate dimensional stability, usually a limitation when using high concentrations of fluorocarbon-11.

Medium Density

The medium density range has the greatest market potential, probably over 80 per cent of the total pour-in-place market. Economic and performance standards are stern.

A soft drink dispenser (Fig. 9) developed by the Multiplex Company takes advantage of some of the best known properties of poured-in-place urethane foam: efficient insulation, no sagging out of place, and low moisture vapor transmission. The replacement of fibrous glass insulation which had to be installed by hand and glued in place has cut the production cycle in half. Each dispenser requires about 5 pounds of foam and less than 40 seconds are required for filling. Then, about 15 minutes are allowed before the supporting truss is removed (Fig. 10).
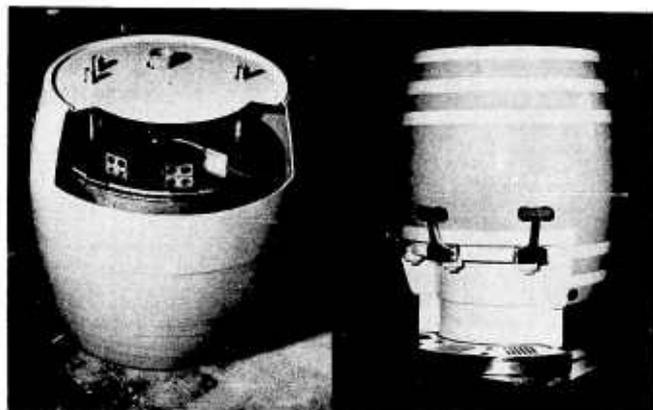
Fig. 9. Multiplex soft drink dispenser foam density 2.4 lbs/cu. ft.

Fig. 10.

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Rigid foam is not a primary structural material. Its main appeal is that it imparts strength and rigidity with little increase in weight and excellent foam-substrate adhesion in sandwich construction. Most current applications take advantage of this because in only a few cases does the foam constitute the entire finished product. (In these cases, any of the several mold release agents must be used.) The high strength to weight ratio provided by rigid foam and the processing advantages of pouring-in-place are especially attractive to the construction industry, particularly for roof and wall panels.

High Density

The high density range embraces 95 per cent of the total useful density scale and provides opportunities for a great variety of foams. For example, compressive strength may range from 100 to 20,000 psi. Insulation value is seldom critical, but mechanical properties must be tailored to suit the particular end use requirements. The greatest usage in this range has been for "packaging;" but in contrast to the low density range where success hinges on favorable economics, performance is the only criterion in the high density region.

Nearly all high density foams are expanded with carbon dioxide. The much lower expanding agent required and the high efficiency of water in this range remove the economic incentive to use fluorocarbon-11. In addition, frequently the pours are large and since density is high, the weight of the foam can be a limiting factor. Carbon dioxide insures that maximum strength per unit weight will be obtained.

The Federal Government is the largest consumer of high density foams, using them for supporting, encapsulation, or shock absorption. One interesting application (Fig. 11) is the "Sonobuoy" produced by Haveg Industries for positioning electronic equipment used to sense undersea noises. The unit is a molded phenolic shell containing high density polyurethane foam which insulates electronically and at the same time provides a shock medium to protect the unit from the impact of hitting water after being dropped from installing aircraft. The high density of the foam is required to give the unit sufficient weight to ride under the surface.

SONOBUOY - HAVEG INDUSTRIES

Fig. 11.

Fig. 12 shows a very current application in the space program for a system formulated to provide a density of 8 pounds per cubic foot.
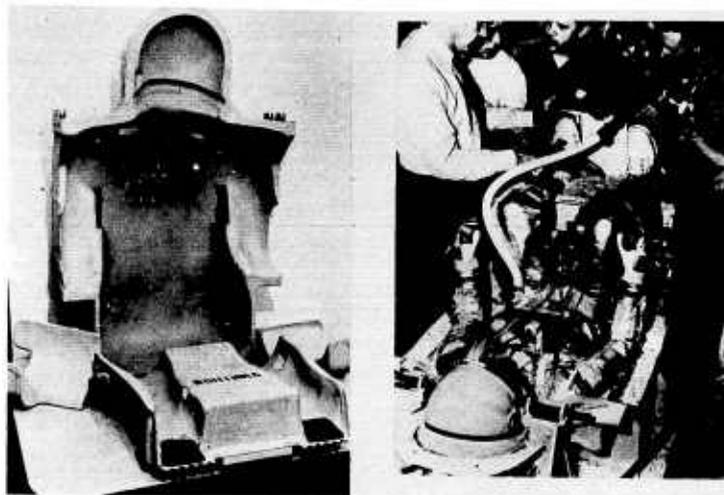
Fig. 12. Project Mercury astronaut couch foam
density >8 lbs/cu. ft.

Each astronaut was encased in a polyethylene film and a contoured plaster
mold was prepared. A reinforced plastic couch was then laminated over the
mold and a foam system was poured between the two surfaces. This is an
excellent example of a complicated molding job of the sort that only rigid
urethane foam can do.

Recent Advances

Three advances in pour-in-place technology are the frothing technique,
one-shot foaming, and "one component" systems. While these are to be treated
in detail in subsequent papers, they are listed here to indicate that each of them
has been derived from conventional liquid pouring-in-place techniques.

It is in the medium density range where properties and economics are
viewed most critically and where the foam users with the greatest volume
potential operate. The advantages in processing and properties claimed for
the frothing method and the minimal costs which one-shots offer may be
realized best when equipment and technically trained personnel are available
to provide control. However, in the low density and high density ranges and
in the medium range for users below about 200 thousand pounds per year, it
will probably continue to be more advantageous to use packaged quasi-
prepolymer systems and conventional pouring-in-place methods.

The third advance, one-can foam systems, may soon constitute a major commercial breakthrough for rigid foams. Such systems have been investigated to date primarily for space applications, but obvious possibilities exist for civilian uses as well.

Conclusion

In conclusion, for a discussion of the more theoretical aspects of foaming, the new volume[1] on polyurethanes written by J. H. Saunders and K. C. Frisch is highly recommended. Furthermore, for those who may be interested in actually developing a new application for rigid urethane foam, a complete discussion of process variables and their significance in restrained and unrestrained pouring-in-place may be found in an article by R. E. Jones which appeared recently in Plastics Technology.[2]

References

1.   Saunders, J. H., K. C. Frisch, Polyurethanes Chemistry and Technology, Part I, Interscience Publishers, John Wiley & Sons, Inc. (1962).

2.   Plastics Technology, October, page 27; November, page 43 (1961).

MOLDING OF ONE-SHOT RIGID URETHANE FOAM

E. A. Dickert, W. A. Himmler, D. E. Hipchen,
M. Kaplan, H. A. Silverwood, and R. Zettler

Introduction

Rigid urethane foam technology during the last six years has had a growth comparable to the phenomenal advance in flexible foam technology. Rigid urethane foam, however, did not find the immediate market acceptance that flexible foam did. This was primarily due to:

1. greater technical and developmental problems;

2. modifications needed to conform to strict construction codes and regulations; and

3. competition from less expensive insulating materials, whereas flexible polyether foam had a price advantage over competitive materials.

It has only been during the past three years that major progress has been made in meeting these challenges. Contributing to the recent accelerating acceptance of rigid urethane foam has been the commercialization of the more economical one-shot method of foaming. Prior to this, all foaming was accomplished by the quasi-prepolymer method, which consisted of blending a premix containing 80-90 per cent of the polyol and all other formulation ingredients with a quasi-prepolymer. The quasi-prepolymer was made by pre-reacting all of the diisocyanate with the remaining polyol. These polyols were initially polyesters; however, in 1958 the lower cost polyethers began to rapidly replace polyesters.

The one-shot method involves only the blending of the premix with the diisocyanate immediately before foaming. Thus, significant saving is accomplished by reducing the manufacture of foam from a two-step (quasi-prepolymer preparation and foaming) to a one-step (foaming) operation. Specifically, the introduction in 1959 of a lower cost modified polyisocyanate* made the one-shot process a reality and at the same time contributed additional cost savings.

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*NACCONATE®4040--Allied Chemical Corporation, National Aniline Div.

An important use of rigid urethane foam presently is for insulation, with refrigeration accounting for an increasing share of the rigid urethane market. The low thermal conductivity, low density, and excellent dimensional stability of rigid urethane foam make it especially suitable for refrigeration. More-over, since low thermal conductivity permits the use of thinner insulation compared with other insulating materials, more inside space is available for storage.

Uses for rigid urethane foam, other than for thermal insulation, are:

1. Construction applications where the load-bearing properties of the foam are important in addition to its insulating ability.

2. Flotation.

3. Packaging.

4. Speciality applications.

There are three general methods of rigid foam application:

1. Poured-in-place. (This paper will discuss the important factors of the one-shot poured-in-place technique.)

2. Slabstock--used in applications where foam can be most economi-cally cut to required shapes.

3. Sprayed--offers advantages of ease of applications and mobility.

The poured-in-place technique offers the following advantages as compared with slabstock:

1. Lower initial thermal conductivity and improved retention of thermal conductivity of the foam.

2. Improved structural strength and resultant cost saving by per-mitting use of thinner gauge skins.

3. Self-bonding characteristics of the foam to the panel skin.

4. Ability to produce a complicated shape.

These advantages justified the development of the special techniques required to mold commercially.

In-place foaming is accomplished by charging the cavity with the proper amount of liquid mix and allowing the expanding foam to fill all voids. Since cavity molding of rigid urethane foam presents difficulties not encountered

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in slabstock production, a specific technology is required. This paper presents a discussion of several aspects of filling a cavity or panel with rigid urethane foam.

Discussion

The production of molded rigid urethane foam panels of good quality is dependent on control of chemical and mechanical variables. The contribution of each formulation ingredient to the properties of the finished foam is chemical in nature, whereas, metering and mixing of the ingredients, mold design, and automation of the foaming operation are distinctly mechanical. Some of these factors are discussed in this paper.

Early one-shot foam formulations produced good moldings having low thermal conductivity and excellent dimensional stability. However, improvements in several properties were desired. These included the attainment of

1. reduced shear (non-uniformity) of the panel surfaces,

2. reduced panel density with little or no change in properties, and

3. improved adhesion of the foam to the substrate.

Several experimental studies involving numerous formulation and processing variables resulted in the solution of these problems through

1. slower foam gelation,

2. optimum mold temperatures, and

3. surface treatment of the substrate materials.

A typical molding formulation and important processing variables are shown in Table 1. Typical physical properties of a foam panel are given in Table 2.

This formulation has been used successfully to mold panels which differed widely in size and shape. Its versatility has been illustrated by molding of intricate shaped refrigerator doors, simple refrigerator panels, and eight-foot high refrigerated truck panels.

Several formulation and mechanical variations have been developed to permit attainment of lower densities, improved adhesion, and low shear. These variations have involved changes in pour patterns to accommodate various mold shapes, changes in fluorocarbon levels or ingredient temperatures to control panel density, and slight catalyst adjustments to improve adhesion or shear by control of gelation rates.

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TABLE 1

One-Shot Rigid Urethane Foam Molding Formulation
and Process Conditions

Foam Formulation	
Ingredients	Parts by Weight

Component A

Polyether Polyol[a] (460 Hydroxyl No.)	100
N,N,N',N'-tekrakis	
(2-hydroxypropyl)ethylenediamine[b]	8
Triethylenediamine[c]	0.3
N,N-Dimethylethanolamine	0.5
Dibutyltin dilaurate	0.02
Silicone Surfactant	1.5
Trichlorofluoromethane[d]	38

Component B

NACCONATE 4040	107

Processing Conditions

TDI Index (ratio of NCO/total active H)	1.03
Isocyanate Temperature, °F	80
Premix Temperature, °F	80
Agitator Design	Screw type
Mixing Speed, RPM	6000
Output, lb/min.	36
Mold Temperature, °F	125
Cream Time, seconds	15
Rise Time, seconds	150
Tack-Free Time, seconds	150

[a]ACTOL* 52-460 POLYOL, National Aniline Division, Allied Chemical Corp.

[b]Quadrol - Wyandotte Chemical Corporation

[c]Dabco - Houdry Process Division

[d]GENETRON® 11 - General Chemical Division, Allied Chemical Corp.

*Trade-mark of Allied Chemical Corporation for urethane-grade polyethers.

TABLE 2

One-Shot Rigid Urethane Foam Molded Panel (48" x 48" x 2-1/2")
Foam Physical Properties

Density, over-all, panel lb/ cu ft	2.35
Density, core, lb/cu ft	2.20
Closed Cells, %	95
Compression Load, psi, perpendicular to rise	
at yield point	23
at 10% deflection	30
Compression Modulus, psi	600
Flexural Strength, psi	60
Flexural Modulus, psi	900
Shear Strength, psi	22
Shear Modulus, psi	210
Moisture Vapor Permeability, perm-inches	2
Water Absorption, lb/sq ft surface area	0.06
"k" Factor, Btu (sq ft)(hr)($^\circ$F/in.)(cut foam sample)	
initial	0.112
after 10 days at 140°F	0.123
Dimensional Stability, % Volume Change	
24 hours at -22°F	< 1
24 hours at 158°F	< 1
24 hours at 230°F	4
24 hours at 158°F, 95-100% RH	8
72 hours at 100°F, 95-100% RH	1

Our work was carried out with a two-component foam system; isocyanate composed one stream and a premix of all other ingredients composed the second stream. Three or more streams have been used on occasion to give greater formulation flexibility without altering results; however, more stringent control of ingredient calibration is needed as the number of streams is increased.

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As is true in all foaming operations, close control of many chemical and mechanical factors is a prerequisite to a high yield of first-quality product. The remainder of this paper is devoted to a discussion of these factors and their effect on the molding operation.

Chemical Factors

Polyethers

Rigid foam polyethers are usually based on sorbitol, sucrose, pentaery-thritol, methyl glucoside, or similar polyols. In general, foam physical properties, especially dimensional stability, improve with increased poly-ether functionality and hydroxyl number. High functionality is helpful in attaining the highly cross-linked rigid polymer that is necessary for good dimensional stability in the finished foam.

The hydroxyl number of the polyether (a measure of equivalent weight of the polyether) usually falls within the range of 300-550 units. High hydroxyl number polyethers (e. g. , 450-550) generally produce one-shot rigid foams having good dimensional stability. However, as the hydroxyl number in-creases, the foams have a tendency toward friability. Since friability has an adverse effect on adhesion and foam strength, a compromise must be made. The best balance of properties of one-shot foam moldings has been attained in a hydroxyl number range of 450-490 (see Fig. 1), the exact hydroxyl number depending on the specific polyether type. Conversely, low hydroxyl number polyethers (300-400) usually produce soft, non-friable foams having correspondingly poorer dimensional stability.
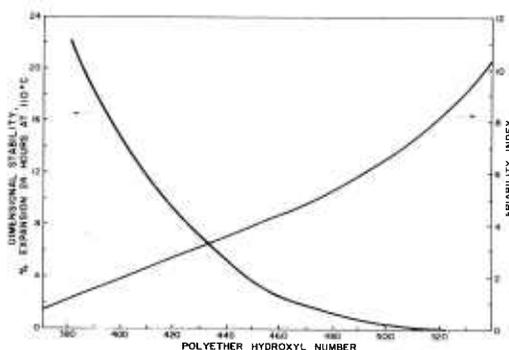
Fig. 1. Effect of polyether hydroxyl number on dimensional stability and friability.

Polyisocyanate

The polyisocyanate* used in the one-shot molding system described here is a modified toluene diisocyanate. Its relatively high acidity (0. 2-0. 3 per cent) gives it a reduced degree of reactivity which permits slow gelation and rise times, both of which are helpful in panel molding.

A TDI Index (ratio of NCO/total active H) of 1. 03-1. 05 produces opti-mum results. Lower isocyanate levels can result in poor dimensional sta-bility. Higher levels do improve

*NACCONATE®4040--Allied Chemical Corporation, National Aniline Div.

dimensional stability but density is
increased (Fig. 2) with a correspond-
ing increase in foam cost.

Silicone Surfactant

The silicone surfactant serves
a dual function. First, it serves to
emulsify the hydrophilic polyether
and the hydrophobic isocyanate and
fluorocarbon into a homogeneous
mixture, thus insuring uniform re-
action throughout the foam mass.
Second, it controls cell size by
stabilizing the rising foam and pre-
venting coalescence of the tiny foam
cells until gelation occurs.

Fig. 2. Effect of isocyanate index
on panel density.

In the one-shot molding process, slightly higher quantities of silicone
surfactant are generally required than are used in slabstock production.
Perhaps this is due to the more critical nature of the molding process arising
from foam movement and packing pressures involved.

Catalysts

The most critical formulation ingredients in rigid foam production are
the catalysts, which control the rate of polymerization and rise of the foam.
The reaction rate is conveniently measured as follows:

1. cream time - start of exothermic reaction manifested by milky
   appearance of foaming mass.

2. rise time - completion of foam expansion.

3. tack-free time - complete gelation or hardening of the foam.

These relative foaming times are especially important in molding formulations.
To insure complete mold fill, low shear, and good adhesion, gelation should be
retarded until the foam has nearly completed rising. This permits foam to flow
into each crevice or void of a complex mold. The close control of reactivity
required for molding has been accomplished by selecting the optimum combi-
nation of catalysts.

Two classes of catalysts have found commercial acceptance in the pro-
duction of rigid urethane foam: tin salts and tertiary amines. The tin salts
are of two types: the organometallic type such as dibutyltin dilaurate and the

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organic acid salts of divalent tin such as stannous octoate. Some of the tertiary amines are:

> triethylenediamine
> N,N-dimethylethanolamine
> N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine
> tetramethylbutanediamine
> tetramethylguanidine
> triethylamine

The preferred catalysts and their contributions to one-shot panel molding are:

Dibutyltin dilaurate. Produces fine cell structure and promotes rapid gelation or hardening of the foam. Because dibutyltin dilaurate is particularly effective in promoting rapid gelation, its use is restricted in the above molding formulation. Concentrations above 0.03 parts by weight/100 parts polyether result in increasing shear and decreasing adhesion.

Triethylenediamine. Gives the rapid initial polymerization that is essential for fine uniform cell structure, yet gelation or hardening of the foam is delayed until rise is almost complete. The catalytic activity of triethylenediamine is not so pronounced as that of dibutyltin dilaurate and therefore it allows more latitude in control of gelation.

N,N-Dimethylethanolamine. Serves to neutralize the acidity in NACCONATE 4040, thereby increasing the basicity of the system and controlling the rate of polymerization. Excessive amounts tend to reduce foaming times slightly but have little effect on moldability. Odor in the finished foams is not a problem since the catalyst becomes part of the polymer through reaction of its hydroxyl group with isocyanate.

Odor in the finished foam is undesirable when the panel is used in the proximity of foodstuffs since the odor can be transferred to the food. The recommended amines do not cause odor in the foam. However, many amines such as triethylamine, tetramethylbutanediamine, and tetramethylguanidine may cause odor problems.

N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine. Improves moldability and adhesion, and reduces shear. This amine polyol also acts as a crosslinking agent and is especially effective for improving dimensional stability of low-density foam panels. Again, foam odor does not occur with this catalyst.

Fluorocarbon Blowing Agent

The fluorocarbon serves two important functions in rigid foams. First, it serves as a blowing agent for expansion of the urethane polymer. Second, the fluorocarbon gas, usually trichlorofluoromethane, trapped in the foam

cells contributes to the low thermal conductivity of the foam, apparently because the thermal conductivity of the fluorocarbon is low.

The over-all panel density is controlled by the level of trichlorofluoromethane, as shown in Fig. 3.

Other factors, such as ingredient temperatures, mold temperature, panel thickness, and panel shape, also have an effect on panel density. All of these factors must be considered when a given panel density is required.
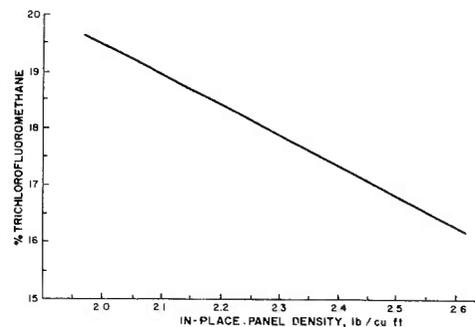
Fig. 3. In place panel density vs. per cent trichlorofluoromethane.

Ingredient Temperatures

The temperatures of ingredients can play an important part in obtaining proper reaction times (i.e., cream, rise, and tack-free) for molding. In general, reaction times decrease with increasing ingredient temperatures. This effect of ingredient temperatures on reaction times for a two-stream system containing identical premixes and diisocyanate is shown in Table 3.

TABLE 3

Effect of Ingredient Temperatures on Reaction Times

	Foam A	Foam B
Premix, ^{O}F	70	78
Isocyanate, ^{O}F	71	123
Cream, seconds	17	9
Rise, seconds	140	100
Tack-Free, seconds	145	110

Ingredient temperatures can also be used as a tool to control panel density of one-shot foams. At equivalent levels of fluorocarbon, significantly lower density panels have been prepared from hot ingredients (Foam B) than from cooler ingredients (Foam A), as is shown in Table 4. Furthermore, Table 4 also shows that panels of equivalent density can be prepared from hot ingredients (Foam B), using less fluorocarbon than required with cooler ingredients (Foam C). The physical properties of Foams B and C are equivalent.

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TABLE 4

Effect of Ingredient Temperatures on Panel Density

Foam	Ingredient Temperature, °F		Fluorocarbon Parts/100 Parts Polyether	Over-all Panel Density*, lb/cu ft
	Premix	Isocyanate		
A	77	77	45	2.3
B	87	125	45	2.0
C	77	77	52	2.0

*Panel Size: 24" x 24" x 1.75"

Most commercially-molded panels have an over-all density of 2.3-2.8 lb/cu ft. It is possible, with certain types of polyols, to achieve densities as low as 2.0 lb/cu ft without substantial sacrifice of foam properties. This can be accomplished by increasing blowing agent concentration or ingredient temperatures.

Usually, too short a cream time is undesirable in molding because it may result in poor foam distribution or knit lines and air voids in the molded part. Surprisingly, however, the short cream time attendant to hot ingredients has not caused processing problems. Foam mix is poured on top of rising foam without deleterious effect. In fact, shear is actually decreased when hot ingredients are used. Perhaps this difference occurs because short cream time resulting from hot ingredients is not necessarily accompanied by rapid gelation; whereas short cream time caused by fast catalysis is accompanied by rapid gelation and it is the rapid gelation that causes poor moldability.

Stability of Ingredients

Component A in Table 1 is stable for several days if kept under a slight dry nitrogen pressure to prevent vaporization of the fluorocarbon.

Component B is stable at room temperature under dry nitrogen.

Deactivitation of the premix is characterized by increased foaming times and foam having coarse, irregular cell structure. Loss of fluorocarbon from the premix is evidenced by an increase in foam density. This loss can be minimized by maintaining about two psi pressure on the premix holding tank.

Mechanical Factor

Mixing Head and Agitator

In one-shot rigid foam molding, the foam machine must deliver two or more components to the mixing head in correct proportions and at controlled temperatures. The function of the mixing head is to provide sufficient mixing so that the streams are thoroughly blended and the resultant foam has fine, uniform cell structure and optimum physical properties. Insufficient mixing will result in weak foam with coarse, irregular cell structure.

Fig. 4 shows a typical mixing head consisting of the agitator, housing, and outlet orifice. The degree of mixing achieved in the head is largely dependent upon agitator design, clearance between the housing and agitator, agitator speed, and the size of the outlet orifice. Each of these is discussed below:

Agitator Design. Typical agitator designs are shown in Fig. 5. At equal operating speeds, the pin-type, screw-pin-type, and screw-type agitator, respectively, will provide low, medium, and high rates of mixing shear. The screw-type agitator is preferred for molding because it has consistently given fine cell structure foam and thorough mixing from first to last shot.

The clearance between the housing and the agitator, particularly with the screw-type, is very important. A clearance of 0.006" - 0.030" between the housing and the screw-type agitator provides a high degree of mixing shear and has been found to produce fine, uniform cell structure foam. The specific clearance to be used for a particular system is dependent on ingredient viscosities. Generally, higher viscosities require increased clearance.

The first ingredients discharged from the mixing head on opening the valves and the last on closing the valves must be thoroughly mixed in correct proportions, in order to make useful moldings. Thorough mixing has been attained with the high shear screw-type agitator; correct proportioning has been obtained by adjusting recycle pressure of ingredient streams to equal pressure during forward flow.

Outlet Orifice. Restriction at the outlet of the mixing head creates back pressure and increases the mixing action. The back pressure is also a function of the throughput rate and, therefore, selection of the orifice size must take this into account. Excessive restriction of the orifice tends to result in foam of increased cell size, which is undesirable. Optimum results have been achieved using the smallest orifice that does not significantly increase cell size.

Agitator Speed. Agitator speed may be increased or decreased to bring about a corresponding change in the degree of mixing. Normal speeds for the screw-type agitator are 4000-6000 RPM.

Fig. 4.   Mixing head.

Fig. 5.   Agitator design.
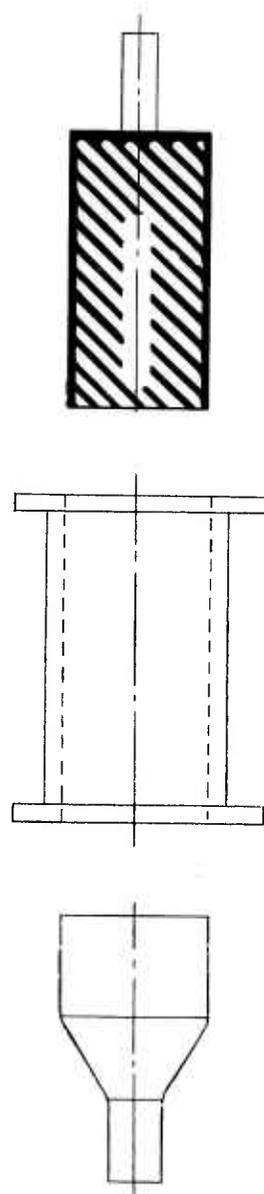
AGITATOR
(Screw Type)

HOUSING

OUTLET ORIFICE
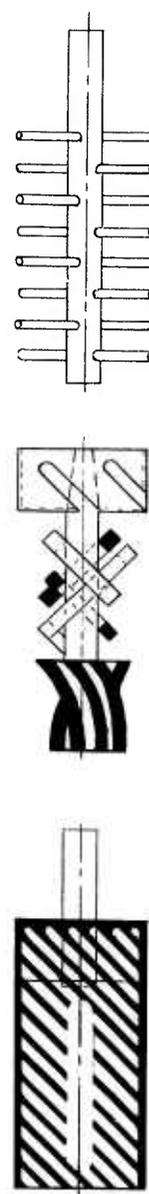
PIN   TYPE
Low Shear

SCREW PIN TYPE
Medium Shear

SCREW TYPE
High Shear

Critical Mixing Level. For the given foam formulation, a specific combination of the above variables will provide a critical minimum level of mixing. Increased mixing beyond this level does not significantly affect foam quality or appearance. Table 5 lists values for these variables which will provide adequate mixing for the foam formulation given in Table 1. In general, these variables will be applicable to most one-shot rigid urethane foam molding formulations. However, it should be noted that some variation should be expected among different foam machines.

TABLE 5

Mixing Head Design Recommendations for One-Shot Panel Molding

Agitator type	Screw
Agitator/Housing clearance	0.015 in.
Housing diameter	1.5 in.
Housing Length	4 in.
Outlet orifice diameter	1 in.
Throughput rate	40 lb/min.
Agitator speed	6000 RPM

Mold Construction

Mold construction is often dictated by the application involved. However, the design of any rigid foam mold cavity must concern itself with materials of construction, adequate jigging for mold support, and venting for release of entrapped gases.

Materials of Construction. Plain and galvanized steel, aluminum, and wood are commonly used mold surface materials. Adhesion of the foam to the mold surface is usually an important consideration. Where strong adhesion is desired, the minimum requirement is that the foam-to-mold surface bond strength should equal that of the foam itself. Surface treatment may be required to achieve optimum foam-to-metal bond. Untreated surfaces ranked in order of decreasing bond strength are: wood, steel, embossed aluminum, mill finished aluminum, and galvanized steel. Surface treatments for metal molds which improve bond strength include:

1. chemical etching, such as with phosphoric acid or chromic acid;
2. application of a primer;*
3. solvent cleaning; and
4. mechanical abrasion.

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*Metalast Washcoat Primer #920, C. A. Woolsey Paint & Color Co., Inc., N.Y.

In general, solvent cleaning followed by a coat of primer gives the best results on metal surfaces.

It is sometimes desirable to release the foam from the mold surface. This may readily be accomplished by applying a wax coat to the mold surface. Mold release agents that have proved effective are Traffic Wax* and Perma-Mold 511-02.**

Jigging. In filling a mold cavity with rigid urethane foam, significant pressures are developed because 5-10 per cent excess foam must be added to insure complete fill. Therefore, the mold surfaces must be supported to prevent distortion of the panel. These pressures may reach 2-4 lb/sq in.

Jigging may be simple or complex depending on the complexity of the panel shape. A straight wall trailer truck or building panel might require only supported plywood. On the other hand, a refrigerator door panel containing shelves and egg trays would require a detailed, complex jig. Jigging is generally necessary when the mold surface has insufficient strength to prevent distortion due to the pressure of the rising foam.

Venting. The one-shot foam formulation discussed previously produces a foam of sufficient flowability to fill narrow and complex mold cavities, e.g., the thin shelf protrusion and egg trays of a vertically filled refrigerator door. However, to fill intricate cavities of this type, it is necessary that air and foam gases be allowed to escape so that voids are not formed within the foamed article.

Small diameter holes, up to 1/16", positioned at the extremities of the mold surfaces permit sufficient gas release to fill intricate sections. Larger holes, up to 1", should be provided at the top of the mold to release the bulk of the gases. The smaller vents will seal themselves as the foam gels. The larger holes at the top surface should be closed when the rising foam reaches that point.

Molding Conditions and Techniques

In addition to mixing head and mold design considerations, the manufacture of quality panels is dependent on other factors, including mold packing, direction of foam rise within the mold, mold temperature, mold thickness and complexity, and curing conditions.

Packing. In order to assure complete fill of mold extremities and optimum foam properties, a foam charge 5-10 per cent in excess of that needed for an unrestrained foam rise should be used for closed molding

*S. C. Johnson & Son, Inc., Racine, Wisc.
**Brulin & Co., Inc., Indianapolis, Ind.

as described by Jones.* Use of too little packing results in non-uniformities and slightly soft foam at the top of the panel. Use of excessive packing results in higher panel densities and higher pressures, which, without adequate jigging, may distort the mold.

Vertical versus Horizontal Pour. The panel mold may be positioned with its walls vertical or horizontal during the foaming operation, as illustrated in Fig. 6. The high vertical rise is the easiest to handle as it may be poured through a single opening at the top of the mold. Panels up to

POUR

HIGH

POUR

LOW
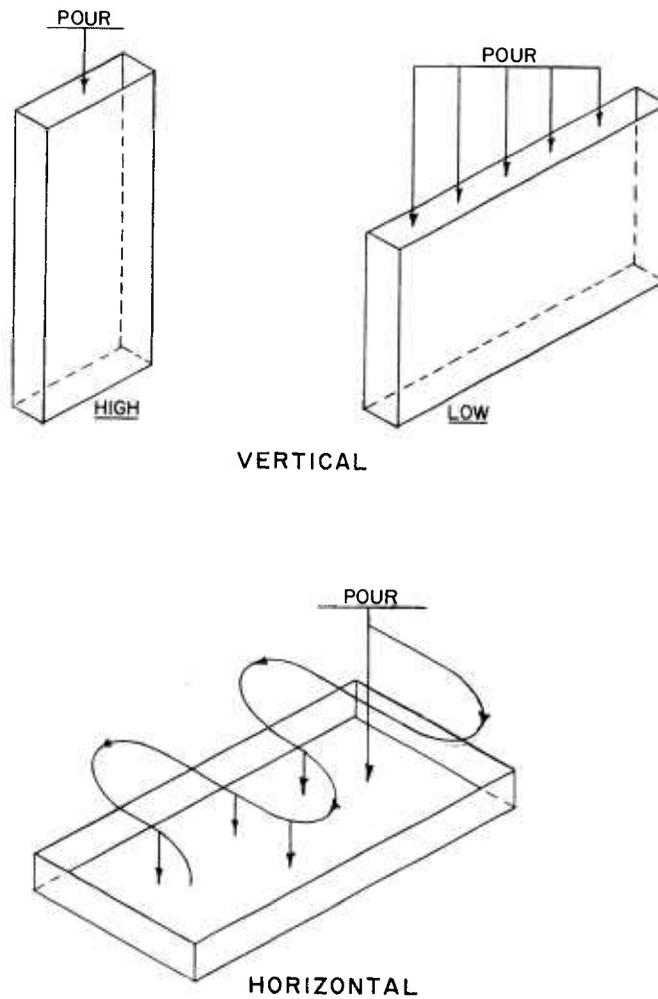
VERTICAL

POUR

HORIZONTAL

Fig. 6.

*R. E. Jones, Plastics Technology, 27-34, October 1961.

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eight feet high have been successfully foamed using only one pour. The foam properties of vertically filled panels are uniform from top to bottom. For example, density and compression load properties of foam from bottom to top of typical panels are shown in Table 6.

A low vertical rise (Fig. 6) may also be used where high panels cannot be conveniently handled. In this case, the foam may be poured through a single hole at one end if the mold is tilted to insure adequate distribution. Otherwise, it may be necessary to traverse the length of the mold.

TABLE 6

Variation of Foam Density and Compression Load in
Vertically Poured Panels (Panel Height, Feet)

Foam Location in Panel	2[a]		4[b]		8[c]	
	Core Density lb/cu ft	Comp. Load,[d] psi at yield	Core Density lb/cu ft	Comp. Load,[d] psi at yield	Core Density lb/cu ft	Comp. Load,[d] psi at yield
Bottom	2.1	21	1.9	16	1.9	16
Middle	2.0	21	2.1	17	1.9	15
Top	2.0	21	2.1	18	1.8	14

[a] 2' x2' x1.75"

[b] 4' x4' x2.5"

[c] 8' x18" x3"

[d] Perpendicular to foam rise

The compressive strength of the foam is greater parallel to foam rise that it is perpendicular to foam rise, e.g., 23 psi versus 16 psi, respectively, at yield point for 2.3 lb/cu ft over-all density. Therefore, maximum compressive strength occurs parallel to the panel walls in a vertical pour. It may be desirable to achieve maximum strength perpendicular to the panel walls. In such cases, the panel can be foamed horizontally. This type of pour requires traversing of the mixing head for uniform foam distribution. It also requires special equipment for closing and jigging one side of the panel after the foam has been charged.

In general, the vertical type of pour offers the greatest simplicity of operation and in many applications, such as refrigerated truck panels, compression load properties should be adequate.

Mold Temperature. Temperatures of 110-130°F are desirable with metal molds in one-shot rigid urethane panel molding to insure low panel densities and optimum "k" factors. Lower mold temperatures result in

high panel density due to loss of heat to the mold. In addition, a thick skin forms at the foam surface which may cause an increase in "k" factor. Fig. 7 shows the effect of the mold temperature on the density of a 1-3/4" panel.

In general, wooden or plastic molds show the same effects. However, due to their lower specific heat and thermal conductivity, as compared to metal molds, lower temperatures are required and the effects of changes in mold temperature are less pronounced.

Mold Thickness and Complexity. High quality panels differing widely in thickness and complexity have been prepared using the formulation shown in Table 1. However, to attain desired panel density, it is necessary to adjust fluorocarbon levels as mold thickness and complexity change. In general, as panel thickness is decreased or complexity increased, the fluorocarbon level must be increased to maintain equivalent panel densities. At a given fluorocarbon level, thick panels will have lower density than thin panels because with thick molds the surface-to-volume ratio is lower and less exothermic heat is lost to the mold. For example, a 1.75" thick panel generally is 0.3 - 0.4 lb/cu ft less dense than a 1" thick panel.
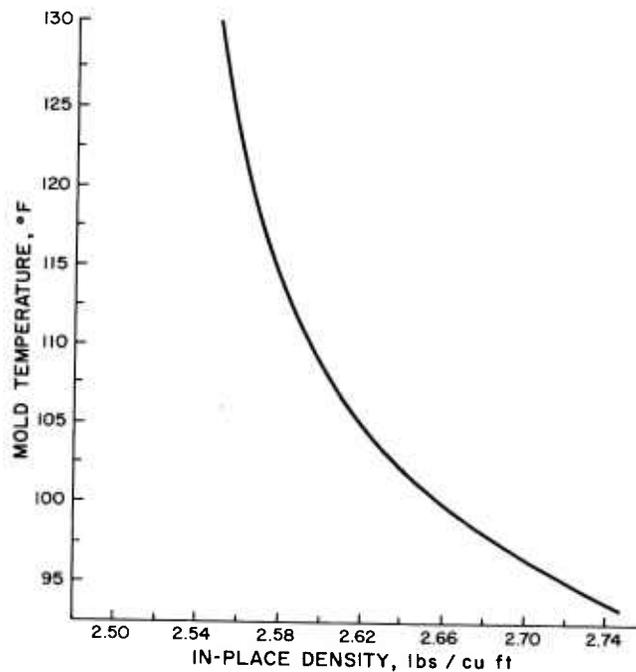
Fig. 7. Mold temperature vs. in-place panel density.

<u>Curing Conditions</u>. Generally, with warm (110-130°F) molds, a panel can be released from the jig in approximately ten minutes. A postcure at 150-175°F may reduce this time to as little as five minutes.

Summary

Some recent advances in the molding of rigid urethane foam have been presented. The contribution of each formulation ingredient (such as polyether, polyisocyanate, silicone emulsifier, catalysts, and blowing agent) on panel molding, as well as effect of ingredient temperatures, have been discussed. In addition, the mechanical variables of panel molding, such as mixing head and agitator design, mold construction, and molding techniques have been investigated.

Acknowledgement

SPRAY APPLICATION OF RIGID URETHANE FOAM

I. N. Einhorn

Introduction

The technology of urethanes was developed in Germany during World War II. This activity reached moderate commercial importance in that country, but did not reach a significant stage of development in the United States until the mid-1950's.

By 1955 laboratory work had yielded a variety of pourable and sprayable rigid and semi-rigid urethane foam formulations. These foams were based on carbon dioxide as the blowing agent and thus did not achieve sufficiently low thermal conductivity ("k" factor) to be competitive on a cost-performance basis.

With the advent in 1958 of foam systems based on fluorocarbon blowing agents, systems were developed which demonstrated improvements in thermal performance. Many foam systems have been field tested on large applications during the past four years.

Application by Spray

Atomization of the foam raw materials by spray technique makes it possible to deposit much thinner layers than can be laid down by pouring with a mixing head, and provides the most effective method of controllably producing foam on vertical as well as horizontal surfaces.

The spray-in-place technique provides a method of applying urethane foam in many types of commercial applications such as exterior tanks, ducts, roofs, and pipes of simple or complex design. Rapid advances are being made in the development of equipment that may be used to apply foam. Use of increased volumes of materials, made possible by this new equipment, should lower the price of the basic raw materials, thus making possible applications that are precluded by current cost structures.

Equipment for Spraying

Spray Guns.[1] Several varieties of spray guns are commercially available for coating surfaces with foam. These may be divided into three basic types:

1. External mix with air atomization. The two reactant streams are

pumped through the gun under pressure and ejected in separate streams. Mixing and atomization are accomplished simultaneously just exterior to the spray nozzle.

2. <u>Internal mix with air atomization.</u> The two reactant streams are blended internally by an air-driven agitator. The components are pumped through the gun under pressure and atomized on discharge by air as a single stream.

3. <u>Internal mix with airless atomization.</u> The two reactant streams are mixed by passing them together through an internal labyrinth under high pressure. Atomization is accomplished on discharge by pressure drop across the spray nozzle.

