EQUILIBRIUM EXPANSION OF POLYPROPYLENE FOAM FILAMENTS
INFLATED IN FLUOROTRICHLOROMETHANE/METHYLENE CHLORIDE BATHS



FIG. I

INVENTOR

FRANK BALDWIN MOODY
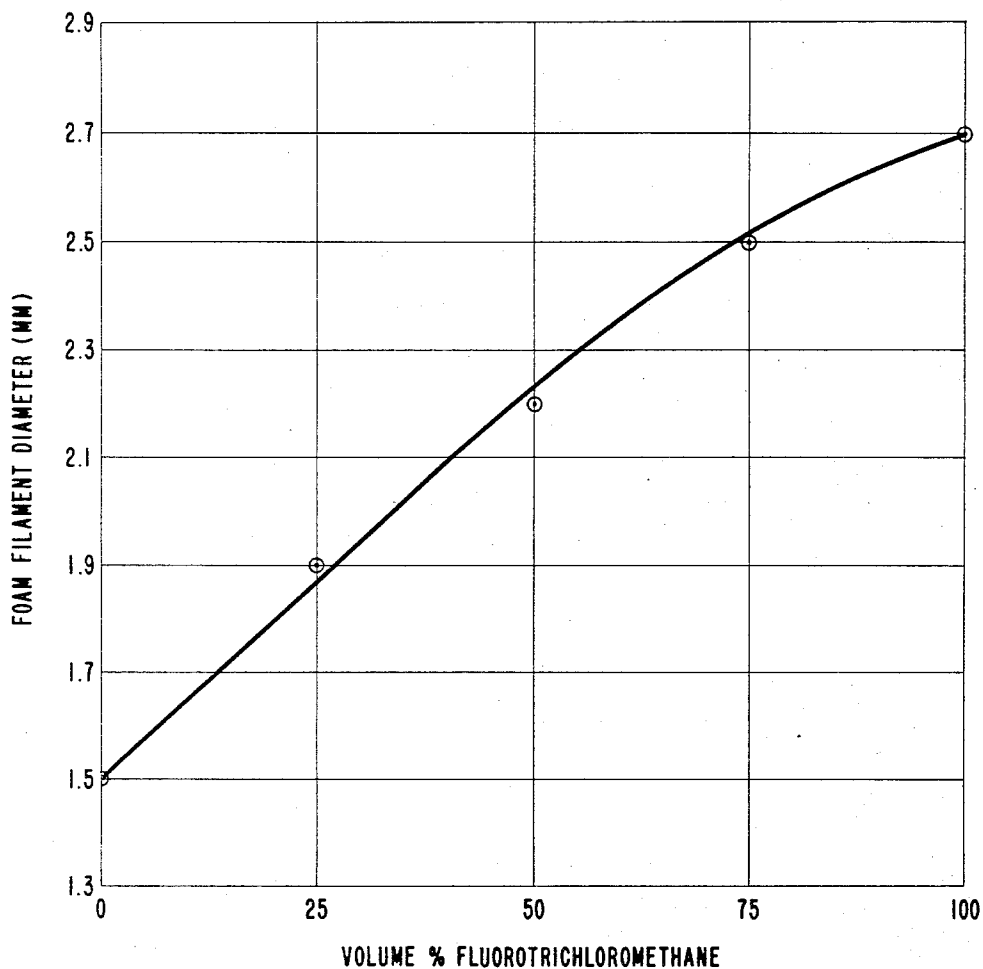ROBERT GUY PARRISH

BY

           ⟨signature⟩ ATTORNEY

YIELDABLE POLYMERIC CELLULAR STRUCTURE
HAVING CLOSED CELLS DEFINED BY GAS
PERMEABLE WALLS AND DENSITY 1 to 75%
OF SOLID POLYMER

IMMERSION IN FLUID PER-
MEATING AGENT (FPA) AT
PRESSURE NOT LESS THAN
ATMOSPHERIC

SAID CELLULAR STRUCTURE HAVING PARTIAL
PRESSURE OF FPA IN CELLS

EXPOSURE TO GAS HAVING
DIFFERENT PERMEABILITY
RATE THROUGH CELL WALLS
FROM FPA TO PROVIDE
OSMOTIC DRIVING FORCE

SAID CELLULAR STRUCTURE HAVING DIFFERENT
BULK DENSITY FROM ORIGINAL

FIG. 2

INVENTORS
FRANK BALDWIN MOODY
ROBERT GUY PARRISH

BY

ATTORNEY

1

This invention relates to yieldable synthetic, polymeric cellular structures having closed cells and more particularly to a process for readily achieving changes in the density or volume thereof.

In recent years yieldable foam materials having closed cells have found increasingly wide acceptance in a variety of applications because of their ability to provide thermal and acoustical insulation, to withstand shock, and to afford buoyancy or other properties. There are, nevertheless, several factors associated with foams which have detracted from their suitability for many end uses. Largely these factors relate in one way or another to the problem that, apart from the application of sustained loads, the foams have not been readily amenable to changes in density as would be desirable for many purposes. Thus the extremely low densities of foams, which are necessary for functional purposes, have resulted in excessively high storage and shipping costs since no satisfactory method has heretofore permitted successive stages of deflation and inflation. Furthermore, many of the foams have not been adapted to be foamed in place but rather have required mechanical shaping techniques to attain a product of suitable dimensions. In addition, a practical means has seldom been available to permit the foam user to effect density changes in the foam as would be desirable for purposes requiring critical product controls.

Recognizing these problems which have been associated with certain foam materials, a number of suggestions have heretofore been made whereby the gaseous content of closed cell foams could be changed with, in some cases, attendant changes in density. Essentially these methods have each relied upon either the application of mechanical compressive forces, the use of subatmospheric pressures, or the employment of condensable gases in order to achieve the desired change. Although such methods have frequently been satisfactory for specific purposes, they have not been widely adopted owing to a number of severe disadvantages. In particular, the mechanics of such techniques have not been well suited to a continuous operation as is commonly necessary for feasible commercial processes. Then, too, such methods have required lengthy processing periods, in many cases for a series of repetitive steps, such that the economics becomes prohibitive. Frequently another disadvantage of prior methods has been the inability to accurately regulate the desired degree of density change, this being particularly troublesome in the case of commercially saleable products. Even aside from the foregoing problems associated with such prior art methods, the products so obtained have not been amenable to more than a single density change, for example a foamed material could not be deflated for purposes of shipping followed by reinflation at a later time.

An object of the present invention is to provide a method for readily effecting a change in the gas content, i.e. regulated inflation or deflation, of yieldable cellular structures. A further object of the invention is a method by which the volume and density of such cellular structures can be reversibly lowered and raised. Another object of the invention is a method for deflating foams without the need for employing mechanical compression, subatmospheric pressure, or condensable gases. Still another object of the invention is a method for consecutively de-

2

flating and inflating cellular foam materials. Another object of the invention is a method for restoring the pneumaticity of foams which have been deflated by compression. Further objects of the invention include foamed products of unique composition and/or structure. Other objects will be apparent from the remainder of the specification and claims.

