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<p>(54) Title: VACUUM INSULATING AND CONSTRUCTION MATERIAL</p>		
<p>(57) Abstract</p>		
<p>Vacuum insulating and construction materials (1) are provided by producing bubble containing, solid materials such as individual bubbles, multiple bubbles, foamed material, and the like in an environment of less than atmospheric pressure and enclosing the bubbles produced in an air-tight encapsulating material (5) while still in the environment of less than atmospheric pressure. On being moved into an environment of atmospheric pressure the bubbles retain their vacuum quality.</p>		

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VACUUM INSULATING AND CONSTRUCTION MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to insulation and construction materials. In one of its aspects it relates to material used for thermal and acoustic insulation. In another of its aspects it relates to vacuum insulation materials i.e. insulating materials containing enclosed spaces in which the pressure is less than atmospheric pressure. In another of its aspects this invention relates to construction materials containing enclosed spaces in which the pressure is less than atmospheric pressure. In yet another of its aspects this invention relates to ultralight construction materials. In still another of its aspects this invention relates to the production of vacuum insulation materials. In still another of its aspects this invention relates to the production of construction materials containing enclosed spaces in which the pressure is less than atmospheric pressure.

2. Description of the Prior Art

Vacuum insulation techniques have been known for use in various applications for both thermal and acoustic insulation material. Such material makes use of the advantage of having a reduced number of molecules in a vacuum chamber encapsulated within the material so that the transfer of heat or sound is reduced as compared to material having chambers encapsulating gases at atmospheric pressure or higher pressures. Obviously, the greater the

reduction of pressure within a vacuum chamber the more effective will be the barrier to the transfer of heat or sound energy through the chamber and increasing the ratio of open space to supporting structure also reduces the transfer of heat or sound through an insulating material.

While several approaches have been tried in the production of vacuum insulation the most common schemes have relied on producing air-tight enclosing structures that are supported from within by loosely packed filler which upon the evacuation of gas from the structure prevents the structure from collapsing on itself, but still provides interstices between the units of filler from which gas can be withdrawn. After the evacuation of gas, the structure is sealed to maintain the vacuum.

Other production approaches enclose within a single air-tight, outer structure a multiplicity of either elongated, relatively flat, air-tight, bag structures or elongated, sausage-shaped, air-tight structures of relatively small diameter, either of which are supported on the inside by microporous insulation material. Gas is withdrawn from the individual, filled structures and each is individually sealed before the multiplicity of structures is enclosed within an air-tight outer structure and the outer structure is sealed.

Although vacuum insulation produced by the processes discussed above is effective, the evacuation and sealing of the filler supported structures can be tedious and costly.

The present invention eliminates the need to evacuate gases from filler supported structures and provides material that can retain its vacuum characteristic after being cut or machined.

5 The technique, described herein, that is used for producing vacuum insulation can be used, by the process of this invention, to produce construction materials i.e. materials, that because of the innate strength of the materials used, can be formed into shapes containing
10 bubbles in which the contained gas is at a pressure less than atmospheric. Such construction materials are useful in constructing products in which the combination of lightness and strength of material is an asset. Among such products are automobiles, airplanes, spacecraft and boats.

15 It is easily understood that bubbles having an internal pressure of less than atmospheric pressure can be incorporated into construction material at sufficiently high ratio to the total amount of solid material in the structure and encapsulating material that the resulting
20 product would be buoyant in a fluid, liquid or gas, of greater density.

 Note that for the purposes of this invention the term "bubble" includes any space surrounded by an enclosing material. It is used herein synonymously with void,
25 chamber, pocket, interstice, area of space and other such terms. Also note that the terminology hereinafter describing the material of the invention as having at least

one enclosed chamber therein refers to material that typically has numerous chambers or is filled with a multitude of chambers.

It is, therefore, an object of the present invention
5 to provide an improved process for the manufacture of vacuum insulating materials.

