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RESEARCH ON CLOSED-CELL SPONGE AS A PRESSURE TECHNIQUE FOR PROTECTIVE ASSEMBLIES

R.M. Heitz, et al.

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SPACE MATERIALS LABORATORY
NORTHROP SPACE LABORATORIES

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AEROSPACE MEDICAL RESEARCH LABORATORIES
AEROSPACE MEDICAL DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This study was conducted by Northrop Space Laboratories (NSL), Hawthorne, California, under Contract AF 33(615)-2953, in support of Project 7164, "Aerospace Protective Technology," and Task 716411, "Aerospace Pressure Outfit." The Contract was administered by the Aerospace Medical Research Laboratories, Altitude Protection Branch, Life Support Division, Biomedical Laboratory, Wright-Patterson Air Force Base, Ohio, with Mrs. Lee Rock as project monitor.

The authors of this report are Dr. R.M. Heitz, co-principal investigator and G. W. Jones, process engineer, both associated with the Space Materials Laboratory. Other contributors of this program include Dr. C. F. Lombard, co-principal investigator, Laboratory Head, Biodynamics Laboratory; Dr. R.D. Johnson, Laboratory Head, Space Materials Laboratory; J.K. Magill and T.W. Brown, associated with the Space Materials Laboratory.

The study summarizes the performance during the contract period from 10 May 1965 through 5 July 1966.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
Technical Director
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ABSTRACT

A closed-cell foam was developed for integration into a partial pressure suit that would produce pressure on the human body to provide protection in a vacuum environment. A survey of literature and industrial organizations was followed by an extensive experimental study on known foam systems and the development of new foam systems. The evaluation and development of the foam composition and processing techniques are described. From this study, the formulation and processing of suitable vinyl closed-cell foams were developed with reproducible properties in controlled processes. Their physical properties passed successfully the required cycling test wherein the foams, properly restrained and exposed to vacuum, exerted a pressure response of 7 psia or 3.5 psia depending upon the process used.

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SECTION I

INTRODUCTION

A potential technique for providing pressure on the human body in a vacuum environment is the use of a closed-cell sponge in lieu of the gas bag normally used under the restraint layer. This program was directed toward the development of a closed-cell foam material which satisfies the requirements of body pressure maintenance, nontoxicity, wearing comfort, ease of mobility and skin secretion capability.

The basic problem was the selection of the resin system that can be foamed under controlled conditions to produce a foam that will effect the response required to counteract "body swelling" pressures. This predesigned mechanical response had to be developed for selected pressure levels and a variety of restraint configurations. The foamed material's properties had to be such that it can be modified to introduce physical paths for transport of water at a controllable rate without altering the specially developed restraint characteristics. The material development had to be accomplished within not only the constraints imposed by foam technology but also the many constraints dictated by intended application as an internal component in a space suit.

NSL proposed a thorough investigation of selected foam systems including their formulations, processing techniques, preparation and evaluation of the resulting foam products. Four basic types of closed-cell foam polymers (polyurethane, vinyl, silicone and rubber latex) were selected to be produced within a confined area under a reduced pressure equivalent to the design working pressure of the foam in the intended suit application. Testing included determination of any deterioration from repeated cycling to vacuum and mechanical response determination for selected configurations.

The major difficulties anticipated in the program were identifiable. Although the development of sufficient response or potential expansion ratio in the foam material appeared feasible, the problem was to produce a high quality uniform foam under a reduced pressure that would withstand cyclic pressure fluctuations without taking on a permanent set. This required rigid process control to produce the required cell size and reproducible pressurizing characteristics as well as to insure a complete reaction to eliminate the possibility of any residual toxic components from the catalyst. Hence, the major effort on the program was placed on material and process development.

SECTION II

TECHNICAL DISCUSSION OF APPROACHES AND SOLUTIONS

A. Foam Formation Technology

In considering applications for foamed materials it is important to understand what they are, how they are made, and what they can do. Foamed materials comprise a versatile new family of low density, cellular materials, which are made in a variety of processes. These synthetic materials are polymers which have been expanded so much by a gas that they have a uniformly cellular structure which can look like an extremely fine honeycomb or a mass of very tiny bubbles or cells fused together. The cells of some foamed polymers are large enough to be seen; cells in others are so fine that a microscope is needed to see them.

All polymers can be expanded by a gas, some much more readily than others. There is no single all-purpose foam, but there are a seemingly infinite number of resinous compositions from which foams can be made. These compositions can be tailored chemically, that is,they can be designed, synthesized, processed, and fabricated to meet the requirements for innumerable types of applications.

1. Foam Formation Chemical Aspects - Foamed polymers are produced from a variety of thermosetting or thermoplastic resins. For instance, among the most important classes of foamed thermosetting resins are the urethanes, epoxies, phenolics, and silicones. Of the thermoplastic foaming resins, polystyrene, vinyls, and polyolefins are among the most common types.

The properties of the base resin and the choice of foaming agent are important in determining the physical properties of the final foam. A close control of the base resin or polymer structure is important to obtain final desired characteristics of a foam. If a flexible, elastomeric polymer is used to produce a foam, the resulting product will be soft and flexible. If a highly cross-linked rigid polymer is used, the resulting foam will be rigid and friable.

When properly formulated and produced, foamed polymers are strong, tough and durable, and lightweight. They derive thair chemical characteristics from the basic polymer used in their production, but their cellular structure gives them useful physical properties not apparent in the base polymer.

The cell structure of a foam may also vary significantly. The cells themselves may be open and interconnected to allow the passage of liquids and gases through the foam, or they may be closed with the membranes of the polymer forming the cell walls so intact that they act as barriers to gases and liquids except by diffusion. The size and uniformity of the cells themselves may be varied from very fine structures barely visible to the naked eye to coarse foam cells half-an-inch in diameter. The cells may occur in a random distribution of sizes within a given foam, or they may be very uniform in size.

Almost any polymer may be foamed by one or more of the following basic processes: (1) introducing gas under pressure directly into a soft plastic mass, (2) incorporating under pressure a low boiling point solvent, which volatilizes when the pressure is released at a temperature above the solvent's boiling point, (3) aeration or frothing of the soft plastic mass, (4) incorporating a chemical or group of chemicals which, when heated, decompose, releasing gas, and (5) reacting chemicals in the formulation which release a gas, such as hydrogen, during polymerization or cross-linking. In another expansion method, solids can be incorporated in the soft plastic mass. After the mass has been formed, the material is leached out by solvents to form an open cell foam. Also, bulky fillers can be incorporated in a binding resin. Partial fusion of the mass produces a porous material. Finally, bonding of loose fibrous structures with resinous materials forms a lightweight porous mass.

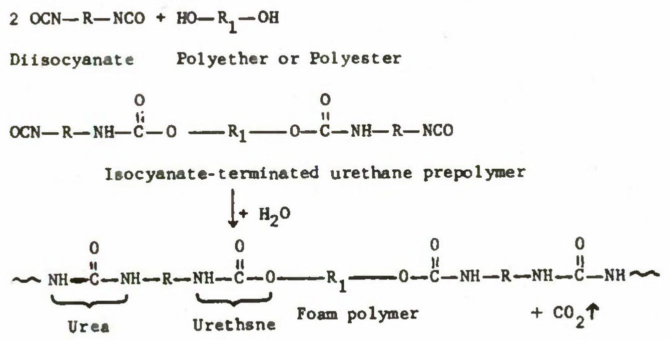
In the foaming of thermoplastic resins, the polymer structure is unaltered during the foaming process, whereas thermosetting resins are foamed simultaneously with polymer buildup, that is, a cross-linking reaction of the constituents takes place to form a three-dimensional network of polymer molecules. Thermoplastic resins are generally foamed by the application of heat to the resin in which the foaming agent is thoroughly dispersed. The function of externally applied heat in this case is to activate the blowing agent and to so soften the resin that it will flow or fuse. In the production of thermosetting foams, two or more reactive components (generally liquids) which form the polymer are mixed together with a blowing agent. Minor quantities of catalysts, foam stabilizers, and activators may be added to facilitate processing. The heat generated from the polymerization is used to activate the blowing agent.

Because of the unique application considered here for the foamed polymer in question, the type of foamed material to be used was of the kind having a flexible organic cellular structure. Its most important properties had to be a high degree of flexibility and softness, a great strength and durability, a low permeability of the cell membrane and the absence of any toxic products or odor.

To find a foam possessing all these qualities, the following four classes of materials were considered: (1) polyurethanes, (2) vinyls, (3) silicones, and (4) rubber latices, with particular emphasis on vinyls. Copolymers prepared from these four classes of material were also suggested. A thorough understanding of the formation of these above enumerated organic foams was necessary to achieve the best results. This involved the consideration of the organic chemistry of the reactions leading to gas formation, molecular growth, and formation of cellular structure, the colloid chemistry of nucleation and stability, the rheology of the polymer bubble system as it cures, and the foaming technique of the material to achieve the pressure varying from 7 psia to 3.5 psia when properly restrained and exposed to vacuum. The understanding of the basic chemistry and the chemical and physical functions of each of the ingredients involved in all four classes of foam materials, was highly important in the selection of suitable foamed polymer systems. A brief description of the chemistry of each of the classes of materials in question is given below.

a. Polyurethane Foams

There are two principal methods of flexible foam preparation: (a) prepolymer; and (b) one-shot. The prepolymer process involves the reaction of a polyether or polyester with a diisocyanate prior to foaming. This process usually employs an excess of isocyanate to yield an isocyanate-terminated polymer, called a prepolymer. Foaming occurs by reaction of the prepolymer with water with formation of urea linkages and evolution of carbon dioxide, which acts as the blowing agent. Catalyst and surfactants are employed to regulate the foaming rate and cell size, respectively. The formation of a prepolymer and the subsequent foaming reaction are represented schematically below:



$$2\ OCN—R—NCO + HO—R_1—OH$$

$$OCN—R—NH—\overset{O}{\overset{\|}{C}}—O—R_1—O—\overset{O}{\overset{\|}{C}}—NH—R—NCO$$

$$\downarrow + H_2O$$

$$\sim NH—\overset{O}{\overset{\|}{C}}—NH—R—NH—\overset{O}{\overset{\|}{C}}—O—R_1—O—\overset{O}{\overset{\|}{C}}—NH—R—NH—\overset{O}{\overset{\|}{C}}—NH\sim \quad + CO_2\uparrow$$

In the one-shot process, the diisocyanate, resin (polyester or polyether), stsbilizers, catalyst(s), and water are mixed simultaneously. In addition, the formulations may include supplementary blowing agents, cell-size regulators, fillers, flameproofing agents, or other additives to impart special properties. The reactions begin immediately, with foam rise starting about 10 seconds after mixing and are completed within 1 or 2 minutes. The foam continues to cure for several hours to a day.

The polyester resins are produced by the reaction of a dibasic acid and a polyol with the elimination of water. These resins, when used for polyurethane foam systems, have a number of alcohol groups which react with the polyisocyanate in converting the low molecular weight-liquid polymer into a high molecular-weight elastomer. Simultaneously, the excess of polyisocyanate reacts with water to generate the foaming agent, carbon dioxide (CO_2). The reaction of the polyisocyanate and water also contributes to the cross-linkage of the structure and its final chemical composition. Less cross-linkage or less branching produces a flexible foam. More cross-linkage or more branching produces a less elastic structure; semirigid or rigid foam.

The polyether resins are produced by the catalyzed addition of propylene oxide to an alcohol by a reaction similar to the curing of epoxy resin systems. In the case of rigid foams, a few molecules of propylene oxide are added to the basic alcohol, while for flexible foams, many hundreds are added.

The polyisocyanates are chemicals derived from basic raw materials. Flexible foams have been prepared from various aliphatic and aromatic diisocyanates. For all practical purposes tolylene diisocyanate enjoys a preponderant position in this field. The 80/20 mixture of the 2,4 and 2,6 isomers is the preferred and lowest cost diisocyanate commercially available in the United States. Being very active and able to react readily with compounds containing active hydrogen atoms (i.e., polyesters and polyethers) the diisocyanates permit combinations leading to many new synthetics. Differences in reactivity with other chemical groups enable control of the formulation and characteristics of the resulting synthetic foams with an infinite range of physical, thermal, and chemical properties. These reactions usually take place quite readily at room temperature or with only moderate heating and the absence of catalysts. However, most of the reactions are greatly accelerated by small amounts of catalyst. The reactivity is usually more pronounced with aromatic diisocyanates than with the aliphatic derivatives. The diisocyanates have a tendency to form the dimers at room temperature when stored for long periods of time and, particularly, when exposed to moisture. The addition of small amounts of phosphorous chlorides and acyl chlorides has been recommended to prevent any loss in reactivity.

In the original foaming method for polyurethanes, carbon dioxide is used as the blowing agent. In the new method, a low boiling chlorofluorinated hydrocarbon (Freon) is introduced into the catalyst portion of the components. When the catalyst is added to the polyurethane resin, an exothermic reaction takes place, raising the temperature of the mass above the boiling point of the Freon causing it to expand and fill the cells. Freon blown foams are, in general, considered more stable than the carbon dioxide blown foams.

The course of the many chemical reactions taking place during the formation of a foam will be to an extent, dictated by the selection of the catalyst. For instance, the catalyst serves to drive the reactions between the prepolymer and the water, or between the isocyanate, resin and water at such rates that the foam rises and cures sufficiently fast to prevent collapse of the foam. The catalyst balances the many reactions taking place by varying its concentration and the type. 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 evolution to maintain its volume without collapse.

The catalysts most commonly used for the polyurethane foams are tertiary amines and tin compounds, such as stannous octoate, stannous oleate, dibutyltin dioctoate, and dibutyltin dilaurate. Some of these catalysts can also be utilized for producing silicone foams.

The catalytic effect and also the usefulness of the tertiary amine for foam formation are greatly influenced by the amine structure.(1,2) Factors generally considered for a catalyst are catalytic strength, odor, vapor pressure, and stability. In the case of the amine for example, the catalytic strength generally increases as the basicity of the amine increases and as steric shielding of the amino nitrogen decreases(3). Relatively low molecular weight dimethyl alkyl amines are strong catalysts, are water-soluble, and have a high vapor pressure. Therefore, their odor leaves the foam quickly. They are good catalysts for the preparation of odorless foams. Being strong catalysts, they are used in low concentration (0.1 to 0.4 percent of the weight of the resin). However, foams made using only these catalysts usually have poor compression set or may cure only slowly to a state having low compression set; that is, the catalyst is not staying in the foam long enough to catalyze adequately the cure required for good compression set.

Contrary to the low molecular weight amines, the higher molecular weight amines (e.g.,dimethylcetylamine) are not such strong catalysts and may be used in concentrations of 1 to 2 percent of the resin weight. With this concentration and the inherent low vapor pressure, this type of catalyst will remain in the foam a long time, helping insure good compression set but leaving an amine odor in the foam.

An intermediate molecular weight amine (e.g., ethylmorpholine)(4) has moderate activity and is often used in concentration of about 0.5 to 1 percent of the resin weight. Its catalytic strength provides a desirable balance of reactions, while its concentration and vapor pressure are such that it generally insures good compression set, yet its odor does not persist in the foam as long as does that of dimethylcetylamine. Therefore, this class of amine catalyst holds the most promise for the formation of the desired foam for the applicable prepolymers.

In general, the tertiary amine catalysts provide satisfactory foaming with either the one-shot polyester or the polyether prepolymer systems. However, the tertiary amines are not adequate catalysts for the one-shot systems for polyether flexible foams, largely because of the low viscosity of the polyethers used, but also in part because the majority of the commercially available polyethers most suitable for foam have secondary hydroxyl groups. Thus, with a tertiary amine catalyzed polyether one-shot system, the gas evolution occurs before the polymer viscosity is adequate to trap and hold the gas. This deficiency may be overcome by using tin catalysts.

Tin catalysts,(5,6) such as dibutyltin dioctoate, dibutyltin dilaurate, stannous oleate, and stannous octoate, are many times more powerful for the isocyanate-hydroxyl reaction than are the tertiary amines, but apparently, are not strong catalysts for the isocyanate-water reaction in a foam system. Thus, the tin catalysts may be used to force the reaction between isocyanate end polyether at such a rate that viscosity is rapidly increased and the gas is trapped and held satisfactorily. Also, contrary to many of the tertiary amines, which evaporate from the foam, the tin catalysts remain in the foam permanently, although they may undergo some change chemically with time, e.g., oxidation of stannous tin to stannic tin or hydrolysis. One must then choose a catalyst system that will have no adverse effect on the foam during its use.

b. Vinyl Foams

A vinyl foam consists of a vinyl resin which when plasticized and

stabilized with an appropriate plasticizer and stabilizer will expand under heat in the presence of a suitable blowing agent. Vinyl alcohol, vinyl acetate, vinyl chloride, vinyl bromide, and vinyl benzene (styrene) on polymerization all form thermoplastic vinyl resins. Most extensive use has been made of polymers and copolymers of vinyl chloride. This type of vinyl resin was investigated in preparing vinyl closed-cell foams during this research program.

Vinyl chloride is prepared most conveniently by treating ethylene dichloride with alcoholic potassium hydroxide, but can be prepared also by passing ethylene dichloride over hot alumina or charcoal; in the latter process, acetylene is a by-product. Pure vinyl chloride polymerizes only slowly in the dark at ordinary temperatures, but the rate of polymerization increases sharply as the temperature is raised. The reaction is catalyzed by ultraviolet light or by the addition of peroxides, ozone, or tetraethyllead. Polymerization in emulsion can lead to higher-viscosity polymers. By control of the various factors, polymers can be obtained ranging in average molecular weight from 4300 to 100,000. In emulsion the vinyl monomer may be polymerized at favorable rates in an aqueous medium containing an emulsifier and a water-soluble initiator.

$$CH_2 = CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl \xrightarrow{\quad KOH \quad}$$

Ethylene dichloride

$$CH_2 = CHCl \longrightarrow \cdots \underset{Cl}{CH_2CH} - \underset{Cl}{CH_2CH} - \underset{Cl}{CH_2CH}\cdots$$

Vinyl chloride monomer

Polyvinyl chloride

A typical simple "recipe" would consist of the following ingredients with their proportions indicated in parts by weight: 100 of monomer, 180 of water, 2 to 5 of fatty acid soap and 0.1 to 0.5 of potassium persulfate. Cationic soaps (e.g., dodecylamine hydrochloride) may be used instead of the fatty acid soap, and various other initiators may replace the persulfate (e.g., hydrogen peroxide and ferrous ion, or a water-soluble organic hydroperoxide).

The polyvinyl chloride resin obtained shows rubberlike characteristics when plasticized by the addition of another ingredient. This plasticization forms a vinyl dispersion which is a suspension of the finely divided resin in an organic liquid or plasticizer. The plasticizer used does not dissolve the resin but rather exerts a peptizing effect on the dispersed particles. When enough liquid plasticizer is used to disperse the resin particles without the addition of any volatile thinners, the resulting resin-plasticizer dispersion is called a plastisol. If at least part of the suspending phase consists of volatile liquids, the dispersion is normally called an organosol.