In accordance with the invention a method is provided for osmotically effecting a net change in the density of a synthetic, high molecular weight, polymeric cellular structure having a density of 1% to 75% of the density of the polymer in solid non-expanded form; that is, the initial structure, depending upon whether it is to be inflated or deflated, can range from a comparatively high density of only minor gas content to one of low density, i.e. a fraction of a pound per cubic foot. The cellular structures employed have a major proportion of closed cells defined by gas permeable walls. These cells, ranging from either full expansion to almost total collapse in inverse proportion to the density, constitute a structure which in expanded condition is reversibly yieldable such that substantial deformation occurs under internal-external pressure differentials. In a first step the cellular structure is immersed, at a pressure no less than about atmospheric, in a fluid permeating agent which is capable of permeating the cell walls, i.e. by osmotic diffusion of permeating agent molecules therethrough. Accordingly, diffusion is effected of the permeating agent through the walls and into the cells to establish an internal partial pressure of the agent. In some cases, it will be apparent that the original gas contained in the cells will likewise diffuse outwardly, as when the internal partial pressure of that gas (inside the cells) exceeds its external partial pressure (outside the cells or the "environment"). The introduction of enough permeating agent to establish an internal partial pressure thereof which is about 5% of the total pressure (usually about atmospheric depending upon the degree of resilience of the structure) is normally the minimum amount necessary to effect sufficient changes in the density of the structure. In a second step the thusly treated structure having an appreciable content of the agent is subjected to a gaseous atmosphere which is also capable of permeating the cell walls but which has a different permeability rate through the cell walls than does the permeating agent. In the case where the gaseous atmosphere is so selected as to be more permeant to the walls than is the permeating agent and the external partial pressure of the gaseous atmosphere is greater than the internal partial pressure of that atmosphere, then a portion of the atmosphere will diffuse into the cells, at least partially expand and inflate the cells, and give rise to an overall decrease in density. In the case where the gaseous atmosphere is less permeant to the walls than is the permeating agent and the external partial pressure of the agent is lower than its internal partial pressure, then at least a portion of the permeating agent will diffuse out of the cells, at least partially contract and collapse the cells and give rise to an overall increase in density.

In the drawings, FIGURE 1 illustrates equilibrium expansion of polypropylene foam filaments inflated in fluorotrichloromethane/methylene chloride baths in accordance with this invention, and FIGURE 2 is a flow diagram of the process of this invention.

It will be apparent that the invention involves controlled utilization of osmotic pressure differentials to inflate or deflate a cellular structure of the described character. The net change in density can be slight or incremental as for purposes of product control or can be great, i.e. an order of magnitude or more. The invention affords a great number of significant advantages and virtues. Several of these will be mentioned hereinafter al-

though the list is not exhaustive and many others will be apparent to those skilled in the art.

By simple interchange of the gaseous content of certain foams, it now becomes practical by the process of the invention to transport and store deflated foams which can be later readily reinflated for use.

In addition, the use of deflated foams to fashion a material, e.g. a textile, followed by inflation permits the production of products which could not be obtained by fabricating a fully inflated foam.

Similarly, certain types of foams which heretofore could only be shaped by mechanical techniques can now be inflated in place to exact dimensions.

The process of the invention also makes possible the restoration of the pneumaticity of foams which have been damaged by collapse, e.g. under sustained loading such that the gaseous component has largely been removed.

Of particular significance, the process of the invention can be performed simply, even continuously, without the necessity of pressurized or vacuum systems, compression devices, and the like.

Essentially the process of the invention is based upon the finding that the bulk density, or simply density, of a closed-cell yieldable foam may be adjusted at will by varying the volume of the individual cells, and that this may be accomplished by filling the cells with suitable fluid permeating agents or inflatants (e.g. gases or volatile liquids) fulfilling certain permeability conditions. Thus, if a deflated foam is desired, the cells are filled with a substance which permeates the walls faster than does air (or whatever gaseous atmosphere in which the sample is to be used). On subsequent exposure of such a sample to air, the inflatant will diffuse out of the cells faster than air diffuses in to take its place, so that a partially collapsed structure of higher density is produced. By suitable choice of character and quantity of inflatant, the degree of collapse and density increase can be varied at will, the more permeative and larger the quantity of inflatant, the greater the degree of collapse. Conversely, if a gas less permeative than air is introduced into the cells, an osmotic driving force will cause air to enter the cells faster than the inflatant gas diffuses out, and a net increase in volume or decrease in density will be observed. Although the use of air as the gaseous atmosphere is particularly preferred because of its availability and its normally suitable permeability coefficient, there are numerous instances where it is desirable to provide another gas in the final product, e.g. for insulation purposes, one having a lower thermal conductivity.

Inflation of collapsed foams according to the invention is accomplished by introducing into the cell a quantity of a gas or volatile liquid, i.e. a fluid permeating agent, having a rate of permeation through the cell walls lower than that of the gaseous atmosphere (usually air) in which the foam is subsequently exposed. As long as any of this slightly permeant gas remains in the cells, the exterior atmosphere will diffuse into and inflate the cells until its internal and external fugacities, or apparent partial pressures, are equal. Thus, when the foam containing the permeating agent is subjected to a gaseous atmosphere having a pressure of about 14.7 pounds per square inch, the internal total pressure, if allowed to come to equilibrium, i.e. substantially equal internal and external fugacities, will also be about one atmosphere or more depending upon the quantity of inflatant gas retained in the cells. Although decreases in density of 25% or more will normally be effected, intermediate degrees of inflation can also be achieved as by selecting the original inflatant of proper permeation and quantity so that its concentration will have decreased to zero by outward diffusion when the desired degree of inflation has been reached. It is also possible to achieve intermediate degrees of inflation or deflation by charging the cells with a judicious mixture of fast and slow permeating gases or liquids.

The inflation technique can be performed upon almost

totally deflated or collapsed cellular structures, i.e. those having a density of about 75% of the polymer itself, or upon products of relatively lower density, i.e. to as little as 1% of the polymer, where simply a greater degree of bulk is required. A structure having at least a minor residual quantity of gas is necessary to create an osmotic driving force for permeating agent to enter the cells.

Inflation of collapsed foams as described in this invention is to be distinguished from primary blowing processes which are employed to form and blow the cells of the foam. This invention is not concerned with forming new cells nor with appreciable stretching of the walls beyond their original dimensions. Thus, the maximum volume of the inflated foams is substantially that of the foam in its initial state, plus perhaps a minor increase from the slight distention as occasioned when the final internal pressure in the cells is superatmospheric, as when a quantity of impermeant inflatant remains in the cell in addition to the gaseous atmosphere which diffuses into the cells.