It is another object of this invention to provide vacuum insulating materials made by the process of this invention.

10 It is still another object of this invention to provide a process for the manufacture of vacuum insulating materials eliminating the need to evacuate gases from the insulating material structure.

It is still another object of this invention to
15 provide vacuum insulating materials of improved structure.

It is another object of this invention to provide construction materials and a method for producing construction materials having encapsulated therein bubbles or pockets within which the pressure is less than
20 atmospheric pressure.

These and other objects and advantages of the present invention will become evident to those skilled in the art by reference to the following description and drawings and the appended claims.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a cut sample of a honeycomb textured insulating material in which bubbles of less than atmospheric pressure are encapsulated in a matrix of air-tight material with a stratum of reflective laminated thereto.

FIGURE 2 is a cut sample of insulating material in which bubbles of less than atmospheric pressure are encapsulated in a matrix of material that is not air-tight and the matrix of the insulating material is encapsulated in an air-tight material.

SUMMARY OF THE INVENTION

There is provided herein a method for preparing an article of manufacture said article comprising at least one chamber enclosed by a solid, air-tight, encapsulating material, (a) the pressure inside the at least one chamber being less than atmospheric pressure, and (b) the encapsulating material of sufficient strength to maintain the integrity and the vacuum characteristic of the at least one chamber the method comprising: in an environment under less than atmospheric pressure (1) treating a material to provide a treated solid material having at least one enclosed chamber therein wherein the at least one enclosed chamber is under less than atmospheric pressure and (2) encapsulating the at least one enclosed chamber in a solid, air-tight, encapsulating material of sufficient strength to

maintain the integrity and the vacuum characteristic of the at least one enclosed chamber.

In a preferred mode of this invention an article of manufacture is prepared by treating a liquid material in an environment under less than atmospheric pressure to provide a treated solid material having at least one enclosed chamber therein under less than atmospheric pressure wherein the treated material on solidifying is air-tight thereby maintaining the vacuum characteristic of the at least one chamber and of sufficient strength to maintain the integrity of the at least one chamber when formed into an article of manufacture.

In variation of the technique described immediately above the material is treated to produce bubbles under atmospheric pressure or under a slight vacuum and then the material containing at least one enclosed chamber therein is transferred into an environment of greater vacuum so that the enclosed chambers are allowed to expand thereby decreasing the pressure within the enclosed chambers before the material sets or hardens to provide air-tight enclosure of the chambers.

Another aspect of the invention involves (1) treating a molten material to provide at least one chamber therein, (2) while still in the molten state introducing the material with at least one chamber therein into a mold, (3) allowing the material in the mold to cool below the melting

temperature thereby providing a solidified molded article and (4) removing the molded article from the mold.

A further aspect of the invention involves foaming a foamable composition of (a) foamable material chosen from
5 the group consisting of metal, glass, plastic and concrete and (b) foaming agent to provide a multiplicity of bubbles, with the bubbles under less than atmospheric pressure, in a foamed article of manufacture.

10 DETAILED DESCRIPTION OF THE INVENTION

According to this invention there is provided a method for preparing an article of manufacture which entails, in an environment under less than atmospheric pressure (1) treating a material to provide a treated material having at
15 least one enclosed chamber therein in which the at least one enclosed chamber is under less than atmospheric pressure and (2) encapsulating the at least one enclosed chamber in a solid, air-tight, encapsulating material of sufficient strength to maintain the integrity and the
20 vacuum characteristic of the at least one enclosed chamber thereby providing an air-tight, encapsulated article having at least one enclosed chamber within which the pressure is less than atmospheric pressure.

Using the procedure set out above can provide an
25 article of manufacture in which there are (1) a multiplicity of chambers enclosed by the material forming the chamber walls in which the material forming said

chamber walls is of sufficient strength to maintain the integrity of the structure of the chambers and in which the pressure within at least some of the chambers is less than atmospheric and (2) an air-tight covering enclosing the
5 multiplicity of chambers.