TABLE 1

Performance Comparison of Foam Spray Guns

Property	External Mix (Air atomization)	Internal Mix (Air atomization)	Internal Mix (Airless atomization)
Viscosity of reactants	Necessary to maintain low viscosity for each component to insure adequate mixing	Viscosity control not as critical as with external equipment	Viscosity control not as critical as with external equipment
Air supply	Large volume of air required	Volume of air required lower than with external mixing equipment	None required
Overspray	Considerable overspray costly and requires optimum safety precautions	Overspray greatly reduced	Overspray reduced to low level
Intermittent operation	Little plugging	Plugging a problem Requires continuous flushing	Internal mixing sections require self-cleaning, needs constant flushing

<u>Metering Units.</u> The equipment employed to meter the foaming reactants must be capable of delivering the materials in accordance with the material supplier's recommendations. Generally, equipment capable of

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EXTERNAL MIX SPRAY
GUN, AIR ATOMIZATION

A COMPONENT
B COMPONENT

AIR
AGITATOR

AIR MOTOR

INTERNAL MIX SPRAY
GUN, AIR ATOMIZATION

A COMPONENT
B COMPONENT

AIR

INTERNAL MIX SPRAY
GUN, AIRLESS ATOMIZATION

ATOMIZING
TIP

MIXING LABYRINTH

A COMPONENT
B COMPONENT
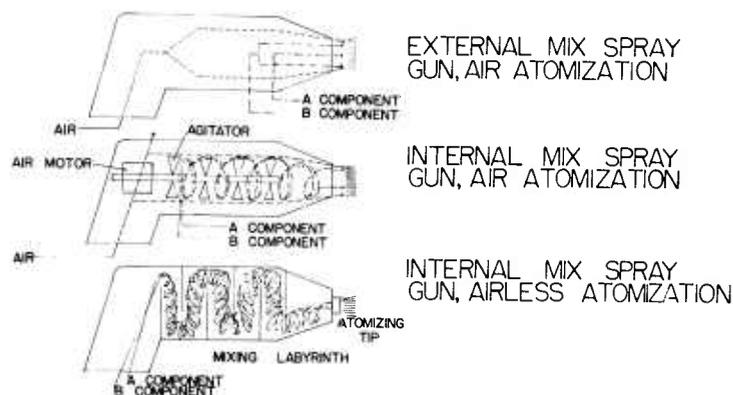
delivering two to ten pounds of material per minute is satisfactory for the majority of field applications. Two systems have been used in commercial applications:

1. <u>Pressure pots</u>. Systems using air to provide pressure and orifice type valves for flow control have been used successfully for small applications. It is necessary to pass the air through a water-extractor and a filter system to minimize pick-up of moisture due to condensation. This system is sensitive to variations in pressure, temperature, and viscosity, and is generally not satisfactory for commercial operation.

2. <u>Positive displacement metering pumps</u>, such as piston or gear pumps, provide accurate, reproducible metering over a wide range of operating conditions. This type of system is more expensive than simple pressure pot systems but has found greater usage because of better control.

<u>Temperature Control</u>. Equipment must be capable of maintaining adequate temperature control (heating and cooling) of the reactants. Controlling the temperature of the reactants reduces variation in viscosity and aids in obtaining good mixing.

Variables Affecting the Spraying of Urethane Foam

Control of the quality of raw materials and recognition of the effects of variables in the application process are vital to the quality and reproducibility of urethane foams.

<u>Climatic Conditions</u>.

1. <u>Temperature (ambient)</u>. The formation of urethane foam involves an exothermic chemical reaction. Variations in the ambient temperature conditions may affect the foaming rate, adhesive bond to the substrate, and

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physical properties of the resulting foam. Unless specifically formulated for other conditions, urethane foam should be spray applied within an ambient temperature range of 65° and 100°F. Loss of volatile components of the foaming raw materials increases at higher temperatures.

2. <u>Substrate temperature</u>. Unless specifically formulated for use at other temperatures, urethane foams should be spray applied on substrates whose temperatures fall within a range of 65° and 100°F. If the substrate temperature is less than 65°F, a thin layer of material can be sprayed and permitted to foam. This "flash coat" will act as an insulation, allowing subsequent layers to foam to the desired density by preventing a loss of exotherm. If the substrate temperature exceeds 100°F, it may be necessary to employ a blowing agent which vaporizes at a higher temperature to prevent flash volatilization and resulting high density foam.

3. <u>Moisture conditions</u>. Moisture (rain, fog, condensation, etc.) will react chemically with the urethane raw materials, adversely affecting foam formation and the resultant properties. Consequently, <u>the substrate must be dry</u> and good industrial practice dictates that the area sprayed be limited by the applicator's ability to protect the insulation from precipitation (rain, snow, dew, etc.) with a temporary cover until the prescribed weather barrier can be applied. If, by conditions beyond control, the insulation is subjected to precipitation, the foam must be allowed to dry before the application of the barrier coat.

4. <u>Wind velocity</u>. Wind velocities greater than 10 to 15 miles per hour can result in excessive loss of exotherm thus affecting foam density and thermal properties. Caution must be taken to prevent overspray and fumes from contaminating adjacent work areas.

Chemical Factors Governing Foam Properties

The formation of urethane foam is a complex phenomenon. In addition to the chemical and physical aspects of a polymerization system, factors peculiar to colloidal systems must be considered. An understanding of the formation of urethane foams involves consideration of the organic chemistry of the reactions leading to gas formation and molecular growth, the colloid chemistry of nucleation and bubble stability, and the rheology of the polymer system as it changes from a liquid to a solid.

Inasmuch as "prepolymer" or "semi-prepolymer" processes have been almost universally employed for spray-in-place applications, emphasis is directed toward a study of the variables in these systems and their relationship to application and performance.

In the prepolymer system the polyol (resin) and isocyanate are reacted to yield a prepolymer:

$$2R(NCO)_2 + HO \sim\!\!\sim OH \longrightarrow OCN\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}O \sim\!\!\sim O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-}NCO$$

Isocyanate   Polyol   Prepolymer
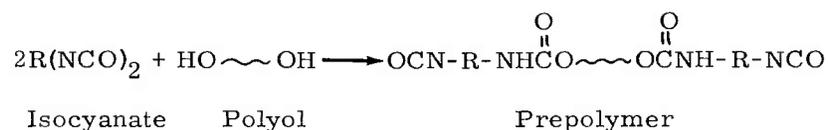
Subsequently water and catalyst (amine) are mixed into the prepolymer to effect foaming:

$$n\ OCN\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}O \sim\!\!\sim O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-}NCO + n\ H_2O \longrightarrow$$

$$\left[-NH\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}R\text{-}NH\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O \sim\!\!\sim O\overset{\overset{\displaystyle O}{\|}}{C}NH\text{-}R\text{-} \right]_n + n\ CO_2 \ .$$
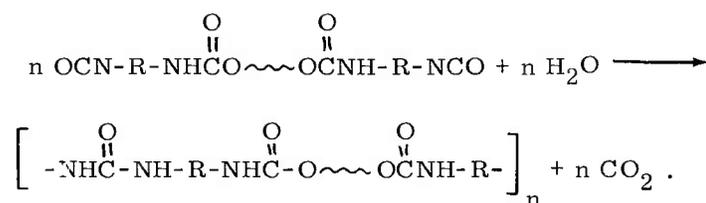
An inert blowing agent (fluorocarbon) is generally incorporated in the system to decrease foam density and improve thermal insulating properties.

Crosslinking is most successfully introduced into the polymer by use of branched resins. Idealized structures can be drawn for trifunctional tetra-functional, etc., polyols.[2] The average weight per branch point has been calculated to be in the order of 400 to 700 for rigid foams and from 700 to 2500 for semi-rigid foams.
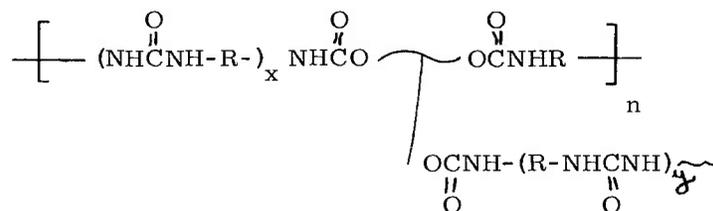
Idealized Structure Based on Triol

The semi-prepolymer (quasi-prepolymer) differs from the prepolymer in that a part of the polyol (resin) is mixed with all of the isocyanate to give a prepolymer containing a large excess of unreacted isocyanate. This pre-polymer is then foamed by reaction with additional polyol which may contain blowing agent, catalyst, and surfactant. Many rigid foam formulations are produced commercially by this process using trichlorofluoromethane as the only blowing agent.

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Chemical Factors Relating to Foam Properties

The stoichiometry of urethane spray systems is normally such that the ratio of total isocyanate equivalents to total hydroxyl equivalents in the reactants is close to unity.

Effect of NCO/OH Ratio on Foam Density. A series of samples were prepared under constant conditions varying only the NCO/OH ratio. Table 2 lists the stoichiometric relationships in the reaction mixture used to produce the test specimens.

TABLE 2

Stoichiometric Relationship of Reactants

Sample Number	NCO Equivalent	OH Equivalent	NCO/OH
1	0.384	1.401	0.274/1.0
2	0.745	1.401	0.532/1.0
3	1.066	1.401	0.761/1.0
4	1.328	1.401	0.948/1.0
5	1.544	1.401	1.102/1.0
6	1.735	1.401	1.238/1.0
7	1.911	1.401	1.364/1.0
8	2.096	1.401	1.496/1.0
9	2.283	1.401	1.630/1.0

Samples 1 and 9 collapsed during the foaming process. All other samples possessed sufficient gel strength to maintain a cellular structure during cure. Fig. 1 indicates the relationship between the NCO/OH ratio and foam density. Foams meeting generally accepted commercial specifications were prepared utilizing an NCO/OH ratio ranging from 0.948/1.0 to 1.364/1.0.

Effect of NCO/OH Ratio on Compressive Strength. Fig. 2 indicates that only a slight increase in compressive strength properties were obtained with a given formulation when the NCO/OH ratio was raised above 1.1/1.0. Table 3 presents the compressive strength properties of a series of foams of varying NCO/OH ratios.

Effect of NCO/OH Ratio on Thermal Properties. The stoichiometry of the foam raw materials governs to a large degree the stability of "k" factor of the finished product. Thus it can be shown, Fig. 3, that the initial "k" factors of a series of foams of different NCO/OH ratios vary only between

EFFECT OF NCO/OH RATIO ON DENSITY OF SPRAYED
RIGID URETHANE FOAM

Fig. 1.

EFFECT OF NCO/OH RATIO ON COMPRESSIVE STRENGTH OF
SPRAYED RIGID URETHANE FOAM
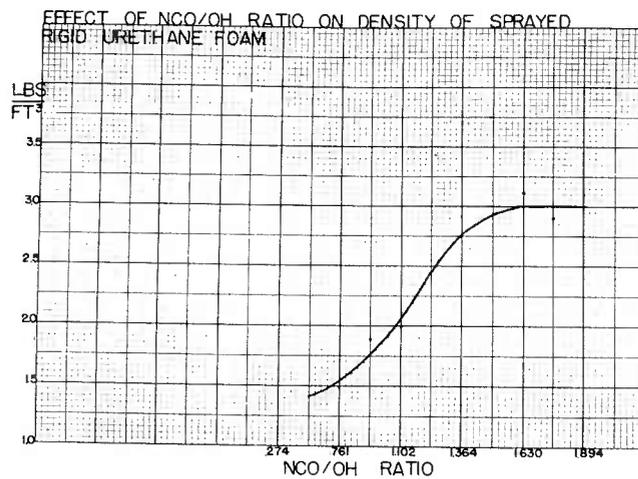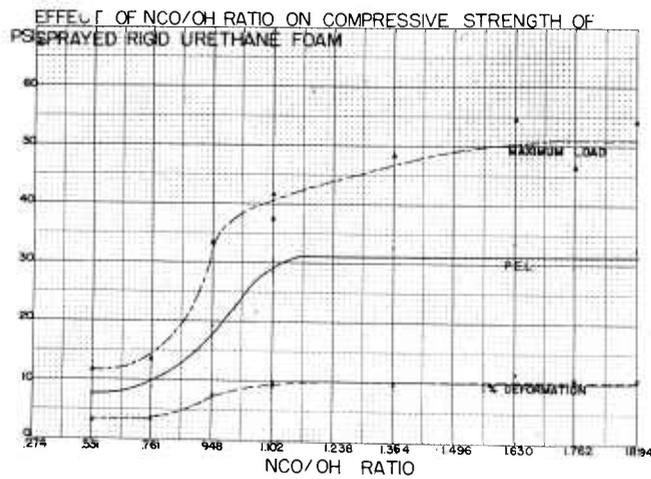
Fig. 2.

0. 136 and 0. 145. The "k" factors of these same foams varied widely when subjected to accelerated aging at moderately high temperatures and varying humidity conditions.

Effect of NCO/OH Ratio on Water Vapor Permeability. Fig. 4 presents data on water vapor permeability vs. NCO/OH ratio. Optimum properties were obtained when the NCO/OH ratio was in the range 1. 102 to 1. 364.

TABLE 3

Relationship Between NCO/OH Ratio and Compressive Strength

| NCO/OH	.532/1.0	.761/1.0	.948/1.0	1.102/1.0	1.630/1.0	1.762/1.0	1.894/1.0
Density, pcf							
avg.	1.42	1.43	1.89	2.11	3.11	2.90	3.10
range	1.40-1.45	1.32-1.60	1.87-1.99	2.05-2.11	3.04-3.20	2.68-3.15	3.03-3.23
Load, psi at 1% deformation							
avg.	3.11	3.08	7.31	9.17	11.61	10.76	10.84
range	2.6-3.9	2.7-3.7	5.8-8.5	8.3-11.8	10.9-14.3	9.9-11.6	9.3-12.7
Load, psi at PEL							
avg.	7.6	8.8	19.1	28.3	33.4	29.6	32.5
range	6.5-9.3	8.0-11.1	17.1-21.6	25.0-37.8	29.0-36.4	29.1-31.3	26.9-37.1
Load, psi at maximum load							
avg.	11.9	13.7	33.3	41.7	54.7	46.6	54.2
range	9.1-14.4	10.6-16.2	30.8-37.1	31.8-41.5	49.0-59.9	44.0-47.8	50.6-55.9

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Fig. 3.

Fig. 4.

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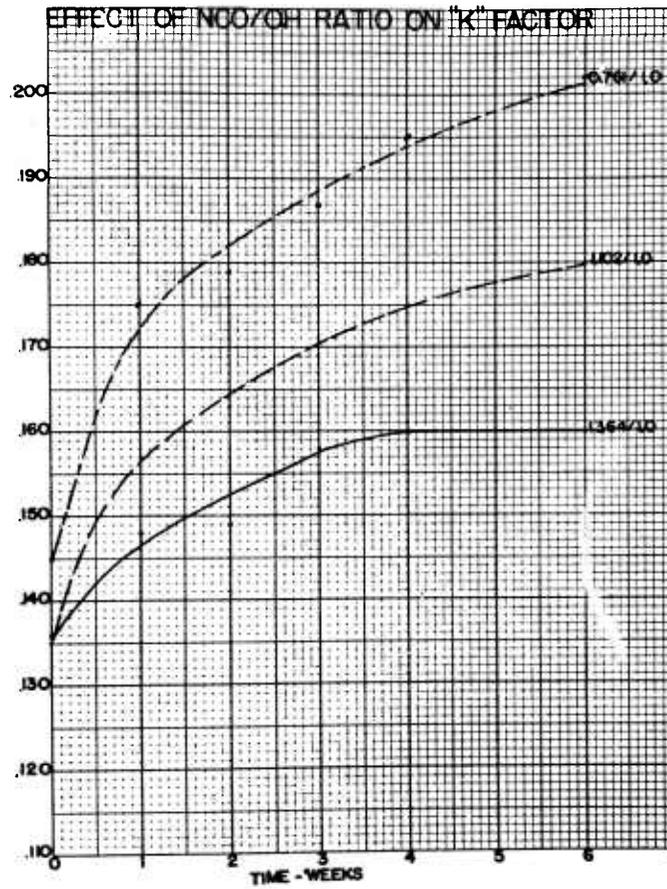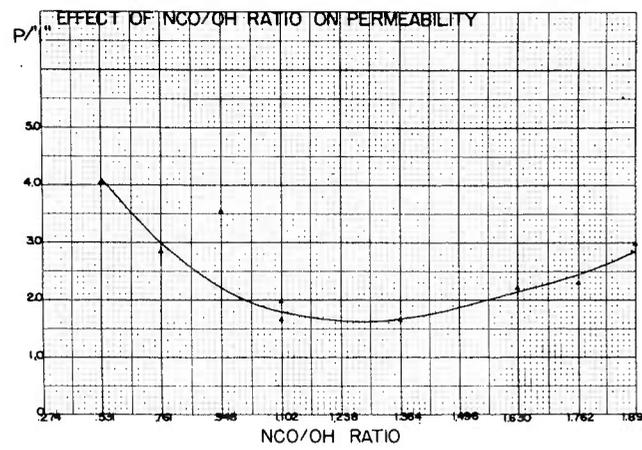
Effect of NCO/OH Ratio on Foam Heat Distortion. The relationship
between the NCO/OH ratio and foam heat distortion properties is difficult to
establish. Samples were prepared in which the NCO/OH ratio varied between
1.102/1.0 and 1.894/1.0. All specimens were permitted to equilibrate at
70^OF and 50 per cent R.H. for 14 days before testing. The samples were
then exposed to each of the following temperatures for a period of 24 hours
(100°, 150°, 200°, and 250^OF). Changes in foam volume and sample weight
were measured. Fig. 5 presents the relationship between the NCO/OH ratio
and sample weight while Fig. 6 presents the relationship between the NCO/OH
ratio and sample volume

Effect of Physical Factors Relating to Foam Properties

Effect of Atomization Pressure on Foam Properties. The atomization
pressure used is of extreme importance in determining foam properties.
Laboratory experiments have shown that density, cell structure, and thermal
properties are directly affected by atomization pressure. Numerous small
voids will occur in the foam structure if excessive pressure is used; this is
probably the result of breakdown of the surface skin during foam rise per-
mitting a release of fluorocarbon blowing agent and simultaneous air
entrapment.
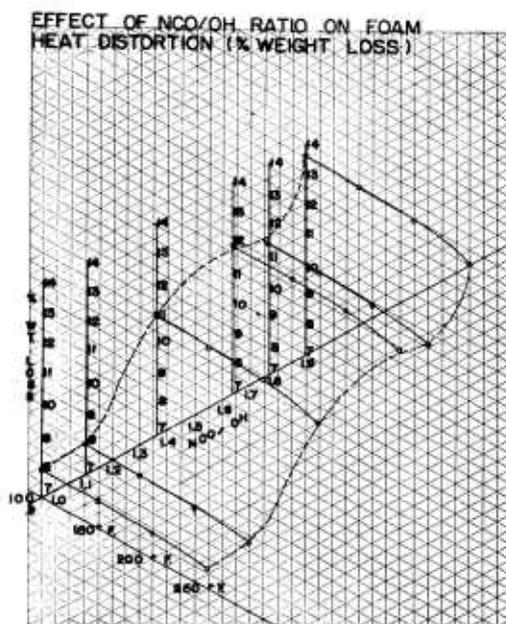
Fig. 5.
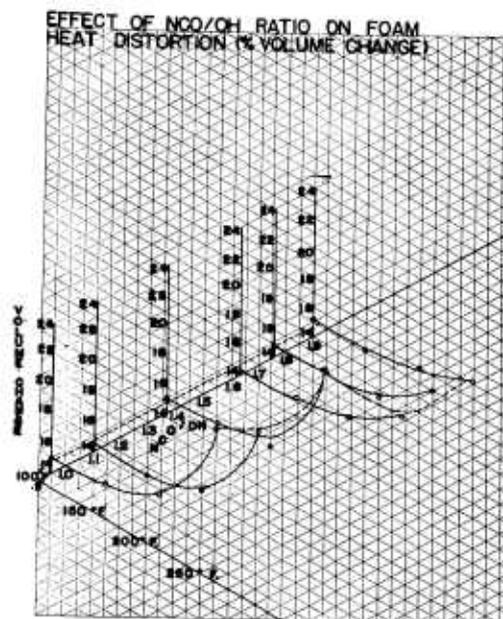
Fig. 6.

1. Effect of Atomization Pressures on Thermal Properties. It is
difficult to assess the entire relationship between atomization pressure and
and foam physical properties. If too little atomization pressure is used
during spray application, insufficient mixing may take place; if an excess
atomization pressure is used, mechanical damage to the foam may result.
A series of samples were prepared (NCO/OH ratio 1. 102/ 1. 0) with the
atomization pressure varied from 25 psi to 90 psi. All samples sprayed
with atomization pressures less than 45 psi exhibited complete or partial
collapse during foaming. Samples prepared with atomization pressures
above 75 psi were characterized by excessive voids or cell collapse.

The initial "k" factors of samples prepared with the atomization
pressure varied between 45 psi and 75 psi fell in a narrow range, i. e. ,
0. 128-0. 139. When the foams were subjected to accelerated aging condi-
tions (Fig. 7), a widening of the "k" factor range was observed. Thus it
is important to determine the optimum atomization pressure for a given
foam formulation and a specific spray gun in order to obtain optimum ther-
mal performance properties.

2. Effect of Atomization Pressure on Compressive Strength. An
analysis of compressive strength properties of foam samples prepared with
various atomization pressures is presented in Fig. 8. Additional insight into
the effect of atomization pressure on compressive strength may be gained by
reviewing the data presented in Table 4.

Fig. 7.

Fig. 8.

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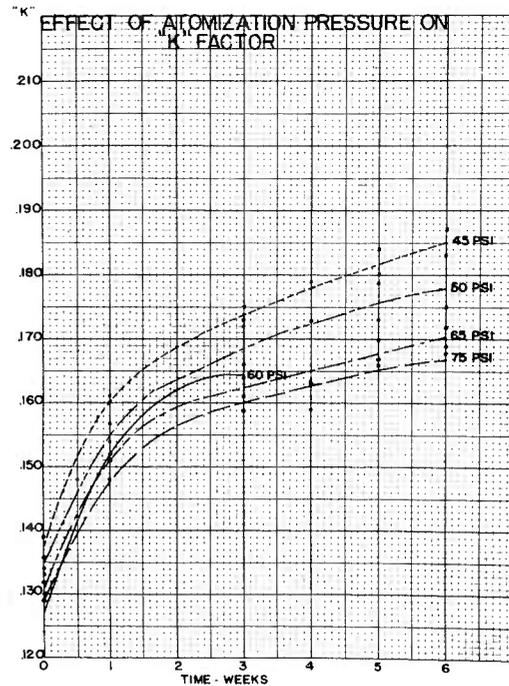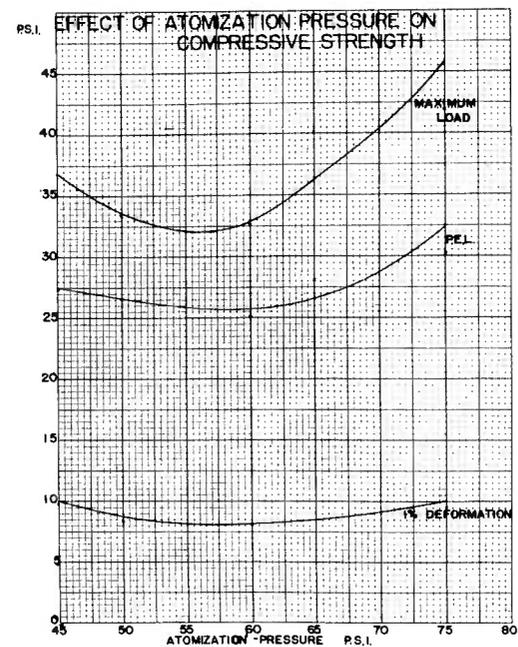
TABLE 4

Effect of Atomization Pressure on Compressive Strength

Sample	Atomization Pressure	Density			PSI - 1% Def.			PSI - PEL			Max. Load		
		Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.
1	45	2.04	2.00	2.08	8.98	7.72	9.59	27.10	22.76	29.40	36.74	30.89	40.69
2	45	2.09	2.17	1.98	10.52	9.78	11.50	28.36	27.05	29.72	36.82	35.29	37.97
3	50	1.83	1.79	1.90	8.25	7.23	8.81	25.21	21.79	28.84	32.53	29.10	35.85
4	50	1.99	1.96	2.07	8.60	7.53	9.36	27.86	22.39	30.90	34.15	32.00	36.11
5	60	2.13	2.09	2.20	8.87	7.62	9.77	25.88	21.20	29.74	34.84	28.81	40.75
6	60	1.95	1.86	2.02	7.45	5.44	8.67	24.17	15.92	28.63	30.37	22.94	34.10
7	65	2.22	2.12	2.29	9.36	7.80	10.99	25.82	22.43	30.17	38.85	36.19	42.08
8	65	2.01	1.96	2.05	9.04	8.43	9.71	30.29	28.44	32.92	41.80	39.42	42.75
9	75	2.23	2.15	2.28	9.56	8.47	10.93	30.10	27.92	32.82	41.85	37.22	47.82

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3. Effect of Atomization Pressure on Water Vapor Permeability. The relationship between permeability and atomization pressure is defined in Fig. 9. As the atomization pressure increases, the water vapor transmission rate decreases.

4. Effect of Atomization Pressure on Foam Thermal Stability. Fig. 10 shows weight loss on heating of spray applied urethane foam samples decreases with increased atomization pressure.

Effects of Substrate Temperature and Substrate Preparation. Experiments were carried out to determine effects of substrate temperature and substrate preparation on the foaming process and foam adhesion. Four temperature levels were employed (45°, 65°, 75°, and 100°F). Substrates included aluminum, cold rolled steel, and plywood. Substrates were free of grease, oil, moisture, and loose particles.

Table 5 summarizes information obtained in this study. The use of a zinc chromate wash and an epoxy prime coat gave improved adhesion to the substrate.

Poor adhension was observed when the substrate temperature fell below 65°F.
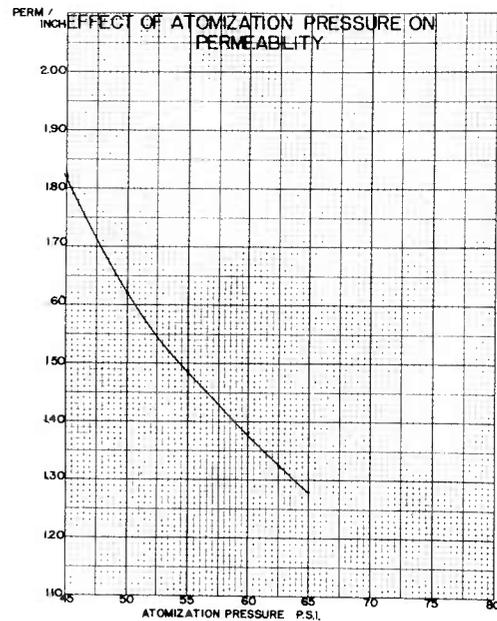
Fig. 9.
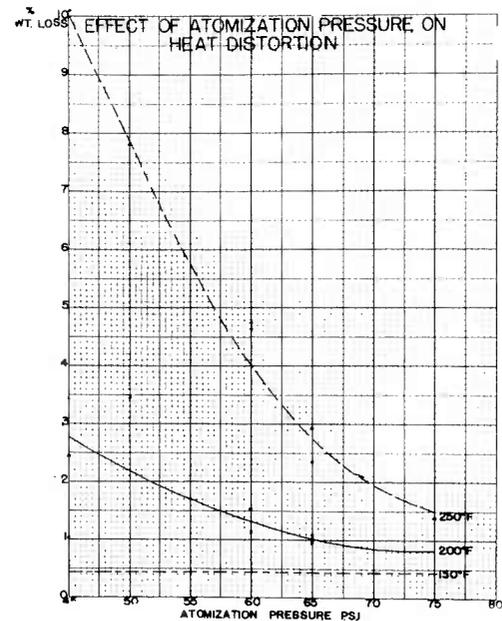
Fig. 10.

TABLE 5

Surface Temperature	Substrate	Remarks
45°F	Aluminum, no wash, no primer	No adhesion, severe distortion of foam
45°F	Aluminum, zinc chromate wash, epoxy primer	No adhesion, severe distortion of foam
45°F	Carbon steel, no wash, no primer	No adhesion, severe distortion of foam
45°F	Carbon steel, no wash, epoxy primer	Very poor adhesion, severe distortion of foam
45°F	Plywood, no preparation	Fair adhesion, moderate distortion of foam
65°F	Aluminum, no wash, no primer	Poor adhesion, slight distortion of foam
65°F	Aluminum, zinc chromate wash, epoxy primer	Fair adhesion
65°F	Carbon steel, no wash, no primer	Fair adhesion
65°F	Carbon steel, no wash, epoxy primer	Good adhesion
65°F	Carbon steel, no wash, bonderite primer	Good adhesion
65°F	Plywood, no preparation	Good adhesion
75°F	Aluminum, no wash, no primer	Poor to fair adhesion
75°F	Aluminum, zinc chromate wash, epoxy primer	Fair to good adhesion
75°F	Carbon steel, no wash, no primer	Fair to good adhesion
75°F	Carbon steel, no wash, epoxy primer	Good adhesion
75°F	Plywood, no preparation	Excellent adhesion
110°F	Aluminum, no wash, no primer	Fair adhesion
110°F	Aluminum, zinc chromate wash, epoxy primer	Good adhesion
110°F	Carbon steel, no wash, no primer	Excellent adhesion
110°F	Carbon steel, no wash, epoxy primer	Excellent adhesion
110°F	Carbon steel, no wash, bonderite primer	Excellent adhesion
110°F	Plywood, no preparation	Excellent adhesion

Effect of Surface Contamination

Carbon steel and aluminum plates were used to evaluate the effect of surface contamination (water and rust) on foam adhesion. Table 6 presents a summary of experimental results. Water on the substrate surface increased the incidence of voids at the foam-metal interface and decreased adhesion to the substrate.

Parameters Pertaining to Product Specification

Insulating Design Factor. Urethane foams applied by the spray-in-place technique have shown initial "k" factors between 0.120 and 0.140. It is suggested for design purposes that a "k" factor of 0.160 be used (based on a mean temperature of 75°F).

Barrier Coatings. Permeability studies of spray foams have indicated that most samples have a perm-inch rating ranging from 1.5 to 3. If the insulation is to be subjected to temperatures below 32°F, a barrier coating having a perm rating of 0.5 perm or lower should be used.

Protective Coatings. If the foam insulation is to be exposed to the elements, a protective coating should be used.

Flammability. It is suggested that urethane foam used as insulation have a nonburning or self-extinguishing classification. If a protective coating or barrier coating is applied, it also should have a nonburning or self-extinguishing classification.

Service Temperature Limitations. It is recommended that urethane foam insulation not be exposed to temperatures greater than 50 per cent of the heat distortion temperature for continuous service and 75 per cent of the heat distortion temperature for intermittent service.

Safety*

Care should be exercised when handling foam raw materials, some of which are classified hazardous. Adequate ventilation must be provided to maintain a flow of fresh air during the spraying operation.

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*Chemical Safety Data Sheet SD-73, "Properties and Essential Information for Safe Handling and Use of Tolylene Di-isocyanate," Manufacturing Chemists' Association, Inc., 1959.

TABLE 6

Effect of Moisture on Foaming Process

Substrate Condensate Condition	Carbon Steel Wet	Carbon Steel Rusted Wet	Carbon Steel Dry	Aluminum Wet	Aluminum Dry
Compressive Strength					
Density, pcf					
avg.	1.79	1.94	2.03	1.66	2.00
range	1.74-1.82	1.86-1.98	2.00-2.09	1.38-1.91	1.90-2.00
Load, psi at 1% Def.					
avg.	6.27	5.33	7.21	4.98	6.48
range	5.8-6.7	4.7-6.0	4.9-8.2	4.0-6.2	4.9-7.3
at PEL					
avg.	25.15	24.50	24.31	19.09	24.00
range	23.5-27.7	18.7-27.4	17.7-29.0	15.2-24.8	18.8-27.2
at Max. Load					
avg.	32.41	33.33	35.44	26.27	32.03
range	31.2-34.6	27.2-37.8	27.4-38.6	20.5-33.2	30.8-33.6
Percent Deformation					
at PEL					
avg.	4.02	4.58	3.39	3.86	3.70
range	3.5-4.4	4.0-5.2	3.0-3.6	3.1-4.6	3.4-4.0
at Max. Load					
avg.	6.08	8.17	6.32	-	5.46
range	5.7-6.4	7.7-8.8	5.3-6.6	-	4.9-6.1
Adhesion to Substrate	Poor	Very poor	Good	Fair-Poor	Good

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Summary and Conclusions

Statistically designed experiments were conducted to determine acceptable limits for spray variables. The relationships between such factors as stoichiometry, temperature of reactants, atomizing pressure, and climatic conditions and their effect on foam density, compressive strength, thermal properties, and permeability were established.

Various types of spray equipment were compared. Emphasis was placed upon equipment requirements necessary to insure adequate metering, mixing, and delivery of foam raw materials.

Results of a study of substrate variables and their effect on the foaming reaction and the physical and mechanical properties of the foam were outlined.

Parameters pertaining to product specification were reviewed, including insulation design factor, barrier and protective coatings, service temperature limitations, and flammability characteristics.

Acknowledgements

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2. "Polyurethanes' Chemistry and Technology, Part I," J. H. Saunders and K. C. Frisch, Interscience 1962.

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DEVELOPMENT OF A ONE-PART
"FOAM-IN-SPACE" POLYURETHANE

Seymour Schwartz

Introduction

In 1958, the Materials Engineering Branch, Applications Laboratory of the Aeronautical Systems Division of Wright-Patterson Air Force Base initiated a number of in-house exploratory investigations to determine the feasibility of producing polyurethane foam at reduced atmospheric pressures, simulating outer space conditions. These tests included mixing of conventional urethane foam components in a vacuum and the use of catalyst-water systems absorbed on silica gels. The results of this preliminary work indicated that polyurethane foams could be utilized at a reduced atmospheric pressure to produce such objects as rigidized inflatable structures, lunar shelters, furniture, thermal insulation, shock absorbing devices, etc. However, it was also demonstrated that conventional formulations and processing techniques would not be suitable for use under these conditions.

As a result of the preliminary work, which established feasibility of the vacuum foamed material, a formal request for proposals was issued by the Aeronautical Systems Division to a number of organizations known to have the desired capabilities. The specific requirements in the directive were as follows:

1. The material must be based on polyurethane chemistry.

2. It must foam reliably in a vacuum environment--with the material directly exposed to the vacuum, of approximately 160,000 feet.

3. The foamed material should be approximately a 2 lb/cu ft density.

4. If pre-mixed material was developed it should have a minimum shelf life of 2 months at room temperature, i.e., it could not be cryogenically inhibited.

5. It should also foam at normal ambient pressures.

6. A minimum of mechanical equipment should be used during the foaming process and no special equipment was to be developed.

7.   Material capability would have to be demonstrated by fabrication of two types of foamed structures, made in a simulated space environment. One was to be an expandable structure, such as a 7 ft diameter ballon, inflated and rigidized with walls 1 to 2 inches thick under conditions simulating an unmanned spacecraft. The other structure, used to demonstrate large mass capability, was to be a full sized chair, made under the same conditions but not necessarily in the same manner.

Hughes' Aircraft Approach

After the receipt of the contract, the Hughes Aircraft Company, on analysis of the problem, came up with several approaches, differing widely because of the vast disparity between the two structures.

1.   In order to foam rigidize the balloon a one part, pre-mixed and pre-distributed material was believed best, since this would require no special vacuum operated equipment to be developed.

2.   On the other hand, the chair, because of its size and shape, (an approximately 2 x 2 x 2 ft block with a back and arm rests) was well adapted for fabrication by metering and mixing a two component material into a mold. Such a procedure, however, would probably have required special equipment in order to operate in a vacuum.

On consideration of all the factors involved in production of each type of material it was decided that if the one part material were produced it would be a very simple approach, and one which could be used for both applications, as well as being potentially a very useful material. It was therefore decided to concentrate solely on production of the one part, pre-mixed foamant. It was also decided that heat would be utilized as the activator. Further, no mechanical equipment was to be used in the vacuum. The basic polyurethane reactions, i.e., diisocyanates reacting with a diol and/or a triol and also reacting with water to produce CO_2 gas, would be adhered to.

Foamant Development

In the development of the desired one component compound, the first step was believed to be a method of deactivating the isocyanate component. This was necessary since in common isocyanate-polyol mixtures the reaction takes place within 5 to 30 seconds, when catalyzed, and not much slower when uncatalyzed. This reactivity, of course stems from the isocyanate, so efforts were concentrated on this component. Two methods were tried. The first consisted of chemical blocking of the isocyanate with a material which would cleave off when heated, thus regenerating the original isocyanate. An example of such a compound, commercially known as Hylene MP, is shown below:

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$$OCN-\bigcirc-\overset{H}{\underset{H}{C}}-\bigcirc-NCO + 2\ \bigcirc-OH \underset{300°F}{\rightleftharpoons} \bigcirc-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\bigcirc-\overset{H}{\underset{H}{C}}-\bigcirc-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\bigcirc$$
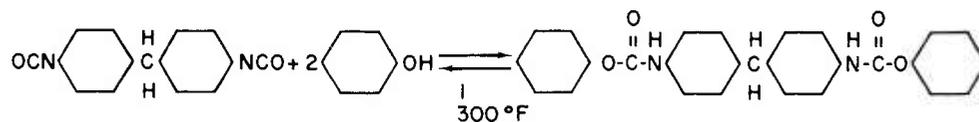
A number of similar compounds were prepared at Hughes using both toluene diisocyanate (TDI) and diphenyl methane diisocyanate (MDI) as the isocyanates and blocking agents such as acetyl acetone, diethyl malonate, phthalamide, and others. A number of blocked compounds were successfully prepared. However, in use it was found that the cleavage temperature in each case was too high (approximately 325° to 400°F), and when reacted in vacuum, the release of the blocking agent resulted in too voluminous a gas evolution. Also, complete stability was not obtained when the blocked isocyanate was mixed with the polyol and stored at room temperature.

The second method of deactivation tried was an attempt to encapsulate the isocyanate in a heat rupturing encapsulant. By this technique it was hoped that the encapsulated isocyanate could be mixed directly with the polyols with no reaction until heat was applied. Contacts were made with all the encapsulators in the United States, and it was found that no one was prepared to encapsulate liquid isocyanates without a long research program. The National Cash Register Company, however, did agree to furnish solid MDI encapsulated in either of two thermoplastic materials melting at 122° and 140°F. In tests it was found that only the 140°F material would resist damage during the mixing with the polyol. However, in attempting to make a foam using the encapsulated MDI and conventional polyols, it was found impossible to get foams much lower than 10 to 15 lb density. In addition the foams were of fairly low strength and poor quality. It was assumed this was due partly to the plasticizing effect of the encapsulant, which was present to the extent of 20 per cent by weight of the MDI, and partly to the solid isocyanate which was used. The reaction was exothermic, however, and it is surmised that satisfactory results might have been achieved with other formulations and more extensive work. Therefore, because of the difficulties encountered in attempting to deactivate the isocyanates, this line of attack was discontinued, in favor of another technique described below.

Concurrently with the work being done on the isocyanates, a number of tests were also made on techniques for furnishing water to the system since this was also considered to be a major problem in development of a one part mixture. This investigation of water sources was also carried out along two lines. The first consisted of investigating a number of hydrates, such as H_3BO_3, $M_gO \cdot H_2O$, $BaCl \cdot 2H_2O$, etc., which would release water of crystallization when heated. The second technique utilized Linde molecular sieves, which would also release their water when heated or in a vacuum. The results of the first tests indicated that boric acid could be mixed with a liquid isocyanate prepolymer for at least a month and a half with no apparent action, when held at room temperature. When heated, the isocyanate-water reaction took place very readily at temperatures of 200° to 300°F. The results secured

with the molecular sieves were not so definite, however. The hydrated sieves appeared to store satisfactorily at room temperature when mixed with the isocyanate prepolymers.* However, when the mixtures were heated in a vacuum, considerable bubbling occurred, which apparently was due to the volatiles in the isocyanate prepolymers rather than the formation of CO_2. Repeating the tests with devolatized prepolymer showed no evidence of reaction although bubbling occurred, which was assumed to be simply water vapor release and not CO_2 since there was no evidence of urea and amide formations which should have occurred simultaneously with the CO_2 liberation. The results with the molecular sieves were therefore considered inconclusive.