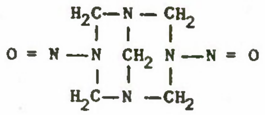
The properties of the vinyl foam in its final use will be determined by the amount and type of ingredients used. The flow properties and aging characteristics of the plastisol will be critical for a successful application of the foam. Those are controlled largely by the choice of the plasticizer and, of course, by the resin itself. The choice of the plasticizer and its viscosity will determine the plastisol viscosity and subsequently its flow properties. To attain the desired end properties of the foam it is necessary to use mixtures of various plasticizers. Mixed plasticizers produce flow properties and aging characteristics of the foam intermediate between those of the individual plasticizers. In all combinations, however, both the undesirable, as well as the desirable, characteristics of each plasticizer may be transmitted to the plastisol and the finished foam. The plasticizer is largely responsible for determining such characteristics as flexibility flow, temperature of processing, odor and tack. Plasticizers may be classified both by chemical structure and by affinity for the resin. Chemically, there are monomeric or ester-type plasticizers and polymeric plasticizers.

As compared to the plastisols, the organosols enable the use of the highest molecular weight, toughest and most chemically resistant vinyl resins. An important factor in the performance of organosol formulation is the choice of a dispersant and diluent. Dispersants are polar compounds which form strong attachments to the resins, aiding in the wetting and dispersing of them. Diluents are aromatic or aliphatic hydrocarbons or a blend of these. They are used to balance and modify the wetting and swelling characteristics of the dispersants. The preferred volatile dispersants are the higher boiling ketones such as diisobutyl ketone. In all cases wherein such volatile liquids are used, there must be a preliminary removal of these liquids before the processing of the organosol.

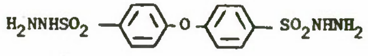
During fusion, the vinyl resin when not stabilized in a plastisol formulation has a tendency to decompose, releasing hydrogen chloride and the formation of conjugated unsaturation. To prevent this decomposition, stabilizers are used. One of the main functions of a stabilizer in a plastisol is to prevent or minimize the discoloration resulting from this action by neutralizing the acid as it is formed. This is important because the reaction is autocatalytic in the sense that the presence of free acid speeds up further breakdown.

Lead stabilizers(7) such as litharge, basic lead carbonate and lead silicate-silica gel complexes, are satisfactory heat stabilizers. The highly basic lead stabilizers perform better in compounds containing organic polyester-type or polymeric-type plasticizers, while the lead silicate-silica gel complex stabilizers appear better suited for use with organic-ester type or oil-type plasticizers. Cadmium compounds in conjunction with barium salts give good all-around heat and light stability. Similarly, di-glycidyl compounds are also found to be good heat and light stabilizers. In general, the amount of stabilizer necessary will depend upon the efficiency of the stabilizer, the composition of the plastisol, and the intended end use.

For the expansion of the plastisol or the formation of a foamed polymer cellular structure, different organic compounds can be used. When heated to a specific temperature, these compounds (known as blowing agents) will decompose and liberate a gas or gases. For instance, two of the most commonly used blowing agents in the vinyl foam preparation are the N,N'-dinitrosopentamethylene tetramine and p,p'-oxybis (benzene sulfonyl hydrazide).



Dinitrosopentamethylene
tetramine

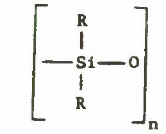


oxybis (benzene sulfonyl hydrazide)

Both are nitrogen-liberating blowing agents.

c. Silicone foams

The silicones are a class of polymers based on a linear, cyclic, or cross-linked arrangement of alternating silicon and oxygen atoms wherein the silicon is substituted by organic radicals or hydrogen. This class of polymers is formulated as follows:



$$\left[-\mathrm{Si}(R)(R)-O- \right]_n$$

$R = CH_3$, C_2H_5, C_6H_5,

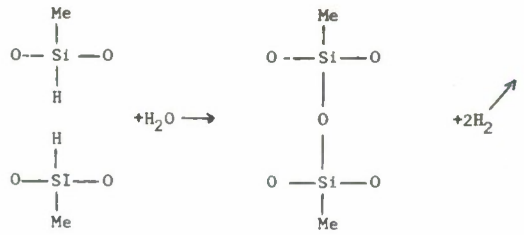
$CH_2 = CH_2$, etc.

Organopolysiloxanes

The usual procedure for preparing silicone polymers is to hydrolize compounds such as R_3SiCl, R_2SiCl_2, $RSiCl_3$, and $SiCl_4$. The intermediates in the reaction are believed to be the corresponding silanols $R_2Si(OH)_2$ which condense very rapidly with elimination of water and formation of the -Si-O-Si-link. If (n) ranges from 3 to 9, cyclic systems are obtained which in the presence of alkaline catalysts open and give high molecular weight, linear silicone gum, and subsequently elastomers. Various curing techniques are available for converting linear and cyclic materials to cross-linked elastomers and resins.

The manufacture of silicone elastomers is divided essentially into two steps; compounding and cross-linking. The first step consists of the intimate mixing under high shear or milling of the polysiloxane gum or resin, a filler, and usually a cross-linking agent, together with miscellaneous additives for obtaining the desired physical properties. The second step involves the cross-linking and curing processes that connect the polymer molecules with one another into an elastomeric mass of the desired properties. The compounded stock may be cross-linked by the action of organic peroxides, such as benzoyl peroxide. The number of cross-links can be controlled by varying the amount of peroxide used.

Silicone foams are obtained by catalyzing a fluid silicone resin which contains hydrogen as a foaming source. In this type of foaming system, the foaming agent hydrogen is released upon mixing of the silicone resin with the appropriate catalyst. A large variety of hydrogen sources exist, but the most interesting one has a releasing mechanism that is initiated at room temperature and then accelerated with the exothermic chemical reaction taking place when the silicone base fluid and catalyst are mixed. Such a hydrogen foaming source could be obtained by the following chemical system:



This reaction is very feasible due to the sensitivity of the silicon-hydrogen bond to acid and especially to base catalysts.

d. Rubber Latex Foams

Rubber latex is a colloidal dispersion of elastomeric particles in water and is compounded with antioxidant, vulcanizing ingredients and soap, and frothed to a creamy low density foam. The liquid foamed rubber latex is cast or shaped prior to gelation, which is carried out through a pH-lowering mechanism, such as the addition of a slowly soluble acid salt. The gelled froth, or foam, is then exposed to elevated temperatures using steam, hot air, or the like to effect the sulfur cross-linking reaction known as vulcanization. Tha produce can then be stripped from molds or casting belts and is usually masked to remove most of the water solubles and reduce odor. It is dried and is then ready for use.

A large variation of elastomeric materials can be used for the preparation of rubber latex foams. Although, generally, styrena-butadiena rubber (SBR) and natural rubber are mostly used for the preparation of latex foams, neoprene or acrylonitrile types are sometimes used. The latter produce foams with outstanding flame resistance and also resistance to oils which normally swell and deteriorate natural rubber and SBR. Acrylonitrile latex is used to make foam with oustanding solvent resistance.

The formation of copolymers using urethane foam formulation and rubber latices results in products with improved physical properties. The latices are added to the isocyanate-terminated prepolymers and the mixture heated in a mold to form flexible foams. The water present in the latex is used in the foaming of the prepolymer mix. Natural rubber, chlorosulfonated polyethylene (Hypalon), chlorinated polyethylene, neoprene, butadiene-styrene, butadiene-acrylonitrile, and other copolymers can be used to modify properties of flexible urethane foams.

2. Foam Formation Physical Aspects - The preparation of a foam involves the formation of gas bubbles in a liquid system which is polymerizing, and the growth and stabilization of these aspects of bubble nucleation (or formation), growth, and stability are of prime importance.

In the formation of a foam, several steps are considered. First the blowing agent generates a gas in the liquid phase with the gas reaching its saturation limit in solution, then becoming supersaturated, and finally coming out of the solution in the form of a bubble. 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 forms new bubbles and diffuses 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 or fusing liquid phase becomes thinner. The bubbles lose their spherical shape as the liquid phase becomes thinner, with the bubbles finally assuming a structure bounded by several membranes of polymerizing or fusing liquid. Where membranes join each other, a rib is present that is thick compared to the membranes.(8)

The cell size of a foam can be controlled by chemical and physical means. One of the physical means is the use of nucleating agents. For instance, finely dispersed silicone oils, especially the dimethylsiloxane type, may serve as nucleation agents in the formation of polyurethane foams. An increase in silicone oil concentration will form fine cells. Fine cells would be the result of faster nucleation and continued nucleation of relatively low degrees of gas supersaturation, so that more cells are formed. Dissolved gases in the reactants will influence the foaming. Therefore, if dissolved gases were sufficient to have the reactants near the saturation before foaming reactions begin, one might expect faster nucleation and finer cells.

The amount of free energy increase (ΔF) necessary to disperse a given volume of gas in a unit volume of liquid will be dependent upon the surface tension (γ) of the liquid and the total interfacial area (A). From this, the following equation can be written:[8]

$$\Delta F = \gamma A$$

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. Further, that the coalescence of cells and foam collapse will be favored energetically unless other factors prevent, i.e., curing of foam before collapse can occur. Also, 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 of A.

The size of the foam cell changes with time by diffusion of gas from the liquid phase into the cell, and also by coalescence of cells. According to classical theory, the gas pressure in a spherical bubble is larger than the pressure in the surrounding liquid by a difference (ΔP) given by the equation:

$$\Delta P = 2\gamma/R$$

in which R is the radius of the bubble. This means that the gas pressure in a small bubble is larger than that in a large bubble. For a given medium, the difference in internal pressure (ΔP_1^2) existing between two bubbles of radii R_1 and R_2 is given by the equation:

$$\Delta P_1^2 = 2Y \left[(1/R_1) - (1/R_2)\right]$$

Therefore, in a liquid system there is diffusion of gas from the small bubbles into the large bubbles. Thus, the small bubbles tend to disappear and the large bubbles to grow. As a result, the average bubble size in a polydispersed system increases with time.

Another factor influencing cell stability is temperature. An increase in temperature reduces the surface tension, thus promoting thinning of the cell membranes, hence promoting rupture. However, increase in temperature also increases the rate of polymerizing or fusing, thus increasing the viscosity of the liquid medium and reducing the thinning of the cell walls, hence stabilizing the foam. These two effects have to be balanced to obtain the best quality foam.

If the cells are too fine, collapse will occur because of the tendency of the too thin cell-walls to rupture. Also, the ribs of these cells are too thin and are not strong enough to stop the rupture started in a membrane. Thus the rupture will continue indefinitely and the foam will collapse. This relation between fine-cell structure and foam collapse results in the well-known difficulty of producing the finest cell foam consistently, compared to the ease of producing a medium or coarse cell foam.

The initial viscosity of a foam system influences greatly the stabilization of the system, although the nucleation of the bubbles will be influenced very little, if at all, by the viscosity.(9) A typical example is the case of polyurethane foams in which the polyesters have relatively high initial viscosities of 10,000 to 20,000 centipoises (cps) at room temperature. No silicone oil is needed for foam stability, although it may be added to control cell size. Similarly, with polyether prepolymers of 20,000 to 30,000 cps viscosity at room temperature, no silicone oil is necessary as a foam stabilizer.

To obtain a complete understanding of foam formation one must be aware of the viscoelastic changes which occur in a foam system, in addition to the chemical reactions occurring snd the colloidal aspects of developing a dispersion of a gas in a polymerizing medium. In the preparation of a flexible foam, the change from a liquid system to a plastic gel and then to a highly elastic polymer can be observed. For instance, in a polyurethane or in a silicone system, one predicts that the growing polymer will change progressively from its initial liquid state into a thermoplastic, soluble, highly viscous polymer or moderste molecular weight; then, as some branching develops into crosslinks, the polymer will become insoluble and take on some elastic

properties. Finally, when the molecular weight reaches very high values, and the polymer is cross-linked into a network structure with moderately long chain segments between cross-links, the polymer will become highly elastic. These changes are shown graphically in figure 1.(10)

In the case of the preparation of a flexible vinyl foam, the basic polymer has already been polymerized to the desired molecular weight and it is in this state that it is mixed or treated with appropriate plasticizers and stabilizers. This treatment is performed at elevated temperatures where the mixture of vinyl resin, plasticizer, and stabilizer go first through a gelling stage, then a fusing stage, and upon cooling the polymer will become highly elastic.

The rupturing of the cells in a flexible foam usually occurs just as the foam reaches its maximum volume. Experimental data indicated that the cells will rupture when the last surge of gas (or maximum gas evolution) is observed and the membranes of the cells have reached a state of high viscosity, but still have very low elasticity.(10) The high viscosity does not permit the membrane to flow fast enough to expand and to relieve the pressure of the gas generated. Also, the elasticity is 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 results in rupture and opening of the cells, leading to further rupture and formation of a void in the foam or total foam collapse.

However, if at the time of maximum gas evolution, the cell membranes do not rupture, the cells are closed, and when the foam cools the cella of a flexible foam will contract due to the reduced internal pressure of the cooling gas. The rupturing of the cell membranes will not take place due to too low a viscosity, so that the membranes will flow as the gas volume increases, thus relieving pressure as it develops. Also, the rupturing will not occur if the membranes are so elastic that they can atretch reversibly to accomodate the last increase in gas volume. In the former case, the polymer cure will not have progressed far enough, at the time of maximum gas evolution, and in the latter case, the cure will have progressed too far.

The formation of closed cells or open cells can be reduced or increased in some polyurethane systems by varying the tin catalyst content. By reducing the tin catalyst, the polymer growth and elasticity ara reduced at the time of the last surge of gas, thereby diminishing the membrane's elasticity and reducing the formation of closed cells. On the other hand, an increase in the tin catalyst content will enhance the cure rate so as to impart elasticity to the membrane and, hence, to increase the formation of closed cells. In some cases in which very low tin catalyst concentrations are used, the percentage of closed cells can be increased due to the low viscosity of the membrane.

An additional observation regarding closed cell formation is the relation between the branching of the resin reactant and the rate of polymerization. With a given rate of reaction of isocyanate with hydroxyl (in polyol) in a polyurethane foam system, a network structure and elasticity are developed faster with a moderately branched resin (or polyol) than with a less brsnched one, thus leading to a higher percentage of closed cells. By increasing the

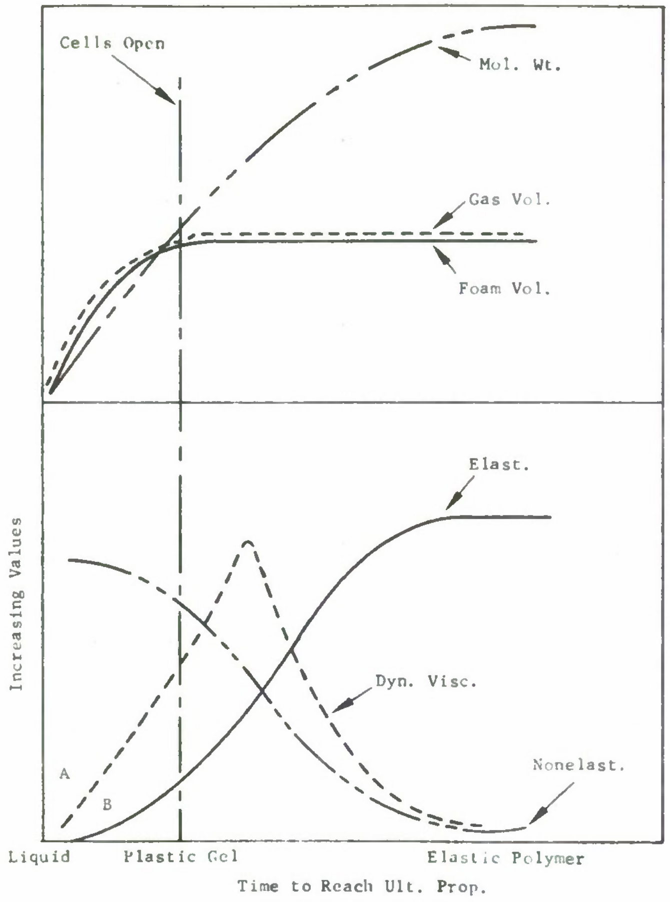


FIGURE 1 TYPICAL CHANGES IN A FLEXIBLE FOAM WITH TIME (TAKEN FROM REFERENCE 10)

isocyanate-hydroxyl reactivity with a given branched resin, the formation of closed cells is increased.

The intimate cell geometry of a flexible foam will affect the mechanical properties of the foam. A change in the percentage of the polymeric material in the cell membrane compared to that in the cell ribs will have an effect. The percentage of closed cells will influence some physical properties of a foam, e.g., a higher percentage of closed cells gives a lower degree of gas permeability, that is, better retention of the gas (blowing agent). Also, as the percentage of closed cells increases, the resiliency of the foam is reduced. However, when the number of closed cells becomes sufficiently large, a pneumatic effect appears to dominate the resiliency so that resiliency increases. This means that, to obtain a good quality closed-cell foam, the percentage of closed cells has to be as large as possible.

B. Foam Development and Evaluation

As mentioned earlier in this section, the objective of this program was to find materials and establish techniques for preparing a suitable closed-cell foam in repeatable processes. The foams were to provide pressures ranging from 7 psia to 3.5 psia when exposed to a vacuum and properly restrained. The pressurizing characteristics of the foamed materials had to be retained through 250 cycles of exposure to a vacuum and 45 days.

The foam development and evaluation was initiated with a thorough survey of information on classes of foam materials followed by a careful experimental screening of foam systems from within each class of material selected from the survey. From this the most promising class of material was retained which was then submitted to a more refined evaluation resulting in suitable foam systems.

1. Survey of Information on Four Classes of Foam Materials - The survey of information on foam systems or foam raw materials covering the four classes of foam materials (polyurethanes, silicones, vinyls, and rubber latices) was conducted in such a way as to (1) screen potential organizations carrying possible suitable foam materials, (2) screen the individual raw materials from each organization selected, (3) evaluate the existing chemical formulations or their possible modifications thereof of each foam system using the screened raw materials, (4) investigate possible existing processing techniques to prepare closed-cell foams under reduced pressure, and (5) gather all information pertinent to this program's research problems through technical literature in government reports as well as technical publications.

From a list of preselected organizations, a selected list of potential industrial organizations was established which is given in Table I. This table summarizes the survey of information which was conducted on the four classes of materials. The four classes of materials are each grouped separately and within each group the following information is given: (1) name and address of organization, (2) how each organization was contacted, (3) raw materials which were available, (4) what information was received after contact, and (5) remarks.