Further according to this invention there is provided a method for treating a molten, encapsulating material in an environment under less than atmospheric pressure to provide a treated, molten, encapsulating material having at
10 least one enclosed chamber therein within which the pressure is less than atmospheric pressure wherein the treated, encapsulating material upon solidifying is (1) air-tight thereby maintaining the vacuum characteristic of the at least one chamber and (2) of sufficient strength to
15 maintain the integrity of the at least one chamber, thereby providing an air-tight article containing at least one chamber within which the pressure is less than atmospheric pressure.

The process described immediately above can provide an
20 article of manufacture having a multiplicity of chambers enclosed in air-tight encapsulation by the material forming the chamber walls in which the material forming the chamber walls is of sufficient strength to maintain the integrity of the structure of said chambers and in which the pressure
25 within at least some of said chambers is less than atmospheric.

Still further, according to this invention there is provided a method for foaming a foamable material and encapsulating the foamed material in a solid material that is air-tight and of sufficient strength to maintain the integrity of the encapsulated foamed material with both the foaming and the encapsulating completed in an environment under less than atmospheric pressure and subsequently transferring the encapsulated foamed material into an environment at atmospheric pressure to provide a material encapsulated in an air-tight covering having at least one enclosed chamber therein within which the pressure is less than atmospheric pressure.

When an article of manufacture is produced by the process just described using a foamable material that at the conclusion of the foaming operation provides air-tight enclosure of the bubbles or vacuum spaces formed in the foaming operation, the product is described as a foamed material in which bubbles or voids formed are enclosed in air-tight encapsulation by the foamed material itself and in which the pressure within the encapsulated bubbles or voids is less than atmospheric.

When an article of manufacture is produced by the process just described using a foamable material that at the conclusion of the foaming operation does not provide air-tight enclosure of the bubbles formed in the foaming operation so that there must be a subsequent encapsulating of the foamed material with another material that provides

air-tight encapsulation, the product is described as being composed of (1) a foamed material in which the bubbles formed are enclosed by the material foamed and in which the pressure within the enclosed bubbles is less than
5 atmospheric and (2) an air-tight covering encapsulating the foamed material.

Essential to this invention is an environment of reduced pressure within which articles of manufacture containing internal open or gaseous spaces can be produced.
10 The means for providing such an environment requires the use of an ample sized production chamber with access through air locks and control of the internal pressure to provide a desired state of vacuum. Means for providing this environment are well known to those of ordinary skill
15 in the art. It is doubted that an amount of vacuum reasonably close enough to a perfect vacuum could be maintained in a facility on the Earth's surface that formation of bubbles in a liquid would be impaired. The pressure at which the production environment is controlled
20 is, therefore, a decision based on the knowledge that the less the pressure in the bubbles formed the greater the insulation value and the practical considerations of maintaining a high state of vacuum in the production facility.

25 In general, for reasons of practicality, the pressure in the bubbles in the finished product is in a range of about 10^{-12} mmHg to about 760mmHg, preferably in a range of

about 10^{-6} mmHg to about 10^{-2} mmHg, and most preferably in a range of about 10^{-4} mmHg to about 10^{-2} mmHg.

The invention is based on the knowledge that forming bubbles, voids or vacuum spaces in an environment of reduced pressure will produce areas of space having relatively the same internal pressure as the external environment in which they are produced. Advantage is taken of this fact in different ways: in an environment of reduced pressure (1) a bubble can be blown or bubbles can be formed within an encapsulating material that itself forms an air-tight encasement for the bubbles or (2) bubbles can be formed in a material which is not itself air-tight but which is then encapsulated within an air-tight encasement and subsequent to the air-tight encapsulation either (1) or (2) is removed from the environment of reduced pressure into an environment of atmospheric pressure. Bubbles can also be produced as in (1) or (2) in an environment that is not of pressure below atmospheric and, prior to the setting or hardening of the material, it can be moved into an environment of reduced pressure allowing expansion of the bubbles. Upon hardening, the material encapsulates the bubbles.