In addition to the work done on the isocyanates and water sources, limited investigations (at that time) were being made on polyols (diols and triols), as well as catalysts and surfactants. In general, during this phase only common commercially available materials were tested. These included liquid diols of equivalent weights of 100 to 200, to insure rigidity, and similar short chain length triols to act as cross-linkers. Similarly, samples of various commercial catalysts and surfactants were also obtained to be tested in the formulations to be made up.

Because of the poor success achieved in attempting to satisfactorily deactivate the liquid isocyanates by chemical blocking or to utilize encapsulated solid isocyanates and liquid polyols, it was then decided to go to an all solids mixture. Such a system, it was reasoned, should have good storage stability and, if it would melt at a low enough temperature, should be capable of being foamed. The problem then resolved itself to finding solid isocyanates, polyols, catalysts, and surfactants of the correct melting point, functionality, and vapor pressure to result in a material which would do the following:

1. Be stable when mixed together and stored in a normal atmosphere.
2. Melt at a temperature below 200°F (arbitrarily selected).
3. After melting the material should foam up and then,
4. polymerize and become rigid while in the foamed condition.

The first such solid mixture prepared had the formula shown below:

Material	Function	MP °F	Equiv. Weight	Equivalents Used
Diphenyl methane diisocyanate (MD1)	Isocyanate component	99	125	0.5
Bisphenol A	Diol	307	114	0.41
Pyrogallol	Crosslinker	271	42	0.1
Boric Acid	Water source			5% by wt.
Silicone Oil	Surfactant			1% by wt.
8 hydroxy quinoline	Catalyst			5% by wt.

*Satisfactory storage was only found with sieves containing less than 7 per cent moisture.

The above formulation resulted in a material which met almost all the requirements. The foam produced, when made in air, was fair foam although somewhat friable. When heated in vacuum, however, the vapor pressure of the ingredients (mainly the isocyanate) was so high that as soon as complete melting occurred the material literally blew itself apart to result in simply a large mass of froth. The importance of this formulation, however, was that it did demonstrate that the solids approach was basically a sound one and that, with improvements, a satisfactory material might be developed along these lines.

Several hundred formulations later such a material was finally developed. The new compound, which used the same type general materials as in the first solids formula, incorporated a higher melting, higher vapor pressure, sterically hindered isocyanate, dianisidine diisocyanate (DADI), as well as different diol and triol, both melting below 200°F. The structural formulas of the resin components are shown below:
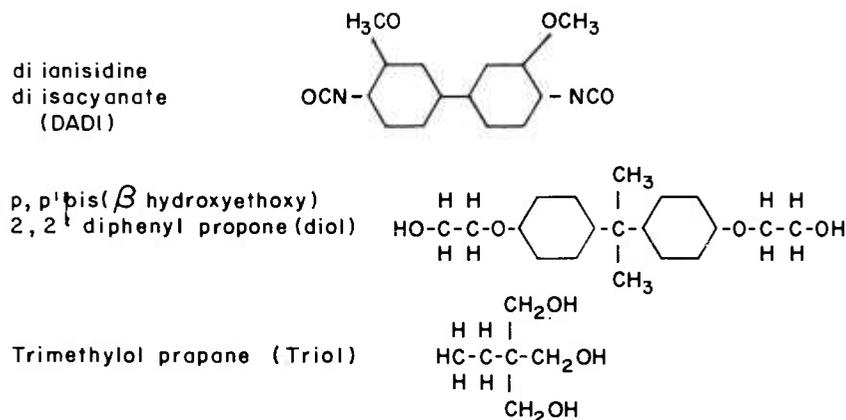
In addition, a commercial silicon surfactant, Dow-Corning #113, was used and a commercial catalyst, Metal and Thermit Company "T-8." The polyols used were selected after a great number of tests on both commercially available solid polyols and synthesis of a number of polyols at Hughes--the great majority of which turned out to be too high in melting point, or were not solids, or were too long in chain length, etc.

The new compound was a material which melted completely at 175°-180°F. It appeared to have an indefinite shelf life when stored at room temperature, although its reactivity apparently is reduced with time. It is not sensitive to normal atmospheric moisture, so needs no special storage conditions. It foamed in a vacuum, without the use of a separate blowing agent (use of vacuum and the vapor pressure of the ingredients turned out to be the key). The resulting foam was 2 to 5 lb per cu ft in density, depending on processing conditions.

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The compressive strength of the material varies from 15 to 50 psi, depending on density, and on being compressed the material did not shatter. In addition, the foamed material showed surprisingly good strength at 300° to 350° F. By addition of boric acid to the basic mixture, a fair foam was obtained at normal pressures. Fig. 1 shows the type of foam made at a pressure corresponding to 16,000 ft (1-1/2 mm Hg approximately).
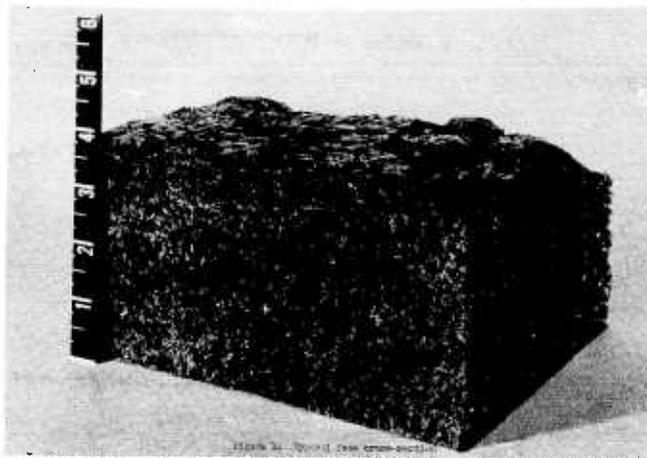

Fig. 1. Typical foam cross-section.

Even with the production of a satisfactory foaming powder it was found that the development problems were far from over. The diol and triol, though solids, were not hard, crystalline materials but were somewhat soft and gummy. Therefore, while small amounts of the powder mixture were easily made by hand using a mortar and pestle, attempts to make large amounts by mechanical mixing and grinding always ended up as gummed up messes. A number of techniques were tried including ball mills, a drug mill, a Hobart paddle mixer, and a counter current muller. A satisfactory process was finally developed when it was found that by working the material to cause the "gumminess" the temperature would rise and when checked at the right point, a prepolymer would form which was plastic when hot and brittle when cold. This brittle material could then be easily ground up to form the desired powder. Using this technique, several hundred pounds of powder were prepared for use in fabrication of the required structure.

Fabrication of Demonstration Units

Prior to actually starting fabrication of the balloon and chair, it was necessary to develop a method of distributing the powder on the balloon surface. It was also necessary to determine the optimum conditions of time and

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temperature for forming large amounts of foam since only small laboratory quantities had been made before. The technique finally adopted for the balloon fabrication utilized the fact that the powder could be pelletized, using a plastic preform press. A number of pellets, 2-3/8 in. diameter by 3/32 in. thick, were adhered to the surface of a two foot diameter balloon using Goodyear Plibond cement. Over the pellets was heat sealed (using the pellets as the sealing media) a thin Dacron marquisette cloth, the purpose of which was to prevent running of the material during the period between liquefication and final polymerization. Tests on a small (2 ft) balloon indicated a satisfactory structure could be obtained. See Fig. 2.

In running a number of tests with various amounts of foam in a vacuum chamber, it was found that the maximum height of foam which could be obtained was approximately 4 inches. This limitation was established by the fact that since the material was endothermic as the reaction progressed, the developing foam retarded the rate of heat input. Thus the inner layers of powder would not receive heat as rapidly as the outer layers and therefore would not foam. Another factor limiting the size of the foam was the fact that after a few minutes of heating, if the powder was too thick, the outer layers would cure
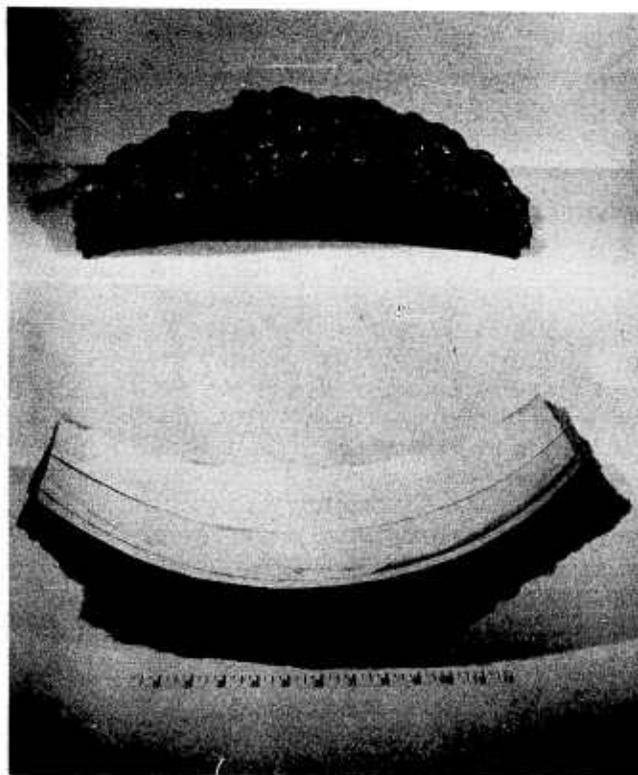

Fig. 2. Section of 2 ft test balloon.

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or set" before the inner layers liquefied. This cured material then tended to prevent any further expansion from the rest of the mass. It was thus found that approximately 1/4 inch of powder was the limit of material which could be foamed.

With the processing information then it was decided that the large balloon could be fabricated using the adhered-on pellet and restrainer cloth technique. It was also decided that the chair could be made, but in this case using multiple "blows" to result in the final 2 x 2 x 2 ft block.

Fig. 3 shows the fabrication techniques employed in coating the large 7 ft diameter demonstration balloon. While the balloon was not extremely flexible, it was possible to pack it in a relatively small container for shipment. At Wright-Patterson Air Force Base the balloon was inflated in the vacuum chamber at a pressure corresponding to approximately 150,000 ft altitude. By suitable pressure regulation, the balloon was maintained at 5 inches of water internal pressure during the rigidizing operation. Rigidization was accomplished by heating a band approximately one foot wide from pole to pole, as shown in Fig. 4. As the area foamed and rigidized, in approximately 15 minutes, the balloon was rotated to expose a new area. Rigidization was complete in 4 hours. Fig. 5 shows the completed structure.

Fabrication of the chair was conducted in a somewhat different manner. The completely vented mold employed is shown in Fig. 6. Fig. 7 shows the set-up employed for the first "blow," with powder and pellets in place. The chair mold is shown laying on its side so the arms may be formed easier. The heat lamps are directly above the mold. The use of pellets, large and small, was found to be distinctly superior to the use of plain powder. The small pellets on the sides would foam and flow into the depressions left by the main mass of foam as it rose up bubble shaped. (Because of lack of back pressure, the material did not follow the mold contours as it foamed.) The large pellets were used since it was found they were more compact and they helped spread the material more evenly than did the powder.

The complete chair was foamed in seven stages since only approximately 4 inches of foam could be formed at a time. Each layer of reactants was therefore put in place, foamed, cured, and allowed to cool slightly prior to addition of the next layer. Each foam cycle took approximately 20 minutes to complete. However, bringing the chamber to altitude, cooling the foam prior to pressurization, and then adding the new material made each stage take approximately 2 hours to complete. Fig. 8 shows the completed chair.

Conclusions

As a result of the preliminary Air Force efforts and the work reported here, it may be concluded that there are a number of approaches which might be used to produce polyurethane foams in a vacuum environment. These
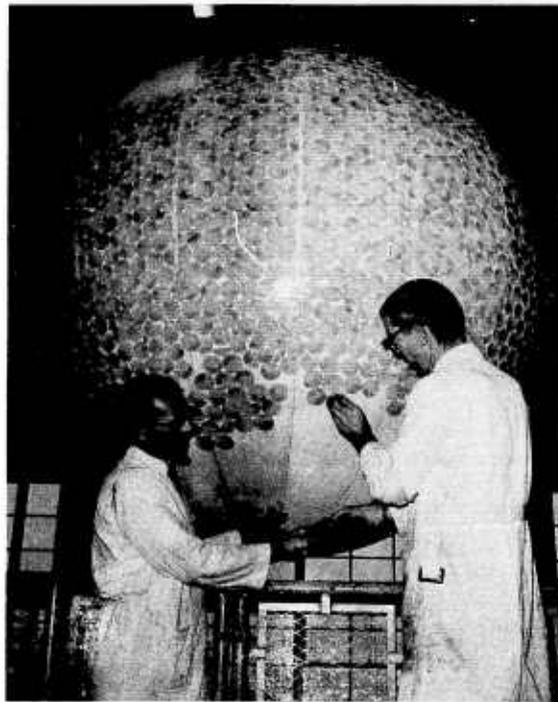
Fig. 3. Technique for applying foam pellets
to balloon surface.

Fig. 4. Method used to activate foam on
balloon at 160,000 ft.

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Fig. 5. Completed balloon structure.

Fig. 6. Chair mold.

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STOP OF CHAIR
RESEARCH OF FOAMED-IN-PLACE PLASTIC MATERIALS
TEST NR. 61-23-52
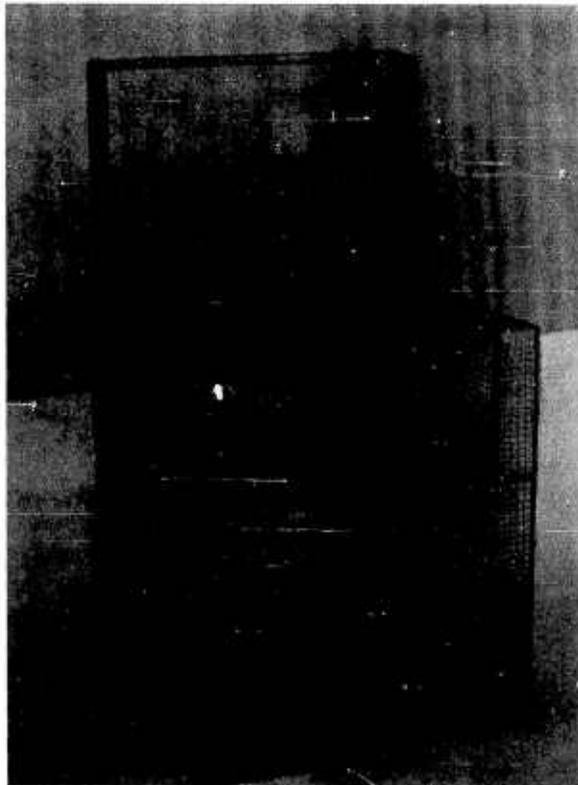
Fig. 7.   Method used to mold chair.

Fig. 8.   Completed chair.

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include the solid reactants, encapsulated components, absorbed catalyst-water systems, and possibly "blocked" isocyanates. Some of these will require longer research and development programs than others to be fully useable.

The one part, solid reactant heat triggered material so far developed, however, is considered to possess many characteristics which make it ideal for space usage; other than the obvious advantage of elimination of the metering and mixing processes. The material can be triggered by the readily available solar heat. The vacuum environment is used to assist in the blowing process. The powder may be very simply packaged with no need for vapor tight or pressure resistant containers, refrigeration, etc. Because of the low vapor pressure of the ingredients, it is believed that the material has much lower toxicity than conventional polyurethane foamants.

There are also, however, a number of improvements which could be made in the material. One of the most desirable would be a technique to cause the material to exotherm, after initial triggering. This might be accomplished by using a more reactive isocyanate, by encapsulation of conventional isocyanates, or possibly by adding a pyrotechnic to supply heat. Another desirable improvement would be development of techniques and materials which could be easily spread in a continuous film over a substrate. Still another desirable improvement would be other methods of activation such as gas catalysis, or use of gamma or ultra-violet rays from the space environment. Further development to improve the uniformity and cell size structure is also desirable.

THE DEVELOPMENT OF A FLEXIBLE, SELF-EXPANDABLE SHEET

Thomas Francis, M. H. Jones, and M. P. Thorne

Introduction

The use of foamed plastics as materials for the construction of shelters and storage facilities for military personnel, particularly in regions of extreme climatic conditions, is attractive because of their low weight and excellent thermal insulation characteristics. To realize their full potential, simple and convenient techniques are required for producing foamed materials in the field over a wide range of ambient conditions.

One concept that would have wide applicability is that of an expandable sheet. It its simplest form this is visualized as a thin tent roll material incorporating the components of a foam system, suitably stabilized, which on heating will react to yield a rigid or semi-rigid foamed product. Two basic types of foam systems have been considered and may be designated as heat-expandable and self-expandable systems. The first consists of a thermoplastic material containing a blowing agent. Application of heat from an external source would melt the resin and cause it to expand through decomposition of the blowing agent. The second type involves a reactive foam system in which the components are deactivated by chemical or physical means so that the mixture is stable under normal storage conditions. Once activated in a localized area, foaming could be self-propagating in sheet form by virtue of the exothermicity of the chemical reactions involved. Because of the obvious advantage of a system with a minimum heat requirement, the research effort has been directed towards the development of a self-expandable sheet.

Ideally, the properties and operating conditions that should be met are as follows:

1.   storage stability for 12 months in the range -55° to $70^{\circ}C$ (-65° to $160^{\circ}F$).

2.   an operational range of -45° to $50^{\circ}C$ (-50° to $125^{\circ}F$).

3.   an initiation temperature of not less than $70^{\circ}C$ ($160^{\circ}F$).

4.   a uniform foamed product of core density 2-4 lb/cu ft and compressive strength of 20-80 psi.

5. a foamed product of low thermal conductivity and good low temperature resilience.

6. a product stable to atmospheric conditions of temperature, moisture, U.V. radiation, etc.

Foam systems considered to be of potential use in a self-expandable sheet include the phenolics, epoxides, and polyurethanes. Experimental work has been confined to the epoxies and the polyurethanes with the initial emphasis on the latter because their technology is well advanced and, potentially, they possess most of the characteristics necessary to meet the desired end use.

The principle requirements of a self-expandable system are storage stability at ambient temperatures and a high reaction exotherm so that foam propagation can be self-sustaining once initiated. Two logical approaches to the problem of obtaining storage stable mixtures of the foam components may be suggested. These are encapsulation of the individual reactive constituents in an inert polymeric film, or the use of more stable solid components in finely divided form where molecular interaction is restricted to the limited area of particle-particle contact. Micro-encapsulation techniques, as developed by the Southwest Research Institute,[1] National Cash Register Company,[2] and others, have been considered. However, attention has been concentrated on possible all-solid systems since the difficulties inherent in the encapsulation of reactive liquid materials, such as the diisocyanates employed in urethane foams, are obvious.

With regard to the second requirement, the approach must be towards foaming compositions which have a high chemical functionality per unit weight and a fast reaction rate. For systems involving the same basic chemical reactions, the heat output is determined largely by chemical functionality, but rapid reactions are also necessary to minimize radiant heat loss to the surroundings. The combination of these factors controls the temperature rise in the system which is a measure of the facility for self-propagation. Throughout the paper the term exothermicity is used in this sense rather than in the conventional thermodynamic one of heat of reaction.

As will be shown later, it appears improbable that an all-solid epoxy or polyurethane system can be devised which is self-propagating in sheet form on localized initiation, if the initiation temperature is appreciably above the ambient temperature. In practice, the compromise that has been adopted is a system which is sufficiently exothermic to foam and cure when heated uniformly to the initiation temperature. This has necessitated the development of a suitable auxiliary heating source.

Polyurethane Foams

In a conventional polyurethane foam formulation, the isocyanate component represents the logical point for approaching the problem of storage stability because of its sensitivity to any compound containing reactive hydrogen atoms, and particularly to water. One method of achieving this end is chemical deactivation since isocyanates form heat labile adducts[3,4,5] with a variety of organic compounds. The formation and thermal cleavage of these derivatives is typified by the reaction given below for phenol and 2,4-tolylene diisocyanate.
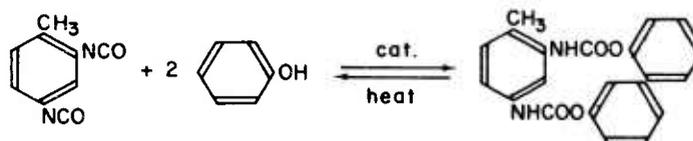
A large number of adducts employing phenols, 1,3-dicarbonyl compounds, and carbodiimides as blocking agents were synthesized using commercially available diisocyanates. These were substituted for the isocyanate component in a standard formulation which gave rise to a rigid, low density foam in an exothermic reaction when 2,4-tolylene diisocyanate was employed. Apart from such disadvantages as high initiation temperatures and the deleterious effect of the blocking agent on foam properties, in no instance was evidence obtained of a significant degree of over-all exothermicity with the systems. Similar results were obtained with blocked prepolymers and with isocyanate dimers. Although it is probable that storage-stable polyurethane foam compositions based on isocyanate adducts can be developed, their high thermal requirements would constitute a severe handicap in field applications.

Epoxy Foams

Isocyanate Adduct-Epoxy Systems. It is evident that the lack of exothermicity in adduct-based polyurethane systems is due to an essential heat equivalence between the endothermic decomposition of the adduct and the exothermic reaction of the liberated isocyanate with the polyol. Consequently, consideration was given to systems combining isocyanate adducts with epoxides. In principle, the following series of reactions would be expected for compositions employing water as the gas generating source.

$$RNHCOA \text{ (adduct)} \longrightarrow RNCO + AH \quad \dots\dots\dots \text{endothermic}$$

$$RNCO + H_2O \longrightarrow RNH_2 + CO_2 \quad \dots\dots\dots \text{exothermic}$$
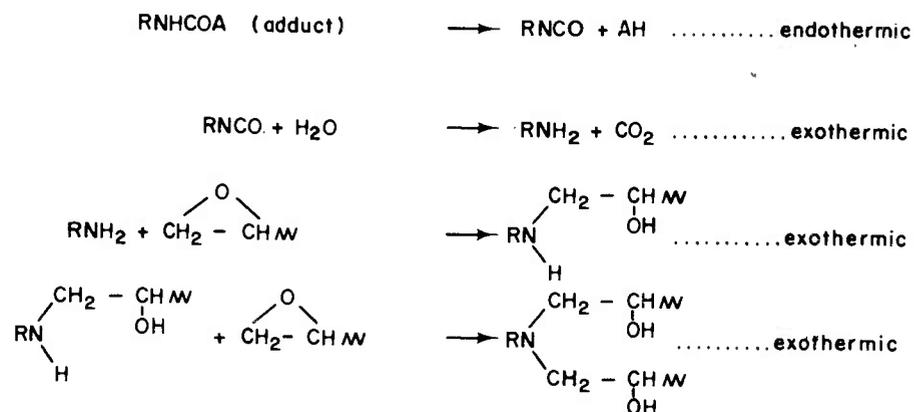
Obviously this represents an idealized scheme since a number of side reactions are possible, for example, that of the isocyanate with the aliphatic hydroxyl or the amine. However, under almost all circumstances, such a system would be expected to have an appreciable over-all exotherm. This was found to be the case with a number of adducts, particularly phenol derivatives, when employing liquid epoxy resins but not with solid epoxides. One of the major problems encountered with these combinations was an imbalance between the blowing and curing reactions leading to foamed products with relatively poor properties.

Amine-Epoxy Systems. A number of examples of cellular materials based on the curing of epoxides have been reported in the literature[6,7,8,9] but the technology of epoxy foams is not nearly as advanced as that of the polyurethanes. For the most part, published formulations yield high density products and employ liquid components, as a result of which they lack storage stability.

The majority of commercially available epoxy resins are glycidyl ethers based on the condensation of epichlorhydrin with bisphenol A to give products of the type
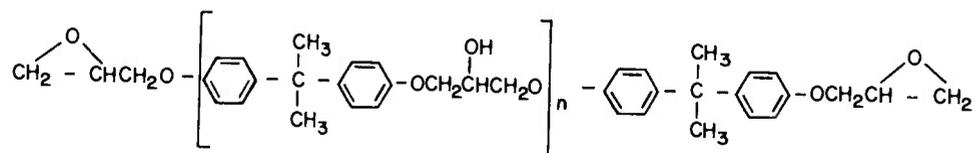

where n = 0 - 20. These range from viscous liquids to low melting solids depending largely on molecular weight. A few solid resins of higher epoxide functionality, such as the tetraglycidyloxy derivative of symmetrical tetra-phenyl ethane (Epon 1031), are also available.

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In general, the curing of a multifunctional epoxide to produce a thermosetting product is achieved by:

1. Catalysts which promote epoxy-epoxy condensation reactions such as Lewis acids or bases. Examples of these are tertiary amines and boron trifluoride. The base catalysed reaction may be represented as follows:

$$R_3N + CH_2\overset{O}{-}CH\sim \longrightarrow R_3\overset{+}{N}CH_2 - \underset{O^-}{CH}\sim$$

$$R_3\overset{+}{N}CH_2 - \underset{O^-}{CH}\sim + CH_2\overset{O}{-}CH\sim \longrightarrow R_3\overset{+}{N}CH_2 - \underset{O-CH_2-\underset{O^-}{CH}\sim}{CH}\sim$$
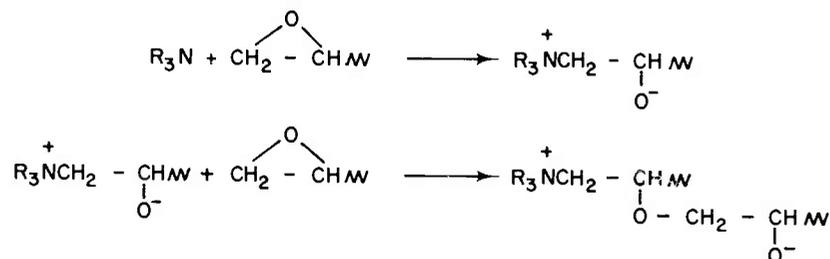
2. Crosslinking agents with functional groups that react with the epoxide linkage. Typical examples are multifunctional carboxylic acids, anhydrides, amines, and hydrazides. The condensation reactions are illustrated for the case of a primary amine by the following scheme:

$$RNH_2 + CH_2\overset{O}{-}CH\sim \longrightarrow RN\underset{H}{\overset{CH_2-\underset{OH}{CH}\sim}{<}}$$

$$RN\underset{H}{\overset{CH_2-\underset{OH}{CH}\sim}{<}} + CH_2\overset{O}{-}CH\sim \longrightarrow RN\underset{CH_2-\underset{OH}{CH}\sim}{\overset{CH_2-\underset{OH}{CH}\sim}{<}}$$
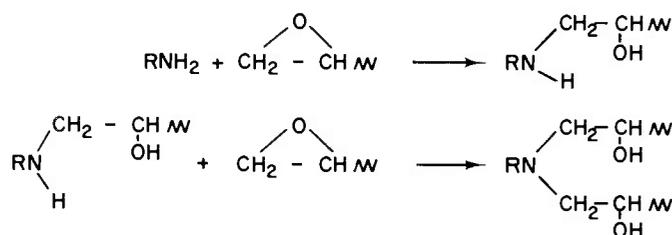
Considering once again the requirements for a self-expandable sheet of storage stability and exothermicity, attention was focused on epoxy-amine combinations because of the range of solid components available and the fact that the amine-epoxide condensation is one of the most rapid curing reactions for epoxy resins. Initially, a preliminary investigation was made of the curing characteristics of various commercially available epoxides with multifunctional amines to obtain information on reactivity and flow properties. This was used as a guide in selecting components for evaluation in foam formulations. Volume expansion in epoxy systems to give cellular products may be achieved by the use of suitable chemical blowing agents which are thermally unstable compounds that liberate a gas on decomposition. These may be either inorganic or organic, the latter having wider applicability because of their greater ease of dispersion in organic resins.

Using a standard formulation comprising epoxide, amine, blowing agent, and surfactant, an extensive study was made of combinations of the individual components listed in Tables 1(a), 1(b) and 1(c). Over 1,000 formulations were examined and assessed on the basis of initiation temperature, peak temperature, foaming characteristics, and physical state of the product. The most promising systems were found to be those employing an epoxy-amine combination of Epon 1031 - 4,4'-diaminodiphenyl sulphone with di-phenylether - 4,4'-disulphonylhydrazide (Celogen) or diazoaminobenzene as the blowing agent and were examined in greater detail.

Appreciable differences were noted in the behavior of the two blowing agents. With Celogen, foam initiation occurs at 120°C and the decomposition of the compound contributes significantly to the exothermicity of the system so that internal charring is observed at foam densities below 6 lb/cu ft. Also, the material or its decomposition products[10] react with the epoxide and rapid curing occurs, leading to irregularly shaped products in the low density range. The importance of this contribution to the over-all curing reaction can be judged from the fact that thermosetting foamed products can be obtained from Epon 1031 and Celogen alone although they have low strengths. Recent work has indicated that a related blowing agent diphenylsulphone-3, 3'-disulphonyl hydrazide (Porofor D 33) may be advantageous as a replacement for Celogen since it results in less internal charring.

With diazoaminobenzene as the blowing agent, foam formulations based on Epon 1031 and diaminodiphenyl sulphone have an initiation temperature of 160°-170°C and foamed products can be obtained with densities down to 3 lb/cu ft without significant charring. The main disadvantages of this system from the viewpoint of its use in an expandable sheet are a high initiation temperature, a very fluid melt stage, and a slow foam rise and set period. As opposed to Celogen, the decomposition of diazoaminobenzene is less exothermic, and neither the parent compound or its products appear to be involved in crosslinking reactions with the epoxide.

In attempting to optimize these systems, consideration was given to methods of obtaining better control of the exotherm, the flow properties during foaming, and the rate of cure. As Celogen and diazoaminobenzene suffer from opposing drawbacks, formulations were examined containing mixtures of the two in various ratios. Using such combinations foams can be prepared with core densities as low as 3 lb/cu ft without appreciable charring and with reasonable curing characteristics. It is interesting to note that the combined blowing agents result in somewhat lower initiation temperatures which is also advantageous. Further improvements in specific formulations can be made by the addition of inorganic fillers to reduce the exotherm, such as aluminum dust, and compounds which may be employed to control viscosity during foam rise. Examples of the latter are octyl phenol and the more reactive amine: 4,4'-diaminodiphenyl methane.

Three preferred formulations which possess the best balance of properties for the planned end use are listed in Table 2 together with data on their

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TABLE 1(a)

Epoxides Examined in Foam Formulations

Type		Soft. Pt. (^{O}C)	Epoxy Equiv.	Source
Diglycidyl Ethers				
EPON 1001	Bisphenol A	65-75	425-550	Shell
DER 542	Tetrabromobisphenol A	50-60	c. 405	Dow
	Tetrachlorobisphenol A	70	240	Lab. Prep.
Tetraglycidyl Ether				
EPON 1031	Tetra(hydroxyphenyl)ethane	75-85	245-255	Shell

TABLE 1(b)

Amines Examined in Foam Formulations

Type	Equiv. Wt.	M. Pt. (^{O}C)
Aliphatic		
Hexamethylene diamine	29	40
Octamethylene diamine	36	51
Decamethylene diamine	43	61
Dodecylmethylene diamine	50	
Heterocyclic		
Piperazine	43	104
Piperazine hydrate	97	44
2,6-Diaminopyridine	30	120
Aromatic		
p-Toluidine	53.5	45
p-Anisidine	61.5	59
m-Phenylene diamine	27	63
m-Tolylene diamine	30.5	99
N,N'-Diphenyl-1,4-phenylene diamine	130	c. 142
N,N'-Diphenylethylene diamine	106	66
4,4'-Diaminodiphenyl methane	49.5	93
4,4'-Diaminodiphenyl sulphone	61.5	165

TABLE 1(c)

Blowing Agents Examined in Foam Formulations

Type	Trade Name	Decomp.[12,13] Temp. (°C)	Decomp. Temp. In Foams (°C)	Source
Inorganic				
Ammonium carbonate		58	90	
Calcium sulphate dihydrate			75	
Copper sulphate pentahydrate			70	
Magnesium sulphate heptahydrate			75	
Sodium sulphate decahydrate			100	
Ammonium alum			95	
Boric acid		185	85	
Organic				
Benzenesulphonyl hydrazide	Porofor BSH	103	110	Bayer
Benzene-1,3-disulphonylhydrazide	Porofor B 13	163	110	Bayer
Diphenylether-4,4'-disulphonylhydrazide	Celogen	150	120	Naugatuck
Diphenylsulphone-3,3'-disulphonylhydrazide	Porofor D 33	148	130	Bayer
Nitrourea		130	90	Lab. Prep.
Urea oxalate		c. 115	125	Lab. Prep.
Dicyandiamide oxalate		120	120	Lab. Prep.
Diazoaminobenzene		150	160	Nat. Aniline
Azobisformamide	Celogen AZ	190	150	Naugatuck
Azobisisobutyramide oxime		148	120	Lab. Prep.
N,N'-Dimethyl-N,N'-dinitrosoterephthalamide	Nitrosan	105	100	du Pont
Dinitrosopentamethylene diamine	Unicel NDX	195	150	du Pont
Argon clathrate		160	80	Nat. Lead

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TABLE 2

Preferred Formulations

FORMULATION	1	2	3
Epon 1031	100	100	100
4,4'-Diaminodiphenyl sulphone	12.5	25	18
4,4'-Diaminodiphenyl methane	-	-	5
Celogen	12	10	8
Diazoaminobenzene	6	10	10
Octyl phenol	8	-	-
Aluminum powder	32	40	-
Pluronic F-68*	2	2	2
DENSITY (lb/cu ft)	3.3	3.0	3.0
COMPRESSIVE STRENGTH (psi) (0.2% offset yield)	27	25	27
% CLOSED CELLS	95	75	90

*Wyandotte Chemicals Corporation

properties. These are all-solid systems that tests to date have shown to be storage stable in the form of loose powders for at least five months at $21^{\circ}C$ ($70^{\circ}F$). Formulations 1 and 2 also yield acceptable foamed products after storage at $38^{\circ}C$ ($100^{\circ}F$) for three months although the components fuse to form a hard cake.

The formulations mentioned above represent the present state of development, but it is anticipated that systems yielding products of lower density without charring can be achieved. Recent work has shown that combinations of Epon 1031 and various amines with nitrourea as the blowing agent have an initiation temperature as low as 80°-$90^{\circ}C$ and give rigid foams with densities as low as 0.8 lb/cu ft with no evidence of internal charring. However, the indications are that these systems are not storage stable because of interaction between the amine and the blowing agent.

Auxiliary Heating Source

The original concept visualized a foamable composition with sufficient exothermicity to be self-propagating in sheet form once reaction is initiated in a localized area. However, it is improbable that this objective can be attained with an all-solid epoxy foam system. Even with the most exothermic formulations, it has been shown experimentally that the foaming reaction

will not propagate in a thin layer when the initiation temperature is 80°-100°C above the ambient temperature. A similar result was obtained when conditions for heat transfer were made more favorable by allowing a foaming layer to flow over an adjacent unfoamed area. Supporting evidence is also provided by a simple thermochemical calculation. From approximate values of the heat of reaction for an epoxy system and the heat required to melt the components and raise the temperature to that for initiation, it is found that 70-80 per cent of the heat output must be utilized for self-propagation. The limitation of these systems is then obvious when consideration is given to such factors as the large surface to volume ratio, the radiant heat loss to the surrounding, and the poor heat transfer characteristics across sections of partially foamed material.

The formulations that have been developed are self-propagating when heated completely to the initiation temperature. Thus, a self-expandable sheet can be obtained by employing an auxiliary heating source. To provide uniform heating, it is evident that the heating device must also be in the form of a flexible sheet that can be bonded to the foamable section. Initially, consideration was given to the use of combustible sheets or films impregnated with an oxidant, but pyrotechnic compositions were favored because better control can be achieved together with an absence of flame or smoke. The requirements of a suitable pyrotechnic are that it should:

1.   involve gasless and smokeless reactions.

2.   propagate uniformly at a reasonable rate in the substantial absence of oxygen and at sub-zero temperatures.

3.   have a relatively low burning temperature to avoid charring of the foamable composition.

4.   be obtainable in the form of a flexible sheet.

The so-called gasless pyrotechnic compositions[11] are essentially mixtures of inorganic materials; one component of which is oxidizable, representing the fuel source, while the second is an oxidant. A number of compositions were evaluated, in terms of the characteristics listed above, by visual observation of the behavior of a thin layer of loose powder on ignition. Some of the systems studied are given in Table 3 together with a brief description of their characteristics. The oxidant contents listed in the table are those which give the best properties for each type. In all cases a range of component ratios was examined to establish limits of propagation.

The most suitable pyrotechnic composition was found to be that based on the oxidation of iron powder with elemental sulphur.* Consequently, a number of methods of obtaining this finely divided mixture in flexible sheet

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*This composition was originally suggested to the authors by Dr. J. M. Humphries and Dr. R. Tremblay, Explosives Division, Canadian Industries Limited, Brownsburgh, Quebec.

TABLE 3

Pyrotechnic Compositions Examined as Potential Heat Sources

Type	Wt. % Oxidant	Comments
Fe/S	25	Gasless. Medium burning rate and temperature. Hard continuous residue.
Zn/S	33	Gassy. Violent reaction. Little residue.
Pb/S	14	Gasless. Medium burning rate and temperature.
Si/PbO_2	90	Gassy. Burns rapidly. Little residue.
Si/Pb_3O_4	96	Gassy. Burns rapidly. Little residue.
$CaSi_2/Pb_3O_4$	80	Gassy. Violent reaction.
$CaSi_2/Fe_2O_3$	50	Gasless. Very hot. Medium rate. Porous slag.
$CaSi_2/Fe_3O_4$	50	Gasless. Very hot. Medium rate.
$Zn/PbO_2/Pb_3O_4$	55	Gassy, violent reaction. Little residue.
$Si/Al/PbCrO_4$	88	Gassy, fast rate.

form were studied. Packaging techniques such as quilting the powders between noncombustible supporting sheets and the use of flammable binders such as nitrocellulose were investigated, but both were found to have an adverse effect on propagation. A simple method that proved to be particularly effective is to employ a loose fibrous material as a bonding agent. By compounding the iron-sulphur mixture in a liquid medium with a small quantity of asbestos fibers, a pulp-like material is obtained which can be filtered to give a mat or sheet. Although of low strength, flexible sheets of the pyrotechnic composition can be prepared in this manner with from 2 to 20 per cent by weight of asbestos without serious effect on the burning properties. The sheets show no evidence of dusting and the strength can be improved by replacement of part of the asbestos fiber with fiberglass.

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To obtain information on the optimum composition of the pyrotechnic sheet, its heat output in relation to the requirements of the foam formulation, and the amount of insulation required between the pyrotechnic and foamable compositions, a simple test was devised using an aluminum disc to represent the foamable layer. The dimensions of the disc were chosen such that the heat capacity was approximately equivalent to that of a foamable layer of equal surface area that would yield a three inch product of density 3 lb/cu ft. Pyrotechnic sheets were burnt in contact with the disc and the temperature-time profile recorded automatically.

Using this test it was established that pyrotechnic sheets containing iron and sulphur in ratios from 75:25 to 65:35 by weight and bound with from 2 to 10 per cent of asbestos fibers give acceptable burning characteristics. The sheets are self-propagating above a total weight of 0.1 lb/sq ft and have an average burning rate of 1 ft/min. Also, with an arrangement in which the foamable layer is sandwiched between two pyrotechnic sheets, the total weight of heat source required should correspond to 40-60 per cent by weight of the foam composition for initiation temperatures of 100°-150°C above ambient. In general, surface temperatures encountered in the test were of the order of 300°C but lasted for only a few seconds. Glass fiber fabrics and glass-asbestos papers were found to be acceptable insulating materials.

Construction of the Composite Sheet

The final phase of the investigation has been to combine the pyrotechnic heating device with the foamable composition to demonstrate the concept of a self-contained, expandable sheet. In the first instance, a method was required of converting the powdered foam formulation into flexible sheet form. On a laboratory scale, the procedure that was found to be the most convenient was to package the powder in a channelled envelope of polyethylene-coated aluminum foil. This had the additional advantages of providing a continuous barrier between the pyrotechnic and foamable materials, thus preventing ignition of the latter, and of giving some heat distribution. The channels were prepared by heat sealing through the inner polyethylene linings and as this bond is readily destroyed at the temperature of the foaming reactions, uniform foam rise can be achieved.