In general, the contacts made with each organization mentioned in Table 1

TABLE 1 - LIST OF POTENTIAL INDUSTRIAL ORGANIZATIONS AND THEIR RAW MATERIALS

A. Polyurethane Foams

Name and Address of Organization	How Organization Was Contacted	Raw Materials Available	Received After Contact	Remarks
1. Union Carbide Chemicals Co., Mfg. Plant, South Charleston, West Va.	Personal contact with representatives.	Polyethers, Catalysts, Surfactants, Blowing agents and Isocyanates.	Free sample of each with technical literature.	The company is mainly interested in open-cell foams and no information could be obtained on how to make closed cell foams under reduced pressure. Were highly interested in knowing how.
2. American Latex Products Corp., a Division of the Dayco Corp., Hawthorne, California	Personal contact with representatives.	Polyethers, Catalysts, Blowing agents, Mold release agents, Isocyanates.	Free samples of polyethers and isocyanates.	Both open-cell and closed-cell foams are of interest to the company but no information on how to make closed-cell foams under reduced pressure could be obtained.
3. Polytron Co., Los Angeles Office (Mr. J. Wernack) 11934 Riverside Drive, Suite 101, N. Hollywood	Representatives were contacted by telephone.	Prepolymers and Catalysts.	Free samples of each with technical literature.	Open cell foam technology of interest to the company. No information available on how to make a high-strength, closed-cell foam under reduced pressure. Highly interested in knowing how.
4. Foemade Industries, 1220 Morse St., Royal Oak, Michigan	Representatives were contacted by mail.	Polyurethane foam systems.	One free sample.	Open-cell and closed-cell foams interested but no information on durable closed-cell foams made under reduced pressure.
5. Scott Paper Company, (Foam Division) 1500 E. 2nd St, Chester, Penn.	Representatives were contacted by mail.	Polyethers, Catalysts, Blowing agents, and Isocyanates.	Free polyether sample with technical literature.	Mainly open-cell foams interested. Nothing available on how to prepare high durable closed-cell foams under a reduced pressure.
6. Phalan's Resins and Plastics, Oak Street and Bluff Road, Burlington, Iowa.	Representatives were contacted by mail.	Polyethers, Polyesters and cyanates.	Free foam system already premixed.	Open-cell and closed-cell foams interested but no information on how to make closed-cell foams under reduced pressure. Highly interested in knowing how.
7. Wyandotte Chemicals Corp., Pacific Dist. Sales Office, 232 N. Lake Street, Pasadena, California	Representatives were contacted by telephone.	Polyethers, Isocyanates, Catalysts	Free samples of each with technical literature.	Involved in intensive research on open-cell and closed-cell foam systems. However, no information available on how to make high strength, closed-cell foams under reduced pressure. Highly interested in knowing how.
8. Witco Chemical Co., Inc., Urethane Chemicals Dept., 75 East Wacker Drive, Chicago, Illinois	Representatives were contacted by telephone.	Polyesters, Polyethers, Catalysts and Coupling agents	Free samples of polyester and isocyanate and technical literature.	Open-cell foams mainly and no information available on how to make closed-cell foams under reduced pressure. Were interested in learning how.
9. Emerson and Cuming, Inc., 604 West 182nd Street, Gardena, Calif.	Personal contact with representative.	Mold release agents	Samples were purchased.	----
10. Nopco Chemical Co., Plastics Division, 60 Park Place, Newark, New Jersey	Representatives were contacted by phone.	Prepolymers and Catalysts	Free samples of prepolymers and technical literature.	Open-cell and closed-cell foams technology but no information on how to make closed-cell foams under a reduced pressure.
11. DuPont de Nemours Co., Elastomer Chemical Dept., Room 2269-A, Wilmington, Delaware	Representatives were contacted by telephone.	Blowing agents, Isocyanates.	Free sample of each plus technical literature.	No information on making closed-cell foam under reduced pressure. Were interested in learning the technique.
12. Plastomer Corp. 6433 Epworth, Detroit 10, Mich.	Representatives were contacted by mail.	Polyethers, Catalysts, Isocyanates	No samples but useful technical literature.	Not aware of how to make closed-cell foams under reduced pressure.
13. Olin Chemicals Div., 2041 Pioneer Court San Mateo, Calif.	Representatives were contacted by telephone.	Polyols, Isocyanates	Several free samples of polyols and isocyanates plus technical literature.	Open-cell and closed-cell foams but no information on how to make closed-cell foams under reduced pressure and were interested in knowing how.

	Name and Address of Organization	How Organization Was Contacted	Raw Materials Available	Received After Contact	Remarks
14.	Allied Chemical, National Aniline Division, 40 Rector Street, N. Y.	Representatives were contacted by phone.	Polyethers	Free samples of polyethers.	Large interest in open-cell and closed-cell foams. No studies had been made in preparing closed-cell foams under reduced pressure. Were highly interested in knowing how.

B. Vinyl Foams

	Name and Address of Organization	How Organization Was Contacted	Raw Materials Available	Received After Contact	Remarks
1.	B.F. Goodrich Chemical Co., Adhesive Products Division, Los Angeles, Calif.	Representatives contacted by telephone.	Plastisols, Polyvinylchloride resins, Plasticizers.	Free samples of each and technical literature. Large samples of plastisols were purchased.	Large interest in closed-cell foams prepared under high pressures. Very much interested in our program, on how to make closed-cell foams under reduced pressure.
2.	R. T. Vanderbilt Co., Inc., 1248 Wholesale St., Los Angeles	Representative was contacted by telephone.	Blowing agents	Free samples plus technical literature.	Interested to know more about how to make closed-cell foams under reduced pressure.
3.	United States Rubber Co., Ensolite Products Dept., Mishawaka, Indiana	Representatives were contacted personally, by phone and by mail.	Plastisols, Blowing agents, Foam samples (closed-cell)	Free samples of each plus technical literature.	Large interest in closed-cell foams prepared under high pressures and one atm. Highly interested in our program, that is, how to prepare closed-cell foams under reduced pressure.
4.	Diamond Alkali Co., Union Commerce Bldg. Cleveland, Ohio	Representatives were contacted by mail and by phone	Vinyl organosol in form of powder.	Free sample plus technical literature.	Involved in vinyl foam formulations. However, no information on how to prepare closed-cell foam under reduced pressure was available.
5.	DuPont Co., Elastomer Chemicals Dept., Wilmington, Delaware	Representatives were contacted personally, by phone and by mail	Blowing agents	Free samples and purchasing of larger samples. Technical literature.	----
6.	Monsanto Hydrocarbons and Polymers Division, 6670 E. Flotilla St., Los Angeles, Calif.	Representative was contacted personally and by telephone.	Plasticizers and Polyvinylchloride resins	Free samples of each plus technical literature.	Highly interested in our research study on how to make closed-cell foams under reduced pressure.

	Name and Address of Organization	How Organization Was Contacted	Raw Materials Available	Received After Contact	Remarks
7.	Union Carbide Chemicals Co. South Charleston, West Virginia	Representative was contacted by phone.	Plasticizers, Polyvinyl chloride resins	Free samples of each plus technical literature.	Mainly involved in the fabrication of polyvinylchloride resins and plasticizers. No information available on how to make closed-cell foam under reduced pressure.
8.	Stay and Dey Paint Materials Co., 363 S. Mission Road, Los Angeles, California	Representative was contacted by phone.	Stabilizers	Free samples and purchasing of large samples. Technical literature.	Distributor of stabilizers.
9.	Firestone Tire and Rubber Co., Industrial Products Division, 6333 Telegraph Road, Los Angeles, California	Representative was contacted by phone.	Polyvinylchloride resins	Free samples	Involved in closed-cell foam technology but no information was available on the preparation of closed-cell foam under reduced pressure.
10.	The Goodyear Tire and Rubber Co., Chemical Division, 6666 E. Washington Blvd., Los Angeles	Representative was contacted by telephone.	Polyvinylchloride resins	No samples have been received to date. Technical literature received.	Large manufacturer of polyvinylchloride resins. Highly interested in our program of preparing closed-cell foam under reduced pressure.
11.	The Ware Chemical Corp. P.O. Box 783 Westport, Connecticut	Representative was contacted personally and by phone.	Prespersion of blowing agents	Free samples and purchasing of samples. Technical literature.	Prepares prespersions of dinitrosOpentamethyione tetramine (blowing agent) in oils or plasticizers.
12.	Rohm and Haas Co. 1920 S. Tubeway Avenue Los Angeles, Calif.	Representative was contacted by phone.	Plasticizers	Free samples plus technical literature.	Manufactures a long series of high molecular weight plasticizers. Very much interested in our study of preparing closed-cell foams under a reduced pressure condition.

Name and Address of Organization	How Organization Was Contacted	Raw Materials Available	Received After Contact	Remarks
13. Rubatex Corporation 2655 Commerce Way Los Angeles, Calif.	Representative was contacted by phone.	Plastisols	Free samples.	Investigates plastisols in a liquid and a solid form in the process of making closed-cell foams. The company was highly interested in our closed-cell foam research program.
C. Silicone Foams				
1. General Electric, Silicone Products Dept. Waterford, New York	Representatives were contacted personally and by phone.	RTV Silicone base polymers and catalysts	Free samples and technical literature.	Open-cell and closed-cell silicone foams.
2. Dow Corning, Engineering Products Division, Midland, Michigan	Representative was contacted personally and by phone.	RTV Silicone base polymers and catalysts	Free samples and technical literature.	Open-cell and closed-cell silicone foams. Were highly interested in our research program on closed-cell foams prepared under reduced pressure.
D. Rubber Latex Foams				
1. Goodyear Chemical, Data Center, F-16, Box 9115, Akron, Ohio	Representative was contacted by mail.	Pliolite latices	No samples but technical literature was received	Large manufacturer of rubber latex foams.
2. The Dow Chemical Co., Plastics Sales Dept., Midland, Michigan	Representative was contacted by mail.	Styrene-butadiene base polymers, Vinyl resins, and Nitrile base polymers	No samples and no literature received.	Large manufacturer of rubber latex foams.
3. Enjay Chemical Co., 615 S. Flower Street, Los Angeles, Calif.	Representative was contacted by phone.	Butyl latex	No samples were received due to the butyl latex not being satisfactory in preparation of closed-cell foams. Technical literature was received.	Major manufacturer of butyl latex.

were fruitful in acquiring foam raw materials, verbal suggestions and technical literature. These three factors were very helpful in initiating the experimental program, that is, the preparation and evaluation of suitable flexible closed-cell foams. However, preliminary testing proved that none of the available commercial foam formulations would give closed-cell foams which would meet this program's requirements. Therefore, it was necessary to establish a program to develop suitable formulations. Two different approaches were taken in the establishment of these formulations: (1) the use of existing commercial formulations which, with modifications, would yield a suitable foam, and (2) the employment of raw materials obtained from industrial organizations to prepare new formulations. Both approaches were pursued experimentally for every class of foam materials selected, with the exception of the rubber latex.

In comparing the practicality, advantages and repeatability of these two approaches, the first offered the advantage of using premixed reactive solutions in most cases, thus speeding the formulation and preparation of the foam. In the second, the improvement of the formulation was simplified since each individual raw material used was chemically known and handled separately. The proportion of the raw materials used in every formulation was known and the physical and chemical properties of each individual raw material could be fully used to its best advantage. In the first approach, this was only possible in certain cases. For instance, premixed solutions of polyurethane foam systems were obtained for which the formulations and mixing proportions were only partly known. A similar situation existed for some silicone foam systems and some vinyl foam systems. In some cases, the formulations and mixing proportions were made known by the vendor after the formulation of potentially suitable foams was shown in preliminary tests. Also, each premixed reactive solution was given a formulation code number which allowed the formulation to be repeated and to fulfill one of this contract's requirements.

In addition to establishing suitable foam formulations and using the appropriate procedure for mixing the selected ingredients, processing techniques for making high strength, flexible, closed cell foam under a reduced pressure condition, had to be investigated and developed for every class of foam material.

A large number of the contacted organizations were highly interested in this research program. Most interested organizations were the organizations whose businesses were directly involved in the preparation of flexible closed-cell foams either through research and development programs or production.

2. <u>Experimental Preparation and Screening of Selected Foam Systems From Survey</u> - Foam systems were experimentally evaluated using the raw materials obtained from the above survey. In a first preliminary step, foam samples were prepared according to the organization's formulations using their processing techniques, if available, or an NSL-established processing technique. These foam samples were analyzed for their quality such as cell structure uniformity, expansion capability under vacuum, strength, durability and toxicity (emanation of nauseous gases). None of the foam samples was satisfactory so the formulation was either modified or completely changed. The processing technique was also modified or completely changed. Each foam system was

thoroughly investigated either physically or chemically before its rejection as a possible candidate. From the innumerable tests performed, one class of material was retained which was then submitted to further evaluation and screening to enable selection of the foam which would best suit this program's requirements. A description of some of the tests performed with each class of polymeric materials is given below.

a. Polyurethane Foam Systems

The foam formation chemical aspects for this class of material will not be repeated here since it was thoroughly discussed in Section II, A-1. From this discussion we learned that the polyols (polyethers or polyesters) and the isocyanates are the most important ingredients in the preparation of polyurethane foams. During the experimental evaluation, the type of polyol used was varied and the type of isocyanate was kept constant. The isocyanate used in each system was the toluene diisocyanate (80/20 TDI). The other ingredients such as catalyst, stabilizer, cell size control agent, and additional blowing agent, participating in the foam formation, were varied and a large selection was used.

The experimental equipment which was used for the preparation of the foam samples is shown in figure 2. As shown, two different foaming apparatus were used, one for the initially low viscosity reactive fluids enabling the utilization of the magnetic stirrer and one for the initially high viscosity reactive fluids where a more powerful stirring device was necessary. To regulate the pressure inside the foaming containers, two separate pressure regulators calibrated for 3.5 psia and 7 psia, were used. Also a manual pressure control system was installed. To attain the minimum change of pressure (due to gas formation) during an actual foaming test at either 3.5 psia or 7 psia, a large container (bell-jar) under similar reduced pressures was installed between the vacuum pump and the foaming reaction flask. The chemical reactions taking place in the formation of the foam being exothermic, required, in many cases, a cooling system to slow down the reactions.

These apparatus described above were used for reevaluation of the selected foam systems. A simplified apparatus was used for the preliminary tests to save time. This simplified apparatus consisted of a beaker and a manual stirring device.

A large variety of polyurethane foam systems was tested and the suitability of the resulting foam samples determined. Many systems were rejected after a few preliminary tests had been conducted. From among the most promising systems, six were retained for further evaluation. For these foam systems the modifications and changes of formulation and processing technique with subsequent improved foam quality, are discussed below.

One of the polyurethane foam systems evaluated uses a glycol-adipate type polyester resin which when properly reacted with toluene diisocyanate (80/20 TDI) and activated by an "activator solution" (mixture of water, catalyst, and coupling agents) resulted in a flexible foam. By using the commercial formulation, a low density predominantly open-cell (over 90%) structure foam was obtained. To increase the percentage of closed-cell structure

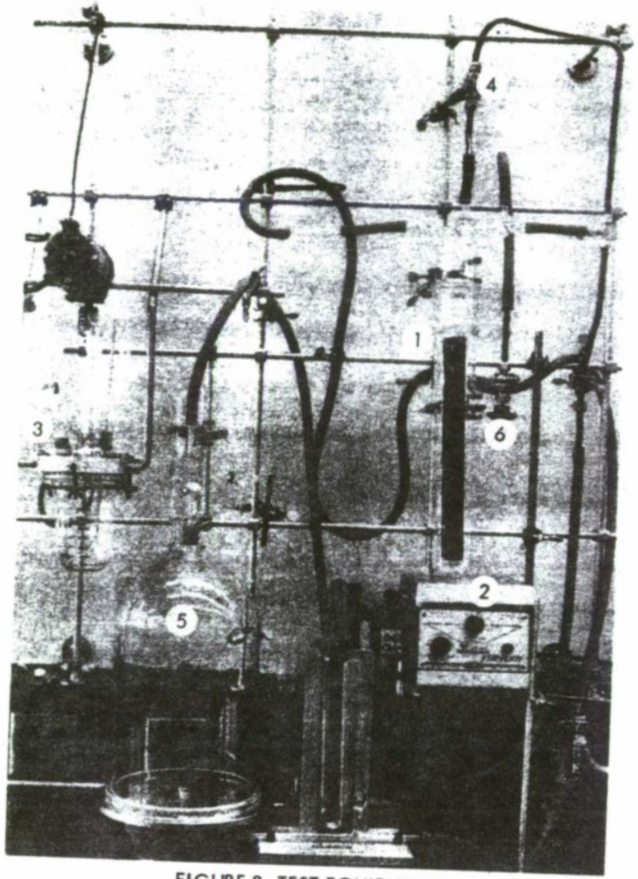


FIGURE 2 TEST EQUIPMENT

PART CODE

1. FOAMING SET-UP FOR LOW VISCOSITY REACTIVE FLUIDS
2. MAGNETIC STIR-PLATE
3. FOAMING SET-UP FOR HIGH VISCOSITY REACTIVE FLUIDS
4. PRESSURE REGULATOR CALIBRATED FOR EITHER 3.5 PSIA OR 7 PSIA
5. VACUUM BELL-JAR FOR REDUCING THE PRESSURE CHANGE
6. VACUUM VALVE FOR FINE MANUAL PRESSURE ADJUSTMENT

some modifications of the formulation were performed. The changes in the formulation were such as to reduce the foam volume, that is, decrease the cell size, increase the reactivity, and speed the cure time. This was accomplished by a slight increase in catalyst concentration and coupling agents which act as surfactants. Caution had to be taken in increasing the amount of catalyst because an excess of it caused splits and shrinkage of the foam. The volume increase of the foam was also reduced by increasing the stirring efficiency and time in order to evacuate excess gases.

From the different formulations tried, the best obtainable foam contained approximately 30 percent of closed cells. This foam was semiflexible which was probably due to too much cross-linking.

In other foam systems three different types of polyols were investigated, (1) a polypropylene glycol, (2) a polyoxypropylene derivative of trimethylolpropane, and (3) a propylene oxide adduct of trimethylolpropane terminated with ethylene oxide.

In using the type (1) polyol and commercial formula, a good flexible foam was obtained. However, its foam structure was mostly open-cell. To obtain a higher percentage of closed cells, the auxiliary trichlorofluoromethane blowing agent was omitted, the ratio of toluene diisocyanate to polyol was decreased in order to reduce the amount of CO_2 evolved, and the content of the catalyst was slightly increased to speed up the curing rate. From these modifications, a good flexible foam sample was obtained showing fine and uniform cells but with only a slight increase in the percentage of closed cells.

Regarding the type (2) polyol, the commercial basic formula gave a good quality foam with approximately 60 percent of closed cells. By placing the foam sample in a vacuum its expansion was large and it returned to its initial shape when removed from the vacuum. However, after repeating this cycling test a dozen times the sample gradually collapsed and shrank.

Chemically the type (2) polyol, as compared to the type (1) polyol has a higher reactivity and is more reproducible due to the higher percentage of primary hydroxyl groups present. The primary hydroxyl groups react much more rapidly with the isocyanate than the secondary hydroxyl groups. Hence, the performance of the polyol varies with the ratio of primary to secondary hydroxyl group contents.

The type (3) polyol, as compared to the type (2) polyol, contains an even higher percentage of primary hydroxyl groups making it even more reactive. However, by preparing foam samples utilizing the commercial formula, the samples which were obtained were very similar to the foam samples obtained with the type (2) polyol. The samples showed good expansion when exposed to the vacuum indicating a closed-cell content of approximately 60 to 70 percent, but nevertheless they shrank after several exposures. The only difference noted between the two types of polyols, type (2) and (3), was finer cells for the type (3) polyol due probably to its higher reactivity.