When the air-tight, encapsulated articles having bubbles produced at less than atmospheric pressure are transferred into an environment at atmospheric pressure the internal pressure of the bubbles remains at the reduced pressure at which the bubbles were produced and because of

the strength of the structure surrounding the bubbles the difference between the external pressure and the pressure within the bubbles does not cause the structure to collapse. Relative to the external atmospheric pressure
5 the articles can be described as having a chamber or chambers therein within which there is a reduced pressure or as having a chamber within which there is less than atmospheric pressure.

The present invention can take advantage of such
10 technology as the use of production stations in space and the use of robotics. A space station can easily provide the environment of reduced pressure required in the present invention. Production chambers in space can more easily be provided with a desired, subatmospheric, operating pressure
15 than can similar work places on the Earth's surface. Programmed robots can operate effectively in an environment of reduced pressure either on a space station or on the Earth. Among the useful products that can be made by the process of this invention are:

- 20 (1) monoliths of insulating material that can be sliced or shaped, as by machining, as desired;
- (2) sheets of insulating material suitable for incorporation into walls of housing, refrigerators, ovens and other assembly items;
- 25 (3) custom molded objects such as thermos bottle liners, insulated cups, items molded to fit specific areas of assembly and the like;

(4) individual spheroids or clusters of spheroids of various relatively small sizes suitable for use as loose fill as in insulation for hollow walls or packing boxes;

(5) self supporting individual or clusters of foamed
5 or bubbled material suitable for mixing into concrete or other building material for original construction or for later application to existing walls;

(6) strings of bubbled material or interlocked bubble
10 beads that can be incorporated into fabric for use in clothing, upholstery and the like;

(7) bubbled or foamed, pliable sheeting or blanketing material;

(8) extruded hollow, cylindrical insulation for pipes
and conduits,

15 (9) light weight engineering materials and

(10) as set out in (1), (2), (3), (7), (8) and (9) that has another material such as a layer of reflective material laminated on at least one of its surfaces.

Among the materials most useful in the construction of
20 the products of this invention are those that: (1) are liquid- for the purposes of this invention liquid can include a true liquid, a molten material or a liquid slurry; (2) can be manipulated to enclose at least one bubble therein and (3) then can be solidified to
25 encapsulate the at least one bubble in an air-tight enclosure. The useful materials include, among others, metals, metal alloys, polymeric materials (preformed

polymers), glass, glass-ceramics, metallic glass, wax, concrete and mixtures thereof. members of these groups can provide the necessary structural strength, the ability to provide air-tight encapsulation and the ability to be
5 manipulated into the desired products.

Metals, glass and thermoplastics can be melted and molded into desired shapes, and in the molten state can be blown into bubbles or can be treated to disperse bubbles therein. With sufficiently rapid cooling all of these
10 materials can be solidified with structure that will maintain the integrity of the bubbles and provide an air-tight encapsulation of the bubbles. The techniques for producing molded articles useful in this invention are well known in the art and do not constitute a novel feature of
15 this invention.

In one of the preferred modes of this invention any of the materials useful for making foams that do not in the preparation of the foam form air-tight encapsulation of the bubbles formed can be foamed in an environment of pressure
20 less than atmospheric pressure and subsequently the foamed product or any portion thereof can, while still in the environment of pressure less than atmospheric pressure, be encapsulated in an air-tight covering material. Among the foamed materials suitable for this mode of the invention
25 are such flexible plastic foams as polyurethane, rubber latex, polyolefin and vinyl polymers; such rigid plastic foams as polystyrene, polyurethane, polyepoxy and polyvinyl

chloride. Techniques for producing foams, either as free forms or in molded shapes, are well known in the art.