An especially desirable system in accordance with the invention is obtained when the inflatant gas has substantially zero permeation through the cell walls. In this case, air can be allowed to diffuse into the cells until the fugacity of air is equal inside and outside the cells, i.e., until the partial air pressure inside the cells is essentially one atmosphere. The total internal gas pressure may, therefore, be greater than one atmosphere, and the foam will be fully inflated. When such a pneumatic inflated product is used for cushioning purposes where it may be exposed to static loads for sustained periods of time, slow diffusion of air out of the cells may lead to partial collapse of the foam; but so long as the impermeant inflatant gas remains in the cells, the foam will recover by self-reinflation upon removal of the load as osmotic pressure drives air back into the cells. Post-formation introduction of such an impermeant gas may be accomplished by a temporary "loosening up" of the polymer in the cell walls with a volatile plasticizer which is rapidly removable by vaporization when the desired amount of impermeant gas has penetrated the plasticized cells. In this regard polyethylene terephthalate is a preferred polymer for preparing permanently pneumatic foams since certain halogenated organic gases, particularly octafluorocyclobutane, may conveniently be used as substantially impermeant agents.

In another embodiment, the invention is particularly advantageous in the preparation of deflated cellular products such as filaments. In addition to economies in storage and shipping, such products have special utility as post-expandable stuffing materials (as in life jackets, sleeping bags, etc.) and textile yarns. Although the strength of an inflated cellular filament, for example, is adequate for power weaving operations, its high surface friction makes the operation difficult, and its extremely high bulk means that only a relatively few yards of yarn can be held on conventional bobbins, beams or shuttles. However, when a collapsed cellular yarn is used, not only are these problems effectively overcome but also a very open scrim-like fabric, i.e. loosely woven, can be economically prepared which, on subsequent inflation of the filaments, expands to a tight, highly opaque, pneumatic, bulky fabric. The resultant fibers without fusion or permanent adherence to one another can therefore constitute a more tightly woven fabric than could be produced by the weaving of an expanded filament.

A technique suitable for deflating preformed foams, e.g., those having a density of less than 25% of the polymer of the cell walls, is to immerse the sample in a highly permeant gas or volatile liquid, i.e., permeating agent, which will replace the previous or original gas content since the latter diffuses out of the cells as a result of the osmotic pressure difference caused when its external partial pressure is less than its internal partial pressure. Since the highly permeant material can enter the cells faster than the original diffuses out, the structure may temporarily be super-inflated or turgid.

5

After the exchange has progressed to some predetermined extent, usually to the point where at least 90% of the orginal gas volume has diffused out, the structure can be partially deflated by exposure to a less permeant atmosphere. The degree of deflation is governed by how fast the concentration of the highly permeant substance drops which depends on its permeation rate and original concentration. If allowed to proceed to a concentration of about zero, the internal partial pressure of the inflatant will also be about zero. In any event an increase of the density of the structure by 50% or more will normally be desired.

Exchange of either the fast or slow diffusing gas or volatile liquid with the previous contents of the cells may frequently be hastened by exposure of the system to elevated temperature, so long as the softening point of the polymer is not exceeded and the cellular character of the product destroyed. For many permeating agents it will be desirable to operate near its boiling point, whether at normal or superatmospheric pressures, and for this reason the selection of an agent having a boiling point below about 150° C., usually below 85° C., is preferred. The elevated temperature can assist either in effectively "plasticizing" the polymer cell walls and thus increasing the permeability rate of the diffusing materials, or by raising the activity, and hence the osmotic driving force, of the diffusing species. For example, it is possible, in reasonable periods of time, to introduce gases which have very low diffusion rates at room temperature by carrying out the exchange process at elevated temperatures.

It is also possible to speed up the exchange process by exposing the foam to a plasticizing gas or volatile liquid concurrently with the exposure to the desired exchange material. A preferred plasticizing agent has a high diffusion coefficient and high volatility so that when the desired quantity of exchange material has penetrated the cells, the plasticizer may be rapidly removed (as by a heat treatment) and the exchange material "locked" in the cells. This technique is particularly useful for introducing "impermeant" gases into cellular structures. The action of the plasticizing agent may be assisted by operating at elevated temperatures. The step of immersing the initial foam structure in the fluid permeating agent should be effected at pressures no less than about one atmosphere with a large excess of the agent in order to achieve diffusion into the cells in practical periods of time. Then too this eliminates the need for special equipment. Although not essential, the subsequent exposure to a gaseous atmosphere is also desirably conducted at no less than about one atmosphere of pressure.

The time required for completion of the process of this invention is frequently of the order of a few minutes, as will be apparent from the specific examples hereinafter. The speed of sample inflation is governed principally by the speed of inward air diffusion, and sample deflation must, of course, occur faster than this rate. Obviously, the time required for complete gas equilibrium will, therefore, depend on many factors: sample size, cell wall thickness, permeability coefficient of original gas, permeating agent, or gaseous atmosphere in the polymer in question, temperature, presence of plasticizing agent, etc.

The cellular structures employed in accordance with the invention require certain essential characteristics and properties. A great many of the commercially available foam materials as well as others less well known nevertheless possess such features and hence can be satisfactorily utilized. A particularly essential characteristic of a suitable foam is that it has a major proportion, by number, of closed cells since open cells do not confine liquids and would not afford osmotic pressure differentials. For practical purposes mere visual or microscopic examination will often readily reveal whether or not a particular cellular structure predominates in closed or open cells. Particularly this is true in the case when the

6

identity of the polymer and the conditions of foam formation are known. Otherwise the closed-cell content of a yieldable foam sample may be determined by the gas displacement method of Remington and Pariser, Rubber World, May 1958, p. 261, modified by operating at as low a pressure differential as possible to minimize volume changes of the yieldable closed cells.

Necessarily the cell walls must be gas permeable in the sense that they must be capable of being permeated by at least some gases, although not all. Thus certain gas molecules or inordinately large size could be virtually incapable of permeating the walls. Also such large molecules would frequently be unsuitable because of unduly low vapor pressures.

A further essential characteristic of the foams to be employed in the process of the invention is that they be yieldable, i.e., resilient such that substantial deformation occurs under internal-external pressure differentials, meaning differences, of one atmosphere or less (since this is the order of magnitude of the pressure differentials available for collapse and inflation). By substantial deformation is meant that the cellular structure in expanded condition, i.e., having an internal pressure of about one atmosphere with few if any buckles and wrinkles in the walls, is yieldable such that its volume can be compressed by at least about 10% under a load of 10 lbs. per square inch sustained for a period of 1 second with recovery of at least about 50% of its original volume on release of the load. Foams which do not compress to that extent are entirely too rigid and hence do not afford a sufficient degree of resiliency to respond to pressure differentials. Moreover if the foam does not sufficiently recover after release of the load, then it is not sufficiently flexible to resist fracturing and rupturing of the cell walls.

The wall portions of cellular structures are composed of a synthetic, high molecular weight polymer, usually organic polymers. These may be a wide variety of addition or condensation polymers, provided, of course, that in the form of a cellular structure they possess the described essential characteristics. Typical of such polymers are the polyolefins such as polyethylenes, linear or branched, polypropylene, polyamides such as nylon 6 or polyesters such as polyethylene terephthalate, halohydrocarbon polymers such as polychlorotrifluoroethylene, etc. A highly suitable class of cellular structures is that wherein substantially all of the polymer is present as filmy elements of thickness less than 2 microns, since the walls are extremely thin and diffusion of gases through the cell walls is easily facilitated. A particularly desirable type of cellular material is the ultramicrocellular structure described in copending U.S. application, Ser. No. 170,187, filed Jan. 31, 1962, now U.S. Patent 3,227,664, issued Jan. 4, 1966, wherein additionally the structure is a crystalline organic polymer having thin walls exhibiting uniplanar orientation and a uniform texture. These preferred cellular structures contain at least $10^3$ cells per/cc. and the average transverse dimension of the cells in expanded condition is under 1000 microns.