For testing the combination of expandable and pyrotechnic components, a multilayered construction was devised and this is illustrated diagramatically in Fig. 1. It does not necessarily represent the most suitable design for manufacture. Basically, the two pyrotechnic sheets are sandwiched between thin fiber glass fabrics and these components are bonded to each face of the aluminum envelope. In the test, the composite sheet is placed in a wire mesh basket and the two pyrotechnic components are ignited simultaneously. The temperature-time profile within the foamable layer is recorded with a suitably placed thermocouple.

Glass Fabric   Pyrotechnic Sheet

Aluminum Foil   Foamable Powder   Polyethylene Film
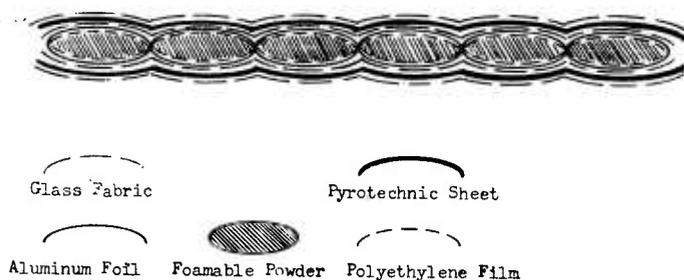
Fig. 1.   Construction of composite sheet.

Using this procedure, several composite sheets containing preferred epoxy formulations have been shown to yield acceptable foamed products with densities in the range 3-5 lb/cu ft. An illustration of the volume expansion that can be achieved is given in Fig. 2 which is a photograph of a composite sheet and a cross-section through a foamed layer. The large pores that can be noted in the foam are believed to be caused by air trapped within the aluminum envelope, and it is anticipated that this problem can be overcome by vacuum packaging or alternative methods of containing the foamable composition.
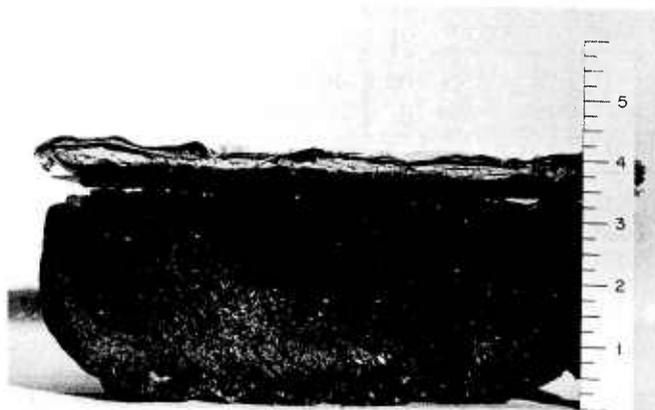
Fig. 2.   Photograph of composite sheet and cross section through a foamed layer.

Preliminary results suggest that for a foam system which initiates at 110°-$120^\circ C$, a weight ratio of pyrotechnic to foamable components of 30-40 per cent is required when the ambient temperature is $25^\circ C$. Work is in progress to determine the performance of these systems at temperatures

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of -40° to $0^{\circ}C$ and to establish their flexibility from the viewpoint of the operable temperature range for any given combination. An indication that they possess a fair degree of versatility can be judged from the fact that identical composite sheets have given suitable products at ambient temperatures of -5° and $25^{\circ}C$.

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NEW BRITISH DEVELOPMENTS IN FOAM EQUIPMENT

J. B. Blackwell

Microwave Heating

The first process I would like to talk about is the microwave curing of flexible molded foams.

The ability to use electrical energy for heating the foam depends upon several factors. The first is the applied voltage; the second is the frequency of the electrical supply; and the third is the specific inductive capacity of the material subjected to the energy.

At a particular frequency, an increase of applied voltage will give increased heat energy if the material--and this is the problem--can accept the energy. Considerable amount of work has been done in the past few years on radio frequencies in a wave band of 36 megacycles and possibly up to 100 megacycles per second; however, the problems encountered were that the voltages used to cure foams were too high. If we have two electrodes and we apply the correct voltage across these electrodes and if the space between the electrodes was completely filled with foam, then the foam would heat and cure. However, when dealing with molded foams, we have complex shapes. There is bound to be a certain amount of air space between the molded objects and electrodes. In this respect, the voltage gradient across the air is greater than the voltage gradient across the foam and to obtain the correct foam cure there tends to be voltage break-down across the air gap.

The next point was to try higher frequencies. The particular frequency depends upon the acceptance by the Post Master General or your Federal Communication Commission. Microwave frequencies were considered as a possibility.

One factor which was discovered at the beginning of the study of microwave heating was that uncured foam would accept microwave energy and that as soon as the foam became cured the energy was no longer absorbed. This is fine up to a point because we can then pour the foam into a mold and place the mold into what is termed a resonant cavity and apply the microwave energy. The mold must be of some non-conducting material such as epoxy fiber-glass construction.

The foam heats, cures, and rejects the energy after curing. We have a problem now that the mold itself stays cool as the epoxy fiber-glass construction does not readily heat up. Thus we have a molding which can be

cured internally but impossible to release from the mold. It was then dis-
covered that the introduction of what is termed lossy material into the mold
construction adjacent to the foam caused a rise in temperature. We have
found about sixty per cent incorporation of finely divided iron powder into a
gel coat will cause the temperature to rise sufficiently so that the conventional
mold release agents of various types allow the foam to be released.

As shown in Fig. 1, we have a microwave cavity and rotating carousel
under construction. The magnetron unit used was about 1.1 to 1.2 kilowatts.
The magnetron is housed in a position shown and the microwave field is fed
by means of wave guides into the cavity. The dimensions of these cavities
are critical and in general should be proportional to multiples of half the wave
lengths in all directions. We have to distribute this energy in the resonating
cavity, and this can be done by a mode stirrer on the inside of the cavity.
After the microwave energy comes along the waveguide, it enters the cavity
and strikes the rotating mode stirrer which interrupts the flow and caused
reflection of the radiation.

How can this be translated into an industrial practice? Credit should
be given here to the British Motor Corporation, who for the past nine months
have been pioneering this work. This effort resulted in the design of a
carousel which is basically a fabricated structure in which we take the elec-
trical supply in the center via slip rings to these individual magnetrons. The
carousel unit can accept up to twelve magnetrons. Cold water is used for
cooling the magnetrons. This unit, of course, is only part of the molding
process. It could be built into an existing foam molding line which carries
the mold from the foam head. By incorporating a mechanical arm, we can
push the mold in and out of the cavity. The back of the cavity is hinged and
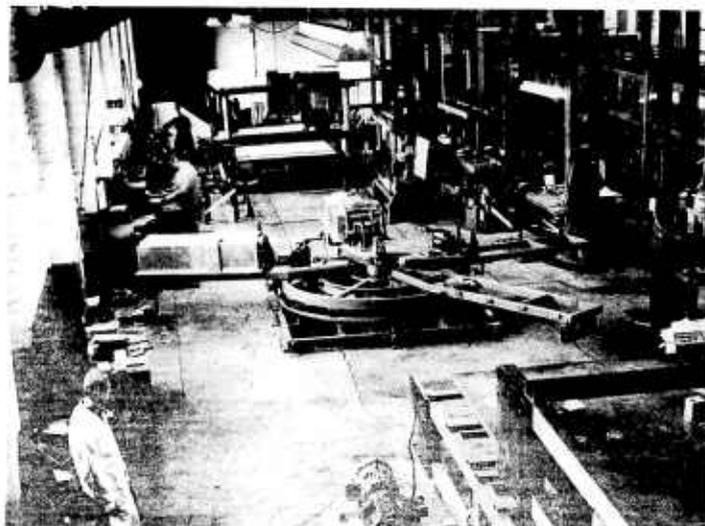
Fig. 1.

the front is raised and lowered as the microwave cavity moves into position. The first unit is now being installed at the B.M.C. factory.

The advantages of microwave heating are: one, the heating is more uniform and generally independent of shape; two, the use of high frequencies result in a lower applied voltage and consequently no breakdown in the air; three, the most important factor is that mold occupation time is reduced.

The mold occupation time can be determined by the use of a cushion or a topper pad somewhere around two pounds. The foams are being cured inside six minutes.

These are the claims and advantages made for microwave heating.

"Hold-Up" Mixing

The next topic is "hold-up" mixing heads. In most foam molding plants, the mixing heads which are used are based on three stage "intermittent" types. These heads were all based on early du Pont designs and operated by pumping, mixing, and pumping through the stirrer. The big problem with "intermittent" mixing heads has always been surge control. Surge control is combatted in four ways:

1. by eliminating all the air from the pipe lines.

2. by pressure balancing the liquids.

3. by velocity balancing the liquids as they enter the mixer basket.

4. by eliminating the effect of compressibility.

If one paid particular attention to these details, one could operate "intermittent" mixing heads. This is done successfully in many companies in the United States and Europe. If ureas are allowed to form in the T.D.I. or if build-up occurs, jets can become blocked resulting in improper balancing and poor moldings. A considerable amount of high speed Cine work was carried out in England by I.C.I. It was found that even with pressure balancing and velocity balancing, it took up to 20 or 30 microseconds to establish the jets of liquid.

About 1957, I.C.I. took out a patent on a method of batch mixing in which a number of foam chemicals were injected into a mixing cup, with the bottom sealed and the contents stirred. At the end of the stirring period, the bottom was opened and the stirrer used to push the liquids into the mixing head. This has been exploited commercially by B.M.C. in England, and for eighteen months they have had a "hold-up" mixing head in operation.

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Consider a valve block into which the chemical streams can feed. Through the valve block runs a hollow stirrer shaft. A mixer cup sufficient in size to take the charge is fitted (normally this is about 1.5 times the maximum volume of the liquids dispensed), and a seal disc is placed on the bottom of the cup. The stirrer is of a helical design which assists considerably in cleaning out the inside after foam ejection.

An air cylinder turns the valve and feeds the liquids inside the stirrer cup for a pre-determined period of time. This is the equivalent to the normal method using an "intermittent" mixing head. At the end of the dispensing period (which may be up to five seconds), the stirrer continues to rotate for a pre-set time. When the cycle for the stirrer is completed, an air cylinder pushes the shaft disc down, opening the seal and causing the disc to come in contact with the rotating friction pad. This causes the disc to rotate as it opens. This has two advantages. First, the foam is distributed in the mold. The second advantage is that the surface of the seal at this point is kept clean by the spinning action of the disc. In this period, the speed and shape of the mixer head have considerable influence on a cell structure, and a variable speed drive is essential. This factor caused Viking to look into the power requirements.

Fig. 2 shows a power/speed curve for a Viking "hold-up" head. The curve goes from 1,000 up to 2,500 rpm. The maximum power is 4 HP. For this particular experiment, 450 grams (one pound) of polyol and a helical stirrer was used. We tried to find the best stirrer shape for operation at the lowest possible speed to give the best possible cell structure.

The "hold-up" stirrer does have certain advantages. If there is any surge, the error is distributed throughout the whole mass. However, it does have a limitation in distribution. If you imagine the bottom disc opening, there is a limited amount of distribution which can be effected by this method.

In making a topper pad, one, of course, likes to distribute the foam down the center of the mold. Therefore, we found it desirable, in addition to the "hold-up" head, to also have the use of an "intermittent" stirrer for distribution over large thin moldings.

Mark V Gun

The third subject is a mixing head for rigid foams which does not use a mechanical stirrer. Air is used to promote mixing. The actual output from the gun depends upon viscosity and the formulation of the chemicals used. This is a two components mixing head. Using M.D.1. and low viscosity polyols, we have been able to mix 70 pounds a minute, and with the same gun, spray down to half a pound a minute. It has quite a wide range of application.
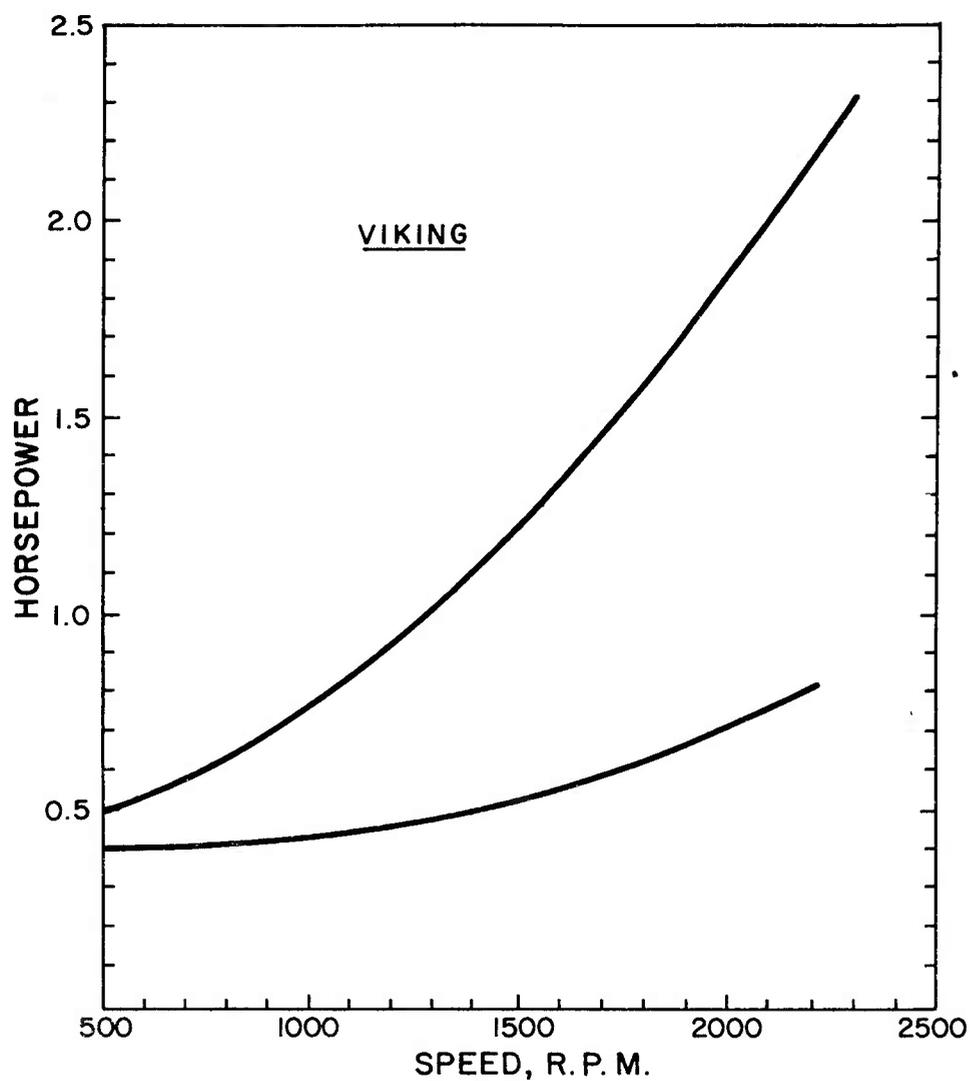
Fig. 2. Horsepower curve with 450 grms. of polyol only
in hold-up cup helical stirrer.

The gun is composed of four parts:

1. the body,
2. a handle which has a trigger,
3. a dispensing tube, and
4. a special type of non-return valve.

This type of non-return valve is based on a bicycle valve principle.
At the back of the gun there are three inlets. Two of the inlets are for the

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chemicals. The third is for compressed air at 80 pounds per square inch. The air is channelled across to each of the raw material streams, and closely controlled quantities of the air is admitted to the raw material streams. The control of this air is by means of a needle valve on the top of the gun. The liquids and air then pass from the back of the gun into a small mixing chamber which is about five eighths of an inch cube. The mixture leaves by means of its own speed of liquid flow, the compressed air moving with it. The high turbulence created by the liquids gives a good cell structure. It is important to control the quantity of mixing air. This can be done by inspection, and for normal in situ work this is quite sufficient, but for refrigerator production work, we have had to go to the reflinement of flow meters and fine control needle valves.

There is one other device on this mixing head which is worthy of note: the self cleaning device. A cam action valve by-passes the needle valve mixing air and feeds scavenging air from the back to the front of the gun, forcing out any residual material.

The trigger on the handle is for starting the metering unit. When the trigger of the gun is pulled, the pumps start and the liquids are delivered to the mixing head. The delivery of liquids will stop if the gun trigger is released or the timer on the metering unit finishes the pre-set dispense period. For safety purposes, the electrical lead from the mixing head is at 12 volts potential.

Over 400 metering units and guns of this type are now in commercial operation on ships, building and transport insulation. The guns are also especially set for use with different metering units for the production of insulation for domestic refrigerator cabinets and doors.

SESSION NO. 3

FOAMED PLASTICS APPLICATIONS
AND REQUIREMENTS

Mr. John Lacz, Chairman
Atlantic Research Corporation
Alexandria, Virginia

ARMY INTERESTS IN FOAMED PLASTICS

Bruce Fisher

The Army has a continuing and growing need to increase the efficiency and decrease the weight of items of combat and supply equipment. In satisfying this need, substantial quantities of foamed plastic materials are already being utilized. For example, foams have been introduced into such items as refrigerators and insulated food carriers, landing crafts, aerial delivery platforms, prefabricated structural panels, mattresses, and packaging.

The introduction of foams in such items has resulted in improved performance. Such utilization of foams will continue. However, present uses have incorporated the foam into the end items while they were being manufactured under controlled plant conditions. There are many uses for foams, however, in areas where it is logistically or tactically unsatisfactory or even impossible to use foams manufactured in a base area and shipped to the point of use. Thus, the ability to produce foamed plastics under field conditions is of paramount importance.

It is easily apparent that field requirements can vary widely: from conditions of large foam-volume needs requiring specialized van-mounted equipment and trained personnel; through conditions of moderate foam-volume needs requiring a few drums of materials, simple hand-operated equipment, and semi-skilled operations; to conditions of small foam-volume needs requiring only a small amount of materials and unskilled personnel. Furthermore, climatic conditions can range from tropical to arctic.

Since field use requires a minimum of equipment, attention has been devoted to exothermic liquid systems with the greatest effort to date being devoted to the urethanes. Other foaming systems are also being investigated now.

One of the early interests in foams was their use as energy dissipators for aerial delivery. For this use, a high strength, rigid, non-resilient foam that could be produced in the field with the minimum of equipment was required. Urethane formulations based on castor oil and Quadrol and modified by copolymerization of vinyl monomers that had excellent energy dissipation properties were developed. In connection with field production of such foams, a simple hand-operated peristaltic action pump and mixing unit fed from fifty-five gallon drums by gravity was developed.

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Another early interest has been the use of foams as a structural, insulative material for shelters. There are two general lines of approach in this area. One concerns the construction of sizable, rather permanent shelters which require considerable amounts of materials and considerable quantities of equipment and personnel. The Corps of Engineers (Fort Belvoir) have been quite interested in this approach and have been investigating van-mounted equipment for casting foam pieces in molds that can be assembled subsequently to form a shelter (Camp Century). A spray equipment could be used to spray-foam over air-supported shelters (the mold) under favorable climatic conditions. With this type of equipment, commercial urethane formulations can be used quite satisfactorily.

The second approach to foamed shelters has been the production of small, temporary shelters under rigorous field conditions, with little equipment and by untrained personnel. This area has been of primary interest to the Natick Laboratories as early as 1958. To learn the problems and techniques as well as obtain shelters whose properties could be investigated, commercial spray equipment and formulations were used at first. A number of small and large shelters were made by spraying over air-supported shelters over a time period ranging from April to December. A stress analysis of hemispherical and Quonset type shelters has been carried out, and a nomograph relating foam strength, density, and wall thickness has been developed. An aerosol foam kit was developed which would deliver fifteen pounds of a two lb/cu ft density when using commercial formulations. This kit could be used by unskilled personnel.

All experience indicated that at low field temperatures the normal urethane foam formulations would not be suitable because of viscosity increase with temperature, crystallization of toluene diisocyanate, and lack of sufficient exotherm. It has also become obvious that the equipment or method for applying foams must be made quite simple and that, in fact, formulation and equipment development are interrelated and must be carried out simultaneously.

Present research and development effort is centered largely in two areas: low temperature liquid foaming systems and solid foaming systems.

In the liquid foaming systems, work is being devoted to the urethane system that will be operable down to around $20^\circ F$. By selection of low viscosity urethane precursors, vinyl monomers, solvents, crude diisocyanates, etc., suitable formulations are expected to be developed in this area. To reach still lower temperatures ($-65^\circ F$), research is being conducted on ionic catalyzed vinyl monomers which previous investigations have shown to be a feasible approach. Simultaneously, equipment for utilizing these formulations under field conditions is being developed. Propulsion by gas pressure developed by low boiling materials, from burning propellants, or by mechanical hand pumps are under consideration.

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The other area of investigation is solid foaming systems. Here again two major lines of investigation are in progress. One of the most interesting is the development of a sheet of material that when treated by some simple method will initiate a self-propagating foaming reaction. Such a sheet would be the ultimate in simplicity of use by the individual but offers the greatest technical difficulty in development. This work is being sponsored by the Canadian Government under the U.S./Canadian Development Sharing Program and is being conducted by the Ontario Research Foundation. A paper on this work was given earlier in the program of this Conference.

The other approach to a solid foaming system is the use of a "heat gun," a simple unit that will produce a blast of hot air that can be confined and used to foam solid compositions. This approach has certain advantages over the liquid systems in that the use of solids obviates the problem encountered with liquids: large viscosity increases with temperature decrease. Furthermore, it widens the choice of foamable systems since highly exothermic reactions will not be required. Thus, materials such as foamable styrene beads, epoxy resins with heat decomposable foaming agents, blocked isocyanate systems, and many other solid systems could be used. Successful development of this area will, of course, be largely dependent on the development of suitable equipment.

There are many uses for foams. Among the easily forecastable applications are: small shelters, flotation rafts for equipment or personnel, insulation for shelters, camouflage, packaging of materials for cushioning, use of higher density foams for a landing area in boggy conditions. Besides what might be described as the normal, expected uses of foams, there are a number of other, farther out, suggestions for uses of foams. These uses are generally referred to, for more than one reason, as "Project Bubbles." One of the ideas in this area is the use of an aerosol of foam particles to act as radioactive scavengers—the idea being that the combination of the light foam particles with the heavy fallout particles would yield a lighter and hence slower falling particle so that the radiation would decrease before reaching ground and would also be spread over a wider area. Another idea is the production of a low density, very sticky foam which might be useful by adhering to enemy equipment causing malfunctioning.

There also exists the possibility of making foams out of polymeric materials that are capable of reacting with and destroying or neutralizing biological warfare and chemical warfare agents. Such foam could be of use in construction of self-decontaminating shelters and packaging to protect personnel and material.

Before such objectives can be obtained, there lies a long road of research and development. New basic polymers capable of the proper reactions must be developed. A deeper understanding of the foaming processes and the relation between polymer composition and foam structure with foam properties must be acquired.

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APPLICATION OF RIGID FOAM TO LIGHTWEIGHT STRUCTURES

C. Herbert Wheeler

No new material has captured the imagination of architects and structures designers more than rigid plastic foam. In this age of new materials and new building techniques, which serve people living a new way of life, it seems uncanny that rigid foam appears on the horizon.

Architects have been searching for lightweight, easy-to-handle, mass produceable, structural components to shelter our work and living environments. Aerospace designers are even more diligently searching for lightweight structure materials for space capsules and space shelters.

Instead of listing applications and charting properties, I am taking the pictorial approach to point out "design criteria" and show you an architect's view of the applications of rigid foam to lightweight structures. I am grateful to my friends at Dow Chemical, Monsanto, Mobay, Thiokol, and Nopco for permitting me to show their work and some of their forward looking ideas.

In showing photographs of a broad spectrum of structures applications, I hope to stretch your imagination. I hope you will use your "Jules Verne vision" to imagine the possibilities of better lightweight structures, lighter mobile structures, and even more graceful configurations to shelter man.

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The science of thermally isolating the inside and outside faces of a weather-resisting wall achieved new proportions with the advent of a structural non-conductive core material. An early example of the rigid foam sandwich panel exists in this experimental house built in Midland, Michigan, in 1955. Redwood plywood (1/4") on the exterior and 1/4 inch gum plywood on the interior are separated and supported by a 2 inch thick core of rigid foam. Soon afterwards a new dimension for the sandwich panel (the translucent panel) appeared in a Saginaw, Michigan house. The translucent roof panels, made with clear reinforced polyester sheets and foam cores, are interspersed among opaque panels faced with pigmental polyester sheets.

(DOW)

This skylight is made of a new highly transparent foam core material called Styrocel.

(DOW)

Color pigments are added to the translucent panels in this small office building.

(DOW)

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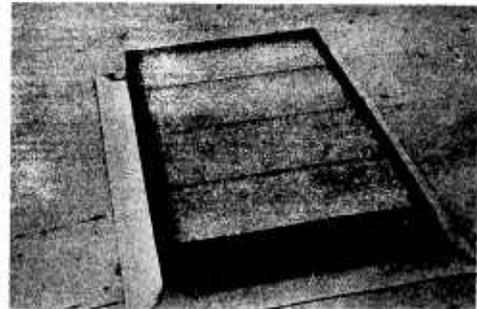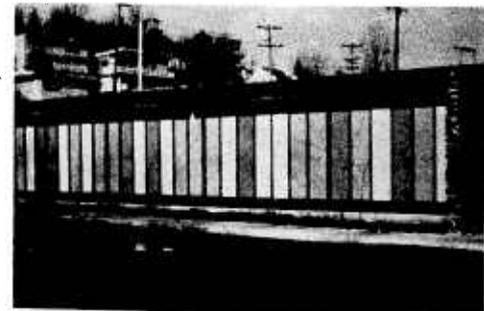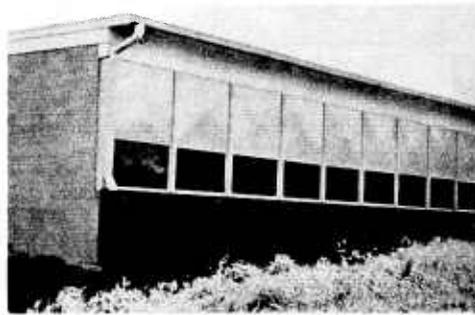
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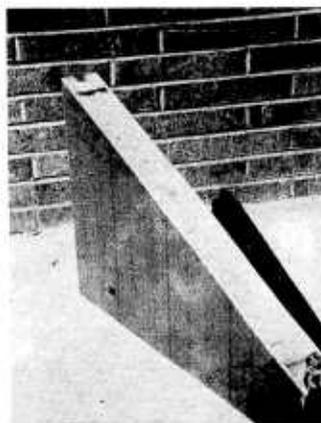
Section Through Aluminum Skin
Foam Core Panel (DOW)
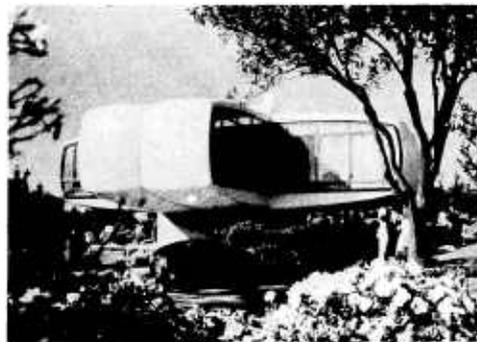
(Monsanto)

Glare of direct sunlight and bright skies, a critical factor in classroom design, is minimized through the use of translucent panels in the upper portion of these windows. The panel offers the combination of good light transmission and good thermal insulation and also eliminates the cost and nuisance of adjustable blinds and window cleaning.

Thermal leaks are thwarted by the use of wood edge strips in this section through a typical sandwich panel. Good design requires that the through structural members and reinforcements of a panel be isolated to stop heat loss and lessen structure-borne sound transmission.

Multicurved panels, a natural for rigid foam sandwich type construction, are shown in Monsanto's House-of-the-Future. This beautiful shell sandwich structure was conceived in an Applications Research program at MIT, sponsored by Monsanto, for the purpose of showing "the application of plastics to structures." The house was designed and subsequently built in Disneyland. The design utilizes the formability and high strength-to-weight ratio of plastic materials to achieve lightweight and adequate rigidity. The boat-hull beauty of the exterior adapts itself to pleasing living space on the inside. The 16-foot long and 8-foot wide curved bents are turned perpendicular 4 feet for the sidewall and join at the halfway level. Note the field made joint from inside. The joined cantilevered "U" sections from the floor, wall, and roof of each wing, jutting away from the center utility core. The resulting structure is a "cross," spanning 48 feet, having a pair of sections cantilevered outwards in all four directions. The finished structure demonstrates the potential of large insulated structural components.

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(Monsanto)

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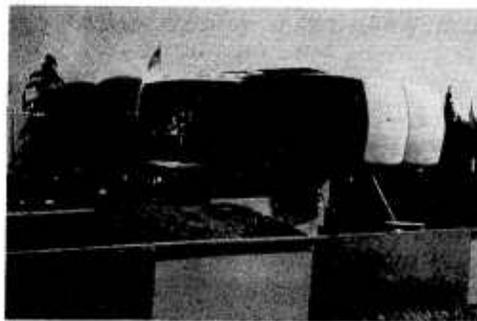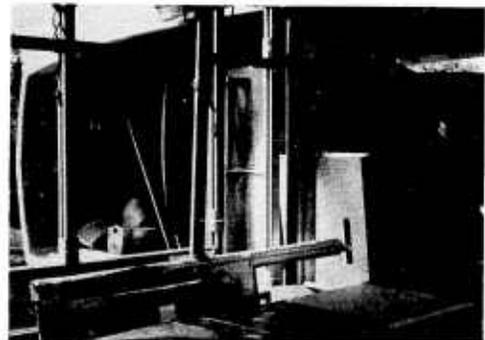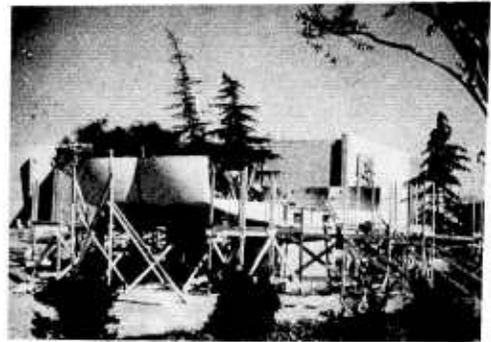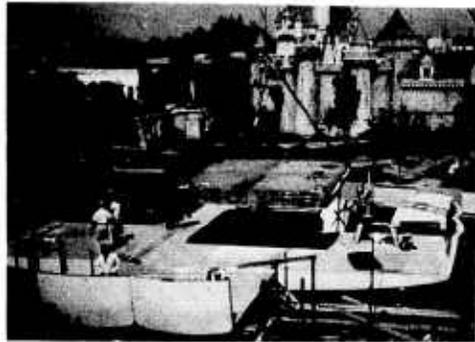
The Golf Starter House at Purdue University is a new type of lightweight configuration—the hyperbolic paraboloid, an inspiring roof structure. This structure resulted from a Dow Chemical research grant to Purdue to build a shelter using the offset wire concept of construction, a design technique which could lower the cost of lightweight construction. The inside complements the outside, especially note how the top of the glass wall panels accentuate the lines of the structure.
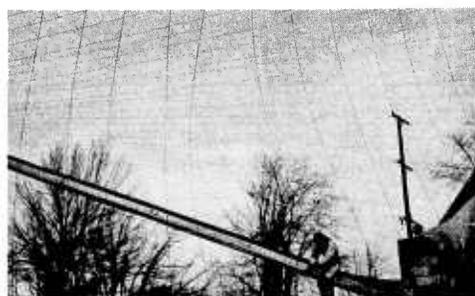

(DOW)

The sequence of erection of this type of construction is shown in these photographs of a Midland, Michigan structure. This hyperbolic paraboloid covers an area 64-foot square and rests on four piers. Light steel ridge and edge beams are erected and wires strung from side to side, showing the natural parabolic trace generated by the shell. Three inch thick rigid foam slabs, 2 feet by 8 feet are laid on the wire system. Top wires are then strung over the insulation slabs in the opposite direction holding the foam securely in place. The wires are adjusted to 600 pounds of tension and the slab joints are sealed with a 1/4 inch layer of grout. A thin concrete top is poured on the shell. After curing, the shell is covered with a plastic waterproofing membrane and the undersurface is stuccoed.

(DOW)

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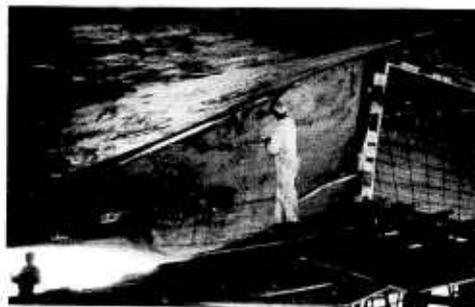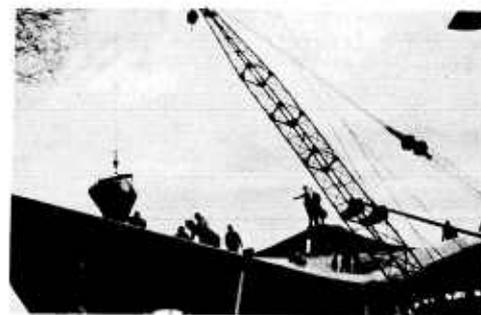
(DOW)
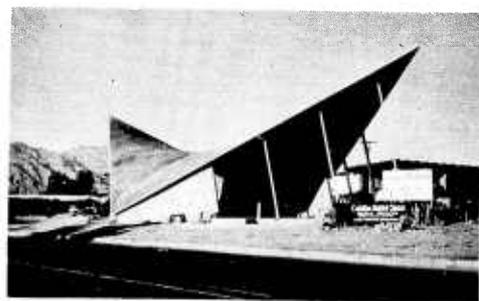
Catalina Baptist Church (DOW)

The use of rigid foam as "forming" in addition to thermal insulation is exemplified by this hyperbolic paraboloid, 60 feet on a side, which will end up as a Tucson, Arizona Church— think of this as a great cost saver.
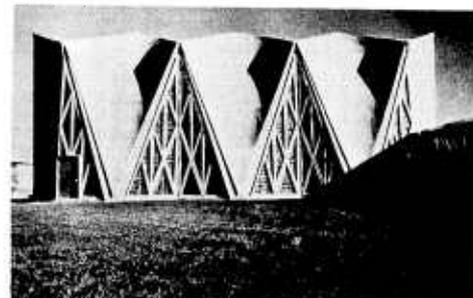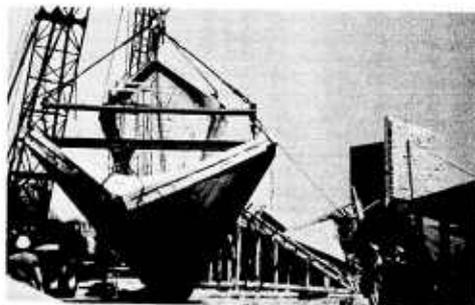
Zion Evangelical and Reformed Church (DOW)

Preforming on the ground and mass forming are the techniques for fabricating six HP's which are then lifted into position to form this church in Milwaukee. This technique for large or small panels bears study.

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Reuseable forms and the triple use of rigid foam slabs as insulation, vapor barrier, and base for interior surface finishing provides economy to the fabrication of a cluster of twelve inverted umbrella type HP's. Its graceful, attractive lines symbolizes the lightweight character of structures made possible by the creative use of structural foams.

Office Building, Eden, Indiana (DOW)

This scallop dome test panel made by Dow for a 100-foot diameter dome portrays the strength of double-curved shells. Rigid foam boards are arched between lateral supports then covered with chicken wire mesh and sprayed with a 1-inch layer of concrete. After curing, the supports were removed. The panel bearing on three corners was loaded to an equivalent loading of 300 pounds per square foot before the shell buckled—ten times the normal snow load.

(DOW)

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The folded plate principle expresses another form of the thin panel, lightweight structure as shown in this Caro, Michigan Church designed to use tapered folded plates.
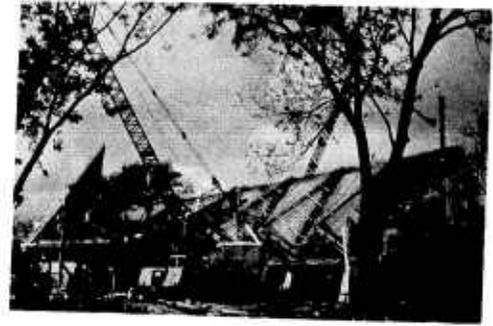
Sacred Heart Church (DOW)

Thin barrel vault shells are readily formed in rigid foam, expressing lightness of character on the interior as well as exterior. Another technique for low cost forming of lightweight structures.


Wayne Federal Savings & Loan, Detroit (DOW)

Another Church School of folded plate design using rigid foam forming.

St. George Church, Houston, Texas (DOW)

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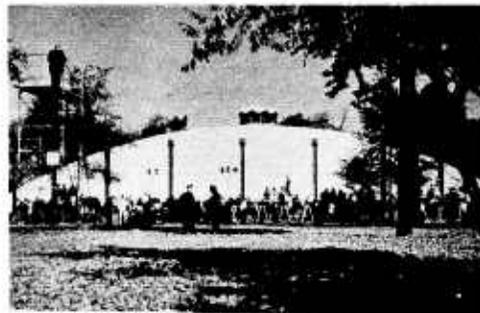
Earth mounding and rigid foam boards, combined with ingenuity, make possible a 250 foot clear span dome in Anderson, Indiana. Earth from a gravel pit is mounded to the desired cross section and then covered with foam board. The boards are covered with reinforcing steel and then concrete. The dome is completed, including waterproofing membrane and exhaust system canopy. Note the hydraulic jacks. The dome is lifted 20 feet up the columns and the building finished. Cost of structural portion including foundation, columns, and dome is $3 per square foot—the entire building housing 7000 seats cost $6.50 per square foot, less than half the cost of a conventional auditorium.

Warner Auditorium (DOW)

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Lightweightness, transparency, better insulation, easier-to-handle, less costly, thinness, attractiveness—these characteristics insure a place for rigid foam as a building material. Architect designed structures, which I have shown, radiate character and portray the enthusiasm which architects are showing for rigid foam. The engineered structures using rigid foam which will be shown next portray imagination also.

A happy Eskimo on Baffin Island, Canada, has an igloo which he constructed himself by whittling blocks of foam and joining the blocks with asphaltic adhesive. The foam was so effective an insulator that, in sub-freezing temperature, the small lamp normally used to heat an igloo made the igloo so hot within 3 hours that its inhabitants had to leave. Isn't this a do-it-yourself material?

(DOW)

The inherent strength and natural beauty of the igloo, shell, or geodesic appears to have captured the heart of today's designers. Buckminister Fuller leads in the penetrating search for globelike structures with his many variations to the geodesic. Hexagonal and pentagonal panels in this geodesic may be assembled in 20 minutes by two men using only wrenches to provide portable housing for any climate. These panels are shipped in a package 6 feet x 7 feet x 1 feet and form this geodesic dome developed by Tool Research & Engineering Corporation in California.
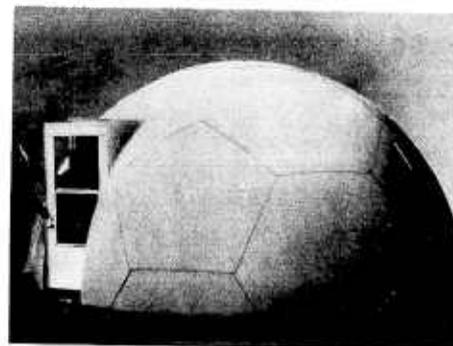
Withstanding high winds and an extreme climate, these preformed sections of rigid foam form the three-quarter sphere structures used on the Dew Line radar installations. Urethane foam was selected because of its high permeability to radar waves, as well as excellent insulation and high structural strength.

Radome, Distant Early Warning Radar Installations (Mobay)

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Rigidity, dimensional stability, and low weight characterize this giant radio antenna which has a 30 foot reflector developed by Boeing. To eliminate sheet metal, heavy supports, and stretching under sunlight, severe cold, and high wind, the bowl is formed of double wall fiberglass shells cured on a mandrel. The cavity between the shells is filled with rigid foam.