In further tests with type (2) and (3) polyols, the amount of CO_2 evolved

was decreased to a minimum by decreasing the ratio of toluene diisocyanate to polyol and by increasing the amount of stannous type catalyst in order to speed up the curing rate. In addition, in order to minimize the shrinkage of the foam when exposed to vacuum repeatedly, a technique was used whereby during the mixing procedure of the foam ingredients, an extra blowing agent in the form of a powder was added which, under heat, will decompose and release nitrogen gas. Thus, upon thorough mixing of all the ingredients at the appropriate low temperature to retard the foaming and curing actions, the mixture was introduced in the reduced pressure (3.5 psia or 7 psia) container and after reaching the desired reduced pressure, the temperature of the mixture was raised to approximately 30°F below the blowing agent decomposition temperature. This was performed in order to partially cure the polymer and entrap the intact powdered blowing agent. Once the polymer had reached a certain cure state the temperature of the mixture was then raised to the blowing agent decomposition temperature to release the gas which remained entrapped. This foaming technique proved to be effective inasmuch as the shrinkage of the foam samples obtained was greatly reduced, but not enough to meet this program's requirements.

In still another foam system, the type of polyol investigated was a trifunctional polyoxypropylene tipped with ethylene oxide. This polyol (or polyether) has an average molecular weight of about 3600 and a hydroxyl number of about 46 which is lower than for many polyether triols for flexible foam and, consequently, requires less toluene diisocyanate in the foam formulation. In combination with the polyol and the diisocyanate, stannous octoate (catalyst), water, triethylenediamine (auxiliary catalyst), silicone surfactant, and trichlorofluoromethane (auxiliary blowing agent), were used as activators. This formulation gave a foam with a uniform cell structure, highly flexible and soft, but with mainly an open-cell structure. Improvements towards obtaining a high percentage closed-cell foam were performed by (1) increasing, cautiously, the amount of stannous octoate thus increasing the curing rate to prevent collapse of the foam,and (2) decreasing the amount of toluene diisocyanate and prolonging the mixing of the components for minimizing the amount of gas evolved, thus keeping the foam sample from expanding excessively. The foam sample obtained showed fine and uniform cell structure with an appreciable increase of closed cells but still not sufficient. A minimum of 80 percent closed cells would be considered sufficient, but the higher the content of closed cells the better the foam quality will be. For instance, a 100 percent closed cell foam would give the most uniform expansion when exposed to the reduced pressure and exhibit the best resiliency.

To further increase the percentage of closed cells in this foam, a formula was established which was similar to the one above with the exception of (1) the silicone surfactant was slightly increased to give an even better control of size and uniformity of the cell structure and to aid the mixing of the various components, (2) the auxiliary blowing agent was omitted to avoid excessive blowing gas, and (3) the amount of triethylenediamine (auxiliary catalyst) was slightly increased favoring the formation of closed cells. The foam sample obtained with this formulation was of good quality showing fine and uniform cells and was highly flexible and soft. When exposed to the vacuum it expanded appreciably and was able to stand more repeated exposures to vacuum than any other foam sample tested earlier. The data obtained from expansion ratio measurements and visual observations under a magnifying glass the percentage of closed cells present in the foam structure was estimated to be approximately 70 percent.

Finally, foam samples were prepared using a 50:50 mixture, consisting of the type (2) polyol described earlier and the latter polyol mentioned above. The amount of toluene diisocyanate utilized was kept to a minimum and was added gradually to the other premixed ingredients (with the exception of the catalysts) in order to effect a better control of the CO_2 formation and evolution. No auxiliary blowing agent was used. The amounts of catalyst, surfactant, and auxiliary catalyst were kept on the high side when compared with the basic formulations. The stannous octoate catalyst was added last to allow a better distribution of the gas within the foam prior to curing. The foam samples obtained were flexible, soft, white, of good quality, and had approximately 80 percent closed cells. Their repeated expansion in vacuum was improved with respect to all the other samples previously prepared but still did not possess the physical properties necessary to withstand the 250-cycle test required by the program. Further improvements could have been achieved by remodifying the formulation but the degree of improvement which would have been realized would not have been sufficient to give a suitable foam. Thus further efforts to effect improvements were discontinued.

b. Silicone Foam Systems

Three different silicone foam systems were evaluated of which one was of particular interest. In preliminary tests, a base polymer (phenylmethylpolysiloxane gum) supplied by Dow-Corning was used. In the preparation of the foam system, 18.5 percent by weight of reinforcing silica filler was added. From this silica-filled gum, a stock was prepared by adding 7.5 parts of Cab-O-Sil MS-7 to 100 parts gum. After the last addition, the compound was stabilized by 4 to 5 days aging prior to addition of a vulcanizing agent and blowing agent. After the aging period, the vulcanizing agents such as tertiary-butyl perbenzoate and 2,4-dichlorobenzoyl peroxide, were added using the rubber mill. The blowing agent, N,N'-dimethyl, N,N'-dinitrosoterephthalamide (Nitrosan 70% active) was added simultaneously. The samples thus prepared, prior to blowing, were press-cured at approximately 300°F for a few minutes. The actual blowing was performed at approximately 450°F for 15 minutes.

The foam samples obtained demonstrated good strength and excellent expansion when exposed to the vacuum. However, it was found that after a few days exposure to vacuum, the foam had shrunk appreciably due to the high gas permeation from within the foam cell structure.

The permeation of the blowing gas could be decreased by using copolymers of silicone with other polymeric species. No steps were taken toward this possible improvement because this study of evaluating silicone foams was conducted in parallel with the highly successful vinyl foams.

c. Vinyl Foam Systems

Several vinyl foam systems were evaluated and compared. These systems

were supplied by different industrial organizations in forms of plastisols. As stated in a previous discussion in Section A-1, a plastisol is a colloidal dispersion of a vinyl resin, plasticizer, stabilizer and filler mixed in the proper ratio and giving an easy flowing milky liquid. Among the most promising systems tested two were retained and were identified as BFG (B. F. Goodrich), and USR (U. S. Rubber Company).

BFG Foam System - The BFG foam samples were prepared by adding an appropriate blowing agent to the supplied plastisol and by heating the mixture in an air-circulating oven at a temperature above the blowing agent's decomposition temperature. The chemistry of the formation of vinyl foam will not be repeated here since this was already discussed earlier in Section A-1.

The furnished plastisol, a flowing milky liquid, was a mixture of: a polyvinylchloride resin (Geon resin 121), dioctyl phtholate (plasticizer), monomeric epoxidized soybean oil (plasticizer), and a Cd-Ba-Zn metallic stabilizer. The formulation code number of this plastisol was BFG 370E1330.

The first polyvinylchloride foam samples obtained were prepared under one atmosphere pressure using a series of blowing agents. The selection of the most effective blowing agent depended upon the melt viscosity, the gelling and fusion temperatures of the vinyl matrix. The ideal decomposition temperature of the blowing agent is approximately 10 to 15°F below the fusion temperature of tbe plastisol. This ideal condition can be obtained if the decomposition of the blowing agent is controlled so that gas evolution does not commence until the plastisol has been converted to a homogeneous system of low melt viscosity just prior to full fusion. In our investigation the decomposition temperature of the blowing agents varied, thus giving foam samples with different appearance and quality.

Among the vinyl foam samples prepared, three were of particular interest. In the first case, dinitrosopentamethylene tetramine (40%) mixed with an inert component (60%) was utilized as the blowing agent. The average decomposition temperature of this type of blowing agent in vinyl is 340°F. When used in a 2 percent proportion and properly dispersed in the plastisol, the heated mixture (above 340°F) released the gas from the blowing agent and fused the vinyl polymer forming the cell membranes and ribs. Upon further heating the gas expanded and the cell structure set after cooling, becoming elastic. The vinyl foam sample obtained was of good quality with a high percentage of closed cells (≈ 100%). No sign of shrinkage or collapse when the foam was exposed to vacuum repeatedly for at least one week.

In the second case, dinitrosopentamethylene tetramine was also used as the blowing agent but in a purer form (100%) that is more reactive. The results obtained were very similar to the above with the exception of the cell structure which was more uniform. Finally, in the third case [p, p'-oxybis-(benzene-sulfonyl hydrazide)] was used as the blowing agent. Its average decomposition temperature is 310°F. The results here too were similar to the results in case one with the exception that finer cells were obtained. In all three cases the gas released from the blowing agents was nitrogen. The foam's quality was good but the samples had been prepared under one atmosphere pressure. Since pressure responses of either 3.5 or 7 psia were required, the next step was to prepare foam samples under these reduced pressures. In a first try, samples were prepared in a vacuum chamber in which the forming foam samples were allowed to expand freely during the processing procedure. However, uncontrolled foam expansion, breakage of cells followed by a collapse of cells, etc., resulted in poor quality foam samples. A technique was then developed whereby the foam sample was prepared under a restraint condition at the desired reduced pressure. This method enabled a better control of the foam expansion and cell structure uniformity. Using this technique, good quality foam sheets were prepared under 3.5 psia and 7 psia reduced pressures.

This latter test indicated that the BFG vinyl foam system was very promising for this program's application. Therefore, it was decided to conduct a further evaluation of this particular foam system. Section C (page 29) covers this evaluation very thoroughly.

USR Foam System - A USR foam system was supplied by the United States Rubber Company with a formulation suitable for preparation of foam samples in one atmosphere pressure. This system was supplied to NSL for exploratory trials. The foam system consisted of a plastisol (formulation code number DC-2113) and a blowing agent paste. Foam samples prepared with the system as received were not of good quality, particularly when prepared under the required reduced pressures using the same processing technique employed with the BFG foam system. However, by eliminating the blowing agent paste and replacing it with the dinitrosopentamethylene tetramine (pure form) blowing agent, the results indicated a drastic change wherein good quality foam was obtained. When compared with the BFG foam system, the USR foams were softer and had finer cells but strength and durability were lower. Nevertheless, this foam system was retained and used effectively in combination with the BFG foam system as shown in tests described in Section C-1 below.

d. Rubber Latex Foam Systems

The investigation of the rubber latex foam systems was conducted after suitable vinyl foams had been successfully prepared. Nevertheless, a consideration of the rubber latex systems was initiated for the purpose of comparing the best vinyl foam with a possible breakthrough in the rubber latex foam class of materials. In other words, were there rubber latex foam systems which could give foam samples whose quality would exceed the quality of our best vinyl foam samples?

Two classes of rubber latex foams were considered, (1) butyl latex foams and (2) acrylonitrile latex foams. The butyl latex was of particular interest because of the known low gas permeability of the butyl rubber itself. Copolymerization of vinyl rubber with either butyl or acrylonitrile rubbers was also of interest.

From the extent of literature research conducted and the number of inquiries made of different industrial organizations, it was concluded that it was improbable that a rubber latex closed-cell foam could be prepared that would be superior in quality to the best vinyl foams produced.

3. Conclusions and Selection of a Class of Foam Materials - In a general statement, the possible suitability of the foam systems discussed above can be summarized as follows:

(I) Two common problems were evident in the evaluation of the polyurethane foams, (a) the control of gas evolution during the foam formation under the specific conditions required, and (b) the retention of gas within the closed cells to prevent shrinkage of the foam.

(II) In the evaluation of silicone foam systems, excellent foam samples were obtained. The percentage of closed cells was high, the cell structure was very uniform and flexibility and softness were very good, but the foam samples shrank badly when exposed to vacuum repeatedly due to the cell-wall membrane's high permeability to gases. This permeability could be inhibited or prevented by use of coatings.

(III) From the literature and inquiries made of industrial organizations on specific rubber latex classes of materials, difficulties in making closed cell foams under the specific conditions required, seemed to be the problem.

(IV) The results obtained with the vinyl foam systems were very encouraging. The preliminary tests conducted on some vinyl foam systems, such as the BFG and USR foam systems, definitely indicated good possibilities in obtaining the foam required for this program's final objective.

From the above, it can be stated that the vinyl foam systems exhibited the most promising prospects.

C. Further Evaluation and Screening of Polyvinylchloride Foam Systems

The very encouraging preliminary results obtained with the vinyl foam systems as described above in Section 2-c led to a more thorough evaluation of this class of polymers. Such problems as (1) establishing the most suitable formulation and the most appropriate foaming technique, (2) the density control of the cellular vinyl foam, (3) the preparation of foam samples under either 3.5 psia or 7 psia reduced pressure, and (4) obtaining vinyl foam samples with the highest percentage of closed cells, the highest uniformity of the foam texture, strength, durability, and stability in the 45-day cycling test, were considered.

Further evaluation and screening of the vinyl foam systems established two alternatives: (1) improvement of the BFG and USR vinyl foam systems, and (2) investigation of new vinyl foam systems.

1. NSL Vinyl Foam Formulations Based on Commercial Plastisols - In the process of improving the BFG vinyl foam system, first a slight modification of the plastisol formulation was performed. This modification had been made possible due to a better knowledge of the BFG plastisol as it was received. This modification gave the following formulation:

(1) BFG plastisol [containing polyvinylchloride resin (100 parts), dioctyl phthalate (90 parts), monomeric epoxidized soybean oil (5 parts), and a Cd-Ba-Zn metallic stabilizer (2 parts), No. 370 E 1330 . . . . 100 parts

(2) Monomeric epoxidized soybean oil (plasticizer) . . . . . 5 parts

(3) Dinitrosopentamethylene tetramine (blowing agent, 100% reactive) . . . . 3 parts

Several foam samples were prepared using this formulation. Three different processing techniques were utilized: (1) "Mold Technique," (2) Regulated Low Pressure Chamber Technique," and (3) "Mill Technique." All three techniques are described in Section C-3 below (page 48). Good quality foam sheet samples were obtained with these techniques. Particularly the "Regulated Low Pressure Chamber Technique" gave excellent samples. This technique is very accurate because of the fine adjustment on the reduced pressure available with the weighted pressure vent. The foam samples obtained responded accurately to the predetermined reduced pressure.

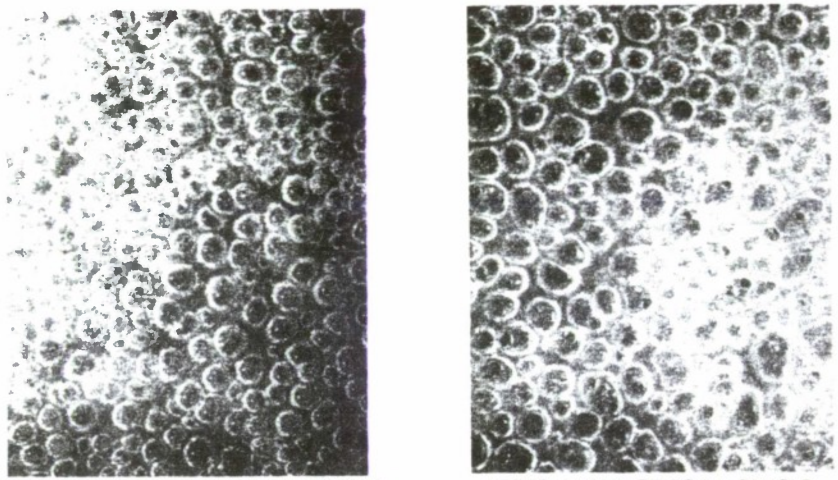
Figure 3 illustrates the high percentage (~ 100%) of closed cells and their uniformity in the foam samples obtained. They demonstrated high strength and good durability when compared to the previous samples.

The mixing of the plastisol ingredients was performed in a mixing flask equipped with a mechanical stirrer. A water bath was used to keep the temperature of the mixture at not higher than 100°F. This equipment set-up was used for mixing all the NSL plastisols based on commercial plastisols.

The first cycling test (Cycling Test I) of 250 cycles in 45 days was performed with two foam samples, one prepared under a reduced pressure of 3.5 psia and the other under 7 psia using the "Regulated Low Pressure Chamber Technique" (see Section C-4, page 52).

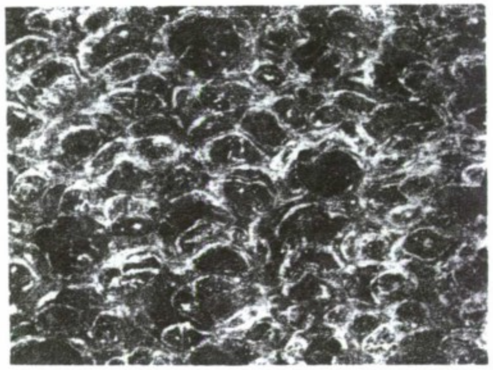
The foam samples cycled shrank unevenly. This suggested some uneven cell distribution or cell wall thickness differences, or both combined. From the shape of the foam sample under one atmosphere as described in the analysis, the discrepancy of the foam structure was probably due to the uneven temperature distribution during the fusing procedure of the foam plastisol. The bottom part of the foam sample was heated by contact in the air-circulated oven and the top part was heated by convection. Thus, the bottom part was exposed to somewhat higher temperatures than the top part during the fusing procedure. This provoked a cell distribution of closed cells with thicker walls on the top part of the foam sample and closed cells with thinner walls on the bottom part, the latter having a higher permeation to the contained gas. This could explain the above-mentinned uneven shrinkage of the foam. Therefore, it is important that, during the fusion and expansion processes of the plastisol, either the convection heating or the contact heating should be used but not both, to avoid temperature differences.

To improve the pressure-response consistency to at least 250 cycles, the



TOP VIEW OF FOAM SAMPLE SHOWING CLOSED CELLS (1/64" ACTUAL AVERAGE SIZE)

BOTTOM VIEW OF FOAM SAMPLE SHOWING CLOSED CELLS (1/64" ACTUAL AVERAGE SIZE)



SIDE VIEW OF FOAM SHOWING CLOSED CELLS (BROKEN DUE TO CUTTING)

FIGURE 3 MACROPHOTOGRAPHS OF A VINYL FOAM SAMPLE PREPARED UNDER 7 PSI REDUCED PRESSURE gas permeation from within the foam matrix had to be reduced. This could be accomplished by (1) the use of the convection heating in the fusion process of the plastisol, (2) the changing of the basic plastisol formulation as for instance, using high molecular weight plasticizer, (3) the coating of the foam sample by a thin rubber film made of unblown vinyl polymer, and (4) the finding of new processing techniques which would affect the foam cell structure to the point of reducing the gas permeation.

In the reorder of a batch of BFG plastisol, B. F. Goodrich agreed to supply NSL with the same formulation (No. 370 E 1330) minus the stabilizer. This arrangement enabled an evaluation to be made of a wide variety of stabilizers. The new plastisol formulation minus the stabilizer was designated No. 370 E 1330-1.

As was elaborated in Section A-1 (page 2), the function of a stabilizer in a vinyl foam system is to neutralize the hydrogen chloride which is released due to the tendency of the vinyl resin in the plastisol to decompose. The foam discoloration is prevented by the stabilizer's action.