In the case of the preferred class of cellular structures, as described in the copending U.S. application, substantially all of the polymer is present as filmy elements whose thickness is less than 2 microns and preferably under 0.5 micron. The thickness of a cell wall, bounded by intersections with other walls, will ordinarily not vary by more than ±30%. Adjacent walls commonly will have nearly equal thicknesses, usually within a factor of 3. Moreover the polymer in the cell walls exhibits uniplanar orientation and a uniform texture. In strand form, such an ultramicrocellular structure will have a tenacity of at least 0.1 g.p.d. The microcellular sheets have in general, a tenacity of at least 5 lbs./in./oz./yd.$^2$ in the machine direction and a TAPPI opacity of at least 70% at 1 oz./yd.$^2$.

The apparent density of these ultramicrocellular products ($\rho$) in expanded condition is between 0.5 and 0.005 g./cc. The number of cells per cc. ($n_f$), is at least $10^5$,

**7**

preferably $10^8$ or greater, as estimated from the equation

$$_nF=\left(\frac{\rho}{3t\rho_0}\right)^3$$

wherein $t$ is the wall thickness in cm., and $\rho_0$ is the bulk polymer density.

The wall thickness and transverse cell dimensions are determined by microscopic examination of cross sections cut perpendicular to the machine direction. Thus 20–60 micron thick sections may be cut from a frozen sample with a razor blade. Large cell ($>50$ microns) samples are frozen directly in liquid nitrogen. Smaller celled samples are preferably "imbedded" in water containing a detergent, and then frozen and sectioned. The transverse dimension of one or more cells can be readily measured by the freezing and sectioning technique mentioned above which at least partially inflates the cells. The cells will then exhibit a general polyhedral shape similar to the shape of the internal bubbles in a foam of soap suds. It is found that the average transverse dimension of the cells is less than 1000 microns, and that the mutually perpendicular transverse dimensions of a single cell in a fully inflated condition do not vary by more than a factor of three. In the preferred structures the average transverse dimension is under 100 microns. The ratio of the cell volume to the cube of the wall thickness can be calculated and exceeds about 200. For very thin walled samples ($<1$ micron), the wall thickness is preferably measured with an interferometer microscope. A layer of the sample is peeled off by contact with "Scotch Tape." The layer is freed from the tape by immersion in chloroform and subsequently placed on the stage of the microscope for measurement.

The term "uniplanar orientation" employed in defining the preferred products of this invention may be fully understood from the following discussion. "Axial," "planar," and "uniplanar" indicate different types of molecular orientation of high polymeric crystalline materials. "Axial orientation" refers to the perfection with which the crystalline axis parallel to the molecular chain axis in a sample is aligned with respect to a given direction, or axis, in the sample. For example, prior art materials which have been drawn in one direction only (e.g., fibers or one-way stretched films) generally exhibit an appreciable degree of axial orientation along the stretch direction. "Planar orientation" refers to the perfection with which the crystalline axis parallel to the molecular chain axis is oriented parallel to a surface of the sample. Conventional two-way stretched films generally exhibit a degree of planar orientation in that their molecules lie approximately parallel to the surface of the film, although the molecules may point in random directions within this plane. "Uniplanar orientation" is a higher type of polymer orientation in that it refers to the perfection with which some specific crystalline plane (which must include the molecular chain) in each polymer crystallite is aligned parallel to the surface of the sample. Obviously, only crystalline polymers can exhibit uniplanar orientation. There is no restriction imposed on the direction of the molecular axis within the plane of the sample. Thus, these three types of molecular orientation may occur singly or in combination; for example, a sample might simultaneously exhibit uniplanar and axial orientation.

Electron diffraction furnishes a convenient technique for observing the presence of uniplanar orientation in the ultramicrocellular structures. A single cell wall is placed perpendicular to the electron beam. Since the Bragg angle for electron diffraction is so small, only crystalline planes essentially parallel to the beam (perpendicular to the wall surface) will exhibit diffraction. If the sample does in fact have perfect uniplanar orientation, there is some crystalline plane which occurs only parallel to the film surface and, therefore, will be unable to contribute to the diffraction pattern. Thus, the observed pattern will lack at least one of the equatorial diffractions normally

**8**

observed for an axially oriented sample of the same polymer. If the degree of uniplanar orientation is somewhat less than perfect, there may be a few crystallites tilted far enough to contribute some intensity to the diffraction pattern, but at least one of the equatorial diffraction intensities will be appreciably less than normal. Thus, for the purpose of this invention, a sample is considered to have uniplanar orientation when at least one of the equatorial diffractions appears with less than one-half its normal relative intensity as determined on a randomly oriented sample of the same polymer.

Other techniques of measuring uniplanar orientation and their correlation with electron diffraction measurements are described in the J. Pol. Sci., 31, 335 (1958), in an article by R. S. Stein.

The term "uniform texture" applied to the polymer in the cell walls means that the orientation, density, and thickness of the polymer is substantially uniform over the whole area of a cell wall, examined with a resolution of approximately ½ micron. This is best determined by observing the optical birefringence in the plane of a wall of a cell removed from the sample. For microcellular samples with a net over-all axial orientation, the individual cell walls will also normally exhibit an axial orientation in addition to the required unipanar orientation. In the birefringence test, such products will show a uniform extinction over the whole area of the cell wall. Samples with no net axial orientation must show a uniform lack of birefringence over their whole area rather than numerous small patches of orientation with each patch oriented at random with respect to the others. Lacy or cobweb-like cell walls, of course, do not have uniform birefringence over the whole area of a cell wall, and such products are readily distinguished from the uniform textured products preferred in this invention.

The polymers suitable for the preferred ultramicrocellular structures in accordance with this invention are members of the class of synthetic crystallizable, organic polymers which includes polyhydrocarbons such as linear polyethylene, stereo-regular polypropylene or polystyrene; polyethers such as polyformaldehyde; vinyl polymers such as polyvinylidene fluoride; polyamides both aliphatic and aromatic, such as polyhexamethylene adipamide and polymetaphenylene isophthalamide; polyurethanes, both aliphatic and aromatic, such as the polymer from ethylene bischloroformate and ethylene diamine; polyesters such as polyhydroxypivalic acid and polyethylene terephthalate; copolymers such as polyethylene terephthalate-isophthalate, and equivalents. The polymers should be of at least film-forming molecular weight.