(Mobay)

This balloon house consists of a vinyl-covered nylon air-supported structure which is spray coated with flame resistant rigid foam on the inner surface. The foam having a density of 2.3 pounds cubic foot is applied about 6 inches thick and then foam-ribbed or foam-thickened for extra strength as desired.
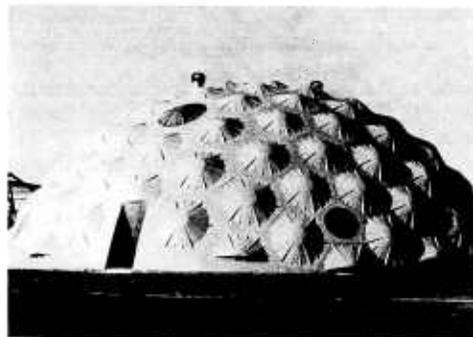
(Mobay)

Sprayed-in-place foam adheres to the inner side of this 80 foot diameter geodesic dome. Effective as insulation on the lightweight molded fiberglass panels, rigid foam makes it possible to heat or cool this structure for one-fourth the cost of conventional buildings of equal size.

(Mobay)

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In contrast, geodesics can be small and inexpensive. Geospace Gardenettes made of "fomecor," a rigid foam paper-faced material, are de-mountable, movable polyhedra having no end of possibilities for use as storehouses, farm shelter, pool-houses, second homes, and so on.
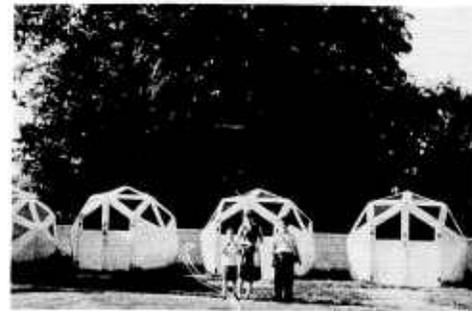

(Monsanto)

Another prototype house demonstrates the possibilities of Ribcore, a rigid foam slab material with reinforced paper ribs.


(Monsanto)

Where does the shelter industry stop and the container industry start? This well-designed case for a Hawk Missile shows weatherable seals, hinges, shock-mounts, cushioning, and ribbing for lightweightness. Rigid foam makes possible this lightweight shipping container for a Polaris guidance system.


(Nopco)

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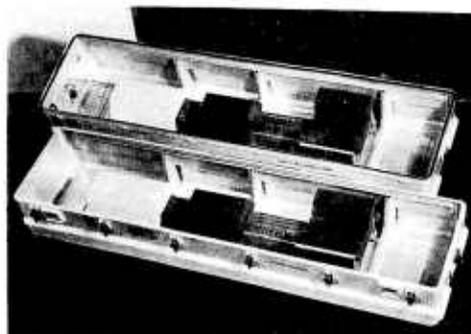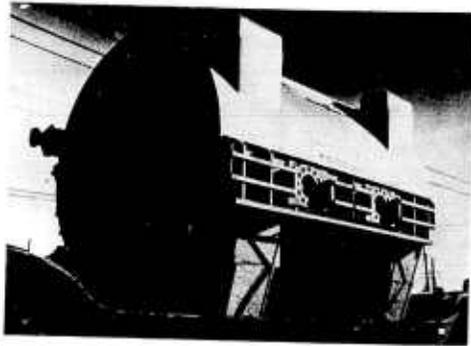
Turbine Generator, General Electric

Lightweight structures using rigid foam can have great strength. The high load-bearing capacity of rigid urethane foam is dramatically demonstrated by the use of 200 pounds of rigid foam which replaces a 6800 pound hand-built hardwood skid formerly needed to support this 120 ton turbine generator during shipment.


Bell Laboratories (Mobay)

Urethane foam protects the electronic heart of "Telstar" against the rigors of space travel. Over two thousand transistors and diodes are encapsulated in foam forming a supporting structure which helps to resist shock, vibration, and temperature changes.
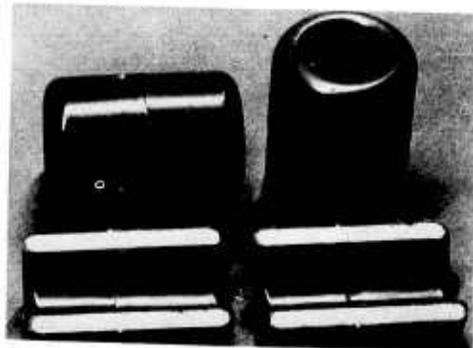

Minesweeper Floats (Nopco)

Buoyancy is another characteristic of rigid urethane foam. This foamed plastic cable float for a minesweeper is made of high impact styrene filled with foamed plastic.

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The Welin fiberglass and foam lifeboat uses rigid foam to great advantage. Foam fills the void between double fiberglass hulls rendering it unsinkable, virtually maintenance-free, structure-reinforcing, and hull-sealed. The boat survives a drop of 10 feet into the water with a 10 ton load aboard.
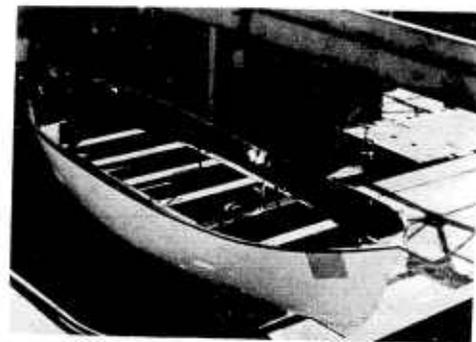
(Nopco)
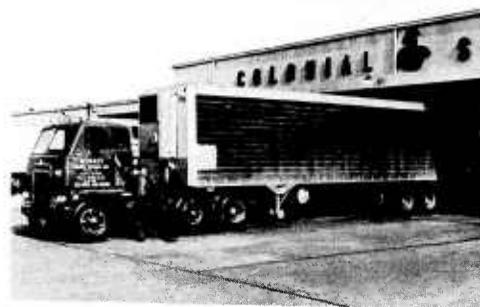
(Mobay)

Lightweight and mobility go hand in hand. The new "reefer" vans by Fruehauf provide land transportation for perishable cargoes. Lightweight foam insulation fills every minute space between trailer shell and lining to block air, weather and heat penetration, and improves the strength-to-weight ratio of the trailer.

(Nopco)

This buoyant foam-filled drome, a missile target, is held together in flight and kept afloat in the sea indefinitely by foam.

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The suburban air-car of the future utilized urethane foam to fill the void in the rear annular duct to reduce resonance and metal fatigue.

Avian 2-180, Gyroplane (Mobay)

Designed for helicopter mobility is the foam core sandwich panel "helicop-hut"—lightweight and strong to meet all types of military tests for both air and land mobility.

Craig Systems, Inc.
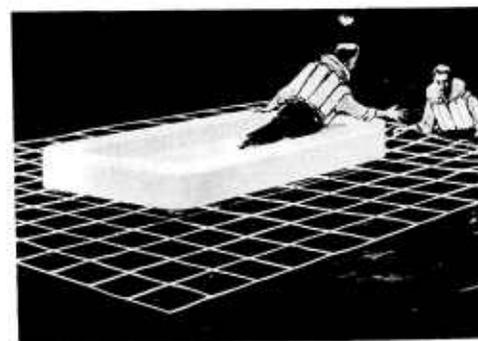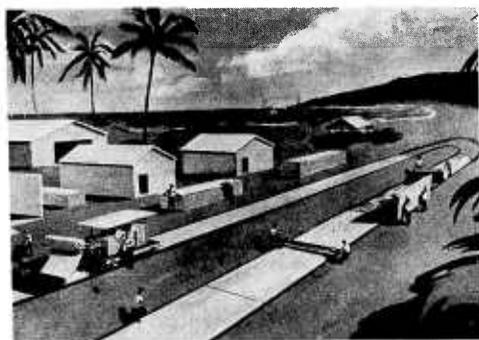
(Thiokol)

A whole new approach to the use of field-made foam comes from my friends at Thiokol who have developed a portable foam generator. They visualize on-site construction of building panels. They visualize a non-deflatable foam-inflated life raft.

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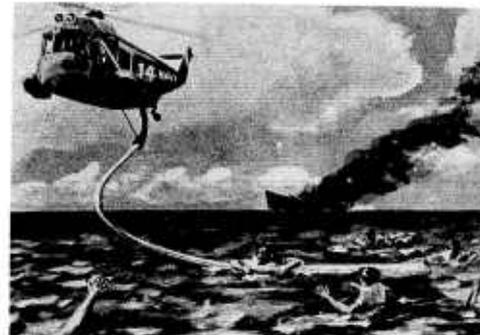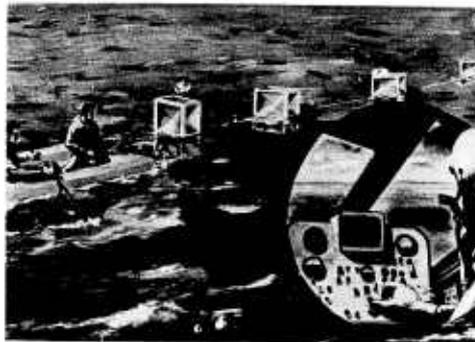
Floating corner-type radar reflectors add to the survival system by permitting rafts to be spotted by radar from search planes, increasing the survival target area by 400 to 1 ratio. A unique approach is the extruding equipment which will foam within a tubular formed plastic film making a rope having flotation provisions for floundering survivors.

Why not a rigid foam rescue island which can be carried in barrels as a safety device on a troop transport, aircraft carrier, or intercontinental plane. Here is the new material rigid foam performing like no other material.

Another new approach for space travelers is a urethane package which, when heated by solar energy, triggers a foaming action which results in an igloo type shelter and an armchair. Powdered urethane chemicals are cemented to a deflated 7 foot balloon and a crude wire chair frame. These models were formed in a simulated space environment at Wright Patterson Air Force Base by Hughes Aircraft.
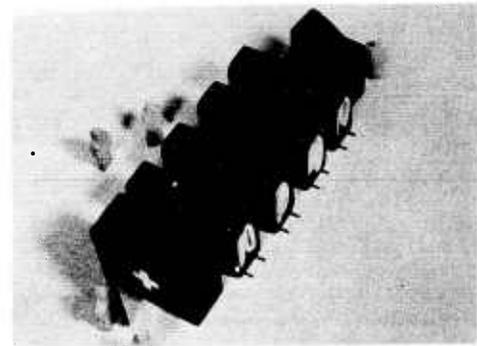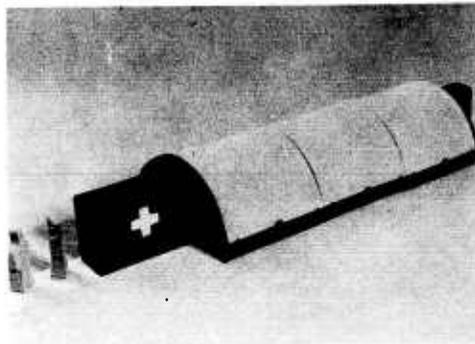
Curtiss-Wright has recently completed the study of a mobile army hospital for the Medical R&D Command which consists of an integrated shelter container system of plastic and foam primarily. The medical equipment is secured to the center floor skid and housed in a panelized rigid foam core container.
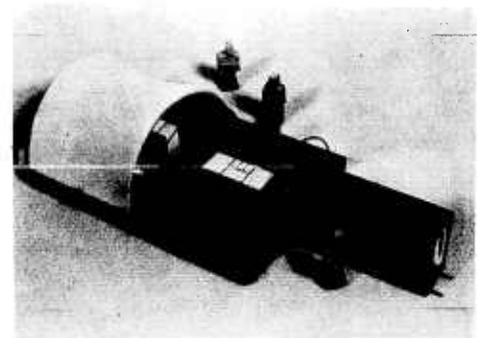
Three years ago, we developed a lightweight componentized building consisting of floor, wall and roof panels, beams, and footings all of rigid foam. The light weight foundation has great bearing strength.

(Curtiss-Wright Corp)

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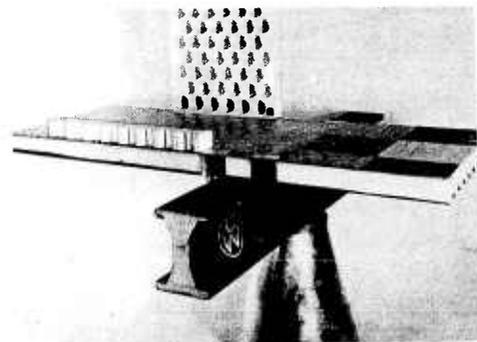
This is a solar heat collector panel. The experiment showed the possibilities of using rigid foam as a fully integrated structure. Corner details shows a frame, a back panel, back insulation, a potting material (for the water jacket)—locking the components together to heat the hot water for house and swimming pools in the future.
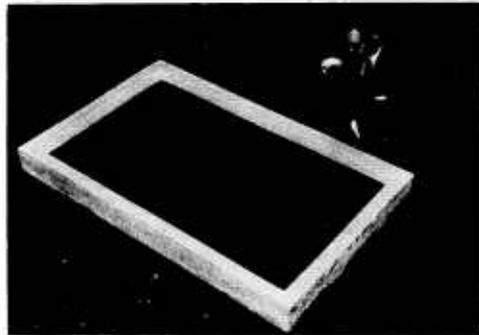
(Curtiss-Wright Corp)

As you have seen, rigid foam plays an important part in almost all types of lightweight structures now. Without stretching our imagination, this "young-in-years" building material should have a great future.

URETHANE FOAM PACKAGING AT THE AIR FORCE PACKAGING LABORATORY

Bernard A. Domning

In addition to test equipment normal to packaging laboratories, the Air Force Packaging Laboratory has several unique instruments designed for research and testing that should be mentioned.

Our El Fam (Force Analyzer) has the ability to record and analyze any force or condition (such as impact, stress and strain, pressure, temperature, humidity, and so forth) that can be converted into an electrical signal. This feature allows us to record high frequency signals, such as impact, at a fast speed and play them back at a slow speed for read-out on graphic recorders or a memoscope for analysis. Slow changing data, such as pressure or temperature changes, are recorded at a very slow speed and played back at high speed, thus condensing hours of data into a few minutes. The test data may be picked up from within sealed packages in conditioning rooms, vacuum chambers, ovens, or from the impact head of the drop tester. The equipment was designed for maximum flexibility and to cover the wide range of application required by our laboratory.

An Analog Computer has given us the capability of reducing the mountainous problems associated with material or cushion selection in package design. Virtually any packaging engineering problem that can be reduced to a mathematical formula can be resolved by this computer. Its limitation is basically the imagination, ability, and skill of the engineers operating it.

A high vacuum chamber is presently being installed. It has a volume of approximately 12 ft^3, a vacuum capacity of 10^{-9} mm of Hg, and a temperature variation capability of 260° to -195°C.

We at the Air Force Packaging Laboratory believe urethane foam packaging to be one of the more promising packaging concepts today. This cellular material may be easily sprayed or poured into a container and around an item to be packaged. Either method gives satisfactory results. In theory, this material offers many advantages:

1. It insures firm support and restraint for the item by adapting itself to the item's complex contours. This greatly reduces damage risks that exist in conventional packaging materials (Fig. 1).
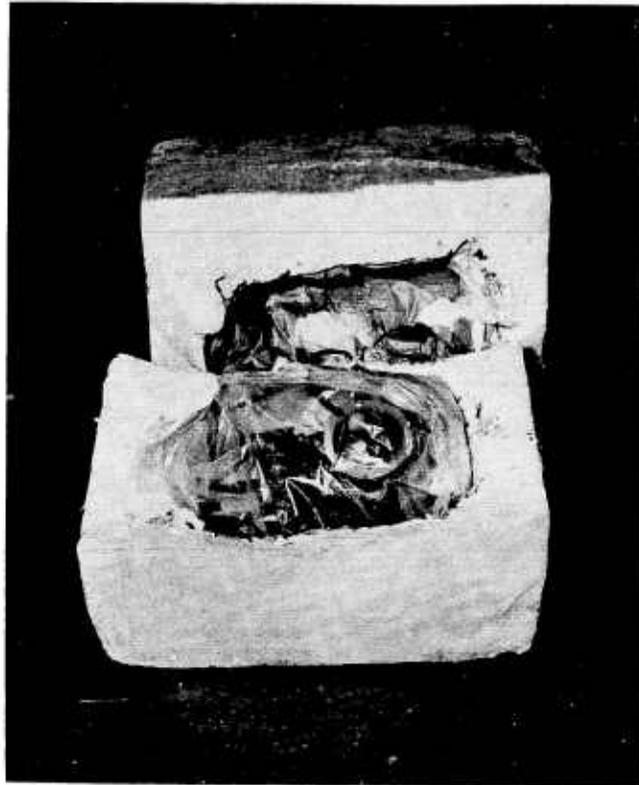
Fig. 1

2. Simple equipment at low cost can produce foams at atmospheric pressures and temperatures.

3. Its high impact energy absorbing properties provide excellent shock protection.

4. It is extremely stable dimensionally if good quality control is exercised in its preparation.

5. It is fungus resistant and will neither support mold growth nor be degraded by mold growth originating from some other substratum.

6. After repeated compression within its load limits, it is free from compressive set.

The Air Force Packaging Laboratory has conducted rough handling and cyclic exposure tests on two J-69 engines encapsulated in 2 lb rigid poly-urethane foam.

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The first was tested in the fall of 1961. The engine was prepared for foaming by first wrapping in MIL-B-121 paper. After the first wrap, a tear wire was wrapped horizontally around the largest periphery of the engine to facilitate opening of the foamed package. The engine was then wrapped in kraft paper, making sure that only paper tape was placed in the path of the tear wire.

To prevent adhesion between the foam and fiberboard box, the inside was coated with paste wax. A layer of foam was then sprayed in the fiberboard box and allowed to expand until it was firm enough to support the engine (approximately 180 seconds).

The engine was then positioned on the foam, and ends of the tear wire exposed to facilitate opening. The engine was surrounded with sufficient layers of foam to fill the container. The maximum thickness of each layer after expanding was approximately eight inches. The foam is not tacky after approximately 240 seconds; therefore, each successive layer was sprayed within this time to prevent seams in the foam. The results of the tests conducted on this package are as follows:

1. When subjected to edgewise drop test in accordance with MIL-P-116 using a 24-inch drop height, there were no visible signs of damage. The maximum "G" force recorded was 41 "G's."

2. When subjected to cornerwise drop tests in accordance with MIL-P-116 using a 24-inch drop height, there were no visible signs of damage. The maximum "G" force recorded was 42 "G's."

3. When fibrated at 260 rpm, with a 1-inch amplitude, synchronous motion for one hour with the largest dimension parallel to the motion of the table, there were no visible signs of damage.

The second container was tested by us in September 1962. The engine was prepared and foamed-in-place the same way as the first one with the following exceptions:

1. Engine was sealed in MIL-B-131C, class 1, material in an attempt to provide Method II protection. Method II protection is described in MIL-P-116 as "waterproof barrier with desiccant."

2. Engine was set on two prefoamed blocks prior to foaming to insure 4 inches of cushioning on bottom.

The engine was received encapsulated in foam retained by a W_{6_s} fiberboard sleeve (Fig. 2). Note instrumentation, accelerometer, and humidity sensing element leads. Fig. 3 shows damage during shipment, probably by fork lift (loss of center leg).

Fig. 2

Fig. 3

During vibration the remaining four legs were compressed and abraded until flush with the base.

The container was subjected to the following tests in order:

- a. cornerwise drop,
- b. edgewise drop,
- c. vibration,
- d. cyclic exposure,
- e. cornerwise drop, and
- f. edgewise drop.

The results of these tests are as follows:

When subjected to cornerwise drop tests using a 24-inch drop height in accordance with MIL-P-116, the "G" forces imposed on the item were recorded for each drop. The maximum resultant "G" force recorded was 13.6 G.

When subjected to edgewise drop tests using a 24-inch drop in accordance with MIL-P-116, the maximum resultant "G" force recorded was 14.0 G.

When vibrated according to ASTM D999 (modified), the total vibration time imposed was one hour and fifteen minutes. The package was unrestrained during the first 45 minutes of vibration and was restrained for the final 30 minutes. During the initial 15 minutes, the starting frequency of 3.33 cycles per second (200 revolutions per minute) was increased at increments of 20 rpm every five minutes to 4.34 cycles per second (260 rpm) and then maintained at this frequency for one hour. "G" forces were recorded for each applied frequency and at points throughout the test. The "G" readings varied from 9-26.1 "G's" with little or no change between restrained and unrestrained reading.

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The package was subjected to the Cyclic Exposure Test, Test B, of M1L-P-116. There was no visible damage to the package as a result of the cyclic exposure test. No definite conclusions could be drawn from humidity readings due to the ruptures in the MIL-B-131 barrier. Also, the lead wire to one of the indicators was completely severed during the tests.

The final drop tests were not completed due to development of cracks in the base of the container (Fig. 4), indicating we feel that the corner legs induced concentrated forces to the base. Smooth rounded portions of the foam at several of the breaks indicated that a good bond or "marriage" was not obtained between layers (Fig. 5). Numerous voids, shear lines, discolorations (light brown areas), and sections of extreme varied densities were found within the upper section of the container (Fig. 6). These samples were cut from the container after completion of all tests.

The container failed to meet Method 11 as the condition of the M1L-B-131 barrier indicates (Fig. 7). Note holes in barrier.
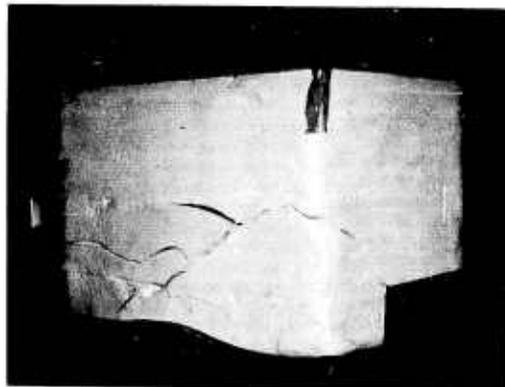
Fig. 4

Fig. 5

Fig. 6

Fig. 7

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The vibration test produced a tremendous amount of dusting (inside the container) which passed through the holes in the barrier and literally covered the engine (Fig. 8). Also, the vibration caused the engine to "settle" in the foam (Fig. 9). Note loss of cushion on bottom.

Fig. 8

Fig. 9

Defects and failure of this nature do not rule out consideration of this type container for shipment of engines. For example, elimination of the legs in lieu of a pallet might decrease chances of foam cracking. Variations in the formulation may correct the poor bond, voids, shear lines, discolorations, etc.

This test simply shows that more work needs to be done on the application of foam techniques in order to refine this type of packaging. We are sold on the foamed-in-place packaging concept.

Our objective in all packaging is "Optimum Packaging at Minimum Cost." The following is a cost comparison between a metal engine container and a foamed-in-place package for a J-69 engine. This comparison shows a considerable savings in cost, weight, and cube.

Comparison of Metal Engine Container
versus "Foamed-in-Place" Package for J-69 Engine

	Metal Container	Packaging "Foamed-in-Place"
Initial Cost	$340	$50
Rehabilitation	$ 70	-----
Container Weight	696 pounds	80 pounds
Container Cube	73.7 cu. ft.	31 cu. ft.
Cushioning Thickness	-----	4 inches

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We have published a Military Specification MIL-P-9969 (USAF) dated 8 April 1963 and entitled <u>Polyurethane, Rigid, Unicellular, Foam-In-Place for Packaging,</u> which sums up our work to date in this area.

The following is some of the work programmed for the future in this area by the Air Force Packaging Laboratory.

1. Analyze characteristic changes of foamed-in-place packaging under conditions encountered during air shipment. This will include:

   a. Selection and development of data on the most favorable foams which may be used in Air Force packaging. Consideration being given to variances in formulas, densities, and rigidity as well as exterior containers used.

   b. Preparation of charts on these foams showing changes undergone from sea level to an altitude attained by jet cargo aircraft, and possibly higher altitudes.

   c. Preparation of charts on these foams showing reaction to rapid decompression of the cargo compartment at selected altitudes.

2. Study cushioning characteristics of foams at varying densities utilizing the El Fam and Analog Computer.

3. Prepare military specification on flexible and semi-rigid foamed-in-place polyurethanes for packaging.

4. Investigate utilization of solid reactants for polyurethane foam packaging.

5. Conduct research on expanded polystyrene for Air Force packaging. Prepare specification on expanded polystyrene for packaging.

6. Conduct research on flexible polyethylene foam for packaging.

Our engineering personnel are presently conducting a rather extensive study of these materials to establish design parameters. Ultimately, we plan to publish an Air Force Packaging Manual or Handbook on the application, design characteristics, and limitations of the various polyfoams. However, our initial work is limited to rigid and flexible polyurethanes.

FIELD FOAMING SYSTEMS AND DEVICES

Robert J. Palchak

Introduction

The Quartermaster interest in foamed plastics is directly related to its responsibility to provide the military with food, clothing, and shelter. In this regard they have investigated or are now investigating the use of foams, not only as thermal barriers in clothing and food containers, but as energy dissipaters for air delivery of military supplies, as a camouflage technique, and as instant shelter for troops and/or supplies.

In January 1957, Atlantic Research Corporation (Contract DA 19-129-QM-838) initiated a program of research and development to produce energy dissipating foams under Army Quartermaster sponsorship.

Requirements

Ideally, energy dissipating foams should (1) exhibit high energy dissipation at low density, (2) have very low resilience, (3) crush at constant stress to a high percentage of its original height, and (4) be producible in the field at the point of use without an external heat source.

Formulation

A one-shot polyurethane foam process, starting with toluene diisocyanate (TDI) and castor oil appeared to be the best approach to the successful solution of this problem. Castor oil is multifunctional—the three hydroxyl groups per molecule favor the formation of a three dimensional network which is characteristically brittle, and the three double bonds per molecule could react with vinyl monomers to yield additional cross-linking with a further decrease in resilience. Finally, castor oil is a low-cost raw material. Because the uncatalyzed castor oil-TDI reaction to yield urethanes is quite sluggish, a variety of catalysts were evaluated to hasten the reaction. The most favorable catalysts were glyceryl monoricinoleate and quadrol. Using these catalysts, two promising formulations were developed (Table 1).

The foams obtained from these recipes possessed marginal energy dissipation values and both were quite resilient.

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TABLE 1

Preliminary Formulations

	T-38C	T-63C
Castor Oil	30	25.0
Quadrol*	--	75.0
Glyceryl Monoricinoleates	3.0	--
Ethyl Cellulose, N-100, 86 CPS	2.0	7.5
Emulphor-EL-719**	0.2	0.50
Water	0.25	0.63
TDI	40.3	70.0
Energy Dissipation (in-lbs/in^3)	50	80

* $[CH_3CH(OH)CH_2]_2N\ CH_2CH_2N\ [CH_2CH(OH)CH_3]_2$
** "A Polyoxyethylated Vegetable Oil"

Several vinyl monomers were next evaluated in these and related formulations to decrease the resilience by further cross-linking through the carbon-carbon unsaturation. Formulations containing either diallyl phthalate or vinyl toluene (Table 2) yielded foams with the desired physical properties.

TABLE 2

Castor Oil-Quadrol-Vinyl
Monomer Foam Compositions

	100C	108C
Quadrol	60	60
Castor Oil	40	40
Diallyl Phthalate	20	--
Vinyl Toluene	--	20
Petromix Number 9	2	2
Witco 77/86	2	2
Ethyl Cellulose	6	6
Water	Variable	Variable
TDI	Variable	Variable
Energy Dissipations (in-lb/in^3)	135	110

Physical Testing

Foam samples were tested for their energy dissipation at Atlantic Research Corporation by dropping a weight from various heights onto a 4-inch cube of foam supported on a stationary anvil. Much larger samples were evaluated under simulated field conditions at the University of Texas.

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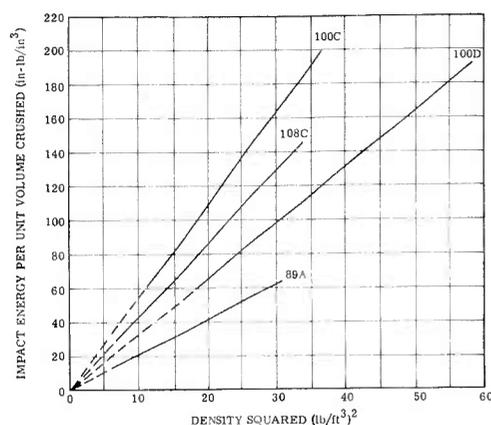
Fig. 1

In general, the energy dissipation of the polyurethane foams is directly proportional to the square of the density (Fig. 1). Since the densities of these formulations could be controlled to a limited extent by altering the water and TDI content, a family of foams differing in density and in energy dissipation properties could be prepared.

Ionic Polymerizations

Because attempts to produce polyurethane foams at low temperatures were complicated by increasing viscosity or solidification of one or more of the components, a limited effort was made to produce foams from ionically catalyzed polymerizations. In a typical experiment, distilled, dried styrene, saturated with CO_2 at $-28^\circ C$ was treated with a 0.5 per cent solution of aluminum chloride in methylene chloride. The monomer polymerized but the CO_2 was lost before it could aid in foaming. Isobutylene saturated with propane and isobutylene-styrene mixtures saturated with propane polymerized vigorously with foaming when treated with BF_3, $SnCl_4$, or $AlCl_3$. However, little gas was trapped and the foams collapsed. Finally, brittle non-uniform foamed structures of low density were prepared from vinyl toluene at $-30^\circ C$ by using Hycar 1312 as a viscosity modifier, dinitrosopentamethylene tetramine (Opex 100) as the blowing agent, and $AlCl_3$, BF_3 etherate, or $SnCl_4$ as the catalyst.

Atlantic Research Corporation is continuing investigations on ionically catalyzed foaming systems for use over the temperature range -65° to $-130^\circ F$.

Foamed Plastic Field Shelters

The polyurethane forms prepared as energy dissipaters were investigated for use as field shelters. In this regard a foamed hut was prepared by spraying a foam onto an inflated sphere. After the foam had cured, the

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sphere was removed, and an opening was made to yield a habitable structure (Figs. 2, 3).

Fig. 2

Fig. 3

Hand Operated Foam Machine

A portable, hand operated foam machine (Figs. 4, 5, 6) was designed and constructed in accordance with the contract requirements.

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TRUARC RING AND WASHER ON SHAFT
(EACH ROLLER)

PUMP CASE

HOSE LOCKING CONE

HOSE LOCKING CONE

INLET

8-32 SCREW AND
RETAINING WASHER

HOSE

ROLLER

ROLLER REEL

CRANK HANDLE
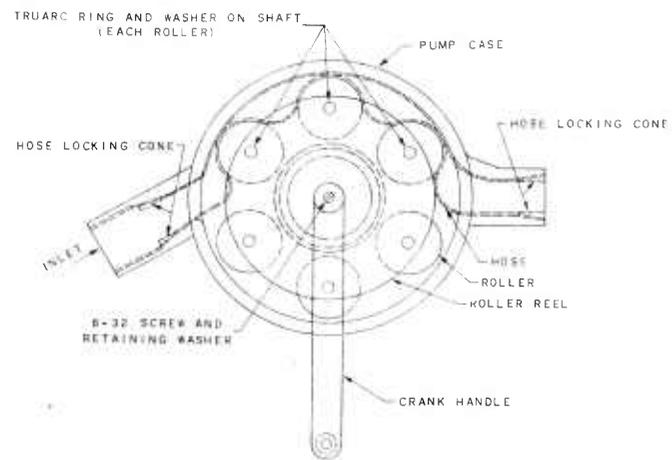
Fig. 4.   Design for hand-operated foam machine

Fig. 5

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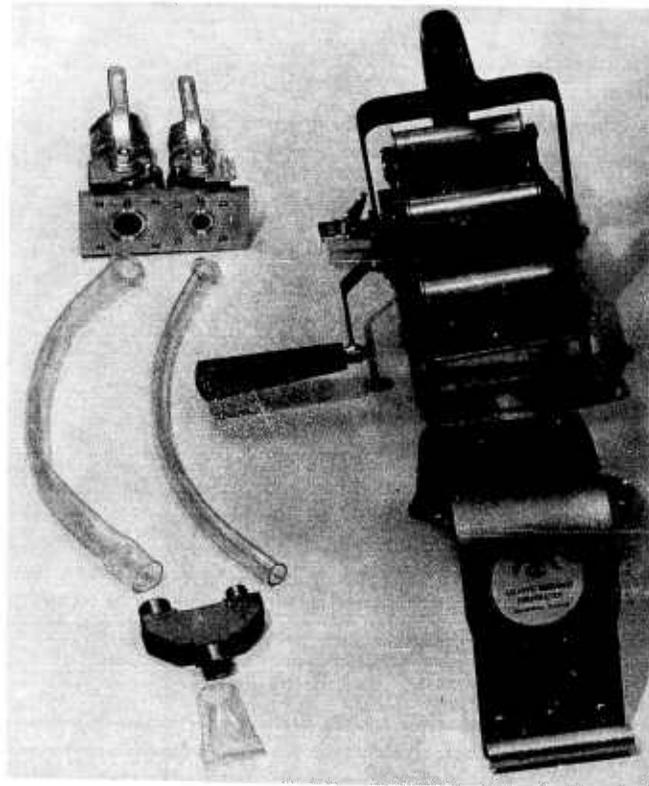
Fig. 6

Heat Foaming Machine

Atlantic Research Corporation is currently developing a system for field foaming heat foamable materials under Army Quartermaster sponsorship, as diagramed in Fig. 7. A mixture of heat-foamable, solid components may be ejected from a feeding device with sufficient energy to carry the components through a heat zone to any impact surface.

Exposing the solids to heat initiates a foaming reaction, which is a function of particle size, residence time in the heat zone, proximity of the ejection point to the impact surface, and the chemical constituents of the mixture. A "mass effect" due to flow rate is another important factor which affects the yield and quality of foam produced.

As indicated in Figs. 7(a) and 7(b), the solid components may be fed with either mechanical or air-operated devices.

Mechanical feeders may employ belts, brushes, or centrifugal action. These devices tend to import the same ejection velocity to all of the solid

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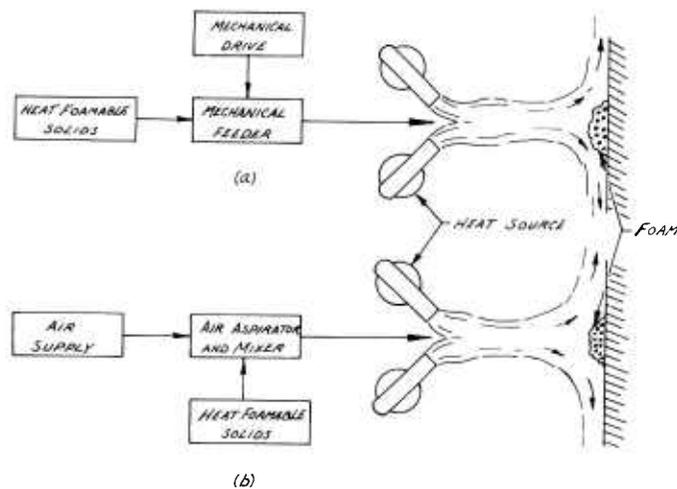
Fig. 7. Methods of heat foaming with solid
components

components. After ejection, the lighter solids tend to separate out due to
air-resistance, but diversion from the main stream is small if the heat source
is relatively close to the ejection point.

Air aspirated feed schemes can be used successfully, but the proportioning of feed elements is more critical than for mechanical feeders. At low
flow rates the concentration of light solids is greater; this affects the solids
mixture ratio unfavorably and lowers the quality and yield of foam.

Heat source requirements, to a great extent, depend on the flame temperature of the heat source. Assuming the parameters to be constant in a
heat transfer analysis for spherical particles—with the exception of the gas
temperature—the time to reach a given temperature drops rapidly in the low
temperature region of 200°-2000°F as gas temperature increases. Above
2000°F the time-to-temperature, or residence time, does not change very
rapidly, and the use of gas temperatures above 5000°F is not necessary.

Acknowledgements

The work on ionically catalyzed polymerizations now in progress is being performed by J. A. Terek and Carl Hassis under the direction of Dr. Robert J. F. Palchak under Contract DA-19-129-AMC-9(X). The design of a heat foaming machine is being done by Mr. Willian Noe under the supervision of Mr. Paul Jensen on Contract DA-19-129-AMC-6(X).

AN ASTRONAUT RECOVERY SYSTEM

John H. Quillinan

Introduction

For the past five years General Electric Missile and Space Division has been investigating an emergency escape system for astronauts. This has consisted of both analytical and laboratory studies. Some of these studies have been reported in other papers. [1,2] This paper will present the results of the past year's work.

General Description

An emergency recovery system for an astronaut is shown in Fig. 1. In the typical sequence, the astronaut dons the plastic covering and folded heat shield, which forms the re-entry vehicle shape, over his space suit. The plastic covering is then folded and secured around the man giving him complete mobility. In addition to the plastic covering and foldable heat shield, the astronaut is equipped with tanks containing foaming plastic, mixer, oxygen supply, recovery aids, and survival gear. The astronaut is also provided with a retro-rocket and orbital measurement package.
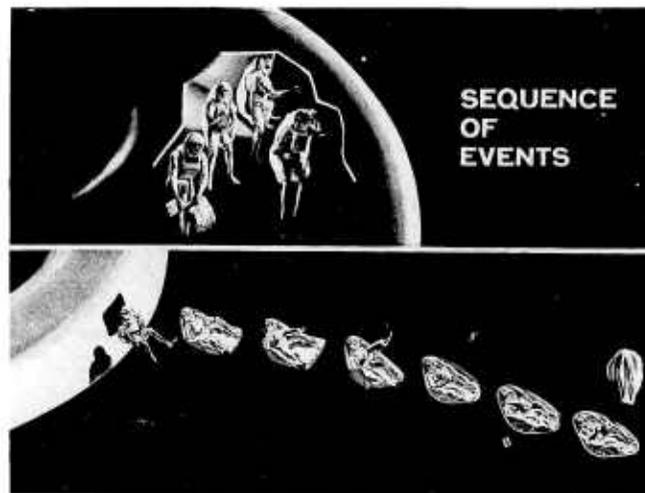

Fig. 1

After abandoning the space craft, the astronaut inflates the foldable heat shield and plastic covering to the designed shape for re-entry. Straps attached to the man and the heat shield-plastic covering position him in the proper relationship to the plastic covering and heat shield. The foaming process then fills the space between the man and foldable heat shield-plastic covering with foam plastic. An elastomeric material forms the foldable heat shield, and a very low density foam of 1 pound per cubic foot "pots" the man and equipment in the vehicle. The astronaut then stabilizes his motion, visually orients himself to the earth and measures the altitude and direction of flight with an optical sight mounted on the retro-rocket. Using the altitude information and pre-calculated range tables mounted in a display on the retro-package, the astronaut is able to aim and fire the rocket motor at the proper orientation in order to achieve re-entry. In many cases the astronaut will have the option of delaying the firing of the retro-rocket until his position in orbit is advantageous to landing in a desirable area. A typical mission profile is shown in Fig. 2. The initial velocity at an altitude of 400 nautical miles is 24,700 feet per second and is reduced by 600 feet per second to 24,100 feet per second by the retro-rocket. Re-entry velocity at a height of 65 nautical miles is 26,400 feet per second.

Fig. 2

The escape procedure then calls for the astronaut to orient the vehicle for re-entry using the cold gas control jets on the retro-package. Prior to re-entry a high intensity flare is fired and a radio beacon is activated. The design shape is highly stable, and maintains the proper orientation throughout re-entry. During re-entry the elastomeric heat shield ablates, protecting the man from the thermal environment while the very low density plastic cushions him against the deceleration and landing shock. After re-entry heating, radar chaff is expelled, another high intensity flare is fired, and a high intensity flashing light is activated. At an altitude of about 30,000 feet

a parachute is deployed on signal from a baroswitch. Impact velocity is designed to be less than 30 feet per second at sea level, which is well below the maximum allowable impact velocity. At impact, SOFAR bombs are released to provide location if impact is on water. The total time from retro-rocket initiation to impact is 45 minutes and total range is 10,100 nautical miles for escape from a 400 nautical mile orbit.