Besides the above-mentioned functions, another function of the stabilizer is to exert a marked and controlled effect upon the decomposition temperature of many chemical blowing agents. Studies have been conducted to determine how the various stabilizers used affected the foam density and cell structure homogeneity at different expansion temperatures on formulations containing a number of different chemical blowing agents. From these studies, specific barium-cadmium-zinc stabilizers were developed by the chemical industry. These new stabilizers promote efficient decomposition of the blowing agents st lower than conventional temperatures resulting in good quality cell structure and low foam densities. They function as true catalysts in that their activity on blowing agents is independent of concentration.

In our investigation of the plastisol formulation No. 370 E 1330-1, four stabilizers were used which were of the barium-cadmium-zinc category mentioned above. Each stabilizer catalyzes nitrogen releasing blowing agents at a specific temperature range. Because the BFG plastisol formulation No. 370 E 1330-1 uses a polyvinylchloride resin of a high fusion temperature, it is essential that it be processed at a high temperature without danger of encountering premature blowing agent decomposition. Therefore, the ideal stabilizer for this particular plastisol formulation would be the stabilizer which catalyzes the nitrogen releasing blowing agent approximately 10 to 15°F. below the plastisol's fusion temperature. From the four stabilizers evaluated one, designated CZ-50*, demonstrated its effectiveness in catalyzing the blowing agent decomposition at the appropriate temperature.

Using CZ-50 ss the stabilizer, the following BFG plastisol formulation was established:

II	(1)	BFG plastisol No. 370 E 1330-1	100 parts
	(2)	Metallic stabilizer CZ-50 (Cd-Ba-Zn complex)	5 parts

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*Supplied by Stay and Day Co. (See Table 1, Section B-1, page 19).

(3)	Monomeric epoxidized soybean oil (plasticizer)	5 parts
(4)	Dinitrosopentamethylene tetramine (blowing agent, 100% reactive)	3 parts

The vinyl foam samples prepared with this formulation were of good quality with a fine, uniform closed cell structure, a good expansion ratio and a degree of strength and softness equal to the foam samples obtained with the plastisol formulation (I). This indicated an excellent repeatability of foam with identical characteristics from different batches but with the same plastisol formulation. However, in improving the processing technique, better foam samples were obtained. One of these samples, made under the 3.5 psia reduced pressure (with a 4:1 increase in volume at 23°C)* using the "Regulated Low Pressure Chamber Technique," and formulation (II), was exposed to a cycling test and the results were compared with a similar foam sample (with a 3:1 increase in volume at 23°C), but prepared using the formulation (I) and the processing technique in its early stages of development. Definite improvements were noted inasmuch as no letdown in the pressure response was recorded after 50 cycles (see Figure 11, Section C-4, page 55, for comparison) indicating a lower permeation of the gas from within the cell structure and a higher foam durability.

To further improve the plastisol formulation (II), a series of tests was performed whereby mixtures of USR plastisol DC-2113, described in Section B2-c (page 26), and BFG plastisol No. 370 E 1330-1, were investigated. It was found that an 8:2 to 9:1 mixing ratio in favor of the BFG plastisol gave the best results. A new plastisol formulation was thus established and consisted of the following:

(III)	(1)	BFG plastisol No. 370 E 1330-1	90 parts
	(2)	USR plastisol DC-2113	10 parts
	(3)	Monomeric epoxydized soybean oil (plasticizer)	4 parts
	(4)	Metallic stabilizer CZ-50 (Cd-Ba-Zn complex)	4 parts
	(5)	Dinitrosopentamethylene tetramine (blowing agent, 100% reactive)	4 parts

Foam samples prepared using this formulation and a new processing technique "Restraint Mold Technique" which is described in Section C-3 (page 48) showed excellent properties.

Particularly the flexibility, softness, and color of the foam were markedly improved. To check the gas permeation of the cell-wall membrane and strength of cell structure, a cycling test (Cycling Test 11) was conducted with a foam sample which was prepared using formulation (111) and the "Restraint Mold Technique." The foam sample was made under a 7-psia reduced pressure with a 4:1 volume increase. This sample passed very successfully the 250 cycles and 45-day cycling test, ss the results show (see discussion in Section C-4, page 52).

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*The volume (at 1 atm.) of the plastisol increased fourfold to the finished foam (at 3.5 psia reduced pressure).

In an attempt to augment the volume increase FVI (1 atm. to red. pr.)*of the foam, several approaches were investigated. For instance, an approach which was very efficient was the approach whereby a foam sample from a previous preparation was heated to its softening point and then reexpanded unrestrained under the desired reduced pressure. Foam samples prepared by this processing approach ("Restraint Mold Technique" coupled with unrestrained technique; for description see Section C-3, page 48) showed excellent volume increases FVI (1 atm. to red. pr.). The foam samples obtained in this manner had a collapsed appearance when exposed to one atmosphere but when exposed to the reduced pressure at which the sample had been reexpanded, the volume increase was approximately 4 to 1 at 23°C. The flexibility and softness had improved greatly while retaining strength and durability. It was also noted that the pH on the foam surface was practically neutral and that no odors could be detected.

The knowledge of the volume increases of either the plastisol to the finished foam,or the foam from one pressure level to another,is important for the fabrication and use of the foam. For instance, if a foam is required having a specific volume increase from one specific pressure level to another, the fabrication of this particular foam is simplified if the volume increases of either the plastisol to the finished foam or of the foam, are known. Knowing these volume increases, the amount of plastisol to be used or the amount of foam to be cut can be easily calculated. Also, the density of the finished foams can be predicted. Obviously, these volume increases will depend upon the type of foam system, the formulation and the processing technique, which will be employed.

In the continuation of improving the physical properties of the foam with special emphasis on the foam volume increase, softness, cell uniformity, high cell wall strength accompanied by a low permeability, good foam reproducibility, good pressure response performance, nontoxicity and no odor, the plastisol formulation (III) was modified slightly and new processing techniques were evaluated.

In a new plastisol formulation, the monomeric plasticizer in formulation (III) was replaced by a polymeric plasticizer which has a better stability (see discussion in Section C-2, page 40) and the amounts of stabilizer and blowing agent were varied. Thus, the new formulation consisted of the following:

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*1. The letters FVI stand for "Foam Volume Increase" of the foam from one pressure level to another. The pressure levels are given in parentheses. In this particular case the pressure levels are 1 atm. to reduced pressure (either 3.5 or 7 psia).

2. Additionally, the symbol PVI (1 atm.) will be used to express the plastisol volume increase to the finished foam at 1 atmosphere.

(IV)	(1)	BFG plastisol No. 370 E 1330-1	90 parts
	(2)	USR plastisol DC-2113	10 parts
	(3)	Polymeric epoxydized soybean oil (plasticizer)	4 parts
	(4)	Metallic stabilizer CZ-50 (Cd-Ba-Zn complex)	5 parts
	(5)	Dinitrosopentamethylene tetramine (blowing agent, 100% reactive)	6 parts

During further evaluation of the processing techniques, two techniques were developed. One of the techniques is designated "Two-Stage Processing Technique" and is described in Section C-3, page 48.

Using the above formulation (IV), a plastisol sample was prepared employing the "Two-Stage Processing Technique." In a first stage, the plastisol was heated to fusion temperature (~ 320°F) and expanded freely (unrestrained) under normal pressure (1 atm.). The oven used in the first stage is shown in figure 4. In a second stage, the temperature of the foam obtained in the first stage, is reduced in order to increase the medium's viscosity and gel strength, i.e., strengthening the cell-wall membrane while keeping it still soft and expandable. At this stage the foam, still in a molten condition, is expanded freely in a vacuum chamber (Figure 5) under a reduced pressure by lowering the pressure gradually to the desired level, either 3.5 or 7 psia. The foam sheet obtained was of excellent quality and had a high FVI (1 atm. to red. pr.). A cycling test was conducted with the foam sample prepared under the 3.5 psia reduced pressure (see Section C-4 Cycling Test III" page 52). Figure 6 shows two foam samples, one prepared under the restraint condition and one prepared under the free expansion condition.

In another new processing technique, designated the "Three Stage Processing Technique," the first stage consists of heating the plastisol under high pressure (small hydraulic press) to the blowing and fusion temperatures. In the second stage, the foam sample is transferred immediately from the press to the oven where heating to blowing and fusion temperatures is continued for a specific period of time. Finally, in the third stage, the temperature of the foam sample is reduced to increase the medium's viscosity and gel strength and free expansion is performed under reduced pressure by lowering the pressure gradually to either 7 psia or 3.5 psia.

This last technique increased even more the FVI (1 atm. to red. pr.) of the foam. The foam had excellent physical properties and particularly higher texture uniformity. This improvement was probably due to a better containment of the nitrogen gas (blowing gas) within the plastisol medium, and a more uniform heating during the processing of the plastisol in stage one. The multiplicity and uniformity of the cells is increased, giving a higher FVI (1 atm. to red. pr.). Figure 7 shows the volume increase FVI (1 atm. to red. pr.) of a foam sample prepared under the free expansion condition.

To increase even further the flexibility of the foam and the volume increases, in both techniques, the foam sample can be reheated to its softening point and then reexpanded freely under the desired reduced pressure.

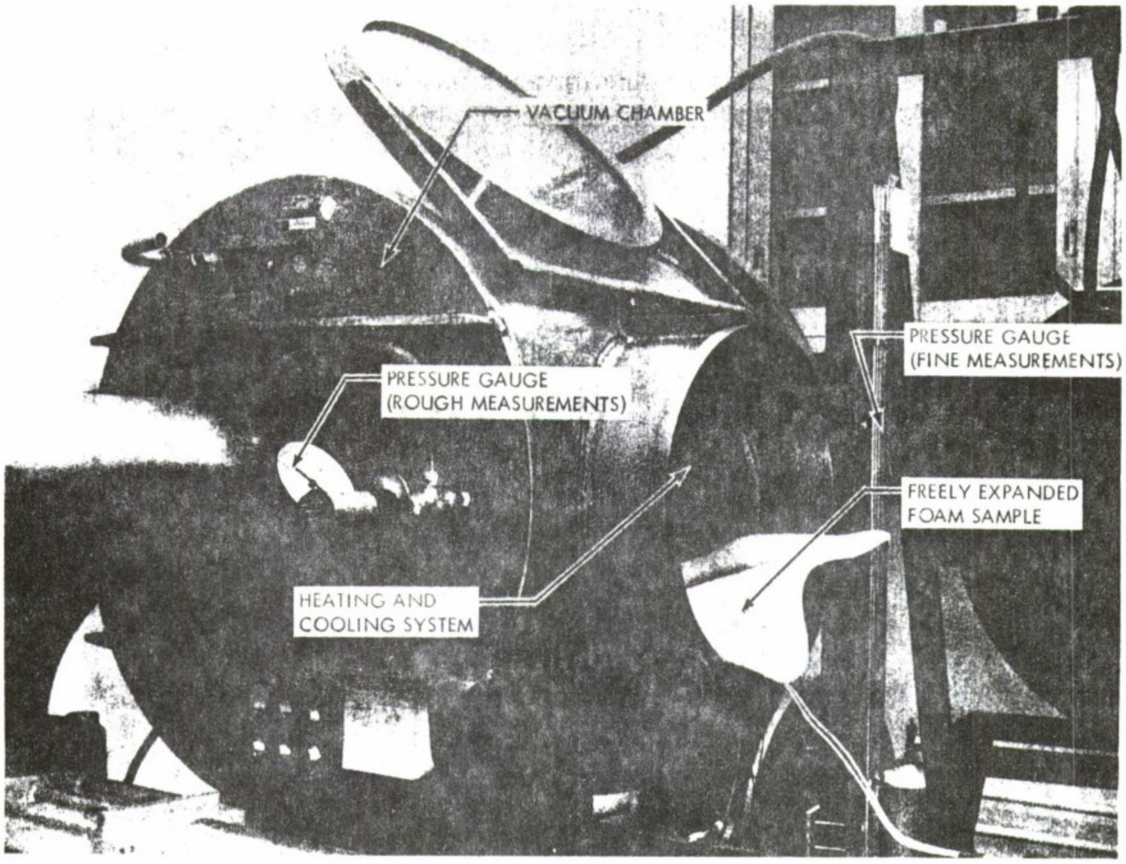


FIGURE 5 BLOWING AND SETTING OF FOAM

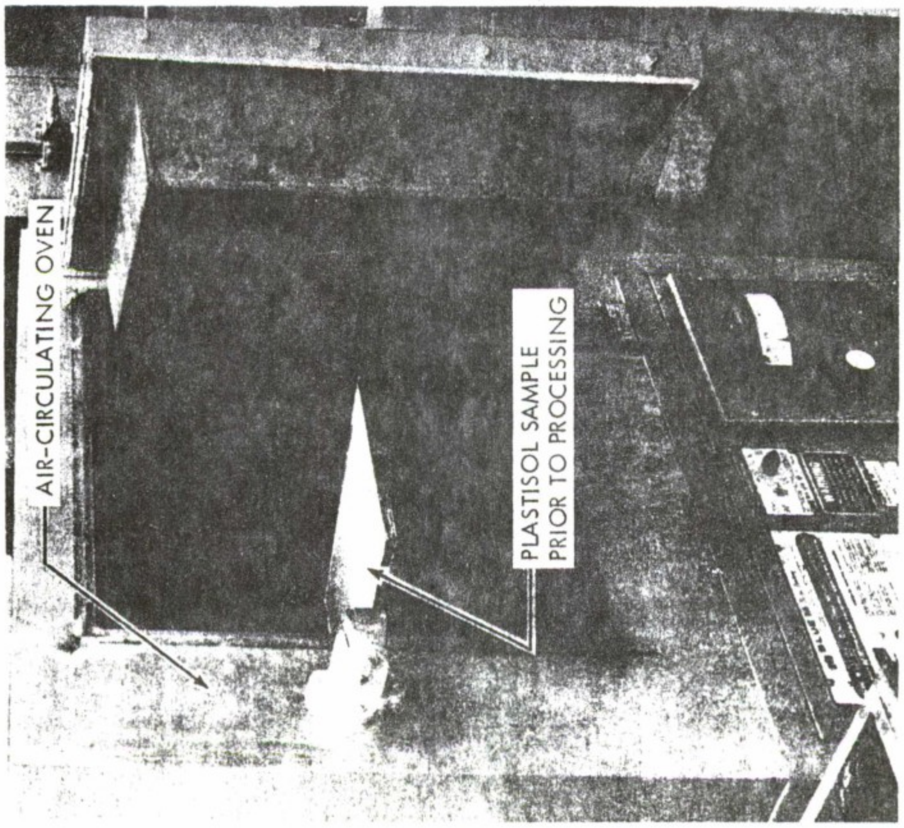


FIGURE 4 GELLING AND FUSION OF PLASTISOL

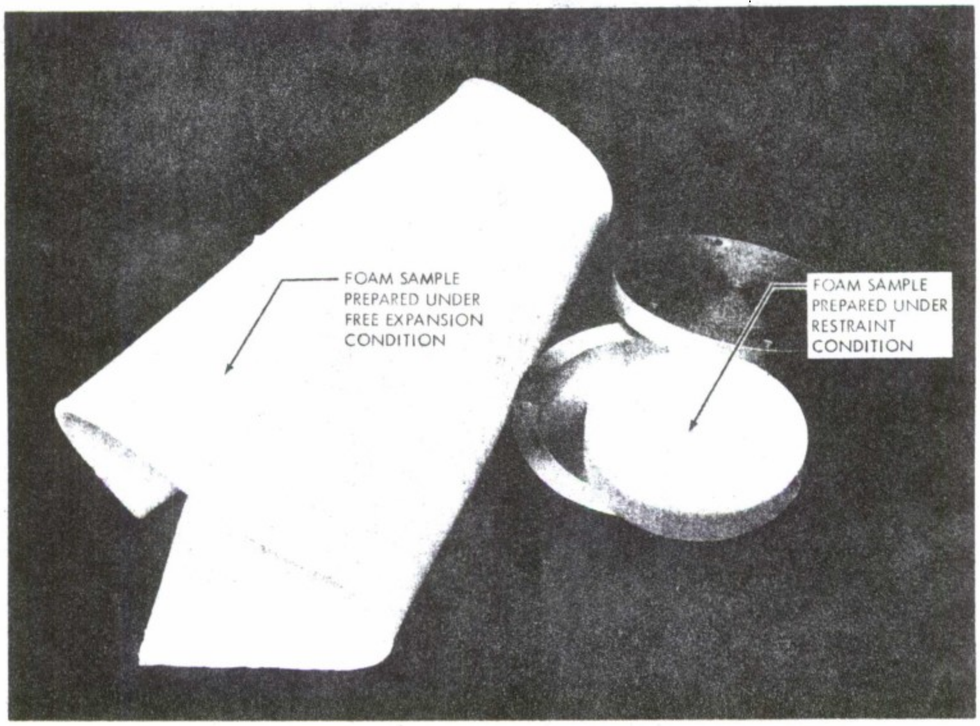
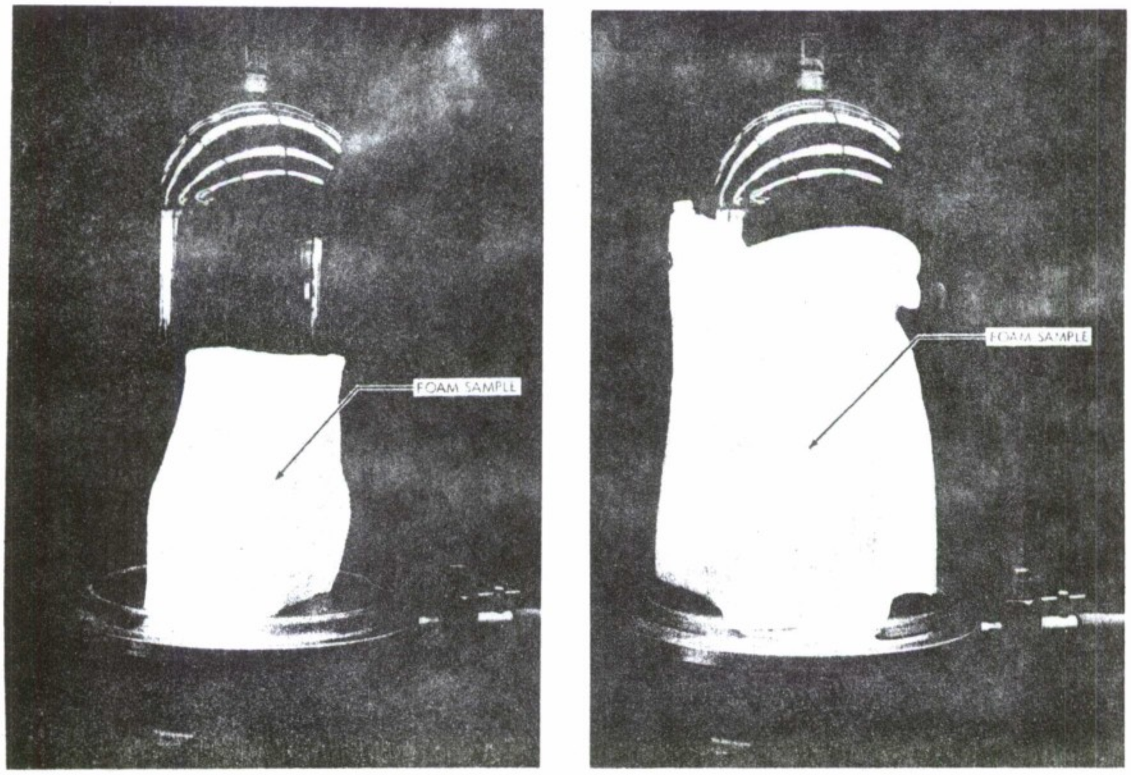


FIGURE 6 FOAM SAMPLES PREPARED UNDER DIFFERENT CONDITIONS



A. FOAM SAMPLE AT ONE ATMOSPHERE

B. FOAM SAMPLE AT 3.5 PSIA

FIGURE 7 VOLUME INCREASE OF A FOAM SAMPLE

This process can be repeated two or three times and each time the flexibility and the volume increase FVI (1 atm. to red. pr.) is improved. Nevertheless, this process should not be repeated more than two times because it may affect the other foam physical properties.