Some of the materials cited above can also be formed so that at least a portion of the bubbles formed therein will be encapsulated in an air-tight enclosure of the foamed material as it is foamed. Among such materials are flexible foams of rubber latex, polyolefin, and vinyl polymers; rigid foams of polystyrene, polyepoxy and polyvinyl chloride.

Any material that can be melted, thereafter treated to form at least one bubble therein and solidified retaining the at least one bubble in air-tight encapsulation is useful by a process of this invention. These same materials are useful by a process of this invention to encapsulate foamed material. Among these materials are glass, metals and thermoplastics. Some of the thermoplastics useful in the present invention are polyolefin, nylon, acrylic resin, polystyrene, polysulfone, poly(arylene sulfide), their derivatives and mixtures thereof. Thermosetting materials that can be caused to form bubbles or that can be applied to form air-tight encapsulation of foamed material can also be used in a process of this invention. Among the useful thermosetting materials are phenolics, alkyds, amino resins, crosslinkable polyolefins, polyesters, epoxides, silicones, natural rubber and mixtures thereof.

Although any metal, or combination of metals with other additives in an alloy, that can be used for construction is suitable for the purposes of this invention among those most favored are aluminum, magnesium, and 5 steel, including carbon steel. It should be emphasized that materials suitable for use as construction materials produced by a process of this invention will innately be superior in thermal and acoustic insulation characteristics to products made in the same manner except for having 10 bubbles therein in which the internal pressure is greater.

Among the procedures for producing at least one chamber surrounded by an air-tight encapsulating material in which the pressure in the enclosed chamber is less than 15 atmospheric are the following: (1) using a material that will form an air-tight encapsulation, (a) treating a molten material to create bubbles therein as by agitation or aeration and thereafter molding the molten material with bubbles therein and causing the molded material to solidify 20 while the bubbles are still retained, (b) blowing individual bubbles or strings of bubbles of molten material and thereafter causing the encapsulating material to solidify, (c) forming bubbles or groups of bubbles from a mixture of plastic in a carrier material, such as a plastic 25 in an evaporatable carrier liquid, from which a solidified bubble results on removal of the carrier and d) foaming a foamable material and (2) using a material that will not

form an air-tight encapsulation, (a) foaming a foamable material and then enclosing the foamed material in an air-tight encapsulating material by a coating method such as spraying, painting, dipping and the like and (b), where
5 there is an economic advantage, forming individual bubbles or groups of bubbles from material that itself will not form an air-tight encapsulation and then enclosing these bubbles in an air-tight encapsulating material by a coating method.

10 Referring now to the drawing, in Figure 1 an insulating material 1 is composed of an encapsulating matrix 5 that is air-tight in which is dispersed a multiplicity of chambers 7 having an internal pressure less than atmospheric and to which is laminated a layer 9 of
15 reflective material such as aluminum foil.

In Figure 2 an insulating material 1 is composed of an encapsulating matrix 5 that is not air-tight in which is dispersed a multiplicity of chambers 7 having an internal pressure less than atmospheric with the matrix 5 encased in
20 an encapsulating layer of air-tight material.

The following examples are meant to be illustrative of the current best mode for carrying out a process of the present invention. These examples should not be taken as restricting the scope of the invention.

Example I

In a chamber having an internal pressure controlled at 10^{-2} mmHg the temperature of 1000 ml of nylon in a beaker is raised to a temperature of 230°C , exceeding the melting temperature of 223°C . The molten nylon is agitated using an agitator blade that introduces gas bubbles from the chamber into the molten material and, while the molten material retains the bubbles, the material is poured into a rectangular bar shaped mold and cooled rapidly to solidify the nylon retaining the bubble structure. The cooled, now solidified nylon bar is removed from the mold. The bubble-containing, nylon bar is removed from the vacuum chamber into ambient conditions as a formed material having contained therein a multiplicity of chambers at less than atmospheric pressure. The formed material is cut in half revealing internal chambers at the cut edges. One of the cut edges is abraded to round the cut end of the bar revealing further evidence of other chambers which are opened by the abrasion. This example shows that a molded bar containing chambers at less than atmospheric pressure can be made of an air tight material which can then be cut or further shaped.