After impact the man releases himself from the vehicle and extracts the survival kit from the plastic foam. The radio beacon continues transmitting as a location aid to search aircraft, ships, and other units. The vehicle can be used as a raft if the impact is on water, and the survival kit is equipped to maintain him in almost any Earth environment.

A weight comparison between the space recovery system and an aircraft recovery is shown in Fig. 3. The space recovery system weighs only 47 pounds more than the aircraft recovery system.
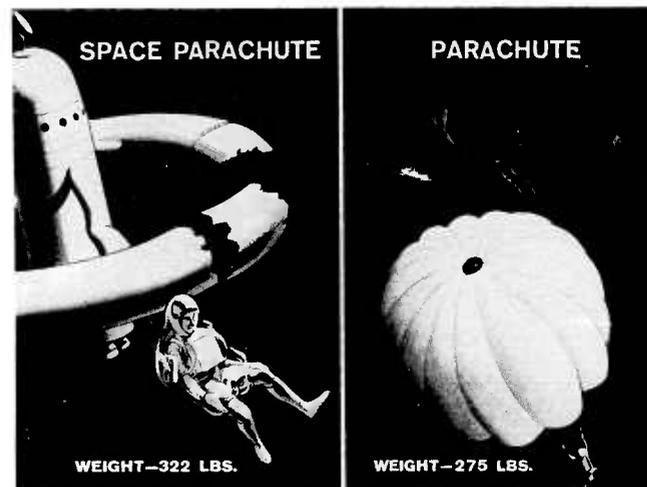
Fig. 3

Analysis

Design Study

Assumptions and Limitations. For the purposes of limiting the computations the following assumptions have been made.

Orbital altitudes have been confined, initially, to the region of 100 to 400 nautical miles. Short orbital lifetimes prohibit extensive satellite operations at lower altitudes, and the inner band of trapped ionizing radiation encountered above about 350 nautical miles will limit most manned satellite

operations to lower altitudes. Results have been limited to that obtained for satellites in circular orbits. Similar information has been derived for elliptical orbits whose apside altitudes lie within the limits given above.

De-orbiting velocity are considered as impulsive changes to simplify the analysis. Transient conditions thus ignored have little effect on the de-orbiting mechanics and re-entry initial conditions, but could affect the detailed mechanical design of the vehicle and the physiological stresses of the occupant. Reference 3 presents a more detailed discussion of limitations involved in such an assumption.

Altitude at initiation of re-entry is approximated at 65 nautical miles for computational simplicity. Although, aerothermodynamic effects will become tangible at altitudes which are a function of W/C_DA, flight path angle, and vehicle velocity, the errors and aerodynamic forces due to this approximation are small for this study.

For a given vehicle, the ballistic factor W/C_DA is held constant at its theoretical hypersonic value during re-entry. Although there will be variations from this value with Mach number and Reynolds number, and with changing shape and weight due to ablation of the heat shield, this effect is negligible for preliminary studies.

Since many of the considerations of these studies involve the anthropometry of the astronaut, it has been assumed that this astronaut is in the 80 percentile category, i.e., his weight is 180 pounds, and height 71 inches. [4]

Design. Fig. 4 shows the design trade-off for the selection of the escape vehicle size. It can be seen that the lowest weight acceptable design is at the minimum size limit of six feet in diameter with a resultant W/C_DA of 10.4. Initial studies have shown that by using a parachute for retardation the weight of the space recovery vehicle was reduced by half for the same deceleration force applied to the astronaut during landing.
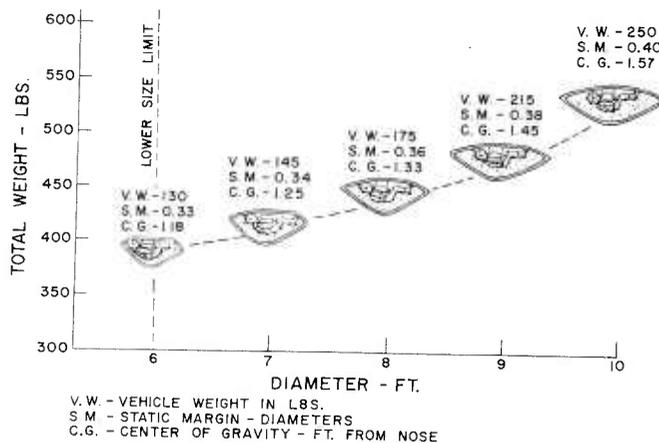
Fig. 4. Space parachute—design trade-off curve

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Fig. 5 shows the vehicle design. Table 1 is a breakdown of the component weight for the space parachute system. The backpack shown will supply oxygen and ventilate the space suit for 2 hours. From the table it can be seen that the weight of the re-entry vehicle is only 130 pounds. The weight
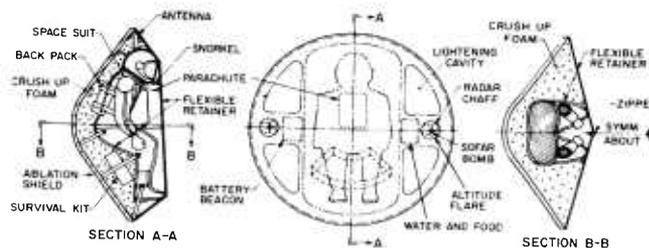
Fig. 5. Design of vehicle

TABLE 1

Space Parachute

Components	Weight (pounds)
Space Suit	25
Moose Back Pack (O_2 Supply; CO_2 and H_2O Removal; Ventilation and Cooling)	11
Survival Kit	12
Beacon, Antenna and Battery	8
Recovery Aids—Radar Chaff, SOFAR Bombs, Flashing Light, Flares (High and Low Altitude), Timer Baroswitch and Ejector, Dye Marker, Programmer	15
Parachute (Standard Design—Personnel Guide Rib Chute)	13
Foamed Re-entry Vehicle	130
Total Vehicle Weight at Re-entry	214
Man	180
Total Re-entry Vehicle Weight	394
Equipment Jettison Prior to Re-entry	
Foam Tanks and Mixer	10
Disorbit Pack (400 N. Miles Orbit)—Propulsion, Gun Sight, Controls, Firing Tables, Timer, Accelerometer, Battery, Pack Frame	93
Shield Container	5
Total Jettison Equipment	108
Total System Weight	502

breakdown of the vehicle is 65 pounds for the heat shield and 65 pounds for the foam. The detailed design of the 6 foot diameter vehicle is shown in Fig. 5. The folding heat shield is on the conical side of the vehicle facing forward. The astronaut is foamed-in facing rearward to withstand the re-entry and landing deceleration. The rear of the vehicle is closed with a sheet of plastic which can be opened with a zipper. The astronaut wears a standard personnel chest parachute. Equipment is imbedded in the foam structure of the vehicle. A snorkel is provided for astronaut breathing in the atmosphere in case of an emergency.

Trajectory Investigation

The satellite in orbit possesses a quantity of energy per unit mass dependent only upon the semi-major axis of its orbit. In order to return the escape device to Earth, this energy must be changed such that the new orbit either intersects the Earth's surface or penetrates the Earth's atmosphere on a flight path that will cause aerodynamic forces to dissipate sufficient additional energy to prevent further sustained orbital flight. By applying a properly aligned rocket thrust to the escape device, an orbit may be established which meets the energy dissipative conditions given above. The curves of Fig. 6 show the initial re-entry conditions for a emergency escape vehicle for 10 per cent greater than minimum disorbit velocity.
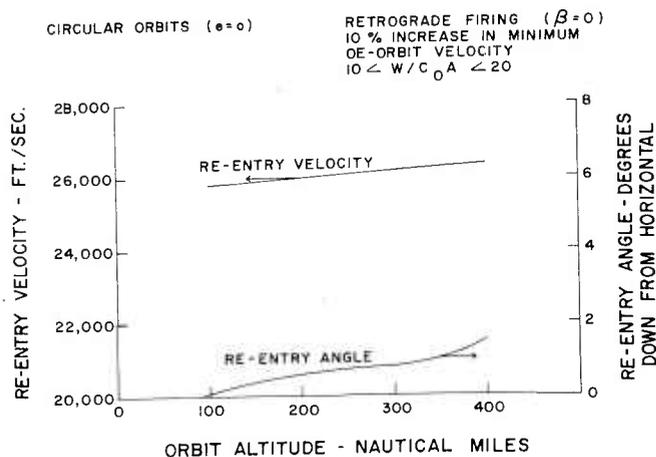
Fig. 6. Re-entry velocity and angle

In order to assess the effect of de-orbiting velocity misalignment (β), the study has included variations in β. A typical case for a 400 nautical mile orbit is shown in Fig. 7. The resulting figure clearly indicates that for all practical purposes β may be varied by as much as ten degrees without seriously affecting re-entry conditions. This will be of major importance in the equipment discussed herein.
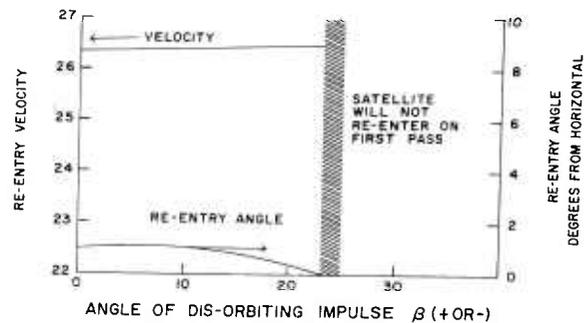
Fig. 7. Effect of angle of de-orbit impulse on
re-entry angle and velocity circular orbit
at 400 nautical miles altitude

Previous studies based on the minimum de-orbiting energies have considered either a cotangential (minimum energy) elliptical trajectory with a terminal point at the Earth's surface thus not taking advantage of the energy dissipative properties of high speed flight in the atmosphere, or considered arbitary, small re-entry angles thus fixing the de-orbiting velocity impulse, which in some cases is not the minimum value. By combining both the elliptical path to re-entry and the re-entry flight to low W/C_DA, non-lifting shapes into a single program, and obtaining a series of complete de-orbiting trajectories, this study has obtained minimum de-orbiting impulse values that avoid the disadvantages imposed in the previous studies.

The danger of attempting to operate with minimum de-orbiting velocities lies, of course, in the occurrence of non-nominal conditions, retro-rocket thrust variations, initial velocity variations, etc. To alleviate this problem, the design parameters were adjusted to allow for a "safety factor" in de-orbiting velocity. Preliminary studies include an additional ten per cent of de-orbiting velocity above the minimum.

Associated with the return from orbit are parameters pertinent to the search and recovery phase of the rescue operations and to the physiological stress on the occupant.

These parameters include time for descent, range transversed during descent, landing point prediction, and deceleration. Fig. 8 presents the relationships of the time and range parameters with initial satellite orbital altitude for emergency escape missions which utilize ballistic (zero lift) re-entry and the specified de-orbiting velocity impulse. Fig. 7 has already indicated that small variations in β, the angle of application of the de-orbiting velocity vector produced negligible effects on the re-entry conditions. Variations in the magnitude of the velocity vector, however, are reflected in down-range dispersion of the landing point. Fig. 9 presents dispersions resulting

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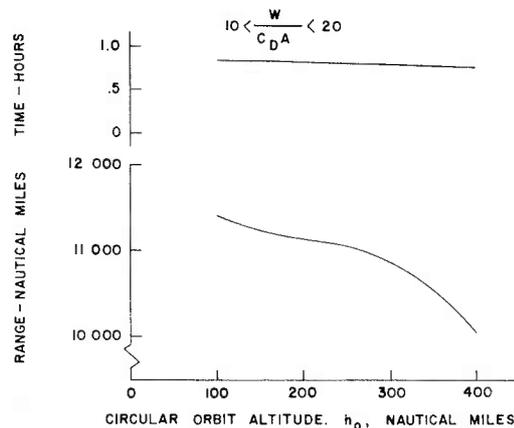
Fig. 8. Range and time from orbit
to impact using nominal de-
orbiting impulse

Fig. 9. Range dispersion due to
de-orbiting velocity variations

from typical variation in the de-
orbiting velocities previously estab-
lished. Fig. 10 presents maximum
decelerations encountered during
ballistic re-entry for the nominal
de-orbiting conditions.

Fig. 11 shows the calculated
resultant ablation of the space para-
chute shield. Ablation tests have
been performed on inclined flat
plate models of the elastomeric
material in the Supersonic Air Arc

Fig. 10. Maximum re-entry
deceleration using nominal
de-orbiting impulse
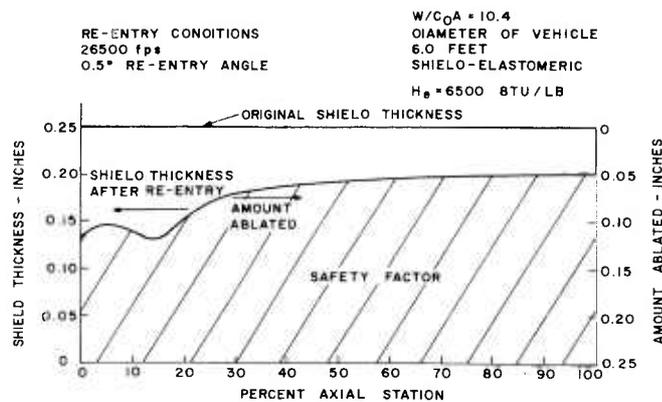
Fig. 11. Ablation shield

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tunnel of the General Electric Company Space Sciences Laboratory.* The elastomeric heat shield material has been tested at a maximum heat flux (for a 0.5 degree re-entry) for nearly the entire re-entry time (300 seconds). Under these conditions the elastomeric materials has proved superior to any other material tested.

Search and Recovery

A major problem in the escape of man from a satellite is finding him after he has landed on earth. If there has been no opportunity to select a landing site, the possible landing area may encompass a large portion of the globe. Such a possibility will require special facilities to find the man. A description of typical procedure and equipment to be used in such an operation follows.

One of the most important search and recovery considerations will be the monitoring of an emergency beacon frequency by a world-wide facility of radio stations. Such a signal will probably be the first indication of a man re-entering from space under emergency conditions. In addition to the signal from the emergency beacon, flashing light and high intensity flares fired before re-entry will be observed against the night sky and against the day sky if not too closely aligned to the sun. In addition, after re-entry, radar chaff will be ejected to provide a large radar target. Furthermore, before the parachute is deployed, another high intensity flare will be ejected to provide terminal point location information. The parachute will be metalized to provide a large radar cross section. Upon water impact, SOFAR bombs will be ejected to provide landing location information. Meanwhile, the radio beacon should continue to operate for several days after impact to provide direction finding information. For water landings, a dye marker will also aid in providing visual sighting aid.

In the actual recovery operation, the most rapid method makes use of aircraft. With sufficient alert time, it may be possible to perform an air snatch, or using a low speed aircraft and the proper equipment, even a water or ground snatch. Studies of vehicles to be employed in the recovery operation indicate that helicopters with their limited range and ships with their limited speed are not suitable for this operation. High speed hydrofoil boats offer an attractive possibility by extending the search capability of ships and possibly providing a landing platform for helicopters.

Human Factors

Design of emergency equipment for man's use must be subject to the limitations of man. For purposes of this study, the limitations of primary concern was man's tolerance to deceleration. Fig. 12 presents results of

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* Detailed results are presented in Laboratory Section of this paper.
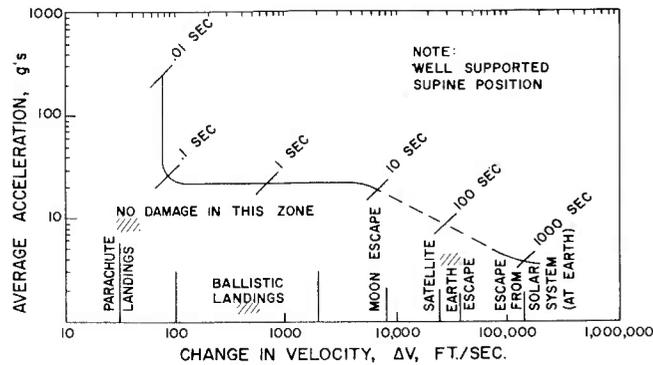
Fig. 12. Man's tolerance to acceleration

the most recent correlation of acceleration tolerance data, covering a wide range of accelerations and durations. Design considerations of this study required maintaining the astronaut well below the limiting curve of the figure. The possible ill effects of foaming a man in place has been investigated by others[5,6] and in the GE-MSD Manned Systems Laboratory as shown in Laboratory Section of this paper. Both man and animals have been foamed in place with no ill effects. In addition, the foam has proved an excellent restraining medium.

Laboratory Program

A laboratory program has been conducted during the past year to indicate the feasibility of the space parachute concept. This program consisted of fabrication of a full scale (6 feet in diameter) foldable ablation heat shield. The shield material was tested for its ablation behavior in a supersonic arc tunnel. A series of experiments were performed on foaming-in dummies and man. This finally culminated in the foaming-in of a man and having him extricate himself from the foam. The details of this work have been reported.[8-11]

Heat Shield

The heat shield system for the space parachute is an elastomeric solid material which can be folded compactly and integrated into an inflatable structure. To permit compact folding, the required thickness of the shield is small (0.25"). The use of a foldable heat shield appears to be most attractive for the following:

1. The shield could be thoroughly inspected prior to flight.

2. Lighter weight heat shield by using high performance elastomeric material.

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Fabrication. A male mold was constructed to the approximate dimensions of the space parachute. The outer shape was basically a sphere cone with a 15 inch radius, a 52 degree half cone angle, and a base diameter of 6 feet. A mylar film (1/2 mil thick) was layed on the mold in the form of sixteen triangular gores to serve as a backing to the heat shield. The mylar skin was placed over the basic mold and secured at its perimeter. The elastomeric shield material was applied by point rollers to the mylar. While the ESM was still wet, triangular gores of capilon (nylon) scrim cloth Nini 1111 (11 x 11 plain weave) was laid on top of the ESM. Three more coatings of ESM formulation was applied over the scrim cloth until a thickness of 1/4 inch to 3/8 inch was obtained. After curing, the heat shield was folded several times to see if any ruptures would develop (Fig. 13). There was no apparent damage and the shield was then packed in a cardboard box measuring 18" x 18" x 6". The total weight of the shield was 29.09 pounds. The scrim cloth composite was used to reinforce the ESM and take the bending loads during folding.

Ablation Testing. Ablation tests of the promising materials were conducted in the supersonic air arc tunnel of General Electric's Space Sciences Laboratory (Fig. 14). The models consisted of aluminum elliptical disks to which 0.5 inches of ablation material was bonded. The specimens were weighed before and after testing. The amount of virgin material remaining after testing was also measured. The specimen was mounted in the arc tunnel at 45° to the air flow. The peak flux was 27.75 Btu-sq ft/sec and the test time was 150 seconds for three runs and 300 seconds for the fourth run. The average heat flux to the test specimens was about 0.50 Btu/second.

Fig. 13. Folding of heat shield
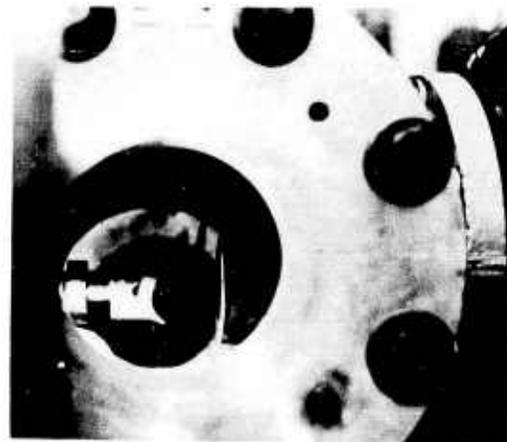
Fig. 14. Ablation test of heat shield

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The test results are given in the following table.

TABLE

| Material | Test Time Seconds | Weight Loss % | Effective Heat of Ablation | |
			Based on Weight Loss	Based on Degradation
ESM 1100	150	1.68	32,496	7,000
ESM 1101	150	4.64	13,300	4,500
ESM 1102	150	4.50	12,870	5,000
ESM 1102	300	8.30	15,086	8,000

The values of effective heat of ablation given in the previous table for the degradation measurements are simply nominal values. For the thickness of the heat shield used for a space parachute the effective heat of ablation obtained based on degradation was used.

Foaming

Materials. The foaming materials were formulated to produce a polyurethane foam. The initial pour was a semi-rigid foam made from castor oil and a polyester prepolymer. It was believed that a semi-rigid foam might be more amenable for extraction of encapsulated personnel and that the castor oil and polyester combination would significantly slow down the reaction and avoid a high exotherm.

The formulation investigated for the first pour is given below:

Pleogen 4050 (Polyester resin)* - 100 pbw
Pleogen 4012 (Polyester prepolymer)* - 112 pbw
Spencer Kellogg XD 1078 (castor oil prepolymer)** - 58 pbw
Benzyl dimethylamine (catalyst) - 0.5 pbw
Water - 2 pbw
Freon - 3 pbw
SF 1034*** - 2 pbw

Subsequent pours were made with a rigid polyester polyurethane containing a sizable amount of blowing agent (lsotron 113)****

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* MolRez Division of American Petrochemical Corp.
** Spencer Kellogg Company
*** SF 1034 size control agent-Silicon Prod., G.E.
**** Isotron 113 - a floro hydrocarbon blowing agent, 134°F boiling point: Penn Salt Chem. Co.

The formulation for pour number 2, 3, and 4 is given below.

Pleogen 4050 - 100 pbw
Pleogen 4012 - 170 pbw
Isotron 113 - 15 pbw
SF 1034 - 2 pbw
H_2O · 3 pbw

The formulation for pour number 5 is shown below.

Pleogen 4050 - 100 pbw
Pleogen 4012 - 166 pbw
Isotron 113 - 17.7 pbw
SF 1034 - 2.0 pbw
H_2O - 2.6 pbw

The formulation for pour numbers 6, 7, 8, and 9 was the following:

Pleogen 4050 - 100 pbw
Pleogen 4012 - 166 pbw
Isotron 113 - 17.7 pbw
SF 1034 - 2.2 pbw
H_2O - 2.6 pbw

Increasing amounts of blowing agent (Isotron 113) were added during the development of the foam formulation. The amount of silicon fluid (SF 1034) was increased slightly and the amount of Pleogen 4012 and H_2O were reduced slightly during the formulation development. As the formulation was developed, it was found advantageous to cool the Isotron 113 to about $0^O F$. This reduced the boil off of the Isotron during mixing and reduced the exotherm of the foam. The blowing agent also decreased the viscosity of the resin permitting better mixing, lowered the density of the foam, and lowered the exotherm.

Fabrication. Two different molds were used for the foaming experiments. The first foam pour was in a female mold that matched the heat shield mold. The subsequent pours were made in a 7 x 3 x 2 feet plywood box. The box was open on top and hinged on four sides. The box was lined with 3 mil polyethylene sheet.

Foam Performance

The first foam formulation performed well in small batches and produced a semi-rigid foam with a density of about 2 lbs/cu ft. This formulation was then used to foam-in a dummy in the conical mold. The mixing of the foam was not complete. Striations were plainly visible during and after mixing. The foam did not completely fill the mold and was unevenly distributed. The temperature peaked at a temperature of $302^O F$ at 7 minutes after pouring the foam. A total weight of 55.48 pounds of foam was made. Upon cooling the

foam was removed from the mold and cut up for examination. The foam was dense (4 lb/cu ft) and showed extensive areas of unmixed resin.

A second pour of foam was made into the conical mold. The rigid polyurethane foam (second formulation) was poured over the dummy. Cardboard baffles were placed around the mold to distribute the foam. The surface of the mold was covered with 1/2 mil mylar film and sprayed with silicone mold release. The foam expanded very nicely producing a fine uniform grain with a density of 2.3 lb/cu ft. The maximum temperature recorded in the foam was $260^{\circ}F$ which occurred at about 13 minutes after pouring. The total weight of the foam poured was 100.5 pounds. The foam contoured nicely to the dummy and would have provided good support to a human astronaut during re-entry and impact (Fig. 15).

A third experiment was performed foaming a dummy into a 7 x 3 x 2 foot box. The objective of this experiment was to see if it was possible to remove a dummy from foam with a cutting cord or wires. The cutting cord was 25 pound test 0.018 inch diameter nylon fishing line. The cutting wires were 0.018 inch, 0.033 inch, and 0.041 inch diameter stainless steel wire. The box was lined with 3 mil polyethylene sheet and sprayed with silicone mold release. The same formulation of foam was used as with the previous experiment. The foam filled the entire box with a total weight of foam

Fig. 15. Cross section of foamed vehicle with dummy

poured of 80 pounds. The density of the foam was 1.65 lb/cu ft with a very fine uniform grain. This was the best quality foam made during the program. The nylon cord and the 0.018 inch diameter stainless steel wire broke while trying to cut the foam loose from the dummy. The 0.033 inch and 0.041 inch diameter stainless steel wire successfully cut the foam but required considerable effort. Upon inspection the nylon cord was found to be embrittled by the foam.

The next series of experiments were concerned with foaming a dummy and man in the standing position. The 7 x 3 x 2 foot plywood box was partitioned off to form a 2.5 x 3 x 2 foot section. The dummy was placed in a 6 mil polyethylene box opened at the front and attached to the front side of the box. The compartment of the box was lined with 3 mil polyethylene and sprayed with silicone mold release. The foam formulation for the pours 4, 5, 6, and 7 are given in the materials section.

A man was foamed-in-place in the standing position similar to the dummy. The man was equipped with long underwear, ventilated underwear, coveralls, three pair of socks, and combat boots. An air line from the laboratory air supply was connected to the ventilated underwear. The pressure was regulated

to 20 to 30 psi. The man was equipped with a breathing mask and bottled air supply. The density and weight of foam poured is given in the following table.

Pour Number	Weight of Foam Pounds	Density of Foam Pounds/cu ft
4	20. 1	2. 6
5	23. 7	2. 7
6	24. 0	2. 43
7	24. 0	2. 28

No temperature readings were taken of the dummy being foamed. The temperature in the foam near the man's calfs was recorded. The maximum temperature in the foam was 160°F. The dummy was easily removed from the foam for all three pours. The man felt no discomfort although he did feel some slight pressure on his legs. The man was able to readily step out of the foam.

The next series of experiments were the foaming of a dummy and a man lying horizontal in the 7 x 3 x 2 foot plywood box. Both the dummy and man were suspended in the box in a sheet of 8 mil polyethylene. The box was lined with 3 mil polyethylene and sprayed with teflon spray and then silicone mold release spray. This was used to reduce the friction between the foam and the polyethylene.

The dummy and the man were extensively instrumented with thermo-couples along with strategic locations on the inside of the box. A total of sixteen thermocouples were used. The man was equipped with, as before, underwear, ventilated underwear, coveralls, socks, and combat boots. In addition, he wore a sweat shirt with hood and a flying helmet. The ventilated underwear was connected to the laboratory air supply and regulated at 20 to 30 psi. The man was equipped with an oxygen mask and air supply.

The formulation for the 8th and 9th pours are given in the materials section. The weight of the foam for the pour with the dummy was 53.4 pounds. The density was 2.5 lb/cu ft. The weight of the foam for the pour for the man was increased to 73.4 pounds since the previous pour did not cover the dummy.

Fig. 16 shows the man encapsulated in the foam. The man was easily able to extricate himself from the foam. The man was restrained very well in the foam. The temperature recording for a portion in the foam and on the man is shown in Fig. 17. The maximum temperature on the neck of the man was 90°F. The maximum temperature in the foam under the man's head was 149°F. The maximum temperature in the foam exceeded 200°F (maximum value on recorder). The man felt no discomfort while immersed in the foam.

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With the present concept of bagging a man in foam, there appears to be no problem in foaming a man in. The Isotron 113 lowers the temperature of the foam quite well. The man is not subject to excessive temperatures. The foam does not exert excessive pressure on the man. It should be noted, however, that the man wore a hard flight helmet. If this is not done, sufficient pressure may be exerted on the head of the man to cause a severe headache. [5, 6]

Fig. 16. Subject being encapsuled in foam
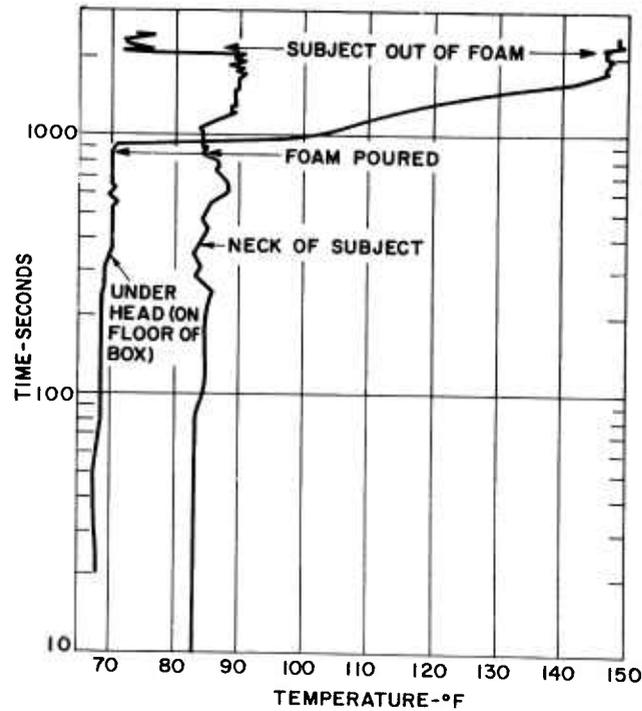
Fig. 17. Temperature vs time

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Symbols

A = Reference Area for Ballistic Vehicles, sq ft
C_D = Drag Coefficient
e = Eccentricity
h = Orbit altitude, nautical miles
R_N = Nose Radius, feet
V = Velocity, feet/sec.
W = Weight, pounds
β = Angle of retro-thrust, degrees from rearward horizontal

Subscripts

I = Retrograde Impulse
re = Re-entry
s = Satellite

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NAVY INTERESTS IN FOAM MATERIALS

Warren S. Bourn

Introduction

Unlike our sister services, the Navy is not confined to operating merely on the surface of the earth or in the air above it; we must also operate in the depths of the sea. These requirements to be "at home" in three media make us interested in practically every application of cellular materials as well as probably many uses that haven't been thought of yet. I shall, therefore, not attempt to detail all of the naval foam applications, but rather touch on our larger uses and some of the more interesting problems which we foresee at this time.

Our uses of foam can be broken down into four main areas: buoyancy, resilience, insulation, and void filling.

Buoyancy

Probably our greatest use of foam is in buoyancy applications. All of our utility and personnel boats such as the twenty-six foot whaleboat shown in Fig. 1 must be able to remain afloat while fully loaded and awash. To obtain this, void areas are filled with low density foam. For years, pre-formed cellular cellulose acetate (CCA) or polystyrene foam was cut and fitted into the voids as shown in Fig. 2. However, because it is so much easier to apply, more and more two pounds per cubic foot density foam-in-place polyurethane conforming to Specification MIL-P-21929 is being used. For the same reason, six to eight pound polyurethane is also taking the place of six to eight pound CCA in buoyancy areas and as a core material in bulk-heads of utility and personnel boats made of reinforced plastics.

As a support for assault units we are using the "UDT Swimmer," an unsinkable fourteen foot plastic boat. It has a five foot beam and can carry eight men. It is made of two pound polystyrene foam plastic cut to size and shape and covered with reinforced epoxy resin. Another fourteen foot boat for assault units is being evaluated. We call it our "instant boat." It is foam inflated and is a supplement to the familiar CO_2 inflated rubber boat which unfortunately has been too vulnerable to bullets. The new unsinkable boat can be taken or carried as a pack to the area where it is needed and the open weave, synthetic fabric form unfolded. The fabric form has six sewn com-partments, each with a zipper running along its length. The components
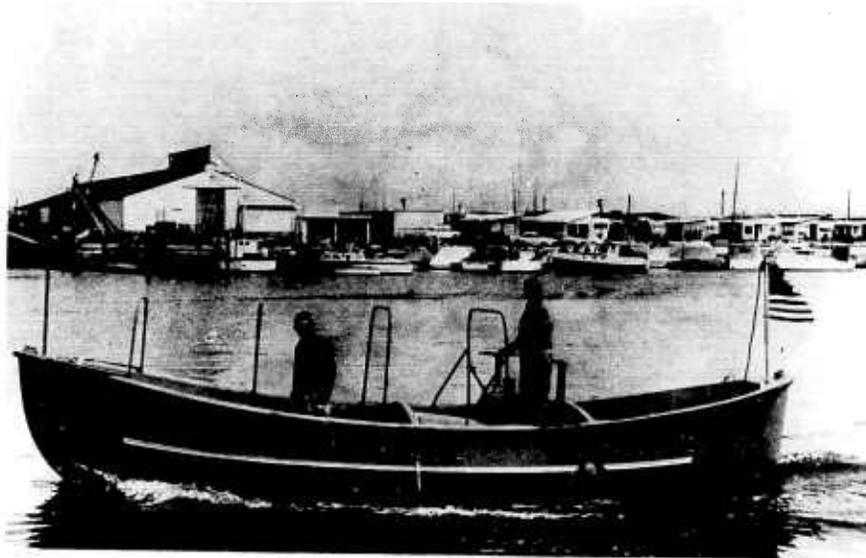
Fig. 1.   26' Whaleboat
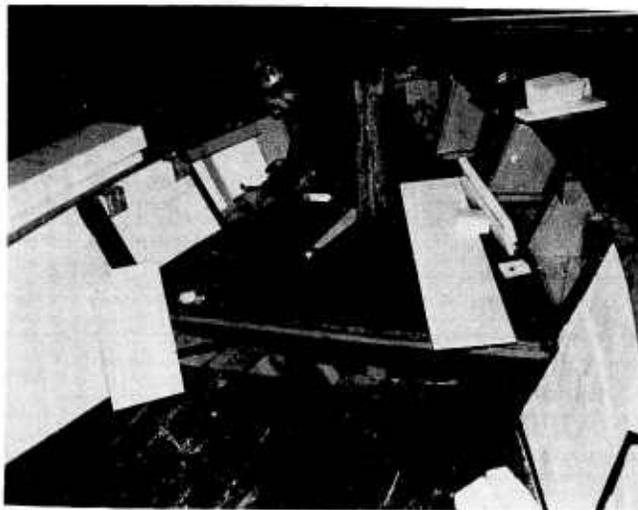
Fig. 2.   Fitting prefoamed foam for buoyancy in
a 28' utility boat

of a two pound polyurethane foam are mixed and poured along the length of each compartment and the zipper closed.   There is a complete foam kit for each compartment.   From start to finish it only takes twenty minutes for one man to have the boat ready to put into the water.   The inflated boat is shown in Fig. 3.   It has a three foot beam and can carry a 500 pound payload.

Fig. 3. Foam inflated 14' assault boat

Foam is also being used in many of our buoys where its use eliminates the problem of maintaining leakproof, airtight compartments and permits the use of a lighter weight, less expensive structure. In our minesweeping operations, a single reinforced epoxy plastic buoy is used to support acoustical minesweeping equipment at a prescribed depth. It is seventeen feet long by two and one-half feet in diameter and filled with two and one-half pound polystyrene foam. Polystyrene foam is also being used in plastic "Dan" buoys to show areas that are to be swept or have been swept clear of mines. These are one foot in diameter and one and one-half feet long. The O-type, size 5G minesweeping float, Fig. 4, used to support minesweeping cable, is made of reinforced plastic and is filled with four pound polystyrene foam. It has a major diameter of one and one-half feet and is about seven feet long.

Large twelve foot diameter plastic floats, six feet long, using two pound polyurethane core material are being evaluated as anchor floats for seaplanes and fuel lines.

In probably the largest single buoyancy application to date, the Norfolk Naval Shipyard poured 40,000 cubic feet of two pound polyurethane foam below the decks of an obsolescent destroyer to make it unsinkable. It will be used as a target ship, Figs. 5 and 6 show some of this installation.

In clothing, a flexible, unicellular polyvinyl chloride (PVC) foam is being used for both insulation and buoyancy as a removable liner in extreme cold weather jackets. Two 1/8 inch thick layers of foam are used in the jacket body and one layer in the sleeves. The foam conforms to Type 1, Class III or Class IV of Specification MIL-P-12420. This foam was selected for use because of its good drapability and cold temperature flexibility properties. The jacket is of particular value for men working in exposed areas who may fall or be knocked overboard by heavy seas. The foam would keep

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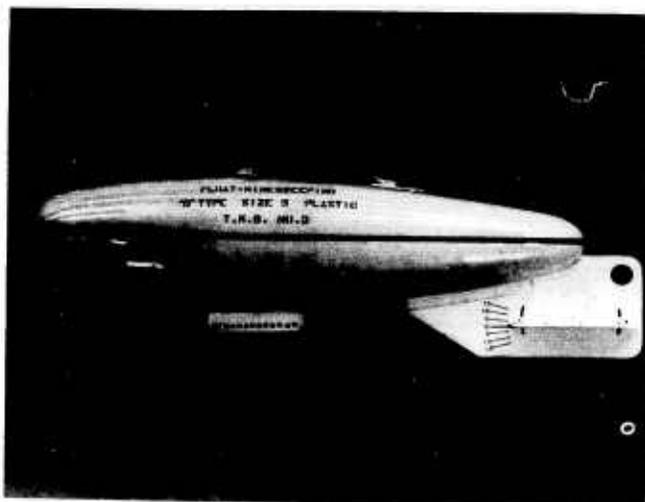
Fig. 4. "O" type plastic minesweeping float

Fig. 5. View of foam through hatch on unsink-
able destroyer
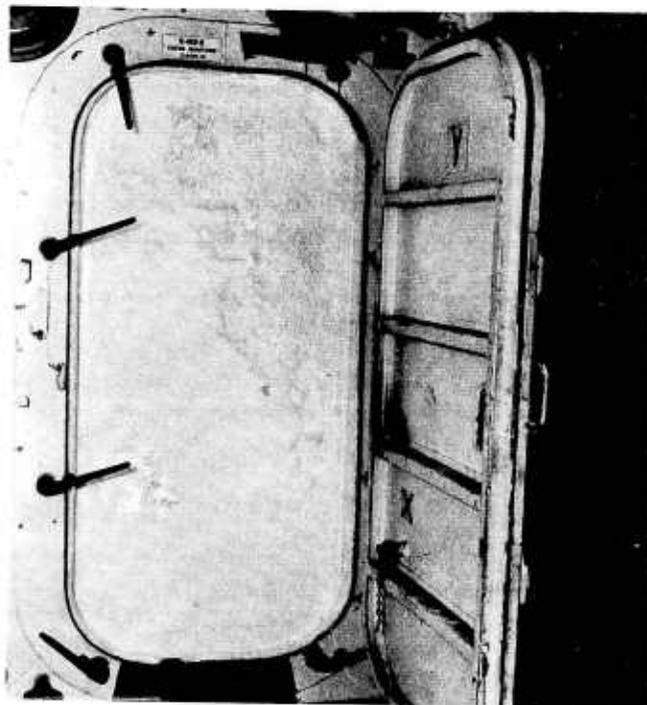
Fig. 6. View of foam through door on unsink-
able destroyer

him afloat indefinitely. In more routine buoyancy applications, PVC foam
conforming to Specification MIL-P-15280, Type 1A is used in life preserver
work vests, and PVC foam is also used in conventional life saving buoys
(rings).

Most of our research work on buoyancy foam applications is concentrated
on their development for deep submergence applications. We need foams that
will retain their buoyancy after long submergence at water pressures up to
10,000 psi. It would be used for static buoy type applications and buoyancy
compartments for research vehicles where the foam is the only means pro-
vided to bring the vehicle back to the surface. At the present time, the best
choice of a foam appears to be a forty to forty-five pound syntactic with an
epoxy matrix using either phenolic or glass spheres as a filler—glass spheres
being used for the greater depths because they give a foam with lower water
absorption and higher strength.

Resilience

Our greatest use of foam for its resilient properties has been in
mattresses and furniture padding, replacing cotton felt. The cotton rapidly

became mat ed and lumpy and was practically worthless after becoming wet. The use of foam has eliminated these problems, and where cotton felt mattresses lasted only about eighteen months, foam mattresses will last more than ten years—some of the foam mattresses originally installed fifteen years ago are still in use. The foam now being used conforms to Specification MlL-R-20092, Class lll. Less expensive PVC mattresses have been tested, but they have not been able to pass the fire resistance requirement which basically restricts the foam to a polychloroprene. Polyurethane mattresses are also being investigated.