Now that a foam can be manufactured under any reduced pressure and exert, when exposed to the vacuum and properly restrained, a pressure response equal to the pressure under which the foam had been prepared, one has to consider a certain number of factors for the foam's application. The volume increase of a piece of foam when exposed from normal atmosphere (1 atm.) to the reduced pressure, either 3.5 or 7 psia, and the volume increase of a plastisol during the manufacturing of a foam sample must be established. These factors will be important when foam sheets are cut in pieces to exert the pressure response desired when properly restrained and exposed to vacuum. The plastisol volume increase must be controlled so as to provide the desired volume increase of the finished foam and the pressure within the foamed cell.

During the development of the foam, these two factors were considered. As was demonstrated, the plastisol volume increase PVI (1 atm.) and the foam FVI (1 atm. to red. pr.) depended on (1) the formulation used, (2) the processing technique used, (3) the reduced pressure under which the foam was prepared, and (4) the amount of plastisol used. In the case of the mold techniques whereby the foam samples were prepared under a restraint condition, the mold spacing or volume was constant and the amount of plastisol was varied in order to obtain foam samples having different values of FVI (1 atm. to red. pr.). In the case of the free expansion techniques, the foam samples were processed in a tray in stage one of the "Two-Stage Processing Technique" and stages one and two of the "Three-Stage Processing Technique."

Tables II and III illustrate the above and gives a comparison of the foam volume increases when either the plastisol formulation, the amount of plastisol used, or the processing technique are varied. Also the density of the foam is given at different pressures.

2. Formulated Plastisols From Raw Materials - Initially, a survey of raw vinyl plastisol ingredients and a preselection of them was conducted. The ingredients of interest were polyvinylchloride resins, plasticizers, stabilizers, and blowing agents of which large varieties were evaluated in formulating plastisols. This study was conducted simultaneously with the study on commercial plastisols discussed in Section C-1, page 29.

The polyvinylchloride resins investigated were each of a different molecular weight and degree of polymerization and were used in powder form. Also they differed in particle size and dry blend characteristics which normally determine the uniform and rapid absorption of the plasticizer involved in the plastisol formulation. Each resin particle must be plasticized through to the core with a uniform concentration of plasticizer.

To attain the best results with each of the resins investigated, the nature and amount of plasticizers and stabilizers had to be varied. The two most important physical properties of the plastisols, that is, flow properties and aging characteristics, were controlled mainly by the use of the selected

Table II FOAM PROCESSING DATA

Foam Sample	Plastisol Formulation Number	(1) Processing Technique Number	(2) Amount of Plastisol in g.	(3) Actual Processing Pressure "p" in psia	(4) PVI (1 atm.) at 23°C Foam: Plastisol	(5) Density of Foam in lbs/ft^3 at 1 atm. and 23°C
A	I	7	62	3.5	3.7:1	19.8
B	I	7	75	3.5	3.4:1	21.6
C	I	7	94	3.5	3.4:1	21.6
D	I	7	110	3.5	3.2:1	22.9
E	I	7	125	3.5	3.2:1	22.9
F	I	7	62	7.0	3.5:1	21.0
G	I	7	75	7.0	3.3:1	22.2
H	I	7	94	7.0	3.4:1	21.6
I	I	7	110	7.0	3.1:1	23.7
J	I	7	125	7.0	3.1:1	23.7
K	III	8	150	4.0	4.0:1	18.4
L	IV	9(6)	150	3.5	4.3:1	17.0
M	IV	9(7)	150	4.5	4.2:1	17.5
N	IV	9(8)	150	4.0	4.3:1	17.0
O	IV	10(6)	150	3.5	4.3:1	17.0
P	IV	10(8)	150	3.1	4.4:1	16.7
Q	IV	9(8)	150	5.5	4.3:1	17.0
R	IV	10(6)	150	6.8	4.4:1	16.7
S	VI	9(8)	150	3.5	4.4:1	16.7
T	VI	10(8)	150	7.0	4.3:1	17.0

Table III FOAM CHARACTERISTICS DATA

Foam Sample	(3) Actual Processing Pressure "P" in psia	FVI (1 atm. to red.pr.) (9) Red.pr. = "P" Exper. data at T°C Foam(red.pr.):Foam (1 atm.)	FVI (1 atm. to red.pr.) (10) Red.pr. = 3.5 psia Data by convers.@23°C Foam(3.5 psia):Foam (1 atm.)	FVI (1 atm. to red.pr.) (10) Red.pr. = 7.0 psia Data by convers.@23°C Foam(7 psia):Foam (1 atm.)	(5) Density of Foam in lbs/ft^3 at 3.5 psia and 23°C	(5) Density of Foam in lbs/ft^3 at 7 psia and 23°C
A	3.5	1.9:1 at 23°C	1.9:1	-	10.5	-
B	3.5	1.7:1 at 23°C	1.7:1	-	12.6	-
C	3.5	1.4:1 at 23°C	1.4:1	-	15.3	-
D	3.5	1.2:1 at 23°C	1.2:1	-	19.3	-
E	3.5	1.1:1 at 23°C	1.1:1	-	21.0	-
F	7.0	2.0:1 at 23°C	-	2.0:1	-	10.5
G	7.0	1.8:1 at 23°C	-	1.8:1	-	12.4
H	7.0	1.4:1 at 23°C	-	1.4:1	-	15.3
I	7.0	1.3:1 at 23°C	-	1.3:1	-	18.4
J	7.0	1.1:1 at 23°C	-	1.1:1	-	21.6
K	4.0	3.0:1 at 30°C	3.4:1	-	5.4	-
L	3.5	3.3:1 at 23°C	3.3:1	-	5.2	-
M	4.5	2.7:1 at 23°C	3.5:1	-	5.0	-
N	4.0	3.4:1 at 32°C	3.8:1	-	4.5	-
O	3.5	3.5:1 at 35°C	3.4:1	-	5.0	-
P	3.1	4.5:1 at 23°C	4.0:1	-	4.2	-
Q	5.5	3.0:1 at 63°C	-	2.0:1	-	8.5
R	6.8	3.5:1 at 45°C	-	1.9:1	-	8.8
S	3.5	3.9:1 at 23°C	3.9:1	-	4.3	-
T	7.0	2.1:1 at 35°C	-	2.0:1	-	8.5

References to Tables II and III

(1) The different processing techniques used are described in Section II-C-3 (page 48).

(2) Each foam sample from "A" to "J" was prepared under a restrained condition in a circular mold of standard dimensions and each foam sample from "K" to "T" was prepared under an unrestrained condition (free expansion) in a rectangular mold of standard dimensions.

(3) These figures were the actual reduced pressures recorded during the expansion of the foam while being prepared.

(4) The ratios foam volume at 1 atm. to plastisol volume at 1 atm. are given. The data were measured experimentally.

(5) The densities were determined in two ways: (a) by dividing the plastisol density (pounds/ft^3) by the volume increase ratio of the plastisol to the foam at either 1 atm., 3.5 psia, or 7 psia, and (b) by measuring the size and weight of the foam sample prepared under either 1 atm., 3.5 psia and 7 psia.

(6) Expansion of the foam was performed one time.

(7) Expansion of the foam was performed two times.

(8) Expansion of the foam was performed three times.

(9) The ratios foam volume at "P" reduced pressure and T°C to foam volume at 1 atm. and 23°C are given. Data were obtained experimentally by measurements of foam sizes and temperatures.

(10) The ratios foam volume at either 3.5 psia or 7 psia and 23°C to foam volume at 14.7 psia (1 atm.) and 23°C are given. These data were obtained by converting the data from FVI (14.7 psia at 23°C to "P" psia at T°C) using the Boyle-Charles law $[p_1 v_1 = p_0 v_0 (1 + 1/273\ t)]$. These data give a comparison of volume increases of the foam from 14.7 psia to two standard reduced pressures (3.5 and 7 psia) at a constant temperature (23°C).

plasticizers. Selected monomeric and polymeric plasticizers such as: dioctyl phthalate, butyloctyl phthalate, tricresyl phosphate, and polymeric epoxidized soybean oil, were investigated either alone or mixed. The viscosity or flow property of the plastisol in its final use depended upon the type of combination of their plasticizers. By utilizing mixtures of plasticizers the desired end properties were more likely to be attained. From the plastisol's viscosity obtained, the processing techniques to be employed in the preparation of the foams, were selected accordingly.

A higher plastisol viscosity had a better chance in retaining the blowing gas during the gelling, fusion, and expansion processes. The solvating effect or peptizing effect of a certain type of plasticizer, used in equal quantities in a mixture of plasticizer and resin at the same temperature and shear rate, differed for each polyvinylchloride resin evaluated, also used in equal quantities. This indicated a different degree of polymerization for each resin. By varying only the amount of the plasticizer in the proper ratio, the solvating effect could be made equal for all resins under study. The obtained plastisols have equal viscosities but when converted into foam, the cell-wall size and thickness will vary for each resin, which undoubtedly will change the physical properties of the finished foam. To enable a more sensible control of the properties, a mixture of plasticizers each having a different viscosity and solvating effect were evaluated. For instance, a mixture consisting of monomeric dioctyl phthalate (high solvating power) and polymeric epoxidized soybean oil (low solvating power), proved to be very effective in controlling the physical properties of the foam. With the resins under consideration, tests indicated that the most suitable plasticizer-to-resin ratio should be between 1:2 and 1:1. Operating beyond these ratios resulted in either too low a viscosity of the plastisol in the case of an excess of plasticizer or a poor plastisol homogeneity in the case whereby not enough plasticizer was used. The latter was due to some resin particles tending to absorb the plasticizer faster than others which do not come into physical contact with the plasticizer as soon.

When comparing the stability properties of monomeric plasticizers to polymeric plasticizers, the facts indicate that the polymeric plasticizers are more permanent. An important factor which controls the stability of a plasticizer is the type of functional groups present in the plasticizer molecule. One of the most effective functional groups in polyvinylchloride plasticization is the ester group as found in the epoxidized soybean oil. For instance, it stabilizes polyvinylchloride against the effect of heat and light. It was found that the plasticizers, either monomeric or polymeric, which contain epoxy groups exhibit dual functionality in that they both plasticize polyvinylchloride and contribute substantially to the stabilization of this resin against humidity and degradation from heat and ultraviolet light. When used in conjunction with metallic stabilizers, particularly liquid barium-cadmium and zinc complexes, the epoxy plasticizers provide a synergistic improvement in the heat and light durability of the polyvinylchloride resin.

With regard to the volatility of the polymeric plasticizers which have higher molecular weights, it will be lower than for the monomeric plasticizers. The tendency of a plasticizer to volatilize from a compound is

largely a function of the plasticizer's vapor pressure and tendency to migrate to the surface. These properties are related to the molecular weight of the plasticizer. Whenever a plasticizer is lost from the material which it plasticizes, the material increases in tensile strength, hardness, and resistance to elongation. This effect was noted on some foam samples which were exposed to a vacuum for a long period of time (see cycling test in Section C-4, page 52).

From carefully selected vinyl resins, plasticizers, stabilizers, and blowing agents, approximately 80 plastisol systems were prepared. To obtain a good dispersion of the polyvinylchloride resins within the liquid mixture of stabilizers and plasticizers and to prevent entrapping excess air in the plastisol during its preparation, the following equipment, illustrated in Figure 8, was used.

In a typical procedure of preparing a plastisol sample using the described equipment in Figure 8, the liquid plasticizers are first measured into the mixing flask; during stirring, the powdered polyvinylchloride resin is added stepwise in order to avoid formation of lumps; after the resin is added, the stirring is continued for approximately one hour until a smooth liquid dispersion is obtained; at this time a premixed smooth liquid dispersion of the powdered blowing agent in the liquid stabilizer is added under continued stirring; at this stage all the ingredients are added and while the stirring is being continued, a 10 mm Hg vacuum is introduced in the mixing flask to eliminate the already entrapped air and to keep from entrapping more air as the stirring is continued for another one or one and one-half hours. During the entire stirring time a water bath was used to keep the temperature of the mixture in the flask at not higher than 100°F. The obtained plastisol has a milky appearance and is practically free of air bubbles which will shorten its deaeration prior to being processed to the final foam. The deaeration process of the plastisol can be very lengthy and difficult if the amount of entrapped air is large.

This described typical procedure of preparing plastisols was varied slightly as the plastisol formulation was modified. Among the plastisol systems formulated initially, the plastiaol formulation given below gave good quality foam samples.

	(1)	Dioctyl phthalate	50 parts
	(2)	Polymeric epoxidized soybean oil	35 parts
(V)	(3)	A predispersed dinitrosopentamethylene tetramine (blowing agent) solution* (60%) in polymeric epoxidized soybean oil (40%)	40 parts
	(4)	Polyvinylchloride resin (B. F. Goodrich 120-174)	100 parts
	(5)	Monomeric epoxidized soybean oil (plasticizer)	5 parts
	(6)	Metallic stabilizer CZ-50 (Cd-Ba-Zn complex)	5 parts
	(7)	USR plastisol system DC-2113	100 parts

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*Supplied by the Ware Chemical Corp. (See Table 1 in Section B-1, page 19.

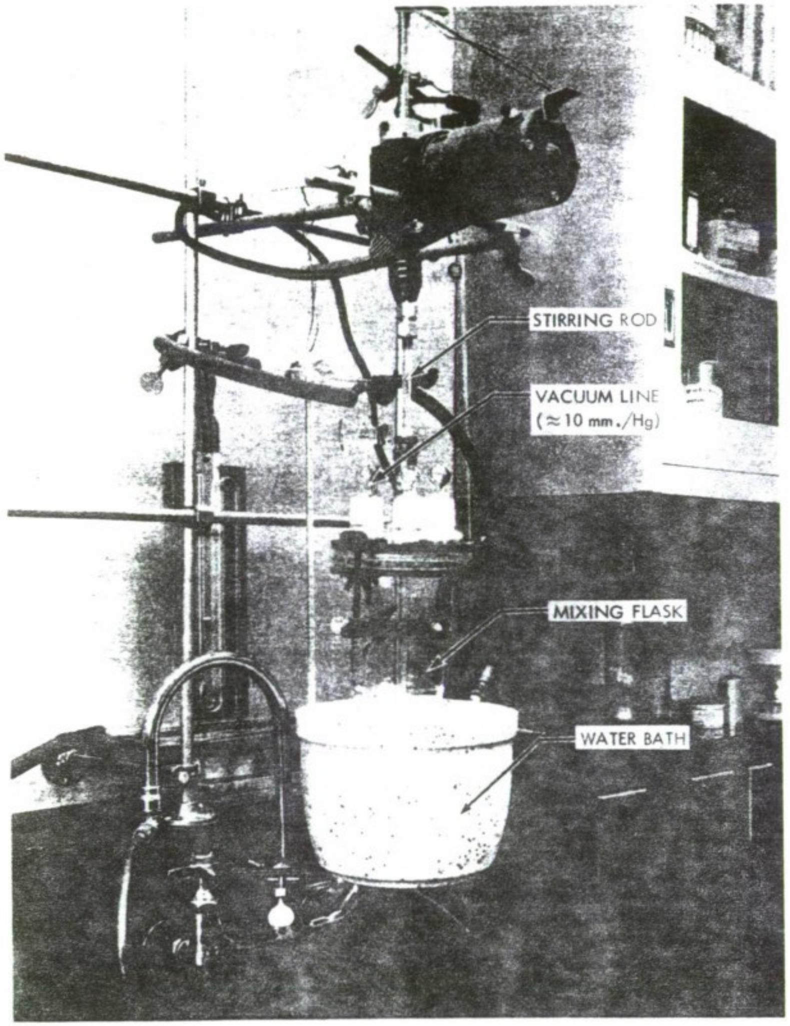

FIGURE 8 PLASTISOL MIXING APPARATUS

The use of the blowing agent (dinitrosopentamethylene tetramine) in a predispersed form was to obtain a more uniform distribution or dispersion within the plastisol mixture. Also under this form the disadvantages of working with powdered blowing agents which can be dusty, explosive, and difficult to disperse, were eliminated. The predispersion is accomplished by mixing the dinitroso compound (66%) with a mineral oil (34%) on a paint mill. This process reduces the dinitroso powder into fine particles while it is dispersed in a mineral oil to give a pasty substance. This paste, in order to accomplish a further dispersion, is mixed manually with a polymeric epoxidized soybean oil resulting in a pourable liquid.

Further improvements of formulation (V) led to the preparation of foam samples with improved durability, volume increase FVI (1 atm. to red. pr.) and cell-structure uniformity. After improvements of formulation (V), the new formulation was as follows:

(VI)	(1)	Polymeric epoxidized soybean oil	85 parts
	(2)	Predispersed dinitrosopentamethylene tetramine (blowing agent) solution (60%) in polymeric epoxidized soybean oil (40%)	40 parts
	(3)	Monomeric epoxidized soybean oil (plasticizer)	5 parts
	(4)	Polyvinylchloride resin (B. F. Goodrich 120-174)	100 parts
	(5)	Metallic stabilizer CZ-50 (Cd-Ba-Zn complex)	5 parts

In the preparation of the foam using the above formulation (VI) and either the "Two-Stage Processing Technique" or the "Three-Stage Processing Technique," excellent quality foam sheets were obtained. They were comparable to the best foam sheets obtained with the best vinyl foam formulation using commercial plastisol (see Section C-1, page 29). Their cell-structure was even finer and their strength and durability were slightly superior due probably to the replacement of the monomeric plasticizer by the polymeric plasticizer which contains the effective ester groups and has a lower vapor pressure.

Cycling tests were conducted to determine the gas permeation from within the cells and the durability of some of the foams prepared. The results indicated that foam samples obtained with formulation (VI) were comparable to those obtained with formulation (IV).

In a foam reproducibility test, several foam samples were prepared using the same formulation and processing technique for each sample. In another reproducibility test, a series of foam samples were prepared using for each sample vinylchloride resin BFG No. 120-174 but taken each time from a different batch. The change of resin batches was the only variable in the preparation of these foam samples. The results indicated excellent reproducibility in each case.