One of the features of the ultramicrocellular structures is the high degree of orientation of the polymer in the cell walls, which contributes to the unique strength of these structures. Therefore, a preferred class of polymers from which to make these objects is that class of polymers which responds to an orienting operation (e.g., drawing of fiber or films) by becoming substantially tougher and stronger. This class of polymers is well known to one skilled in the art and includes, for example, linear polyethylene, polypropylene, 66 nylon, and polyethylene terephthalate. Another feature of the preferred predominantly closed cell ultramicrocellular structures is their very high degree of pneumaticity resulting directly from their uinque structure, which may be looked upon as numerous tiny bubbles of gas enclosed in thin polymer skins. Retention of this gas, and hence of the structure's pneumaticity depends on a low rate of gas diffusion through the polymer walls. Therefore, another preferred class of polymers particularly for preparing microcellular structures where pneumaticity is important, is that class of polymers with low permeability coefficients for gases, such as polyethylene terephthalate. Polymer properties such as solubility, melting point, etc., are usually reflected in the properties of the ultramicrocellular product.

9

In the preparation of cellular structures, whether ultra-microcellular or not, various polymer additives such as dyes, pigments, antioxidants, delusterants, antistatic agents, reinforcing particles, adhesion promoters, removable particles, ion exchange materials, U.V. stabilizers and the like may be mixed with the polymer solution prior to formation of the original foam.

The nature of the fluid permeating agent will largely depend upon the permeability of the cell walls of the cellular structure and whether inflation or deflation is desired. Both gaseous and liquid materials are contemplated by the term although in the case of the latter those liquids having a high vapor pressure are preferred. Such materials should be essentially inert, a non-solvent for the polymer and have a boiling point below the softening temperature of the polymer. The permeating agent may be composed of a single substance or a mixture of two or more materials. For purposes of deflation and for use as a plasticizer with less permeative materials, methylene chloride is particularly suitable. The perhaloalkanes and perhalocycloalkanes of 1 to 4 carbon atoms constitute a highly useful class of such materials whether used alone, in combination, or with other components such as methylene chloride.

The following examples will further illustrate the invention but are not intended to limit it in any respect. Parts are by weight unless otherwise stated.

*Example I*

This example describes the preparation of a deflated ultramicrocellular crystalline polymeric structure for use in accordance with the invention. 400 grams of polyethylene terephthalate (relative viscosity of 50, vacuum dried in an oven at 120° C. for 24 hours) and 250 ml. of methylene chloride (dried over calcium hydride) are charged into a one liter pressure vessel, heated at 210° C. while the vessel is being rotated, held at 210° C. for 10 minutes, cooled to 201° C., held 15 minutes, positioned vertically, and connected to a source of nitrogen pressure at 1,000 p.s.i.g. just prior to extrusion through a cylindrical orifice 0.014 inch diameter by 0.028 inch long. Immediately upon extrusion into the atmosphere, the methylene chloride vaporizes rapidly, generating approximately $10^5$ closed cells per cc., and freezing the polymer in the form of very thin cell walls. The extruded strand has a denier of 1,400 and an estimated density of 0.02 g./cc. but within a few seconds most of the methylene chloride vapor diffuses out of the cells, leaving a highly collapsed strand of 0.13 g./cc. density. The cell walls are composed of filmy elements less than 1 micron in thickness and essentially all of the polymer is present in the walls. The polymer in the cell walls exhibits uniplanar orientation and a uniform texture.

*Example II*

Another deflated structure is prepared for purposes of subsequent inflation in accordance with the invention. Example I is repeated, except that 20 grams of carbon dioxide is added to the mixture, and the extrusion temperature is 191° C. The carbon dioxide serves to assist bubble nucleation so that approximately $10^7$ cells per cc. are now produced. However, carbon dioxide, like methylene chloride, will diffuse out of the cells fairly rapidly so that the 900 denier strand produced is again observed to collapse within a few seconds to a density of 0.08 g./cc. The collapsed yarn will not re-inflate on simple heating.

*Example III*

Portions of the collapsed yarn prepared in Example I are partially inflated by being immersed in several liquid permeating agents at their normal boiling points for periods of time as indicated in Table I. The samples are observed to inflate to some extent in the baths, but collapse immediately on removal from the bath and exposure to the room atmosphere owing to condensation of the internal inflatant on adiabatic cooling when rapid evaporation of residual surface inflatant occurs. The samples rapidly reinflate as they warm up to room temperature and the internal inflatant is converted back to the vapor state, this process being substantially complete in 1–2 minutes. The equilibrium degree of inflation, as indicated by the densities reported in Table I, is shown to be dependent upon (1) the quantity of inflatant introduced into cells during the immersion in the liquid bath and (2) the relative rates of diffusion of air into the cells and inflatant vapor out of the cells. After standing in air the gaseous content of the cells is largely composed of air. These samples, as in all other cases studied, show little change in denier on inflation or deflation, indicating that the machine direction dimension of the cells remains substantially unchanged.

TABLE I.—INFLATION OF COMPACT FOAM YARN

| Liquid | Normal boiling point, deg. | Immersion time, min. | Density after inflation, g./cc. |
|---|---|---|---|
| Control | | | 0.127 |
| n-butane | −.5 | 2 | 0.062 |
| | | 5 | 0.043 |
| | | 15 | 0.037 |
| Ethyl chloride | 12 | 2 | 0.091 |
| | | 5 | 0.036 |
| | | 15 | 0.022 |
| Sym-dichlorotetra-fluoroethane | 4 | 5 | 0.080 |
| | | 30 | 0.042 |
| Sulfur Dioxide | −10 | 1 | 0.087 |

*Example IV*

Polyethylene terephthalate is only slowly permeated by 1,1,2-trichloro-1,2,2 trifluoroethane as evidenced by the fact that less than 2% of this material is lost from an inflated foam even at 100° C. in one hour's time. Since permeation of this material into a pre-formed closed cell foam of this polymer would also be very low, this example illustrates the use of methylene chloride as a volatile, highly permeable plasticizer to facilitate introduction of the less permeant material into a closed cell foam.

Samples of the collapsed foam yarn of Example I are placed in the baths indicated in Table II, the baths being held at their atmospheric boiling points (about 40° C.). The foam samples become somewhat swollen as the vapors diffuse into the cells. Upon removal from the warm baths and exposure to the atmosphere the samples collapse almost immediately, since the inflatant vapors condense at room temperature. The samples are immediately reinflated by being placed in a 100° C. oven to flash off the methylene chloride and maintain the trichlorotrifluoroethane "locked" in the cells as a vapor. After 10 minutes the samples are removed from the oven and cooled to room temperature. In this condition they remain fully inflated because of the internal pressure of air which has diffused into the cells under its osmotic pressure difference.. Much of the trichlorotrifluoroethane remains in the cells, even though it may be predominantly in condensed form at room temperature.

TABLE II

| Mixture v./v. of tri-fluorotrichloroethane and methylene chloride, resp. | Time required to swell in bath | Final density, g./cc. |
|---|---|---|
| 100/0 | | 0.078 |
| 90/10 | 30 min. | 0.068 |
| 70/30 | 1.5 min. | 0.015 |
| 50/50 | 10 sec. | 0.013 |

*Example V*

This example demonstrates the desirability of having a quantity of inflatant which slowly permeates the cell walls of a pneumatic closed-cell foam which is exposed to sustained loading. Portions of a collapsed ultramicrocellular

polyethylene terephthalate foam yarn having cells about 30 microns in diameter (when fully expanded) are inflated with quantites of various permeating agents as follows:

(a) Yarn placed in a mixture of 5 parts perfluorocyclobutane and 1 part[1] methylene chloride in a sealed tube. Heated to 110° C. for 5 minutes, cooled to 25° C. and the tube broken. The yarn spontaneously self-inflated.