To reduce crew fatigue, a flexible PVC foam with a vinyl impregnated glass cloth covering is used as a deck covering in engine rooms of diesel powered submarines. A similar matting material covered by Specification MIL-M-910 is also used to reduce fatigue at watch stations. PVC foam is also being used as a shock liner in crash helmets, while polychloroprene is used as cushioning pads on earphones.

Many foams are being used to provide shock protection. To protect sensitive electronic equipment in missiles during "blast off," the equipment is being potted in polyurethane foam. Silicone foam is used where the temperature extreme may be from -65° to 350°F. Many airborne electrical components are potted in epoxy foams. Both rigid and flexible foams are being used for packaging sensitive equipment for shipment. Normally we do not specify what foam shall be used. The only criterion being that the material being shipped arrives at its destination in a satisfactory condition. The supplier can use any foam he chooses.

Insulation

In our insulation applications, both foam-in-place and sheets of pre-formed rigid polyurethane foam are being used on decks over ballast tanks to prevent condensation of water on the deck and also over hot areas such as an engine room to make the compartments above habitable. A ten pound per cubic foot foam, 5/8 inch thick, with a minimum compressive strength of 100 psi has been satisfactory for this application. Where required, the foam is covered with a trowel on deck covering or vinyl asbestos tile.

A large volume use of foam for insulation is the insulation of submarine hulls. About 40,000 sq ft of hull insulation is used on a Polaris type submarine. Flexible foam conforming to Specification MIL-P-15280, Type ll, Form ll is now used as an alternate to cork for submarine hull insulation. The requirements of the specification characterize a PVC foam which has better fire resistance and is easier to install than cork. The chief disadvantage is material cost, the PVC being about five times the cost of cork. We are currently working on the development of a rigid two pound density, halocarbon blown, preformed polyurethane system. Because of its superior insulating properties, only a 5/8 inch thickness is required to give the same insulation as the 1 inch thick PVC or cork. Use of a thinner insulation

combined with a lower density—two pounds versus five to ten pounds for PVC and cork—should result in a weight saving of about 18,000 pounds per submarine. The material cost is much lower than the cost of PVC foam. A disadvantage will be the need for a covering on the exposed side of the polyurethane for abrasion resistance. Flexible PVC foam would still be used in uneven contoured areas where cementing of rigid foam would be difficult.

Foam-in-place polyurethane is being tried as insulation for the walk-in refrigerator space aboard several surface ships, replacing fibrous glass insulation. Although less fire resistant, the unicellular foam will not become saturated with water and become matted like the glass insulation. Since the polyurethane has better insulating properties, the refrigerator space can also be redesigned to utilize thinner walls and thus provide more usable space. A two pound density foam is used in the walls and ceiling and four pound density in the floor. The 1600 pounds of foam liquid required for the installation are poured through filler holes into the cavity between the preassembled inner and outer liners of the box. The pouring holes are then cemented or welded closed.

There is extensive use of flexible foam, essentially PVC, conforming to Specification MIL-P-15280, Type II as pipe insulation for applications up to 180°F. The chief application is on cold water lines as an anti-sweat material replacing cork. It only weighs about 60 per cent as much as cork, is easier to install, and requires no lagging. It is either slid whole over the pipe before the pipe is installed or it is slit on one side and then sandwiched over the pipe and the slit cemented together again for piping that is already in place. Trial applications of rigid preformed two pound polyurethane foam are under way on chilled water and refrigeration lines on several ships because of the lower price and better insulating properties of the polyurethane. A two pound preformed polyurethane is being used this "winter" for the first time in the antarctic to keep pipe lines from freezing.

Void Filling

Our largest use of foam for filling voids is in areas outside the pressure hull of our submarines to provide both structural support and buoyancy. By providing structural support a lighter weight, less expensive structure can be used. By providing buoyancy the submarine can take on a greater payload. In our newer submarines these areas amount to about 1000 cubic feet and include such areas as the rudder, diving plane, stabilizer, and transition ring. The density of the foam should be as low as possible, but it must still have low water absorption and sufficient strength to resist the high water pressures encountered. Previously, wood (pine) was cut and laboriously fitted in these voids. Hot pitch was then pumped into the void to coat the wood and reduce its water absorption. A pourable forty pound density, phenolic sphere filled polyester resin is now being used. This obviously is easier to apply than the wood, and it gives more assurance of intimate contact and uniform support to the steel plates. The Portsmouth Naval Shipyard pioneered the use of the polyester resin material in submarine structural voids. The approved

formulation for our present material is five parts resin to one part phenolic filler. A performance type specification is being prepared to cover this material. It will also cover polyurethane foam for use in less rigorous pressure applications.

Future submarines will be diving to greater depths, and buoyant material must be found to withstand the greater pressures that will be encountered. The New York Naval Shipyard Material Laboratory is actively engaged in the development and evaluation of foams for this application.

A rather unique application we are going to try soon is probably typical of the many applications we have yet to discover for foam. We intend to fill completely several sea chests (intake water lines) of a ship in our reserve fleet with two pound foam-in-place polyurethane. This is a trial installation to try to keep water leakage to a minimum. When the ship is reactivated the foam will be burned out with a torch.

Summary

I hope that the examples I have given you of some of our current and intended uses of cellular materials in the areas of buoyancy, resiliency, insulation, and void filling have given you an idea of the Navy's broad interest in these materials. I have not been able to cover all the Navy's requirements in this field. In short, however, if it floats and absorbs energy, we are interested in it.

RIGID FOAMS FOR INSULATION APPLICATIONS

Fred O. Guenther

Introduction

Cellular plastics represent a broad spectrum of materials, almost unlimited in application because of the wide range of properties available in the solids and gases of which they are composed. Equations presented graphically in Fig. 1 were developed which relate composition by weight and volume to densities of the cellular material, solid and gaseous components.[9] The gas component is of relatively low density, strength, and thermal conductivity, and represents the major portion by volume. The solid component is of relatively high density, strength, and thermal conductivity, and represents the major portion by weight. The low thermal conductivity and low density of cellular material are attributed to the large volume fraction of gas present in the structure. The high strength to weight ratio in a cellular material is achieved by an efficient use of the strength-giving solid component as illustrated by consideration of the stiffness factor.[9] Stiffness factor occurs in all analysis of deflection of structures and is a frequent design limitation.
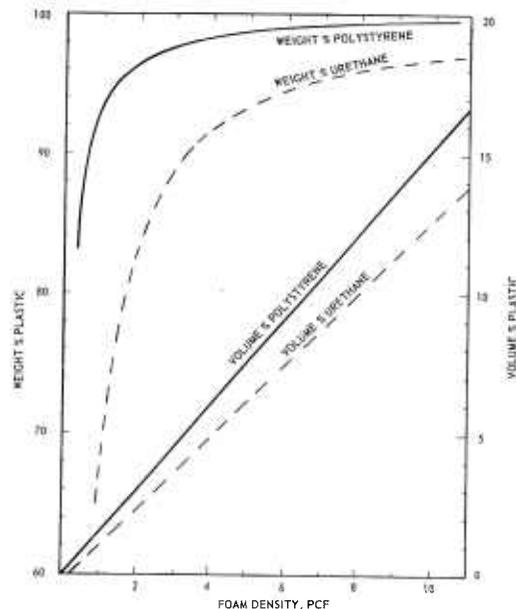
Fig. 1. Composition versus density

By expanding a sheet of solid polystyrene, sixty thousandths of an inch thick, to a cellular material two inches thick with a density of 2 PCF,* it is possible to obtain a stiffness factor equal to that for sixty thousandths thick steel, at a considerable savings in weight (Table 1).

The low thermal conductivity associated with cellular materials is illustrated by expanding a solid urethane to a cellular material with a density of 2 PCF and filling with a gas of low conductivity. The heat loss through the urethane is now reduced by a factor of 480 (Table 2).

Some properties of cellular materials are considerably lower than those expected by simple calculation based on volume fraction solid present.

* PCF = Bulk density in pounds per cubic foot.

TABLE 1

Stiffness Factor, EI

	Polystyrene	Styrofoam	Steel
Size, inches	0.06x2x12	2x2x12	0.06x2x12
Density, PCF	65.5	2.0	489
Modulus of elasticity (E)	5×10^5	1×10^3	3×10^7
I (Flat direction)	2.2×10^{-4}	8	2.2×10^{-4}
EI (Flat direction)	110	8000	6600

TABLE 2

Thermal Conductivity

Material	Thickness (inches)	Thermal Conductivity (K_{75})	Thermal Loss (Btu/hr, ft^2, °F)	Ratio
Solid urethane	0.042	1.0	24	480
R-11 filled cellular urethane	2.0	0.1	0.05	1

The moisture vapor transmission rate of cellular polystyrene is approximately one-sixth of the calculated. The values for urethane are one-sixtieth of the calculated, illustrating how sensitive this property is to the slightest imperfections in cells (Table 3).

TABLE 3

Moisture Vapor Transmission (MVT)

Material	Thickness, Inches		Transmission Rates at 77°F $\frac{cc, \ mm}{sec., \ cm^2 \ cm \ Hg}$		
			Solid	Cellular	
	Solid	Cellular	Observed	Calculated	Observed
Polystyrene	0.058	2.0	1.2×10^{-6}(20)	41×10^{-6}	240×10^{-6}
Rigid urethane	0.042	2.0	0.11×10^{-6}(10) 0.1×10^{-6}(19)	5.2×10^{-6}	240×10^{-6}

The tensile strength of cellular rubber, styrene, and urethane fall in the range of one-fourth to one-tenth of the calculated (Table 4). Gent has treated this subject mathematically for compression, tear, and tensile of cellular flexible rubber.[7,8] The equations he developed were in approximate agreement with the experimental data presented.

TABLE 4

Tensile Strength

| Material | Tensile Strength, Psi | | |
| | Solid | Cellular, 2 PCF | |
		Calculated	Observed
Urethane	$10,000^3$	210	25 to 50
Polystyrene	7,000	200	25 to 50
Natural rubber[3]	relative values	1	0.1

The equations for the basic relationship between cell size, cell wall thickness, density of cellular material, density of solid, and gaseous components were developed.[9] The values calculated for polystyrene-air and urethane-R-11* are presented graphically (Fig. 2). A uniform cell size and cell wall thickness were assumed. This represents an oversimplification of the situation, but the equations are helpful to obtain an estimate of the relationship. For example, a cubic inch of a polystyrene foam with a cell size of 0.04 inch, which may be represented by Styrofoam, has 75 square inches of cell wall with a thickness of 4×10^{-4} inches. If the cell size is reduced to 0.004 inch, typical of some expanded bead polystyrene foam, the area of the cell wall is increased to 750 square inches. The thickness is now only 4×10^{-5} inches. This illustrates the high demand placed on the ability of the solid component to efficiently form thin films.

Thermal Conductivity of Cellular Materials

Introduction

The apparent thermal conductivity of a cellular material is the sum of the effect of heat transfer by three mechanisms: conduction, convection, and radiation. Conduction occurs in the solid and gas and is the transfer of heat energy or kinetic energy due to microscopic motion of molecules. In plastics or high molecular weight polymers, the energy is transferred by movement or oscillation of chain segments or part of a polymer molecule. Convection is the transfer of heat by microscopic motion and is limited to liquids and

* R-11 = Refrigerant-11 = Fluorotrichloromethane

gases. Convection is disregarded usually in gas pockets less than one-eighth inch in size.[13] Radiation is the transfer of energy between two objects at different temperatures by means of a flow of massless particles, photons. Photons are not part of or associated with the working substance. Radiation occurs readily through a perfect vacuum. It is more generally associated with heat loss through gases, but can become appreciable through very thin films.

Losses due to radiation in a cellular plastic are dependent not only on temperature, but on gas fraction, shape, size, and orientation of the cells, and the emissivity of the cell wall. The thermal conductivity unit used in this paper is Btu, inch/hour, square foot, $^\circ$F at a mean temperature of 75°F and is frequently written as K_{75}.

Fig. 2. Cell wall thickness versus cell size as a function of foam density.
Polystyrene - Air Foam _____
Urethane - R-11 Foam _ _ _ _ _

Calculation of Thermal Conductivity

There are a number of equations in the literature for calculating the thermal conductivity of cellular materials.[4, 6, 9, 12, 18, 22, 23, 26, 27, 29] The equations vary in complexity and recently some of them were compared.[9] The application of one of the simplified approaches is illustrated by the calculation of the effect of density on a wide variety of cellular plastics filled with air, Fig. 3. At a density of 2 PCF, most of the plastics considered fall in the narrow thermal conductivity range of 0.205 ± 0.010. The two exceptions to this are polyethylene and Kel-F. Polyethylene represents a solid plastic of low density and exceptionally high conductivity and, therefore, gives a cellular material of higher conductivity. Kel-F represents a high density solid plastic of low conductivity and, therefore, yields a cellular material of lower conductivity. At the lower densities the effect of solid component is of minor significance compared to cell size and composition of gaseous component. As the density increases, the contribution of the solid component becomes of greater importance.

Observed Effect of Density

The observed relationship between thermal conductivity and density was presented[9] (Fig. 4). All insulations have a minimum in thermal

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Fig. 3. Calculated thermal con-
ductivity of cellular plastics
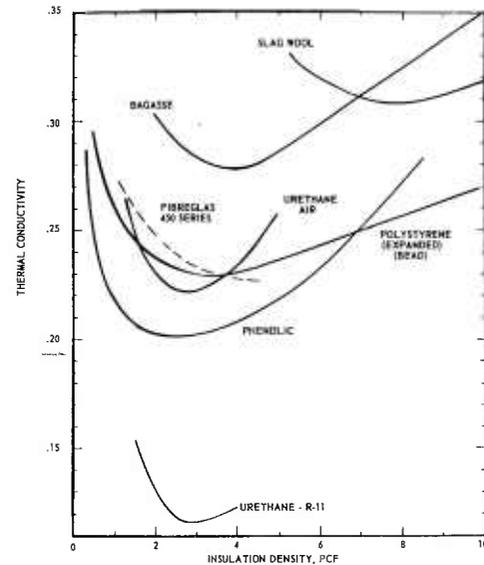
Fig. 4. Thermal conductivity of
insulations versus density

conductivity at some density, in disagreement with the straight line relation-
ship calculated. The location and shape of the curve around the minimum
vary for different materials. The phenomenon is dependent on cell size, gas
content, radiation coefficient of solid component, and temperature. Some of
the more complex equations in the literature have tried to factor in these
variables. The number of constants that must then be obtained by experiment
or approximation greatly reduce the usefulness of the complex equations.

Contribution of Radiation and Convection

The contribution of radiation and convection to the apparent thermal
conductivity of glass fibrous insulation was studied by Verschoor and
Greebler[27] (Fig. 5). The contribution of convection and radiation becomes
appreciable at densities below 2 PCF. At a density of 0.5 PCF, radiation
contributes 32 per cent and convection 15 per cent of the observed conduc-
tivity. The breakdown of conductivity of fibrous glass at 150°F was compared
to the average curve of expanded polystyrene bead at 75°F. The contribution
of convection and radiation was obtained by subtracting the calculated gas and
solid conduction from the observed conductivity. The similarity in the
behavior of the two materials is apparent.

Effect of Cell Size

The effect of cell size on thermal conductivity is presented for three
cellular materials (Fig. 6). The slope of the straight line formed by plotting

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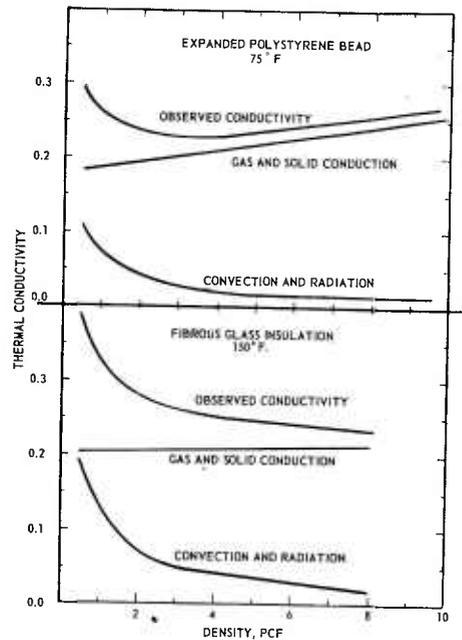
Fig. 5. Contribution of convection and radiation to thermal conductivity

Fig. 6. Effect of cell size

conductivity versus cell size depends on the radiation coefficient of the solid component. This is in agreement with the equation presented by Topper.[26] If the radiation coefficient of the structure changes with cell size, the relationship may then not be as simple as that presented. However, for the cell size range presented in Fig. 6, the straight line relationship is in good agreement with the experimental data.

The change in thermal conductivity per change of 0.01 inch cell size was 0.016 for styrene-air system and 0.021 for epoxy-R-11 system. The value of 0.038 for urethane-R-11 appears to be unreasonably high. The possibility exists that the per cent open cell varied in the experimental samples. The thermal conductivity of this type of foam is directly related to the open cell content[14] (Fig. 7). A change of 15 per cent in open cell content in the cell size range covered would account for the high value. The data presented show the need for reporting cell size with thermal conductivity data as well as open cell content.

Effect of Cell Orientation

The effect of cell orientation is illustrated by the difference in thermal conductivity when heat flow is parallel or perpendicular to foam rise (Table 5).

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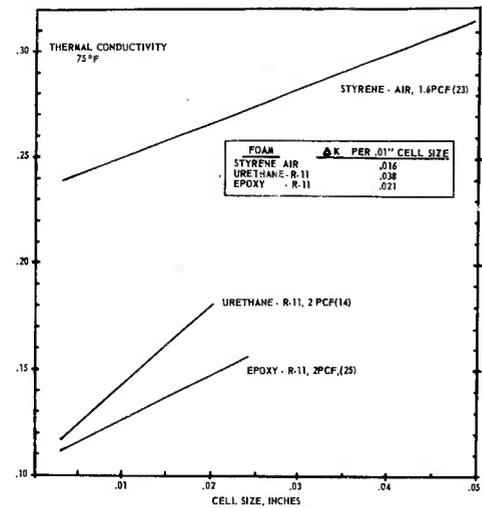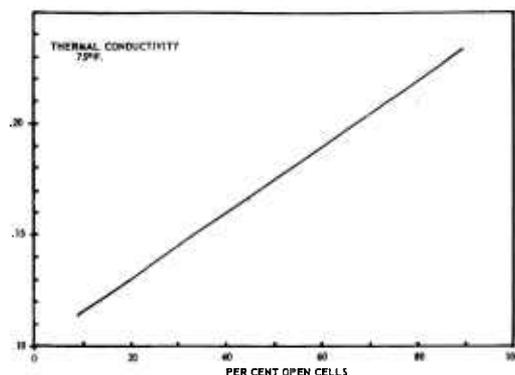
Fig. 7. The effect of open cells on
thermal conductivity of urethane
R-11 foam[14]

TABLE 5

Cell Orientation and Thermal Conductivity

Sample	Density (PCF)	Thermal Conductivity, K_{75}		
		Perpendicular	Parallel	Difference
Molded cube	1.6	0.150	0.162	0.012
	1.5	0.150	0.158	0.008
Free blow cube	2.2	0.114	0.128 to 0.136	0.012 to 0.021
Free blow cube	2.1	0.129 to 0.132	0.149	0.017 to 0.022
Free blow cube[11]	2.0	0.141	0.178	0.037
		0.140	0.172	0.032

Cells in urethane foam are usually elongated in the direction of foam rise.
The conductivity measured parallel to foam rise varies from 0.01 to 0.04
units higher than the values obtained perpendicular to foam rise. The amount
of difference observed would be dependent highly on the processing conditions,
geometry of molded part, and fluidity of the rising foam.

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Effect of Gaseous Component

The conductivity of a gas filled insulation is a direct linear function of the conductivity of the gas. Experimental data are available in the literature for gas filled fibrous glass systems.[16, 27, 28] The data (Fig. 8) obtained by Wilson[28] covers a wide range from low conductivity gases of high molecular weight, such as chlorofluoralkanes, to gases of high conductivity and low molecular weight, such as hydrogen.

The relationship in cellular plastics is illustrated by comparing observed and calculated values for polystyrene and urethane foam[9] (Fig. 9). The solid lines in Fig. 9 are the values for polystyrene. The dashed lines are for urethane. The difference between the observed and calculated lines is due to the failure of the equations used to apply the correction for cell size. As was observed with fibrous glass, a linear relationship exists between conductivity of the gas and the cellular plastic.

Effect of Aging on Thermal Conductivity

The effect of age on the thermal conductivity of cellular urethane and epoxy containing low conductivity gases has been reported by a number of workers.[10, 11, 14, 17, 21, 25] Typical of the results[10] are those presented in Fig. 10. These results are of particular interest because they show the effect of both temperature and humidity on the aging behavior. The authors[10] present permeability values for various gases through solid urethane film. They attribute the major change in conductivity to the inward diffusion of atmospheric gases.

Harding treated accelerated aging data statistically and determined the effect of time, foam density, cell volume, open cell content, and direction of heat flow.[11] The importance of measuring and reporting these variables was emphasized. The data were fit to a general hyperbolic equation.

Effect of Temperature

The relationship between thermal conductivity and temperature approaches linearity over a considerable temperature range for a number of air and carbon dioxide filled systems (Fig. 11). The temperature coefficient for the cellular material is two to three times that observed for the gas alone. The data indicate the significance of radiation losses, which are highly temperature dependent.

The effect of temperature on the thermal conductivity of a cellular urethane filled with a gas, R-11, which condenses at 75°F is complex (Fig. 12). The effect of the composition of the gas mixture plays an important role in the shape of the curve. Experimental data and an approach to calculating the effect for a number of different gases were presented by Patten and Skochdopole.[21]

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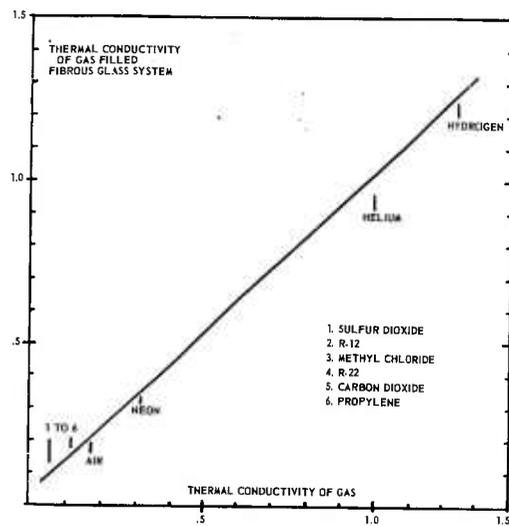
Fig. 8. Thermal conductivity of gas filled fibrous glass systems[28]
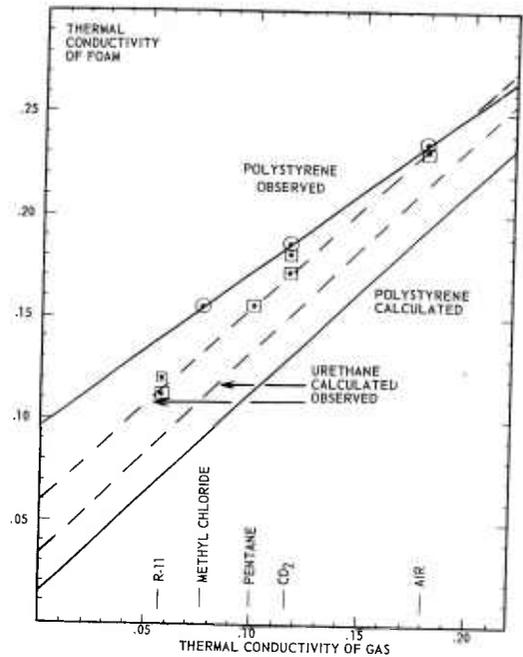
Fig. 9. Effect of gaseous component on thermal conductivity
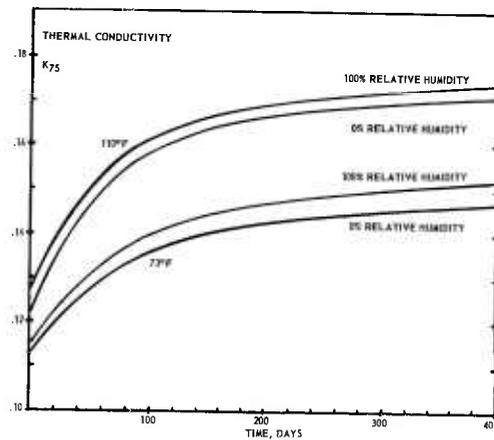
Fig. 10. The effect of temperature and humidity on the aging of R-11 filled urethane foam[10]
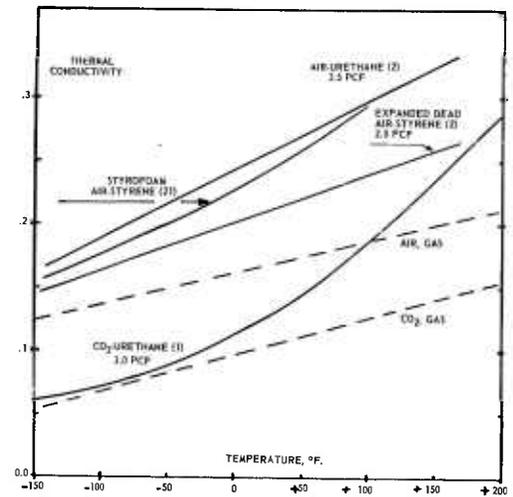
Fig. 11. Effect of temperature on thermal conductivity of cellular plastics

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If only R-11 is present, the effect of temperature is a linear function of conductivity. The cellular material has a temperature coefficient 2.5 times that reported for the gas. As the R-11 is diluted with air, a family of complex curves results, depending on the extent of the dilution and the partial pressure of R-11. The thermal conductivity of the R-11 and air system should never go above the values expected for the urethane-air foam as illustrated by the top line in Fig. 12. This phenomenon again emphasizes the need to report cell size, orientation, and age of foam when reporting thermal conductivity values.

The Effect of Pressure

The effect of gas pressure on the thermal conductivity of fibrous glass insulations has been studied.[24,27,28] The data of Wilson[28] are presented in Fig. 13. The important consideration is the relationship between cell or pore size and mean free path of the gas. The mean free path of a gas is dependent somewhat on structure and temperature, but is directly related on a log-log scale to the gas pressure. The thermal conductivity of a porous material is affected only slightly by gas pressure until the mean free path of the gas is smaller than the pore size. When this occurs, the gas conductivity becomes a direct function of gas pressure, as illustrated, until the total conductivity is lowered to the contribution from the solid and radiation.

Min-K is an example of a commercial insulation with a pore size approximately equal to the mean free path of air at atmospheric pressure.
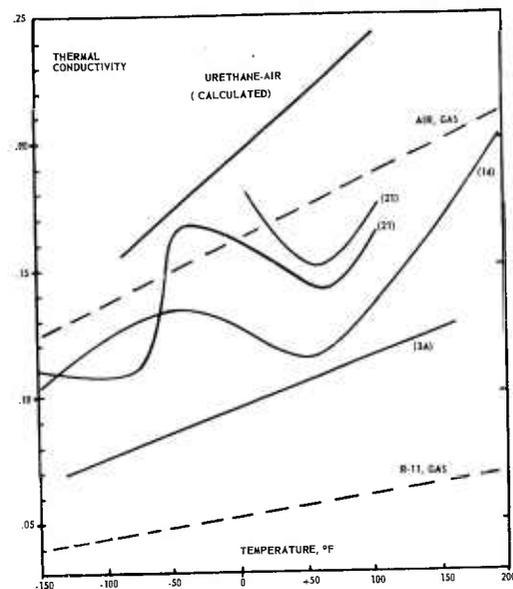
Fig. 12. Effect of temperature on thermal conductivity of urethane R-11 foam
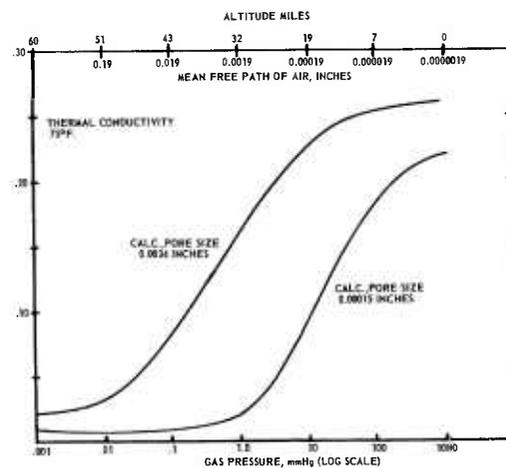
Fig. 13. The effect of pressure on thermal conductivity of fibrous glass insulation (density 10PCF)[28]

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At an altitude of 10 miles, the thermal conductivity is reduced to 1/2 of its original because the mean free path of the gas is now larger than the pore size.

Limited work on the effect of gas pressure in cellular plastics has been reported by Kropschot.[15] Another reference[5] is given by a Russian worker who reported the observation that the conductivity of a foam at 0.1 mm Hg pressure was equal to that of the gas alone at a pressure of 0.00001 mm Hg. These data indicate that the pore size of the foam used was in the range of 0.02 inches.

The data reported were obtained with open cellular or fibrous materials. If similar results are expected with closed cell foams, adequate time must be allowed for the pressure in the cells to come to equilibrium with that recorded on the gauge.

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FLAMMABILITY OF RIGID URETHANE FOAM

Donald W. Mitchell and Edwin M. Murphy

Flammability is a primary factor affecting the underground application of rigid urethane foam in mines and tunnels. The descriptive terms used by the plastics industry—"flame retarded," "nonburning," or "self-extinguishing"—are relative and inadequate. The mining industry requires assurance that foam resists flame penetration to combustible substrate, that flame spread through foam-covered areas is prevented, and that foam does not lose its desirable properties when it is exposed to heated air currents.

This paper summarizes research conducted at the Experimental Coal Mine of the Bureau of Mines on the flammability characteristics and on methods for controlling the burning of urethane foam. The studies show that optimum resistance to flame penetration is obtained from a formulation containing a reactive (chemically bound) phosphorus polyol, a halide, a highly functional low-equivalent-weight sucrose polyether polyol, and a highly aromatic polyisocyanate. When foam made from the recommended polyisocyanate and polyether is exposed to flame or heat, a nonmelting intumescent char develops that insulates the interior portions of the foam from heat and flame and retards penetration. The presence of phosphorus increases the strength of the char and raises the auto-ignition temperature of the solid foam components; the halide inhibits burning, presumably by breaking the chain reaction necessary for sustained combustion and by reducing the flame temperature.

In mining applications, the prevention of flame spread is as important as is resistance to flame penetration. Flame spreads across a foam surface when heat from adjacent burning expands the gas in the foam, causing the cell walls to disintegrate into minute organic particles that provide the fuel necessary for combustion. Flame inhibitors incorporated in the foam do not prevent flame spread because the temperature of the flame is generally too low to produce instantaneous intumescence and to activate the inhibitors. Flame spread can be prevented by a coating of water-emulsion latex paint, alkyd paint, or sodium silicate on foam having a flammability index number of 15 or less. This number is obtained by dividing the flame spread index from ASTM Procedure E 162-60T by the flame penetration time from a newly developed Bureau test.

Foam Flammability

The flammability of urethane foam depends on chemical formulation, foam-application equipment and techniques used, and the atmospheric and

sprayed surface conditions. The data in Table 1 and visual observation of the foams during testing indicate that:

1. Foams made from highly aromatic polyisocyanate char without melting at flame heat, whereas similar foam made from tolylene diisocyanate (TDI) melts and transmits flame readily (lines 1 and 2).

2. Flammability increases with decrease in density (lines 2, 3, and 4).

3. Foams made with a highly functional, low-equivalent-weight sucrose polyether polyol swell and develop an intumescence that inhibits flame penetration. Foams from high-equivalent-weight sucrose polyether polyols develop inadequate intumescence and consequently have higher flammability index numbers (lines 5, 6, and 7).

4. For adequacy, the foams must contain a reactive phosphorus polyol (lines 2 and 5).

5. Flammability is reduced by increasing the roughness and irregularities on the foam surface (line 8).

6. Flame penetrates readily through foams having poor cell structure; these foams have high flammability index numbers [(lines 9(a) and 9(b)].

7. Unreacted isocyanate radicals in foam increase its flammability (line 10). The ignition temperatures of foams studied with and without excessive unreacted isocyanate radicals present ranged from 400° to $600^\circ F$ and from 950° to $1,200^\circ F$, respectively.

The effect of type of flame inhibitor is shown in Tables 2 and 3. Without phosphorus in the foam, antimony trioxide and chloride-containing inhibitors have little effect on flame penetration (lines 2 and 3, Table 2); and presence of phosphorus increased flame penetration time from 1/2 to 10 minutes, the extent of increase depending on the phosphorus content (lines 1, 4, and 7).

The effectiveness of the phosphorus content presumably results from its increasing the autoignition temperatures of the foam and the strength of the char; chloride has no effect on the autoignition temperature or char strength (Table 3).

A phosphorus-based inhibitor containing active hydroxyl radicals is recommended for foam used in mines because excessive deformation occurs when foam containing a nonreactive inhibitor is subjected to $450^\circ F$ for 1 hour (Table 4).

Foam flammability can be reduced significantly by use of a bromine-containing fluorinated hydrocarbon, $CBrF_2$, as part or all of the blowing agent

TABLE 1

Factors Affecting Foam Flammability

Line No.	Iso- cyanate[a]	Foam Formulation Sucrose Polyether Polyol Hydroxyl, No.	Flame Inhibitor	Density[b] Lb Per Cu Ft	Foam Quality	Flamma- bility Index No.
1	TDI	510	None	3	Good	4,200
2	MDI	510	None	3	Good	400
3	MDI	510	None	2-1/2	Good	470
4	MDI	510	None	2	Good	1,500
5	MDI	510	10% P[c]	3	Good	10
6	MDI	460	10% P	3	Good	15
7	MDI	380	10% P	3	Good	210
8	MDI	460	10% P	3	Good surface irregular	10
9(a)	MDI	460	10% P	3	Poor cell[d] structure	300
9(b)	MDI	460	10% P	3	Poor cell[e] structure	500
10	MDI	460	10% P	3	Contains unreacted isocyanate radicals	500

a. TDI is tolylene diisocyanate; MDI is a commercially available highly aromatic polyisocyanate or 4,4'diphenylmethane diisocyanate.

b. ASTM Procedure D 1622-59T.

c. Reactive polyol containing 10 per cent phosphorus; quantity of phosphorus in the foam approximates 2 per cent.

d. Resulting from spraying at 100 per cent relative humidity onto water flowing through surface on which the foam was sprayed.

e. Resulting from inadequate equipment.

TABLE 2

The Effect of Inhibitor on Flame Penetration[a]

Line No.	Inhibitor, % Active Ingredient[b]	Flame Penetration Time, Min.[c]
1	None	1/2
2	30% Sb_2O_3 + 30% Cl	2
3	50% Cl	2
4	5% P	6
5	5% P + 30% Cl	6
6	5% P + 50% Cl	6
7	10% P	10

a. Foam made from MDI, a sucrose polyether polyol having a hydroxyl number of 460, and CCl_3F blowing agent. This foam has adequate adherence and develops a good intumescent char.

b. The total quantity of inhibitor used is 14 per cent of total chemicals in the formulation. The inhibitors tested include a reactive phosphorus polyol (P), a reactive phosphorus polyol containing chloride (P + Cl), chloride (Cl) and antimony trioxide (Sb_2O_3) in the approximate percentages shown.

c. Data from Bureau of Mines flammability test for foam in mines.

TABLE 3

Effect of Phosphorus and Chloride Inhibitors on the
Auto-Ignition Temperature and Char Strength of Foam[a]

Inhibitor		Autoignition	Char
Phosphorus Content, %	Chloride Content, %	°F	Strength
0	0	950	None
0	50	950	None
5	50	1,000	Weak
10	0	1,150	Strong

a. Foam made from MDI, a sucrose polyether polyol having a hydroxyl number of 460, and CCl_3F blowing agent. This foam has adequate adherence and develops a good itumescent char.

used to expand organic plastics into foam (Table 5). Heat from a fire causes this fluorocarbon to expand and rupture the membranes covering the foam cells, the released bromide interrupts the evolution of radicals in the flame and breaks

TABLE 4

Thermal Deformation of Foam Heated to 450°F for 1 Hour[a]

Inhibitor	Area Change, %	
	Foam A	Foam B
Phosphorus polyol (reactive)	2	12
Chlorophosphonate Plasticizer (nonreactive)	40	70
Antimony trioxide and chlorowax (nonreactive)	70	–

a. Data from Bureau of Mines flammability test for foam in mines.

TABLE 5

Effect of a Halide in the Blowing Agent on Foam Flammability

Formulation	Blowing Agent, %		Flame Spread Index[a]	Flame Penetration Time, Min.[b]
	CCl_3F	$CBrF_2$-$CBrF_2$		
C[c]	12.75	0.0	1,400	0.2
C	8.17	8.17	1,100	0.2
C	0.0	14.61	770	0.3
D[d]	12.65	0.0	1,200	0.3
D	8.11	8.11	500	2.5
D	0.0	14.50	240	2.5
E[e]	13.0	0.0	420	19.2
E	0.0	14.0+	80	>60.0
F[f]	13.0	0.0	100	16.4
F	0.0	14.0+	<20	>60.0

a. ASTM Procedure E 162-60T.

b. Bureau of Mines flammability test for foam in mines.

c. 100 parts by weight (pbw) of propoxylated methylglucoside OH No. 433; 101-103 pbw MDI; 1pbw DC 113; 3 pbw C-16. Density = 1.8 pounds per cubic foot (pcf).

d. Basically the same as in 'c' except 20 pbw of a phosphorus polyol replaces 20 parts of glucoside and 1 pbw of tetramethylguanidine replaces 1-1/2 parts C-16. Density = 2.5 pcf.

e. Proprietary formulation.

f. Proprietary formulation.

the chain reaction necessary for sustained combustion.[1] Further, when a carbonaceous material is burned in the presence of a bromide, the gaseous oxidation of carbon monoxide to carbon dioxide is inhibited; this reduces the exotherms in the combustion reaction and results in a substantially lower flame temperature.[2] Bromide in the gas phase exerts greater inhibiting effects than the incorporation of nonvolatile halide salts into the carbon.[3]

Flame Penetration

The Bureau of Mines developed a flame penetration test (Appendix) to assist mining companies and inspectors in evaluating the flammability of foam used in mines. To verify the adequacy of this test, the Bureau made large-scale fire tests in its Experimental Coal Mine. In these tests, a coal zone 5 feet high, 8 feet wide, and 20 feet long was constructed as shown in Fig. 1. The coal was ignited by a kerosine fire, on the floor at the inby end, that burned for 45 minutes and developed flame temperatures as high as $2,300^{\circ}F$.

Coal, without a covering, ignited in 5 minutes (Fig. 2); the flame penetrated into the coal at the rates of 1/4- and 1/2-inch per hour when the ventilating air velocities were 200 and 400 feet per minute respectively.

The coal did not ignite when covered with foam having a flame penetration time of 10 minutes (formulation shown in line 7, Table 2). The maximum temperatures at the juncture of the coal and foam were $250^{\circ}F$ in the inby 5-foot section of the bed, and $160^{\circ}F$ outby this section; after the kerosine fire had burned for 20 minutes, both these temperatures dropped below $100^{\circ}F$. Examination of the test zone after the fire indicated that the coal had been scorched only within 5 feet from the igniting source, and that the surface of the foam was charred but otherwise unaffected.

When covered with foam having a flame penetration time of only 6 minutes (formulation shown in line 6, Table 2), the coal ignited, and temperatures higher than $2,000^{\circ}F$ were recorded.

Flame Spread

Even though a foam can be formulated to resist flame penetration, a second hazard exists—flame spread across the surface of foam covering a wide-spread area. This flame has short duration and a low temperature.