The reproducibility of foams using either formulation (IV) or (VI) and either the "Two-Stage Processing Technique" or the "Three-Stage Processing Technique," was excellent. The foam samples prepared showed similarity in cell-structure uniformity, high percentage of closed cells, softness, flexibility, nontoxicity and no odor, volume increase and pressure response performance. To obtain this reproducibility it was of importance that the procedure and equipment utilized to mix the raw materials and the steps taken in the processing technique were performed in a consistent manner. Also, the mixing proportions and the chemical nature of each ingredient employed in the formulation had to be maintained within limits.

3. Investigation of Processing Techniques and Equipment Used - During the course of this program a large number of processing techniques for the preparation of closed cell foams was investigated. However, here, only the techniques which were used in a step-by-step development of the vinyl foam systems which led to the foam giving the most suitable properties will be described.

This list of techniques which follows contains the techniques which were evaluated in the order given.

Technique No. 1 - Mold Technique

Principle: The plastisol is thoroughly deaerated and introduced in a mold which has an open-face. The mold is then placed between two plates which can be heated. The temperature of the plates is controlled by means of variacs and the temperature of the material in the mold was determined by means of thermocouples. This set-up is located within a vacuum whose pressure can be finely adjusted to the desired reduced pressure. In the actual processing technique the plastisol is gelled, fused, and blown at elevated temperature and set at lower temperature under the desired reduced pressure.

Problems: (a) Overcooking of the foam was experienced due to the inability of controlling the rate of the mold's temperature fall immediately after the blowing process was completed.

(b) Difficulty in controlling the foam's expansion.

(c) Lack of homogeneity of the foam cell structure.

Technique No. 2 - Modified Mold Technique

Principle: Similar to "Technique No. 1," with the exception of a cooling system incorporated into the processing equipment to prevent overcooking of the finished foam. In the new system the mold containing the plastisol is placed into a metal container whose walls can be either heated or cooled to the desired temperature in a short period of time.

Improvement: Overcooking of foam was eliminated.

Problems: (a) Difficulty in controlling accurately the foam's expansion.

(b) Lack of homogeneity of the foam cell structure.

Technique No. 3 - Mill Technique

Principle: It consists of mixing thoroughly the ingredients (plastisol, plasticizer, stabilizer, and blowing agent) under vacuum for a first deaeration operation. With the smooth milky mixture obtained, "pancakes" are prepared on a hot place at 1 atm. pressure. The pancakes are removed from the hot plate while still slightly tacky and then cold rolled (using a rubber mill) into a sheet of material about 3/16 inch in thickness (Figure 9). The sheet material is then laid out flat on a tray and degassed for two or three hours at room temperature in a vacuum chamber. After removal from the chamber an inspection is made for bubbles. If the sample has a uniform texture it is placed in an air-circulating oven and heated at 320°F. The time of heating depends on the size and thickness of the sample. But as a rough guide, the average time of heating was approximately 15 minutes. After heating, the mixture is removed from the oven and placed into the metal container inside the vacuum chamber where the temperature of the metal container is set at 320°F. The desired reduced pressure is then introduced in the chamber while the formation of the foam is observed. The setting of the foam is then performed by turning off the heat and effecting a rapid cooling by allowing cold water to flow through the heater blocks.

The purpose of performing the heating process in an air-circulating oven at one atmosphere is to achieve a uniformly and well-distributed heat over the total area of the foam.

Improvements: (a) A better control of the foam's expansion was achieved.

(b) The homogeneity of the foam cell structure was improved.

Problems: Lengthy operation.

Technique No. 4 - Remodified Mold Technique

Principle: Similar to technique No. 2 with the exception of the gelling and fusion processes being conducted in an air-circulating oven whereas the foaming and setting processes take place in the reduced pressure chamber.

Improvements: The foam's expansion was more accurately controlled and thus the homogeneity and uniformity of the foam cell structure was improved.

Problem: The gelling and fusion processes are critical in controlling the foam's expansion.

Technique No. 5 - Regulated Low Pressure Chamber Technique

Principle: This technique is a modification of Technique No. 4. The deaeration and cooking processes are similar but the foaming and

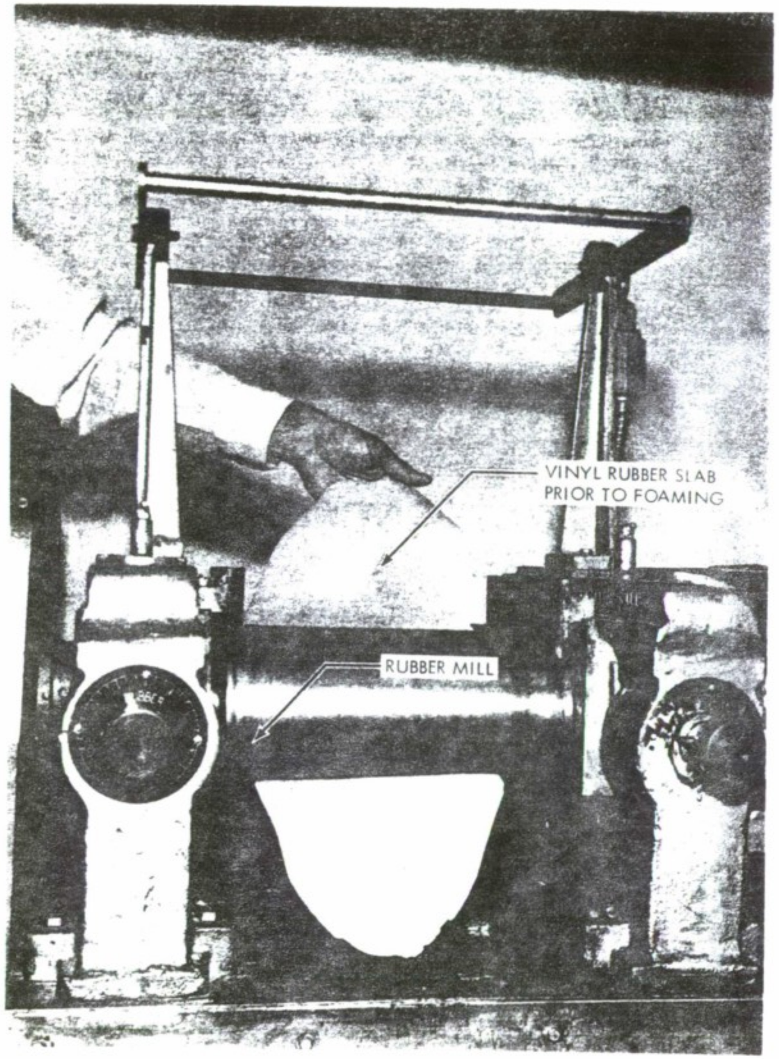

FIGURE 9 STEP IN THE MILL TECHNIQUE

setting processes differ in that the top of the mold is engineered to provide a weighted pressure vent. The desired foam pressure response is attained by varying the weighted pressure vent accordingly. For all desired foam pressures, the mold containing the foam material is exposed to the high vacuum.

Improvements: (a) Excellent control of the foam's expansion was achieved.

(b) A good uniformity of the cell structure was obtained.

Problems: The achievement of a proper seal with the weight used on top of the pressure chamber valve was critical.

Technique No. 6 - Piston Technique

Principle: Largely the principle is similar to Technique No. 5. The difference between the two techniques is that Technique No. 6, a load is calculated to exert a pressure equivalent to one psi on top of the foam mixture while the mold is surrounded by a reduced pressure of one psi below the desired foam pressure.

Improvements: The achievement of a proper seal with the weight was not a problem here.

Problems: (a) The amount of weights which had to be used were too voluminous.

(b) The high temperature during the foam expansion was critical.

Technique No. 7 - Restrained Mold Technique

Principle: The deaeration of the plastisol and the gelling and fusion processes are similar to the above technique. This technique differs from other techniques in the type of mold used. The mold is covered by a lid which is perforated by a number of small holes (1/16 inch diameter). The foaming and setting actions are performed in a vacuum chamber whose pressure is set at the desired reduced pressure.

Improvements: (a) Simplified and accurate technique giving a repeatable foaming process.

(b) The problems encountered with Techniques Nos. 5 and 6 are eliminated.

Technique No. 8 Restrained Mold Technique Coupled with Unrestrained Technique

Principle: A foam sample from a previous preparation is heated to its softening point and then is reexpanded unrestrained under the desired reduced pressure. The foam sample is heated in an air-circulating oven for only a short time (a few minutes) and then is transferred into the vacuum chamber where it is expanded freely under either 3.5 or 7 psia.

Improvements: (a) Significant increase of foam expansion under vacuum.

(b) Higher flexibility and softness of foam.

Technique No. 9 - Two Stage Processing Technique

Principle: A thoroughly deaerated plastisol is transferred from the mixing flask to a tray which is placed in an air-circulating oven at the plastisol's fusion temperature. The gelling and fusion time will depend upon the type of plastisol system used. When fusion temperature is attained the plastisol is expanded freely under one atmosphere.

In a second stage, the temperature of the formed foam is reduced in order to increase the viscosity of the molten foam, that is, strengthen the cell-wall membrane while keeping it still soft and expandable. At this stage the foam is expanded freely in a vacuum chamber under the desired reduced pressure.

Improvements: (a) Exellent foam expansion when exposed to the reduced pressures, either 3.5 or 7 psia.

(b) Flexibility and softness of foam were improved appreciably.

Technique No. 10 - Three Stage Processing Technique

Principle: In a first stage the plastisol is heated under high pressure to the blowing and fusion temperatures. In a second stage, the foam sample is transferred immediately from the press to the air-circulating oven where heating to blowing and fusion temperatures is continued for a few minutes. Finally, in a third stage, the temperature of the foam sample is reduced to increase the medium's viscosity and gel strength. At this stage the free expansion is performed under either 3.5 or 7 psia reduced pressure.

Improvements: Further improvement of the foam's expansion when exposed to the reduced pressures.

4. Cycling Tests - To demonstrate the suitability of a foam developed during this program, a cycling test was conducted. The test consisted of exposing the foam sample to a vacuum for 250 cycles to determine if there was deterioration of the material or its pressurizing characteristics. The cycling occurred intermittently over a period of 45 days.

This test was particularly important in checking (1) the gas permeation (blowing gas) from within the foam's cell structure and (2) the foam's durability which was directly dependent upon the rate of gas permeation and deterioration of the foam polymeric material.

Figure 10 shows the equipment which was used for conducting the cycling experiments. As can be seen the equipment consists principally of two vacuum canisters each containing a container which restrains a foam sample to be cycled. The pressure variation or pressure response exerted by each foam sample when properly restrained and exposed to vacuum, is recorded by the two transducers in microamps which is translated linearly to the pressure.

In a first cycling test (Cycling Test I) [with a plastisol volume increase to finished foam PVI (1 atm. to 3.5 psia) of 3:1 at 23°C] and the other under a 7 psia reduced pressure [with a plastisol volume increase to finished foam PVI (1 atm. to 7 psia) of 3:1 at 23°C] were used. The formulation and processing technique used in preparing these samples are given in Section C-1, page 29.

Both foam samples were cycled simultaneously at the rate of 5 to 10 cycles a day. In each cycle, the pressure surrounding each restrained foam was varied from high vacuum to the respective reduced pressure (3.5 or 7 psia) and back to high vacuum. Thus, the pressure surrounding the restrained foam samples was high vacuum most of the time.

With both foam samples the pressure response was initially excellent. However, as is shown in Figure 11, the 3.5 psia sample experienced a pressure response letdown after approximately 30 cycles. The cycling test was discontinued and the sample was replaced by a 3.5 psia sample with a plastisol volume increase to finished foam PVI (1 atm. to 3.5 psia) of 4:1 at 23°C. This sample showed a slight letdown after approximately 80 cycles, as is shown on the graph. Regarding the 7 psia foam sample, an excellent pressure response was recorded up to the 176th cycle after which some slight letdown appeared to take place. As shown on the graph, the pressure response after 202 cycles was 6.4 psia; after 219 cycles the pressure response was 6.0 psia; after 231 cycles 5.0 psia; and, finally, 3.1 psia after 250 cycles.

After inspection of the foam samples, all samples were found to be shrunk unevenly. The possible reasons of uneven shrinkage were discussed earlier in Section C-1, page 29. When brought to their respective reduced pressure (3.5 and 7 psia) the foam samples did not show any uneven shrinkage. They were uniformly expanded with a very slight overall physical shrinkage. This slight shrinkage prevented the foam from being in contact with the transducer at these reduced pressures which brought about the recorded pressure response letdown, as shown in Figure 11.

As the plastisol formulations and processing techniques were improved, better vinyl foam samples were obtained. In another cycling test (Cycling Test II), a foam sample prepared under a 7 psia reduced pressure with a plastisol volume increase to finished foam PVI (1 atm. to 7 psia) of 4:1 at 23°C was used. For the formulation and processing technique utilized see Section C-1, page 29.

The sample was cycled at the rate of 8 cycles a day. For each cycle the pressure surrounding the restrained foam sample was varied from high vacuum or one atmosphere pressure to the 7 psia reduced pressure. Therefore, for the greatest part of the time, the restrained foam was exposed partly to high

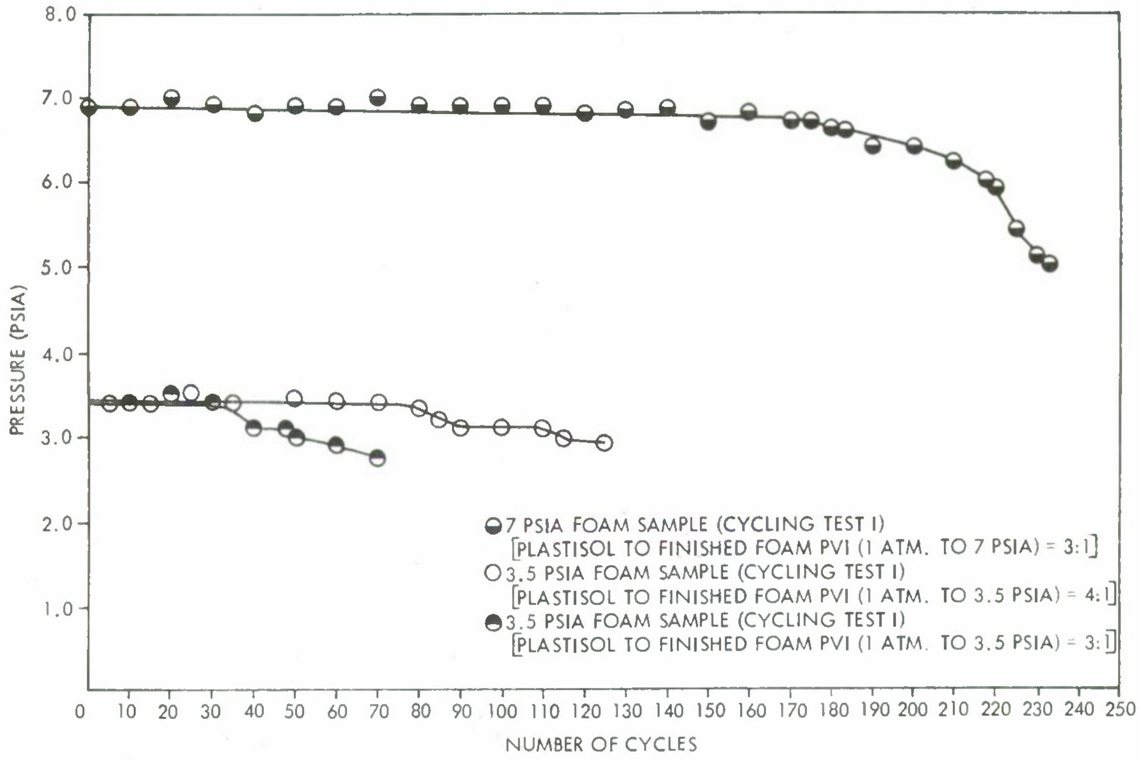

FIGURE 11 FOAM PRESSURE RESPONSE (CYCLING TEST I)

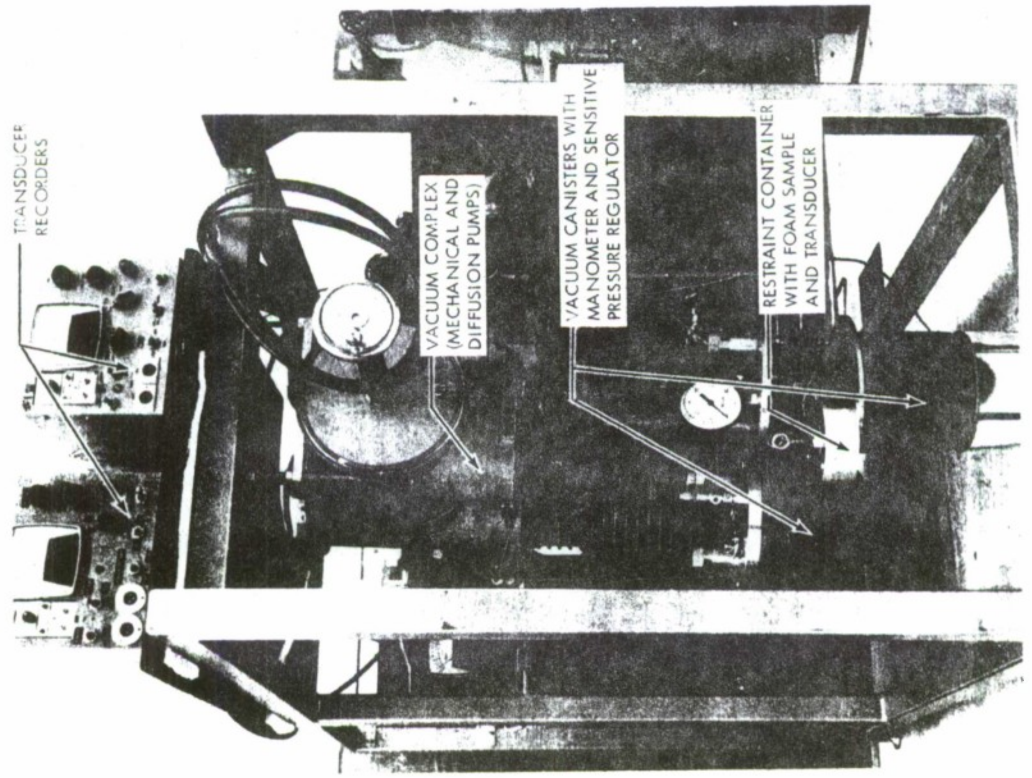

FIGURE 10 CYCLING TEST SET-UP

vacuum and partly to one atmosphere pressure. As is shown in figure 12, the foam sample passed the test very successfully inasmuch as no pressure response letdown was recorded during 250 cycles. In continuing the cycling test beyond 300 cycles the sample still did not show any letdown.

Cycling Test III was performed with a foam sample prepared by using the free expansion technique (for formulation and technique see Section C-1, page 29. It was prepared under a 3.5 psia reduced pressure and was reexpanded three times under the same reduced pressure to increase the foam's expansion. The volume increase FVI (1 atm. to 3.5 psia) of the foam was 4:1 at 23°C.