(b) Yarn refluxed 15 minutes in 1:1 bath of sym-dichlorotetrafluroethane and methylene chloride. Sample heated in air at 100° C. to become permanently expanded even after removal of the heat.

(c) Yarn placed in a 1:1 mixture of bromotrifluoromethane and methylene chloride in a sealed tube at −80° C. Heated to 0° C. for 30 minutes, the tube cooled to −80° C. and broken with the yarn self-inflating upon exposure to air.

(d) Yarn refluxed in 1.1 mixture of fluorotrichloromethane and methylene chloride as per (b).

(e) Yarn refluxed 30 minutes in fluorodichloromethane.

These pneumatic samples are stored under a load of approximately 15 p.s.i. for seven days. During this period the samples show a progressive loss in height as air gradually diffuses out of the cells. In those samples where the inflatant is more permeable, the percent decrease in original height is greatest. At the end of seven days the load is removed and the samples are allowed to recover for three days. The samples containing the inflatants which are least permeable to the cell walls show the smallest loss in height under the sustained load and also the highest recovery. The sequence of inflatants in Table III is consistent with their relative rates of increasing permeability for the cell walls of the polyethylene terephthalate structure, as judged by vapor chromatographic analysis of residual inflatant concentration.

TABLE III

| Inflatant | Percent original height after 7 Days' loading at 15 p.s.i. | Percent original height after 3 days' recovery |
|---|---|---|
| (a) Perfluorocyclobutane_____ | 35 | 83 |
| (b) Sym-dichlorotetrafluoro-ethane_____ | 18 | 84 |
| (c) Bromotrifluoromethane____ | 15 | 65 |
| (d) Fluorotrichloromethane___ | 6 | 13 |
| (e) Fluorodichloromethane____ | 9 | 11 |

In analogous procedures, partially collapsed 6-nylon cellular samples are post-inflated with various agents. Thus partially collapsed 6-nylon foam filaments of density 0.087 g./cc. are placed in a refluxing 50/50 volume mixture of fluorotrichloromethane/methanol for about 1½ hrs., removed and placed in an air oven at 80–100° C. to complete the inflation to a stable density of about 0.013 g./cc. Alternately, the initially partially collapsed filaments may be placed in a boiling methanol bath for two minutes (which presumably plasticizes the polymer to an appropriate degree), then transferred directly to a boiling fluorotrichloromethane bath for 15 minutes, followed by the warm oven drying to achieve the same degree of inflation. Another portion of the 6-nylon filaments is sealed in a pressure vessel with a 50/50 volume mixture of perfluorocyclobutane/ethanol and heated two hours at about 110° C. After the vessel is cooled and vented, the foam filaments are removed and placed in the warm air oven to generate a fully inflated, stable, pneumatic, perfluorocyclobutane-containing sample of density 0.013 g./cc. This sample likewise shows exceptional stability and recovery under sustained load.

Pneumatic polyethyleneteterephthalate foams or 6-nylon foams containing inflatant such as perfluorocyclobutane

[1] In each case a large volume excess of permeating agent was provided and the exposure period extended to promote the introduction of a maximum quantity of the agent.

to which the cell walls are essentially impermeable are preferred stuffing materials for upholstery cushions, sleeping bags, etc., where full recovery after removal of load is desirable.

*Example VI*

100 denier polyethylene terephthalate collapsed ultramicrocellular foam yarn (density=0.2 g./cc.) is woven into a very open scrim-like fabric of 24 ends and 15 picks per inch, having a light transmission of 15.5% and a thickness of 7 mils. When this fabric is dipped in a 1,1,2-trichloro-1,2,2-trifluoroethane/methylene chloride (50/50 volume mixture) bath at the boil and dried for a few minutes at 100° C., the foam yarns are inflated to a density of 0.02 g./cc. and their lateral expansion produces a tightly woven bulky pneumatic fabric of 38 mils thickness and only 4.8% light transmission (comparable to the opacity of a good shirting fabric). There is no appreciable lateral shrinkage of the fabric, indicating that the longitudinal fiber dimension is stable.

In addition to this 100% foam yarn fabric, woven or non-woven fabrics can be constructed from blends of foam yarns and normal dense synthetic or natural textile fibers. When these fabrics contain an appreciable quantity of foam fibers, at least 25%, they may be used in constructing an all-weather garment, using the techniques of this invention to collapse the foam to provide an open, breathable fabric for summer wear, and to expand the yarn to provide a tight insulating fabric for winter wear. It is to be noted in this regard that many common dry-cleaning solvents are suitable inflatants for certain closed-cell foam yarns.

*Example VII*

A sample of fully inflated ultramicrocellular polyethylene terephthalate foam yarn having a denier of 41 and density of 0.022 g./cc. is immersed in a methylene chloride bath at its atmospheric boiling point (40° C.) for 15 minutes. The sample is observed to collapse during the first two minutes or so, as the air diffuses out of the cells. The sample remains collapsed on removal from the bath, since the methylene chloride in the cells diffuses out faster than air diffuses in. The density of the collapsed yarn is 0.55 g./cc. (an increase of 25 times) while its denier remains unchanged at 41. Similar samples collapsed in methylene chloride may be inflated temporarily by taking the yarn from the bath directly into a 100° C. oven which vaporizes the methylene chloride and expands the foam. However, this is only a temporary and unsatisfactory condition as the expanded form persists only for a few moments since the methylene chloride still diffuses out of the cells very rapidly, again leaving the sample collapsed.

The fast permeation rate of methylene chloride in polyethylene terephthalate is related to its plasticizing action on the polymer.

Any tendency of the strands to develop tacky surfaces can readily be overcome by the addition of 10 parts by volume of DC–550 silicone oil (a heat-stable, methylphenyl siloxane polymer, colorless to light straw colored, with a viscosity of 100–150 centistokes and a flash point of 575° F.) for each 750 parts by volume of methylene chloride completely inhibits the sticking problem while still permitting collapse of the yarn to a density of 0.29 g./cc.

These collapsed samples retain their cellular character as evidenced by the fact that they may subsequently be fully reinflated, for example by the techniques of Examples III through VI.

*Example VIII*

Although all the preceding examples have dealt with polyethylene terephthalate foams in order that the various features of the invention may more readily be intercompared, gas permeable cellular structures of other polymers such as linear polyethylene, branched polyethylene,

polypropylene, polychlorotrifluoroethylene, etc. may also be employed in accordance with the invention. In this example, portions of a closed-cell foam of crystalline ultra-microcellular polypropylene in sheet form, wall thickness less than 1 micron, are immersed for several minutes in baths respectively of fluorotrichloromethane, 1,1,2-tri-chloro-1,2,2-trifluoroethane, and methylene chloride at their atmospheric boiling points. Evolution of gas bubbles is observed as air diffuses out of the cells to be replaced by the respective organic vapors. The foam samples collapse on removal from the baths (due to condensation of the organic vapors), but within a minute or two the first two samples reinflate while the third remains permanently collapsed. Thus, the two fluorinated compounds permeate polypropylene slower than air does, while methylene chloride permeates fastest of all and diffuses out before an equal volume of air can enter.