Flame spread was investigated in a 40-foot-long portion of a 9-foot-wide and 7-foot-high entry in the Bureau's Experimental Coal Mine. As shown in the top view of Fig. 3, foam was applied onto the roof and halfway down each rib. The fire was started by igniting kerosine on boards at the lead edge of the foam. The source burned for from 1-1/2 to 2 minutes when the ventilating air velocity was 200 feet per minute, and for 1/2 to 1-1/2 minutes when the

Fig. 1. Test Arrangement for Large-Scale Fires.
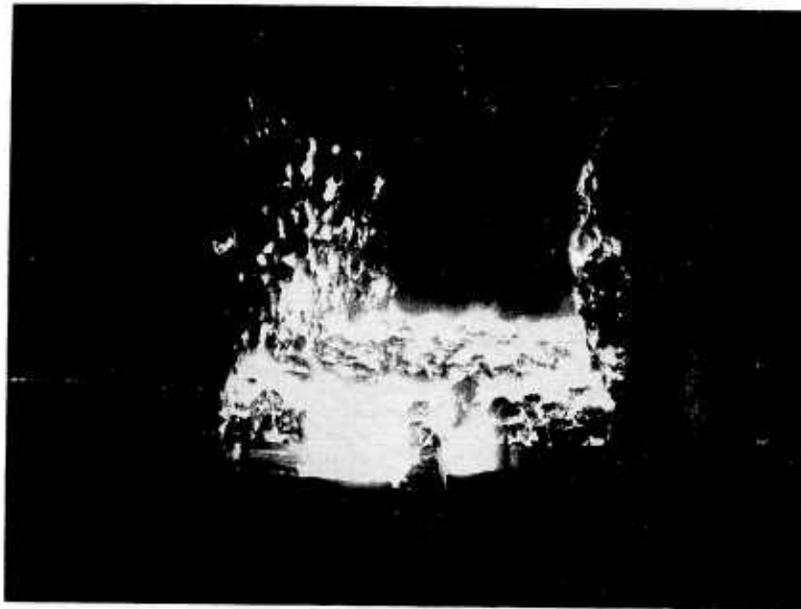
Fig. 2. Coal Ignited by Test Fire.
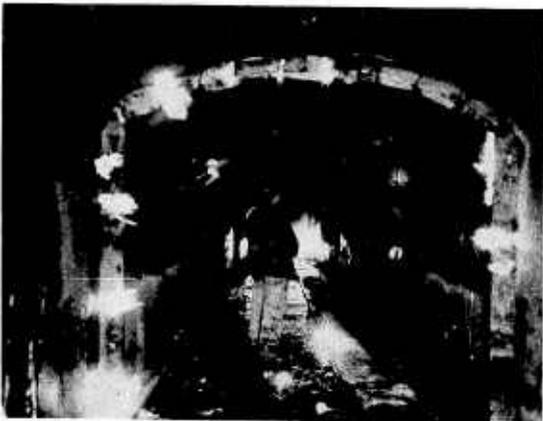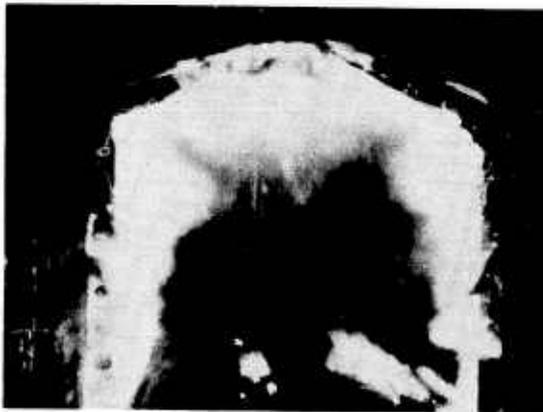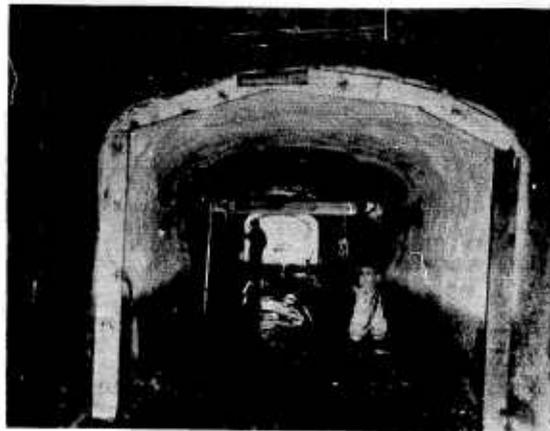
Fig. 3. Test of Flame Spread Across Rigid Foam.

velocity was 1,000 feet per minute. Temperatures were measured every 12 seconds by thermocouples on 10-foot centers on the foam substrate interface and on the exposed foam surface at the roof.

The foam starts to burn within seconds after the kerosine is ignited (middle view of Fig. 3), and flame spreads throughout the test zone at rates of from 20 to 40 feet per minute. Limited data in Table 6 indicates that the flame spread velocity is independent of the velocity of the ventilating air current in the tunnel; it also appears to be independent of the flame spread index and rate of flame progress as determined by ASTM E 162 procedures. However, the velocity of the flame spread in the tunnel test appears to be related to the temperature of the air in advance of the flame and to the heat evolution factor measured in ASTM E 162. This latter observation indicates that the air in advance of the flame is heated by the products of combustion from the foam as well as by the radiation and convection currents from the flame.

Research indicates that an intumescent char is essential to reduce flame penetration. However, during flame spread the foam chars but does not swell; flame penetrates the foam and burning pieces fall to the floor as shown in the bottom view of Fig. 3. The failure to develop an intumescent char apparently results from the low temperature of the flame front and its short duration. In the flame spread experiments, the maximum temperature of the flame front is 600°F; its duration at a given point is only one minute. The charred surface

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TABLE 6

Flame Spread Data from the Bureau's Tunnel
and the ASTM E 162-60T Tests

	Foam[a]			
	1	2	3	4
Bureau Tunnel Test:				
Air velocity 200 feet per minute:				
Air temperature, $^{\circ}$F[b]	–	200	240	600
Flame spread velocity, feet per minute	–	20	25	40
Air velocity 1,000 feet per minute:				
Air temperature, $^{\circ}$F[b]	200	190	220	–
Flame spread velocity, feet per minute	20	20	25	–
ASTM E 162-60T Procedure:[c]				
Flame spread index, I_S	110	140	540	540
Flame progress, F_S	55	35	90	30
Heat evolution, Q	2	4	6	18

a. Foam made from different proprietary formulations having flame pene-
    tration time greater than 10 minutes.

b. Temperatures measured 10 feet in advance of the flame front.

c. $I_S = F_S Q$, all data rounded off to last significant place.

cools below 100°F within 3 minutes after the flame passes. For the foams
tested, the intumescent charring development time at 600°F is 10 minutes;
instantaneous charring requires a temperature of 1,200°F or higher.

Laboratory studies indicate that the fuel for the spreading flame is pro-
vided by minute particles of solid organic matter produced by disintegration
of the foam-cell walls. The disintegration of the cell walls appears to be
caused by rapid expansion of the entrapped fluorocarbon gas. The presence
of flame-inhibiting compounds in these particles has no apparent effect on
flame spread or on the explosibility of dust dispersions.[4] However, halides
such as bromide in the gas phase might reduce flame spread as discussed
previously.

Bureau tunnel tests show that the hazard of flame spread can be elimi-
nated by painting or spraying a protective coat on foam having a flame spread
index below 150; these coatings are ineffective when applied onto foam having

an index of 290 (Table 7). Limited observations indicate these coatings prevent flame spread by increasing the surface strength of the exposed cells, binding the disintegrating particles into larger masses that are not readily consumed by the flame.

TABLE 7

The Effect of Protective Coating for Preventing
Flame Spread Across Foam in the Bureau's Tunnel Test

| Flame Spread Index[a] | Flame Spread Velocity,[b] Feet per Minute | | | |
| | Coating | | | |
	None	Sodium Silicate	Water-Emulsion Latex Paint	Fire-Retardant Paint
140	20	0	0	0
290	40	40	40	40
540	40	40	40	40

a. ASTM E 162-60T flame spread index for 1 sample; coefficient of variation may be from 10 to 45 per cent.

b. Bureau tunnel test; coefficient of variation may be up to 30 per cent.

Related Factors Affecting Underground Foam Application

When exposed to heat, foam should not collapse, melt, pull, or lift off from coated structures. The research indicates that poor dimensional stability upon exposure to heat is generally observed in (1) foams having poor cell structure, (2) foams made from a polyol-isocyanate system having a low degree of crosslinking density, or (3) foams containing a nonreactive liquid phosphorus compound in the formulation.

Foams used in mines should have a flammability index of 15 or less. Foam flammability depends on the condition of the applied surface, the atmosphere in which foam is sprayed, and the application equipment and techniques used, as well as chemical formulation. Thus, specimens subjected to the Bureau's flammability test should be obtained only from foam that has been applied onto average surfaces under typical conditions, and made from chemicals and equipment intended for actual use.

The noxious fumes from heated foam are a major problem over which, unfortunately, there is little control. The principal fumes evolved that exceed the allowable threshold levels are carbon monoxide and isocyanate vapor. For the foams studied, the Bureau observed that when the flammability index was lower, the quantity of carbon monoxide evolved during heating was greater. This finding is in agreement with the previous discussion relating to the effect

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of halides on inhibiting the gaseous oxidation of carbon monoxide. The iso-cyanate vapor concentration evolved is a function of temperature rather than the type of isocyanate used or the flammability index of the foam.

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Appendix

Bureau of Mines Flame Penetration Test for Foams

Specimens should be obtained only from foam applied onto average mine surfaces, and made from chemicals and equipment used underground. At least 8 specimens, 6 inches square and 1 inch thick, without the dense foam skin, should be prepared from foam that is from 3 to 7 days old. Smooth faces and square edges can be obtained by using a band saw with 32 teeth per inch travel-ing at 1,500 feet per minute; fine grit (No. 00 sandpaper) paper is recommended should sanding be necessary.

The specimens should be weighed, and the dimensions of the 6- by 6-inch faces should be measured. The blocks are submerged in a sulfuric acid solu-tion of pH 5 at room temperature for 24 hours to leach nonreactive flame in-hibitors and to simulate aging; foams will normally be subjected to a sulfuric water leaching in mines.

Four of the specimens are placed in a circulating oven at 450°F, and are supported at the 4 corners by 1/2-inch standoffs. After 1 hour the specimens are removed from the oven, weighed, and measured. The maximum recom-mended loss in weight is 30 per cent, and change in the projected area of the

concave face is 5 per cent. These limits are based on tests with foams sprayed on concrete block; foam loosened from the block when the changes in weight and dimension exceeded the suggested limits.

The other four specimens are subjected to an intense flame source for 10 minutes, when the flame must neither penetrate the foam nor cause sustained burning. The equipment illustrated in Fig. 4 consists of:

1.   A fully loaded disposable steel ICC 2826 cylinder of propane.

2.   A pencil-flame burner head with 8 holes complete with 0.008-inch diameter steel colored orifice, a 4-1/2-inch-long burner tube, and a knurled-nut control valve. The burner head should be hand tight.

3.   Qualitative, very rapid filter paper having a diameter greater than 6 inches, or cut into sheets 8 inches square.

4.   A 1/4- to 1/2-inch-thick, 8-inch-square sheet of transite with a 1-1/2-inch-diameter hole in the center.

5.   An 18-gage Chromel-Alumel* thermocouple and potentiometer.
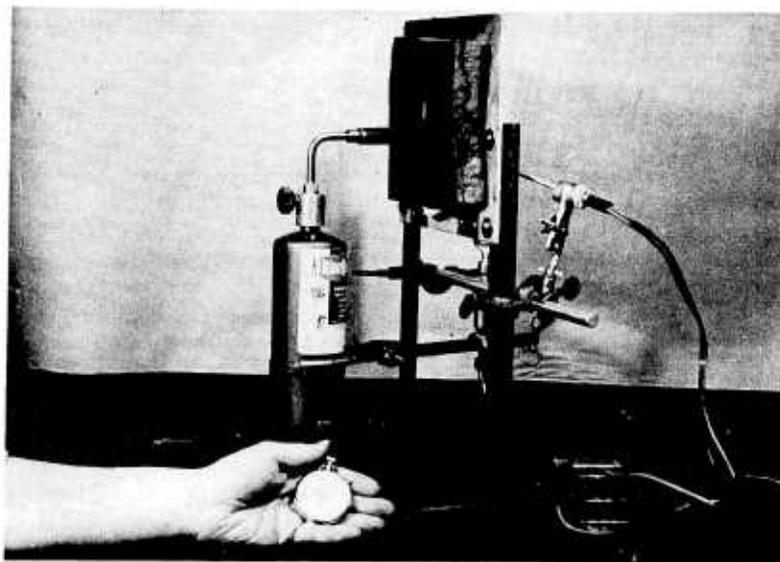
Fig. 4.   Test Arrangement for Flammability Test for Foams.

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*Reference to specific brands in this report is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

The flammability test should be conducted in a ventilated hood or other safe area as toxic and noxious fumes are evolved. The end of the burner head is 1 inch from the sample and positioned so that a 3-1/4-inch-long flame projects into the center of the hole on the transite. With this arrangement, the temperature as measured by the thermocouple 2 inches beyond the burner head should range from $1,910^{\circ}$ to $1,960^{\circ}$F. The flame length and temperature can be regulated by the knurled-nut control valve and by loosening the burner head to adjust the air input to the head. In repetitive tests with randomly purchased torches, there was no significant difference in temperature or test results when using pencil-flame burner heads with 4, 8, or 12 holes, or when using burner tubes bent to angles of 30, 60, or 90 degrees. However, the orifice and burner head must be clean, and the velocity of the air in the hood passing across the sample must be the minimum suitable to maintain a safe atmosphere.

After the flame is adjusted, the foam specimen and filter paper are centered over the hole in the transite. During a 10-minute period, flame should not penetrate the foam. When the specimen is removed from the burner flame, visible burning of the specimen should cease immediately without afterglow. The foam has inadequate resistance to flame penetration should the filter paper ignite in less than 10 minutes; charring of the filter paper is disregarded if flame is not present.

The results of the flammability test are fairly reproducible, as shown by the data in Table 8 for 18 repetitive trials. In evaluating a given foam application, at least three or four specimens should pass the test.

TABLE 8

Reproducibility of the Bureau of Mines Flammability
Test for Foams in Mines

Specimen[a] No.	Weight[b] Change, %	Area[b] Change, %	Flame Penetration Time, Min.
1	-28.9	+ 3.5	30
2	-29.5	0	25
3	-27.0	+ 0.5	18
4	-27.8	0	13.1
5	-28.2	-2.5	16.4
6	-30.0	-4.2	13.4
7	-29.0	-3	8.9
8	-26.7	0	15.8
9	-27.6	0	10.4
10	-25.4	+ 1.2	13.8
11	-26.6	0	14.6
12	-27.2	0	17.5
13	-28.0	-2.0	16.8
14	-25.6	-0.8	9.5
15	-29.4	-2.0	13.7
16	-27.4	-1.0	17.2
17	-28.2	+ 1.8	12.6
18	-30.2	+ 0.3	13.0
Total:	502.7	-8.8	279.7
Average:	-27.9	-0.5	15.5
Standard deviation:	1.4	1.8	5.2

a.   Three samples cut from each of 6 spray applications.

b.   Change in specimen weight and of the projected area of the concave face.

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APPENDIX

APPENDIX A

THE U. S. ARMY "BUILDINGS IN BARRELS" CONCEPT
(Commentary of film presented at banquet)

S. B. Swenson

The report film on the Greenland phase of the U. S. Army Engineer Research and Development Laboratories Plastics Structures Project represents a first effort of these laboratories toward the development of polyurethane foam structures. Being that this was an early effort, and almost two years have elapsed since the termination of the Greenland operations, it seems that a brief resume of the background is appropriate, along with a summary of activities to date.

Some three years ago (June 1960), the U. S. Army Engineer Research and Development Laboratories embarked on a program intended to ease the burden of supplying military housing in the field. The impulse that created this "Buildings in Barrels" approach was the revelation of the possibility of expanding plastics foaming material in the field. The vision of shipping construction materials in liquid form in barrels or drums and expanding them in the field to thirty times their shipping volume presented an amazing logistic advantage.

Six months were spent in developing a working knowledge of foaming materials, designing shapes and structures, and emerging with a structure that might satisfy military requirements. The first model was presented for evaluation in October 1960 with favorable response.

An improved production model was constructed and exhibited at the Pentagon in the spring of 1961. At the same time plans were under way to send a task group to Greenland to construct two buildings as a field test under arctic conditions.

The task group, consisting of four civilians and eight enlisted men, spent the months of July, August, and September in Greenland engaged in setting up a fabricating plant, molding and casting panels, and erecting 100 feet of building. A 30-foot structure was assembled in an ice tunnel bored 1000 feet into the edge of the glacier. A 70-foot structure was erected in one of the snow tunnels at Camp Century—"The Atomic City Under the Ice" situated some 130 miles east of Thule on the ice cap.

These structures, made of expanded polyurethane foam with glass fiber-resin facings, have been in existence close to two years and are today performing as well as when originally installed. From the standpoint of utility, we have not yet made a structure that is stronger, more easily assembled, or more habitable than those constructed as a first venture. However, it was apparent at the close of the Greenland program that the man-hour expenditure in fabricating panels for plastics foam structures, made by the process so far developed, were far too high to justify the logistical advantage. Furthermore, the special support equipment and maintenance parts necessary for the process reduced the logistical advantage realized in the shipment of unexpanded foam.

This evaluation has led to an approach which, hopefully, would reduce or eliminate some of the disadvantages inherent in the original system. Today, due to the reduction in costs of foaming materials, we can afford more generous use of foam and greater latitude of structural design. Improvements in formulae allow simpler processing methods and reduce considerably the complexity and bulk of the support equipment necessary in field operations.

We hope that before the close of 1963 a low cost system will be developed that will afford rapid fabrication of polyurethane foam structures with a wide choice of facing materials, depending on the environment. In fact, a system now in the design stage will be capable of continuously producing face-shaped panels utilizing pre-packaged units of foaming materials which can be hand mixed in buckets and poured into gang molds lined with skin materials which are shipped flat.

APPENDIX B

FOAMED PLASTICS AND HOUSING IN
UNDERDEVELOPED COUNTRIES

Stephen C. A. Paraskevopoulos*

Aspects of the Housing Problem

The population explosion in underdeveloped countries and the exposure of millions of people to the material goods of Western civilization have created an increasing demand for more and better housing throughout the world. Available means and existing housing policies in emerging nations are usually inadequate in coping with this ever-increasing demand; and, consequently, most countries are faced with a serious shortage of housing, including basic shelter.

The provision of adequate housing poses a complex and challenging problem even to technologically advanced countries, let alone the underdeveloped ones. Besides lacking suitable building materials and an effective industrial organization for the production of dwellings, every underdeveloped country has a housing problem that is further complicated by the fact that the people who are most in need of housing usually do not constitute a housing market. In most cases they have no money to pay for any kind of house or shelter.

Governments and international assistance organizations are faced with the immediate problem of helping millions of people in underdeveloped countries to obtain even the barest kind of shelter. Much effort and money are being spent to improve living conditions in villages and shanty towns, and much has been accomplished in this area over the years through aided-self-help community improvement projects. Such emergency projects, however necessary and desirable, have also shed some confusion in the minds of many people and governments as to the true nature of the housing problem.

Various attempts have been made to resolve over-all housing needs by means similar to those used in community improvement projects: to wit, through the development and use of fairly primitive materials and techniques and through some form of direct government subsidy. A basic fallacy of this approach—which is also reflected in some aided-self-help improvement projects—lies in viewing government aid as a direct subsidy intended primarily to improve housing conditions, rather than as an investment to advance a country's economy.

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*Director of the AID sponsored research project on the potential use of foam plastics for housing in underdeveloped areas.

The nature of the housing problem, however, is such that it cannot be resolved just by providing better houses. It requires the development of an economy so that improved living conditions are not only desirable, but also feasible. In the long run, no country can afford any better housing than that which its people can obtain through their own productive efforts.

The housing problem in any country cannot be divorced from that country's total problem of social and economic development. Approaching the housing problem as an integral part of the total problem of national development means that housing must be viewed as a means of raising the national productivity and the national income as well as of providing a rising standard of living for as many people as possible. No country with a shortage of capital or credit, as is the case in the underdeveloped countries, can afford to undertake housing projects because of political expediency or for humanitarian reasons, and to overlook the potential of housing as a capital-producing resource.

To evaluate any proposed solution to a housing problem, the problem must first be placed in its proper perspective. In the case of underdeveloped areas, there are usually two distinct aspects to the housing problem which should never be confused. These are: (1) the immediate need for improvement of housing conditions for people living in squalor and who do not constitute a housing market and (2) the long range problem of providing adequate housing where a housing market does exist or could be created.

The objective of any housing improvement activity related to the first aspect should be the immediate creation of an environment that will enable people to become more productive in national development. This objective should be attained whenever possible without investing scarce capital in items whose contribution towards the industrial development of the country will at best be negligible.

In recent years, for example, some well-meant effort has gone into the development of hand operated machines that will produce a superior type of mud brick. Dwellings constructed of such "improved" building products still represent a relatively low standard of living. As short-term efforts, such projects consume far too much capital for the value of the end result, and the long-range industrial capability of the country is increased not at all appreciably.

Much can be done to improve living conditions through well designed programs offering technical advice on how to improve on sanitation, construction, safety, etc., with locally available means and existing or improved know-how. Such emergency efforts should always be viewed as transitional expedients which are needed in order to educate and prepare the people for a higher standard of living. At the same time, by creating a longing for higher standards, there is also created an incentive for the increased accumulation of savings which is necessary in the development of an economy. From this viewpoint, short-range community improvement programs come under the heading of education, and in terms of government expenditures, they should be treated as part of a nation's investment in education.

Thus, if the short-term community improvement programs are viewed as part of the educational process, any long-term program for the development of more and better housing should in turn be viewed within the framework of an expanding industrial development, and evaluated in terms of its potential contribution towards a country's social and economic growth.

From this viewpoint, the development of a really efficient building industry is of the utmost importance. To encourage a primitive system of home building with large scale expenditures is to negate what should be the primary long range housing objective in a developing society—the creation of a housing market sufficient to sustain the introduction and development of industrial facilities capable of producing housing of an increasing quantity and quality at a price consistent with a steadily rising national income.

The long range problem has to be approached directly as well as indirectly: directly, through the development of really new and improved materials and methods of production and construction; indirectly, through the development of the economy at large on an industrial basis which will provide people with gainful and productive employment so that they can be turned into customers for new housing.

Whenever possible, these two aspects should be complementary. It is believed that much more can be achieved if housing is not seen as an independent quantity and the building industry is not treated as an independent factor; both must be considered as part of an integrated industrial development.

The Need for Re-evaluation of Standards

As soon as we speak of an underdeveloped country, our first impulse is to set our sights very low. Too often a lower standard imitation of what has already been established in a more advanced country is accepted as the immediate housing goal. Too often the available resources of a country are evaluated on the basis of their immediate applicability without thought to the larger good that could be obtained through a long range program of integrated national development. This attitude tends to perpetuate a position of relative underdevelopment; it does not stimulate new development of a truly dynamic sort. A more promising approach is to try to resolve the problem of national development in each country through continuous evaluation and re-evaluation of all the resources, both human and physical, which may become available to that country, externally as well as internally.

In our closely knit contemporary world since any national development will have international implications and ramifications, the utilization of national resources must take into account the resources which are available in other countries. The existence of certain raw materials within a country should not mean that these materials must be used to the exclusion of materials from outside the country unless this is to the advantage of a nation's total economy.

For example, in connection with housing, the prevalence of wooded areas might suggest the development of a structural timber industry. However, from the viewpoint of the total economy, it may be more desirable to use the wood for the development of paper or other synthetic products, or to export the wood as a raw material needed by other countries, or even to leave the wood standing as a reserve against some as yet unrecognized need.

This choice of alternatives in the use of national resources is often overlooked in the development of housing in the emerging countries. The thought usually is that since something is there it must therefore be used. The possibility of doing something else that will be more beneficial in the long run thus becomes obscured by the force of a first impulse. The extent to which any particular material and method of construction is to be used in housing should depend on the degree to which its use will help to increase the national productivity while also raising the standard of living.

The usual theory is that only locally available materials should be considered for housing use to the exclusion of any imported materials. This theory cannot be accepted as a golden rule. If by importing certain materials, a country may upgrade locally available resources or create new resources, then it may be to the advantage of this country to import such materials. In our age of synthetics, we are not limited to natural materials and primitive ways of processing such materials into final products. Natural materials consist of chemical elements which have been synthesized by nature. Today men can synthesize these elements through chemistry and create a great variety of new materials. It should always be remembered that a basic prerequisite for development is the upgrading of resources and the creation of new resources.

A basic premise in approaching any problem, including housing, is that means should never be confused with needs. This means keeping a clear distinction between stating the problem and finding a solution. For instance, if electric power is deemed necessary for housing in a particular country, it would be shortsighted to think only of conventional generators and power lines; the use of fuel cells may be a more desirable solution even though they have not yet been introduced for housing use in even the most advanced countries. Similarly, the creation of large municipal sewage systems is not the only alternative to be considered in replacing primitive systems for the disposal of human wastes; self-servicing household equipment employing chemicals (or some other form of energy conversion) may be a more effective, more readily attained, and less costly solution to this particular problem.

The fact that a particular solution proposed for an underdeveloped country may not have been introduced even in the most advanced countries should not become an inhibiting concern. Any innovation, regardless of its degree of technical sophistication, should be considered for development use, particularly if it holds the promise of being more efficient and less costly to install, operate, and maintain. Many technical possibilities have not yet reached the marketing stage in the more advanced countries simply because

they come in conflict with established codes and other legislation or because they would jeopardize existing investments or drastically upset the traditional way of doing things.

In cases where a new technical possibility has not been fully developed and does not yet meet the high standards of performance demanded by people living in an advanced country, it would be to the advantage of a less developed nation to contribute to the innovations further technical development by becoming an area for any needed field testing. The collaborating nation would itself benefit directly from such experience by building up within its own boundaries a new set of national resources. Instead of being a mere recipient of foreign aid from others, it would become an active participant in a collaborative system of international development.

What is stated here is simply that because the standards of performance in underdeveloped countries are much lower than our own, this does not necessarily mean that such countries should be viewed as good second hand markets for obsolete equipment and production facilities. On the contrary, such attitude in principle should be discouraged. The acceptance of lower standards of performance could very well mean that innovations holding great promise for the future, but not meeting at their present stage of development our own requirements for high performance, should be considered for introduction in underdeveloped areas. Even in their present stage of development, such innovations may be far better than anything a less advanced country has available.

Thus, by perfecting promising innovations in a newly developing country, technologically advanced countries may gain invaluable experience from field application and at the same time truly contribute towards the development of a new nation. Products whose introduction should be particularly considered are those which represent the most advanced efforts of the more advanced countries and which offer great promise for the future growth of all countries. In this regard, the technological advances made in connection with space exploration may prove to have a greater potential for application to housing, both here and abroad, than is presently anticipated.

In our rapidly changing world, under the impact of advances in science and industry, established standards have to be continuously reviewed and re-evaluated. This is especially true with regard to the effect of technological obsolescence in housing. Usually quality in housing has been associated with permanence. If a dwelling could be constructed so that it would last many years this has always been considered desirable, whereas, if the structure were designed so that it could be disposed of without great effort or cost, it has generally had the implied stigma of inferiority by being called temporary.

Technology has made it possible for buildings to be constructed so they will last indefinitely, far beyond their useful life spans. Today, in the United States and other industrially advanced countries, there are many examples of buildings that stand empty because they have become economically or socially undesirable, but they continue to exist as examples of urban blight because of their durability—it would cost more to tear them down than they are worth on

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the open market. Making sure that any new housing can be easily removed when it becomes obsolete and before it turns into a new urban slum is clearly part of the housing problem confronting the newly developing countries as well as ourselves.

Many cultures are not maintenance cultures; instead, the throw-away process is part of every day life. The degree to which cultural evolution is related to maintenance is a question which anthropologists are much better qualified to answer. However, it must be observed that the throw-away process can be encountered in both highly developed as well as underdeveloped societies. The design of houses capitalizing in part or in total upon disposal rather than maintenance may offer great advantages both from the point of view of sanitation as well as that of stimulating an economy through continuous production. Thus, our standards of permanence will also have to be re-examined.

As in the case of housing, a foreign aid program should not be viewed as a liability to the economy of the country offering foreign aid but on the contrary, as a potential asset to further this country's own growth and development. Just as there are various degrees of development, there are various degrees of underdevelopment, not only between countries, but also within countries. A global approach to the problem of development will have to be taken if rapid progress is to be achieved in all countries with minimum human stress. It is believed that such a global approach to the housing problem demands that the most advanced technology be considered for introduction in every country of the world.

The significance of less developed areas is that, at present, they offer less resistance to the introduction of technical innovations, and for this reason they can serve better as testing grounds for the development of new products than can the more advanced countries. Through a cooperative program of development on an international scale in which the experience of those being aided will also benefit those who are providing the technical assistance, there should be continuous progress everywhere in a never-ending cycle of research and development.

Promising Foreign Assistance Programs

The Agency for International Development (AID) of the United States Department of State is administering various programs in the area of international development which will contribute both directly and indirectly towards the resolution of the housing problem abroad. In connection with long range development problems, much emphasis is being given to encourage American business to invest capital abroad either alone or in collaboration with local concerns. Congress has established a series of programs to encourage U.S. investment in underdeveloped countries. These programs offer assistance for investment surveys, dollar loans, local currency loans, and investment guarantees. At the same time our foreign assistance program is also assisting in the establishment of savings and loan institutions abroad to stimulate the accumulation of savings.

It is believed that much can be accomplished in the area of international development if American industry takes advantage and makes good use of these programs. The collaboration of American industry, acting on the basis of enlightened self-interest, is seen as a major potential contribution towards an international kind of development that will benefit all countries involved, including those offering aid as well as those being aided.

Another promising aspect of the foreign aid program has been the establishment of a research unit within AID which is sponsoring projects aimed at placing the whole problem of international development on a more scientific basis. One of its major objectives is to explore the feasibility of new ideas and techniques whose introduction in less advanced areas holds great promise of accelerating development.

One such program administered through AID Research is the project on the potential use of foam plastics for housing in underdeveloped areas, which is being conducted by the Architectural Research Laboratory at The University of Michigan. This paper is a condensed version of a report which we recently published, and which describes in detail the preliminary phase of our plastics research project.

Reasons for Considering Plastics for Housing

Having come to the conclusion, that the use of traditional building materials and techniques alone could not resolve the housing problem, AID decided to investigate the possibilities offered by such new materials as plastics. Although at the beginning these materials were considered primarily for their potential use in short range shelter improvement programs, it was subsequently agreed that they should be explored more importantly for their potential contribution towards the resolution of the long range housing problem.

Many factors have contributed in putting our project on its present broad basis. To wit: the expanded range of aids to business voted by Congress, and the establishment of savings and loan institutions; the international expansion of the American plastics industry; the production of plastic materials offering higher quality at decreasing cost; the technological advances in the area of plastics and the increased use of plastics in building; the encouraging results produced by the Corps of Engineers at Fort Belvoir in building with plastics; and, finally, the increasing interest of people abroad in the potentials of plastics for building construction.

Many new kinds of building materials have been developed in recent years which can be used to advantage in the construction of new dwellings. All these must be considered in any long range housing program involving a specific country or area, but it is believed that special attention should be given the plastics, particularly the foam plastics, for many different reasons.

In recent years, while the cost of traditional building materials has been going up (or at best remaining steady), the price curves for many plastics have

been sloping sharply downward. The cost of components for the production of polyurethane foam, for instance, was around $6.00 a pound only some years ago; in July 1962, at the outset of this feasibility study, the price was 50 to 60 cents a pound, and today it is getting close to 40 cents.

Many different kinds of products can be readily produced with plastics which will meet very precise specifications and conform to a vast variety of requirements and conditions, without great change-over costs in production. The quality of the end product can also be largely controlled in the laboratory, where the prevailing attitude is always to seek to find a better product through research and experimentation (occasionally through accidental discovery).

The production of low density plastics (foam plastics) at a reasonable cost, in addition to providing an excellent kind of insulation, has opened up new possibilities in the construction of dwellings as illustrated by the imaginative Camp Century experiment. This experiment also revealed the interest of the plastics industry in the development of experimental structures and its willingness to contribute resources and know-how when presented with a specific project involving the application of plastics.

Being a synthetic product, the plastics require industrial facilities for their manufacture and processing. Industrialization will therefore be promoted in any country where markets can be created for the various types of plastics. Countries most likely to be benefited industrially from such development are those which have natural resources, such as oil, or by-products and waste resulting from other industrial production that can be utilized in making either the plastics or the plastic building parts.

The main industrial advantage offered by the plastics is their wide variety of possible uses, ranging all the way from tableware and small toys to large structural components. This versatility in turn assures a greater diversification of markets. If production facilities can be created for the building market, potentially the largest, the output would be ample enough to take care of all the other markets (clothing, textiles, furniture, household furnishings, containers, and equipment of all sorts), all of which present equally pressing needs in the newly developing countries.

This diversification of markets should make the use of plastics rather attractive to companies interested in investing in underdeveloped countries. Even if the existing housing market is not immediately large enough to absorb an output of building materials commensurate with low unit costs and a reasonable margin of profit, a manfacturer could justify his investment by producing a number of consumer products which are needed in most of the emerging countries and for which there is already a large market demand. Through the production and sale of allied products, the manufacturer of plastics should be able to amortize a large part of his initial capital investment, which will eventually allow him to produce building materials at lower unit costs.

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The University of Michigan Research Project

It became apparent from the beginning that the project could not be conducted with a reasonable chance of success unless it could obtain the active collaboration and participation of a large segment of the plastics industry. Although the project had been primarily set up to conduct an investigation in the use of materials rather than in the nature of materials, it soon became necessary for us to obtain more background in the latter aspect and the various manufacturing processes than had been originally anticipated. Such background can only be obtained by contacting a great variety of sources.

The response on the part of industry exceeded even the most optimistic expectations. The project is deeply indebted to the plastics industry for its encouragement and assistance and for the many courtesies that the project staff has received. Collaboration with this industry has been a most gratifying experience. In brief, collaboration with industry has involved an exchange of information, a supply of experimental materials, access to laboratory facilities, and general assistance in development work. Most importantly, the project staff has been kept fully informed of developments usually referred to by industry as new "break-throughs."

At the outset, the project staff was faced with a complex problem of analysis. The time allocated, six months, was rather short, and the choice of materials rather extensive. The course of research was determined by the decision reached during the stage of procedural analysis, which established the foam plastics as the basic materials to be investigated for structural use. Besides offering advantages in terms of global logistics and such other virtues as ease of fabrication at low investment cost and light weight, as their density decreases so also does their cost when measured in volume. This fact did not necessarily mean that the lowest density foams would produce the most economic structures, but it did indicate that in order to achieve maximum economy in a total dwelling unit the density of structural materials would have to be taken into careful consideration. The investigation finally concentrated on five foam plastics which seem presently to be the most promising for structural application. These are two thermosetting materials, polyurethane and epoxy, and three thermoplastic materials, polystyrene, vinyl, and ABS. The extension of the investigation to other materials has been primarily for their potential use with foam plastics as surfacings or as fillers and reinforcements or as joining materials.

Another decision which formulated the course of research was that plastics should not be viewed as substitutes for other building materials but for their own intrinsic value in building construction. It was further agreed that, in the interest of the project's own development, the project staff members should divorce their thinking from any traditional or preconceived ideas of house form and approach the problem of structure from a purely analytical point of view, without any specific application in mind. Only after a theoretical structure has been developed as a result of analysis should its possibilities for adaptation to house design be explored.

Our approach to plastics has been from the point of view of the architect, the structural engineer, and the manufacturer, rather than that of the chemist. Thus a 20-pound density urethane foam is for our purpose a different material than a 2-pound density urethane foam, while for the chemist it may only be a different form of the same material. In general we have not limited our comparison of materials to cost and physical properties. In comparing two materials, such as polystyrene and polyurethane, we were primarily interested to determine what could be done with the one as a thermoplastic material and the other as a thermosetting material, and to establish use factors for each case.

Economy is a factor that always has to be considered and especially in the case of underdeveloped countries. However, it is misleading to compare plastics on a pound or board-foot basis alone. It all depends how these materials are being used. Foam plastics have many properties, and if one makes use of only one property, for example insulation, they may appear to be very expensive, while if more properties are being used, they may prove to be very cheap. The only realistic cost figure with regard to plastics, which offer such a high degree of versatility and flexibility both from the viewpoint of production and erection, is their cost in place. Finally, cost figures established in this country may greatly differ in other areas since the relationship of factors is entirely different. For example, a plywood skin may be cheaper in this country than a thin plastic skin, while in many other countries this will definitely not be the case.

Since the success of our program will greatly depend on the willingness of manufacturers to invest abroad, we have to be sensitive to the fact that incentive for investing can only be created if there is a reasonable promise for profit. Therefore, we have to pay attention to materials or forms of materials which can be marketed on a sufficiently wide basis to make the situation attractive for investment. Thus, our approach is not only to specify properties, but more often to accept relative shortcomings and try to design around weaknesses as well as strengths.

There are a number of problems involved if foam plastics are to be considered for structural application at their present stage of development. However, it is believed that these are not insurmountable. They can be resolved through chemistry or design or both. More importantly, industry has the talent and other needed resources to resolve many of the problems, if the potentials of an international housing market become apparent.

As foams receive consideration in primary structural applications, a more comprehensive testing procedure will have to be established, especially since many foam products are today far from ideal homogeneous materials. In many instances, present day testing practices cannot be considered representative of the structural behavior of certain materials, and very often do not offer adequate design criteria.

Also more field experience is necessary to determine the long term weathering characteristics of such synthetic materials. Accelerated weathering

(weatherometer) tests may offer good indications as to color stability, but they are of little value in predicting the weathering properties of plastics under long term exposure. Actual test structures will have to be set up in the field for such purpose. In the meantime, if structures are to be erected, they can be protected with materials which have an established performance record.

The low ultimate strength of some plastics is relatively unimportant when considered by itself. In other words, a material having seemingly inferior mechanical properties may turn out not to be difficult or impossible or uneconomical when used in structural design. The geometry of the structural section and the over-all geometry of the structure are major influencing factors.

The problem of structure was approached from three aspects, to wit, that of mechanical properties, of production methods, and erection techniques. Through a preliminary investigation of mechanical properties, we have drawn certain assumptions as to the family of structures that can be designed, which will be most logical from the structural engineer's point of view.

Possibilities of using materials in equal density as well as in varying densities have been investigated. Structural economy has also been studied on a mathematical basis. Such a study has resulted in the formulation of an equation which determines the most economical use of materials (that is, maximum flexural rigidity from the given weight of materials) for sandwich panels. This equation involves the ratio of core to skin, in terms of thickness, density, modulus of elasticity, and price per unit volume.

A similar investigation of production methods revealed the shapes and sizes as well as the kinds of structural components (or even total structures) which may most readily be obtained. Finally, various possible erection techniques also suggested and limited ways in which structures can be developed. On the basis of this three-fold analysis, we have formulated certain structural ideas which we believe merit further investigation.

Our present program is to study selected structures and develop within this year full scale sections of the most promising of these structures for testing purposes. The intent is to evaluate structures for their efficiency in the use of materials and in the light of such design factors as facilities required for production, space utilization, economy, and the like.

It must be pointed out that we are not involved in either designing or developing a universal house. This, we believe, would be a snare and a delusion. Plastics offer great versatility from the standpoint of both application and production. This advantage has been recognized in the production of other items and should not be overlooked in respect to housing. The objective should always be to develop the total system, (design, production, and marketing) and to make whatever adjustments may be needed within the system to enable it to cover as wide a range as possible of housing requirements in each developing country. In short, our objective is to investigate structural systems through which we hope to develop a better understanding of the potentials of foam plastics for structural application.

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Since this is a basic study, the project will use insofar as possible widely available materials produced by a large cross section of the plastics industry. However, it will be a major aim of the project to encourage companies with proprietary products to use these products in developing suitable structures in collaboration with our project staff, particularly if such products offer the possibility of improving structural performance and economy, or if they utilize other materials which are or could become available in the underdeveloped countries. Thus, the project is offering its own resources to industry in the development of structures that conceivably and hopefully will be of value to the newly developing countries, to the plastics industry as a whole, as well as to individual companies.

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