The rate of cycling was 8 cycles a day and in each cycle the restrained foam was exposed to high vacuum and 3.5 psia reduced pressure. Overnight and weekends the foam was exposed only to high vacuum. Under such conditions, a pressure response letdown was recorded only at the 240th cycle as shown in figure 12.

5. Exploratory Investigation of Foaming Around Irregular-Shaped Objects - This investigation consisted of a series of preliminary tests to demonstrate the feasibility of the present available foam materials to be foamed around irregular-shaped objects. The suitability of the presently available processing techniques was also established.

In a first "foaming-around" experiment an actual size hand was modeled with masticene. This model was then cast in casting plaster from which a hand was molded with plaster. Using this hand, different techniques for foaming around it were investigated. It was found that, for instance, a promising technique would be to cut and sew a glove from a preprepared foam sheet to which a restraint cloth is bonded. The glove would be fitted to the hand whose assembly would be placed in the air-circulating oven to bring the foam to a molten state which would then be expanded in a vacuum chamber under a selected reduced pressure.

A vital point in this technique is the bonding of fabric to vinyl foam sheets. The laminate obtained, with the fabric as the restraint layer, has to be highly flexible to allow easy bending. To date a large amount of work is being conducted wherein a large variation of bonding techniques is being investigated. As was found during this program, vinyl foam can be produced by any of the means by which vinyl products are made, such as calendering, plastisol, molding and extrusion. Because of this versatility of making vinyl foam, many techniques in bonding a vinyl foam to a fabric are possible. In order to obtain the right vinyl foam-fabric combination for a specific application, the right plastisol formulation, the right fabric and the right processing technique have to be selected. To date, two main methods in making vinyl foam in yard goods are (1) vinyl coating of fabric and (2) vinyl foam laminating. The latter is the newer method and the resulting vinyl foam laminates have some outstanding advantages over the conventional vinyl coated fabrics, such as strength, softness and good recovery of the foam. Some techniques in making vinyl foam laminates are presently being developed and some of the most promising ones are (1) the technique in making a three-ply laminate having a layer of vinyl foam sandwiched between a solid vinyl skin and substrate of fabric, (2) the technique in making a laminate whereby the

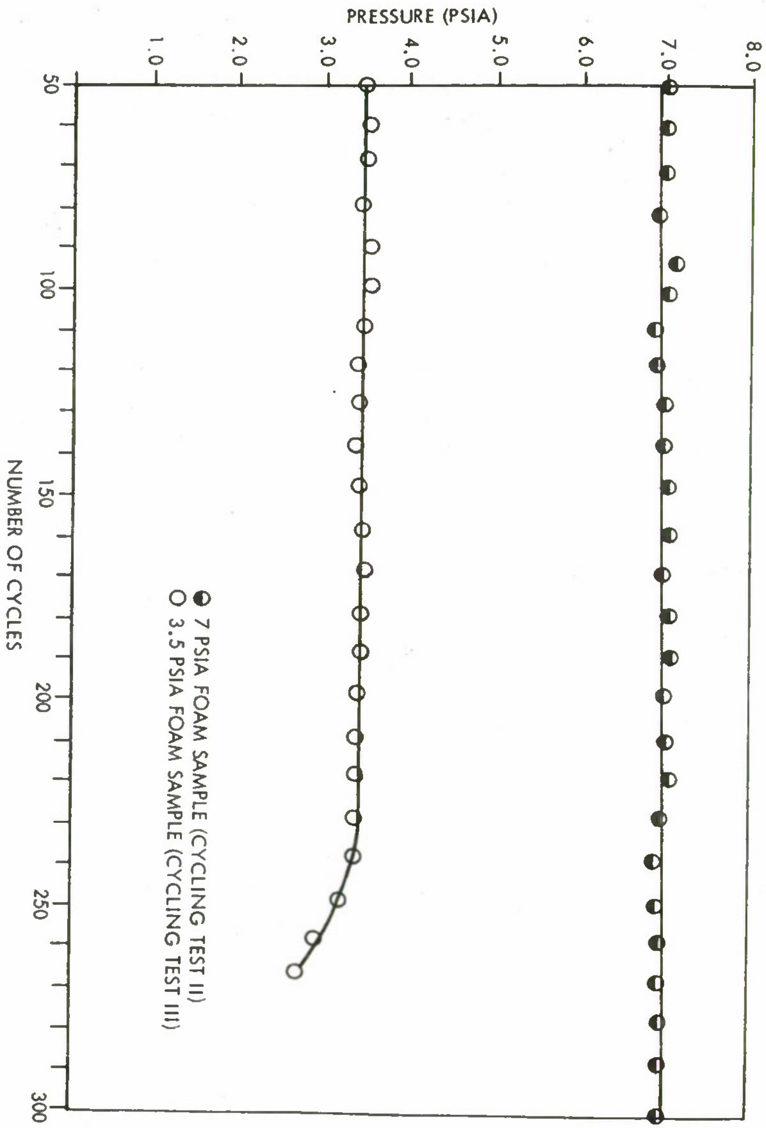

FIGURE 12 FOAM PRESSURE RESPONSE (CYCLING TESTS II AND III)

fabric is between the solid vinyl and the foam vinyl and (3) the technique in making a two-ply laminate wherein the foam is backed by a fabric. Some of these laminates have had an immediate and spectacular acceptance in apparel.

In the search for possible techniques to foam around irregular-shaped objects, a number of techniques was evaluated. The tests conducted to demonstrate the feasibility of these techniques were crude but detailed enough to draw preliminary conclusions. For instance, the following techniques were investigated: (1) dipping, (2) coating by rotation, (3) foaming around an irregular-shaped object with foam thickness varying, and (4) foaming around an irregular-shaped object with foam thickness kept uniform.

The dipping technique has some promising application depending upon the object to be coated. It was found that by keeping the viscosity of the plastisol as high as possible and by applying several coats of plastisol by repeated dipping and heating (below the blowing agent activation temperature) and followed by a final expansion of the foam, good results were obtained.

The "coating by rotation" technique could be worked out as a feasible technique but would require quite sophisticated equipment in order to control the different variables involved. Thus, this technique could be feasible but expensive to demonstrate and to develop the processing.

The number (3) technique consists of foaming around an irregular-shaped object which is contained in a cylindrical container which plays the role of the restraint layer. In this technique the foam can be applied to the object in three different ways, (a) by pouring the selected plastisol in the void between the irregular-shaped object and the restraint layer of the cylindrical container and by subsequent foaming of the plastisol, (b) by incorporating a prefoamed vinyl foam sheet in the void followed by a reheating and reexpansion process, and (c) by incorporating a solid vinyl; that is, unfoamed but containing the blowing agent (unreacted) in the void and by heating the solid vinyl sheet to the blowing agent activation temperature, thus provoking the expansion of the material and formation of a foam. These techniques were all tried and each gave some promising results. However, because the foam thickness varied around the irregular-shaped object, the cell structure of the foam varied (mixture of large and small cells) and so did the properties of the foam. The foam gave a good pressure response but its density varied and its strength and durability would also be affected.

Finally, the number (4) technique was to some extent similar to technique number (3), with the exception of the irregular-shaped object being confined in a similar shaped object (restraint layer) in order to obtain, more or less, a uniform spacing between the irregular object and the restraint layer. As was described above in technique (3), the application of the foam in this technique (4) could also be performed in three ways. Figure 13 shows two examples wherein technique (4) and way of application (a) were used. The foam is of a good quality with a uniform cell structure. The smallest irregular details put purposely in the objects were reproduced in great detail on the foam indicating an excellent molding capability of the vinyl foam. In another test, technique (4) and method of application (c) were used. The resulting foam was of a good quality and of a significantly lower density.

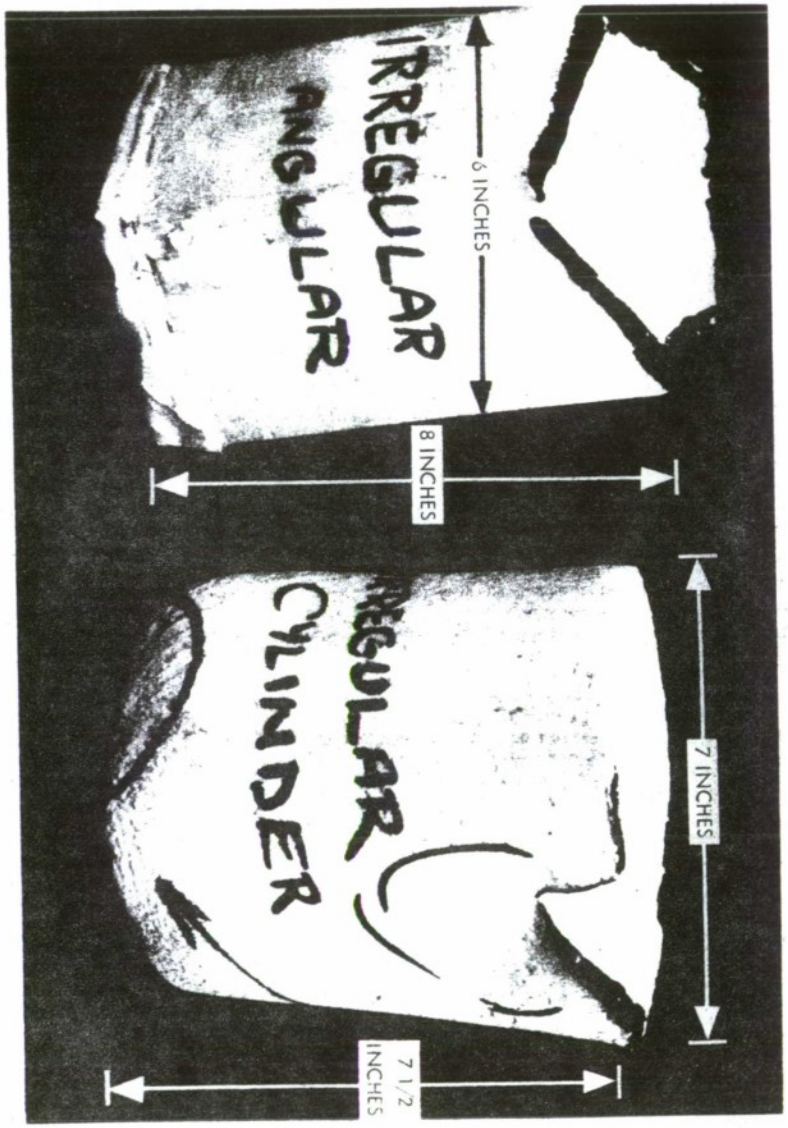

FIGURE 13 FOAMING AROUND IRREGULAR-SHAPED OBJECTS

All details of the irregular objects were shown and the pressure response was good.

In the techniques (3) and (4), the irregular-shaped objects had to be hollowed so as to allow uniform heating of the plastisol or foam, from all sides.

The above discussed "foaming-around techniques" show definite promise. Successful techniques could be worked out with additional testing and refinements.

6. Fabrication of Large Foam Sheets - A 4 ft. by 6 ft. foam sheet was prepared by using the presently available vinyl foam formulations and processing techniques. For this preparation, formulation (IV) and the "Two-Stage Processing Technique" were utilized. The gelling and fusion of the plastisol were performed in a large air-circulating oven. The outgassing and expansion of the plastisol under reduced pressure (3.5 psia) were conducted in NSL's space simulation chamber (Figure 14) which main tank measures 12 feet in diameter by 15 feet long. The following factors had to be watched, (1) thorough outgassing of the plastisol, (2) uniform heating of the plastisol in the large air-circulating oven, and (3) the free expansion of the plastisol had to be accomplished at the appropriate temperature

The 4 ft. by 6 ft. foam sheet obtained exhibited good properties, such as strength, flexibility, softness, durability, and uniformity of cell structure. This demonstrated the feasibility of making large foam sheets under a reduced pressure.

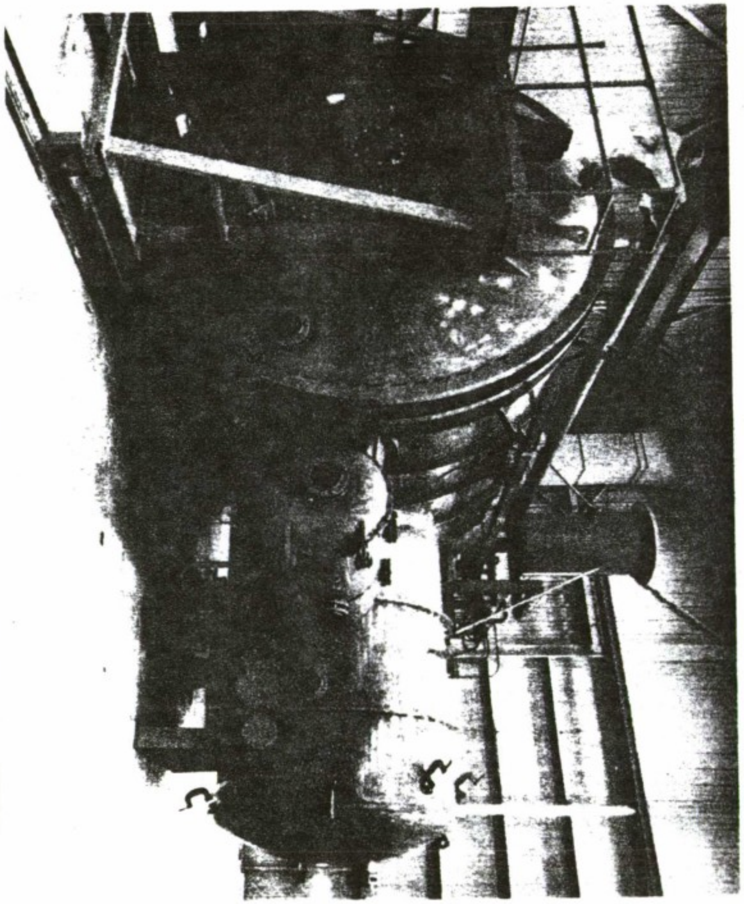

FIGURE 14 NORTHROP SPACE LABORATORIES SPACE SIMULATION CHAMBER

SECTION 111

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

A suitable foam system has been developed which can be formed in a repeatable process and is capable of providing pressures varying from 7 psia to 3.5 psia when exposed to a vacuum and properly restrained. The foam is of the vinyl polymer class and several formulations and processing techniques were established for its preparation. It passed successfully the specifications required by this study and was effectively used in exploratory investigations such as, (1) foaming around irregular-shaped objects, and (2) fabrication of large foam sheets, while still providing pressure responses varying from 7 psia to 3.5 psia when exposed to a vacuum and properly restrained.

B. Recommendations

The closed cell foam which was developed during this program should be utilized in a continuation of a research program on materials and the application in an integrated technique for pressurizing the human body when exposed to a vacuum. This new effort should be directed toward the application of this foam as the expandable medium to provide (1) the intimacy of fit when in a vacuum thus preventing body swelling, and (2) a loose comfortable garment at ground level. For comfort and biothermal control, the normal body perspiration should be removed in a manner comparable with that experienced in shirt sleeves at ground level and during flight where the cabin environment is maintained at 7 psia, 5 psia or 3.5 psia.

This effort should also include a continuation of the foam technology investigation; the reason being that, as the work progresses and concepts and techniques are being developed for foaming around irregular shapes and for removal of perspiration, the foam formulation or processing technique might require some modifications.

One objective should be to continue the development of techniques for foaming around irregular shapes so as to obtain an intimacy of fit and desired repeatable pressure responses in the range from 3.5 to 7 psia when exposed to a vacuum environment. The irregular shapes should simulate actual body sections and should be made of flexible expandable material. The pressures exerted by the foam and the body section when confined within a restraint layer and exposed to a vacuum should be equalized at the point of contact. Using a flexible restraint layer to contain the foam around irregular shapes, mobility, particularly around joints, should be investigated.

A second objective should be to investigate and develop the specific design of a material such as to provide for removal through the closed cell sponge of water when exposed to a vacuum. A method of increasing or decreasing the water loss should also be presented.

More specifically, this research program should consist of:

Task 1

Determine the amount and thickness of expandable foam required to obtain the pressure response of either 7 psia or 3.5 psia when confined in circles varying in diameter from 1/2 inch through 18 inches and exposed to a vacuum. The predetermined pressure response shall be the same in all circles and at different foam thicknesses. The containers with diameters within the range from 1/2 inch to 18 inches shall be of a rigid material and nonflexible or nonexpandable. The foam must exert the above predetermined pressures over an irregular shape confined within the rigid constraint circle. The irregular shapes shall represent cross-section of diameters of the body such as from fingers, arm, leg, hips, chest, etc., and should be cast initially in solid shapes.

Task 2

In a more realistic test, actual body sections should be cast using a flexible expandable material which can simulate the body swelling when exposed to a vacuum. The body sections should be confined within a flexible restraint layer ("state-of-the-art")*. A prepared foam with desired pressure response should be incorporated between the restraint layer and the flexible body section. This foam will have to equalize the pressure exerted by the flexible body section while being confined within the restraint layer and exposed to a vacuum.

Task 3

A more realistic space suit restraint layer should be located or developed. If the existing "state-of-the-art" restraint layers are not suitable for this particular application, a study should be conducted wherein a suitable flexible restraint layer should be fabricated. This effort could be performed concurrently with, or prior to, Task 2, if necessary.

Physical means should be investigated in reducing the foam permeability but still retain its softness and other vital physical properties so as to meet the necessary requirements. This step should be investigated only if the foam should require it,as concepts and techniques are being developed in the steps discussed above.

If necessary, techniques could be investigated whereby deteriorated foam, that is, foam which was used repeatedly for a long period of time and thus lost a quantity of gas from its cells large enough to interfere with the pressure response, would be reconditioned by refilling the cells with an appropriate gas.

Task 4

Because in certain areas of the body (particularly in joints) the foam involved in the space suit will be subjected to compression which will interfere with the ease of movement of the arm, concepts should be

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*For new or more suitable restraint layer, see Task 3.

investigated whereby this interference would be eliminated or minimized. Mobility tests should be conducted on a typical arm section. Concurrently, compression, flexure and extension or elongation tests should be performed with the foam used in each concept in order to check the foam quality and performance for each concept. These tests should be conducted in either the selected reduced cabin pressure or vacuum.

Task 5

Techniques and concepts should be investigated for incorporating a water transmittal capability through the foam/restraint configurations into vacuum. The method developed for extracting water should be demonstrated.

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13 ABSTRACT

A closed-cell foam was developed for integration into a partial pressure suit that would produce pressure on the human body to provide protection in a vacuum environment. A survey of literature and industrial organizations was followed by an extensive experimental study on known foam systems and the development of new foam systems. The evaluation and development of the foam composition and processing techniques are described. From this study, the formulation and processing of suitable vinyl closed-cell foams were developed with reproducible properties in controlled processes. Their physical properties passed successfully the required cycling test wherein the foams, properly restrained and exposed to vacuum, exerted a pressure response of 7 psia or 3.5 psia depending upon the process used.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Protective clothing Partial pressure suits Space flights Vacuum environment Closed-cell sponge research Pressure protection Sweat Personal protection in space environment						

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