*Example IX*

The preceding example demonstrates that trichloro-fluoromethane permeates polypropylene foam slower than air while methylene chloride permeates faster than air. This example illustrates controlled intermediate degrees of expansion achieveable with mixtures of these two liquids.

Closed-cell yieldable polypropylene foam filaments are prepared by extruding a mixture of 1,000 grams polypropylene of melt index 0.7 (Hercules Powder Company's Profax), 1,000 grams methylene chloride, 5 grams "Santocel" (Monsanto trademark for silica aerogel) nucleating agent and 300 grams 1,1,2-trichloro-2,2,1-trifluoroethane heated to 150° C. for 16 hours in a three liter pressure vessel. The autogenous pressure of 255 p.s.i. was increased to 300 p.s.i. by connecting the pressure vessel to a source of nitrogen gas just prior to extrusion through a 20 mil orifice into air. These ultramicrocellular filaments self-inflate to an equilibrium diameter of 1.8 mm. as air diffuses into the trichloro trifluoroethane containing cells. Separate portions of this yarn are then dipped for 5 minutes (to allow adequate time for equilibrium permeation) in fluorotrichloromethane/methylene chloride baths of various composition. The samples are removed from the baths, dried for thirty minutes at room temperature and the new diameters determined with results as indicated in FIGURE 1. (These diameters are remeasured four days later with identical results, indicating that equilibrium degree of air inflation is achieved at least within thirty minutes.) Since the foam yarn density is inversely proportional to the square of the yarn diameter, it is obvious from the data of FIGURE 1 that the density of these particular samples may be varied by a factor of almost 4, and adjusted to any value within this range by pre-selection of the inflatant bath composition.

*Example X*

Ultramicrocellular polypropylene foam filaments of 0.72 g.p.d. tenacity, 563 denier, wall thickness less than 1 micron, are collapsed in methylene chloride prior to being woven into a fabric of 14 ends and 8 picks per inch. This loosely-woven fabric is expanded by a 30 seconds' immersion in fluorotrichloromethane at room temperature. It shrinks momentarily on removal from the bath, but re-expands within 15 seconds at room temperature to a tight, opaque fabric of 1.7 oz./yd.²

A portion of this fabric is partially collapsed under load of 1.5 p.s.i. applied overnight. The loaded area remains depressed even when the load is removed, indicating that the original fluorotrichloromethane inflatant has diffused out of the cells and that there is no osmotic driving force for air to reinflate the fabric. However, the damaged fabric is completely restored by re-immersing the sample in fluorotrichloromethane for 20 seconds followed by a 30 seconds room temperature air drying whereupon the

whole fabric is reinflated to its previous state with no residual evidence of the compression damaged areas.

*Example XI*

Although fluorotrichloromethane permeates ploypropylene foams slowly enough to be a good inflatant the cell walls are not completely impermeable thereto as illustrated in Example X. Perfluorocyclobutane employed in this example is an inflatant with a much lower permeability rate.

Polypropylene filaments are prepared as in Example IX, except that 82 ml. of perfluorocyclobutane is substituted for the 300 gram trichlorotrifluoroethane and the spinning pressure is 465 p.s.i. Osmotic pressure drives air into these foam filaments, and, since no appreciable quantity of the perfluorocyclobutane diffuses out, the total internal pressure developed in the cells is appreciably greater than one atmosphere, making these filaments quite turgid. The low permeation of this inflatant is further evidenced by the fact that samples of these filaments remain inflated even after being stored for many months under the appreciable pressure generated in a closed bound, laboratory record book.

*Example XII*

Pneumatic closed-cell synthetic polymer foam filaments are excellent stuffing materials for buoyancy devices, such as life jackets, because of their conformability, high specific buoyancy and water insensitivity. By employing the post-expansion techniques of this invention, one may avoid to a considerable extent the difficulties of inserting inflated foam filaments into irregular shapes such as are found, for example, in life jackets.

720 grams of vinyl foam buoyancy blocks are removed from a commercial coast guard appproved work vest and replaced with 180 grams of collapsed polyethylene terephthalate foam filaments similar to those described in Examples I and II. The various sections of the vest are then quilted in such a way as to restrict maximum bulk and assure maximum body conformability and comfort, and the collapsed foam yarn is then expanded in place. The foam expansion is accomplished by immersing the vest for 15 minutes in a refluxing bath of 47.6 volume percent methylene chloride, 47.6 volume percent fluorotrichloromethane and 4.8 volume percent silicone oil (DC–550). The vest is then rinsed in a fluorotrichloromethane bath containing 5 volume percent DC–550 and placed in a circulating air oven at 100° C. for 15 minutes to complete the inflation process until the foam filaments expand to the dimensions of the vest. This vest now has a buoyancy of 20 lbs. The silicone oil serves to lubricate the fiber surfaces and enhance the compliance of the structure.

*Example XIII*

Part (a) of Example V describes a technique for introducing perfluorocyclobutane into polyethylene terephthalate ultramicrocellular structures which requires heating the sample in a sealed tube containing perfluoro-cyclobutane and methylene chloride. Superatmospheric pressure was utilized since perfluorocyclobutane is not miscible with methylene chloride at room temperature and atmospheric pressure. The present example describes two emthods for achieving the introduction of perfluoro-cyclobutane at atmospheric pressure.

Methylene chloride and perfluorocyclobutane may be made miscible at room temperature by addition of a suitable third component. Thus 100 ml. of liquid perfluoro-cyclobutane (measured at −7° C.) are added to 100 ml. of methylene chloride and 65 ml. of 1,1,2-trifluoro-1,2,2-trichloroethane to form a miscible liquid system. A portion of collapsed polyethylene terephthalate ultramicrocellular 25 denier yarn of density about 0.2 g./cc. is placed in the refluxing (at atmospheric pressure) liquid for 30 minutes and subsequently removed and dried 15

minutes at 120° C. in an air oven. The yarn inflates permanently to a density, measured at room temperature, of 0.026 g./cc., and contains 6.3 ml./g. of perfluorocyclobutane measured as a gas at room temperature and pressure by standard vapor chromatography techniques.

It is also possible to work at atmospheric pressure with a 2-component liquid system, provided a plasticizing agent miscible with perfluorocyclobutane is chosen. A 50/50 volume mixture of perfluorocyclobutane/fluorodichloromethane is miscible at room temperature. A portion of partially collapsed polyethylene terephthalate ultramicrocellular yarn of density 0.064 g./cc. is immersed for 15 minutes in the refluxing mixture, removed and dried 10 minutes at 120° C. The yarn inflates immediately, and after cooling has a density of 0.018 g./cc. The perfluorocyclobutane content is determined to be 1.2 ml. of gas at room temperature and pressure per gram of foam. When the immersion time is increased to one hour, the perfluorocyclobutane content increases to 4 ml./g.

What is claimed is:

1. Method for osmotically effecting a net change in the density of a synthetic, high molecular weight, polymeric cellular structure having a density of 1% to 75% of the density of the polymer in solid non-expanded form, said cellular structure having a major proportion of closed cells defined by gas permeable walls and being characterized in that in expanded condition it is reversibly yieldable such that substantial deformation occurs under internal-external pressure differentials, which method comprises the steps of (a) immersing said cellular structure at a pressure no less than about atmospheric in a fluid permeating agent capable of permeating the said cell walls, thereby effecting diffusion of the said agent into the cells to establish an internal partial pressure of said agent, and subsequently (b) subjecting the thusly treated structure to a gaseous atmosphere also capable of permeating the said cell walls but which has a different permeability rate through the cell walls than does said agent, further provided that if said gaseous atmosphere is more permeant to the walls than is said agent then the external partial pressure of the atmosphere is greater than the internal partial pressure thereof whereas if said gaseous atmosphere is less permeant to the walls than is said agent then the external partial pressure of said agent is lower than the internal partial pressure thereof thereby effecting a net change in the quantity of fluid within said closed cells.

2. The method of claim 1 wherein the cellular structure in expanded condition is yieldable such that its volume can be compressed by at least 10% under a load of 10 pounds per square inch sustained for a period of 1 second with recovery of at least 50% of its original volume on release of the load.

3. The method of claim 1 wherein (a) said internal partial pressure of said agent is at least 5% of the internal total pressure.

4. The method of claim 1 wherein (b) said gaseous atmosphere is air.

5. The method of claim 1 wherein step (a) is conducted at a temperature near the boiling point of the agent.

6. The method of claim 1 wherein step (b) is conducted at a pressure no less than about atmospheric.

7. The method of claim 1 wherein the said polymer is a cellular structure which has substantially all of the polymer present as filmy elements of a thickness less than 2 microns.

8. The method of claim 1 wherein said polymeric cellular structure is an ultramicrocellular structure of a crystalline organic polymer having substantially all the polymer present as filmy elements of a thickness less than 2 microns, with the polymer in the cell walls exhibiting uniplanar orientation and a uniform texture.

9. The method of claim 8 wherein the ultramicrocellular structure has at least $10^3$ cells/cc. and wherein the

average transverse dimension of the cells in expanded condition is under 1000 microns.

10. The method of claim 1 wherein the cellular structure is in the form of a strand.

11. The method of claim 1 wherein the cellular structure is in the form of a sheet.

12. The method of claim 1 wherein the cellular structure is in the form of a fabric.

13. Method for osmotically increasing the density of a synthetic, high molecular weight, polymeric cellular foam structure having a density of less than 25% of the density of the polymer in solid-non-expanded form, said cellular foam structure having a major proportion of gas-containing, closed cells defined by walls which are permeant to said gas, and being yieldable such that substantial deformation occurs under internal-external pressure differentials, which method comprises the steps of (a) immersing said cellular foam structure at a pressure not less than about atmospheric in a fluid permeating agent capable of permeating the cell walls, thereby lowering the external partial pressure of the said gas causing diffusion thereof from the cells while effecting diffusion of said agent into the cells to establish an internal partial pressure of said agent and (b) subsequently subjecting the thusly treated structure to a gaseous atmosphere wherein the external partial pressure of said agent is less than the internal partial pressure of said agent and which gaseous atmosphere diffuses more slowly through the cell walls than does said agent to thereby effect at least partial diffusion of said agent out of the cells.

14. The method of claim 13 wherein immersion of the said cellular foam structure in said permeating agent causes diffusion of at least about 90% by volume of said gas from the cells.

15. The method of claim 13 wherein (b) exposure to said gaseous atmosphere is continued until the internal partial pressure of the said agent is about zero.

16. The method of claim 13 wherein the bulk density of said cellular foam structure is increased by at least 50%.

17. The method of claim 13 wherein said polymeric cellular foam structure is composed of polyethylene terephthalate and said agent is methylene chloride.

18. The method of claim 13 wherein said polymeric cellular foam structure is composed of crystalline polypropylene and said agent is methylene chloride.

19. Method for osmotically lowering the density of a synthetic, high molecular weight, polymeric cellular structure having a density of 1% to 75% of the density of the polymer in solid non-expanded form, said cellular material having a major proportion of closed, at least partially collapsed cells defined by gas permeable walls and being characterized in that in expanded condition it is yieldable such that substantial deformation occurs under internal-external pressure differentials, which method comprises the steps of (a) immersing said cellular structure at a pressure not less than about atmospheric in a fluid permeating agent capable of permeating said cells, thereby effecting diffusion of the said agent into the cells to establish an internal partial pressure of said agent and (b) subsequently subjecting the thusly treated material to gaseous atmosphere capable of permeating said cells and which diffuses more rapidly through the cell walls than said agent and which has an external partial pressure greater than its internal partia lpressure.

20. The method of claim 19 wherein (a) diffusion of said agent into the cells is effected until the internal partial pressure of said agent is at least 5% of the internal total pressure per square inch.

21. The method of claim 19 wherein (b) exposure to the said atmosphere is continued until the internal and external fugacities thereof are substantially equal.

22. The method of claim 19 wherein the bulk density of said cellular structure is lowered by at least about 25%.

23. The method of claim 19 wherein (b) said cellular structure containing said agent is subjected to said gaseous atmosphere within a shaped confining zone to thereby expand the said cellular structure to substantially the dimensions thereof.

24. The method of claim 19 wherein said agent contains a first component which slowly permeates said wall and a second component which rapidly permeates said walls.

25. The method of claim 19 wherein said agent contains a compound selected from the group consisting of perhaloalkanes and perhalocycloalkanes of 1 to 4 carbons.

26. The method of claim 25 wherein said polymeric cellular structure is composed of polyethylene terephthalate.

27. The method of claim 25 wherein said polymer cellular structure is composed of crystalline polyethylene.

28. The method of claim 25 wherein said polymeric

cellular structure is composed of crystalline polypropylene.

### References Cited

#### UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,659,935 | 11/1953 | Hammon | 264—321 |
| 2,746,088 | 5/1956 | Lindemann et al. | 264—54 |
| 2,795,008 | 6/1957 | Lindemann et al. | 264—54 |
| 3,126,432 | 3/1964 | Schuur | 264—53 |
| 3,189,669 | 6/1965 | Goldfein | 264—321 XR |
| 3,192,300 | 6/1965 | Pehn | 264—321 XR |
| 3,202,998 | 8/1965 | Hoffman | 343—833 |
| 3,227,784 | 1/1966 | Blades et al. | 264—53 |

#### FOREIGN PATENTS

| | | |
|---|---|---|
| 891,943 | 3/1962 | Great Britain. |

ALEXANDER H. BRODMERKEL, *Primary Examiner.*

P. E. ANDERSON, *Assistant Examiner.*