Example II

In a chamber having an internal pressure controlled at 10^{-2} mmHg the temperature of a 1000 ml steel crucible filled with glass beads is raised to a temperature of 1200°C ,

exceeding the melting temperature of about 1100°C. The molten glass is aerated by introducing gas from the chamber in the form of small bubbles into the molten material and, while the molten material retains the bubbles, the material is poured into a rectangular bar shaped mold and cooled to solidify the glass retaining the bubble structure. The cooled, now solidified glass bar is removed from the mold. The bubble-containing, glass bar is removed from the vacuum chamber into ambient conditions as a formed material having contained therein a multiplicity of chambers at less than atmospheric pressure. This example shows that a molded bar containing chambers at less than atmospheric pressure can be made of glass.

15

Example III

In a chamber having an internal pressure controlled at 10^{-2} mmHg the temperature of a 1000 ml steel crucible filled with aluminum beads is raised to a temperature of 700°C, exceeding the melting temperature of about 660°C. The molten aluminum is aerated by introducing gas from the chamber in the form of small bubbles into the molten material and, while the molten material retains the bubbles, the material is poured into a rectangular bar shaped mold and cooled to solidify the aluminum retaining the bubble structure. The cooled, now solidified glass bar is removed from the mold. The bubble-containing, aluminum bar is removed from the vacuum chamber into ambient

conditions as a formed material having contained therein a multiplicity of chambers at less than atmospheric pressure. This example shows that a molded bar containing chambers at less than atmospheric pressure can be made of metal.

5

Example IV

In a chamber having an internal pressure controlled at 10^4 mmHg polypropylene glycol is treated with diisocyanate in the presence of water and a tin soap catalyst to produce
10 a polyurethane foam. The foam contains a bubbled structure which, because the material is not air tight, has bubbles at the pressure of the chamber. A 10 inch x 3 inch x 3 inch bar is cut from the foam and encased in a 1/16 inch nylon wrapper which is heat sealed around the bar to form
15 an air-tight enclosure. The sealed bar is removed from the reduced pressure chamber to atmospheric pressure. The bar is then laminated on one side with aluminum foil to produce a bar foamed at reduced pressure, covered with an air-tight sealing layer and laminated on one side with a
20 reflective surface.

Example V

A polyurethane foam is produced as in Example IV except the foam is produced at atmospheric pressure. The
25 non-air-tight foam is then moved into a chamber having an internal pressure controlled at 10^4 mmHg and allowed to come to equilibrium of internal and external pressures. A 10

inch x 3 inch x 3 inch bar is cut from the foam and encased in a 1/16 inch nylon wrapper which is heat sealed around the bar to form an air-tight enclosure. The sealed bar is removed from the reduced pressure chamber to atmospheric
5 pressure.

Example VI

In a chamber having an internal pressure controlled at 10^{-4} mmHg, bubbles of molten nylon are blown. As the bubbles
10 are blown the pressure on the inside of the bubble seeks to equilibrate with the outside pressure providing an internal pressure of less than atmospheric. The bubbles of approximately 1 mm diameter can be blown to detach as individual bubbles or can be blown to form a continuous
15 string. In either case the individual bubbles or portions of a continuous string of bubbles are allowed to solidify to provide air-tight encasement of the bubbles and are removed to an environment of atmospheric pressure and used in large amounts as fill-type insulation.

20 The invention thus being described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the following
25 claims.

What is claimed is:

1. A method for preparing an article of manufacture said article comprising at least one chamber enclosed by a solid, air-tight, encapsulating material, (a) the pressure
5 inside said at least one chamber being less than atmospheric pressure, and (b) said encapsulating material of sufficient strength to maintain the integrity and the vacuum characteristic of said at least one chamber said method comprising: in an environment under less than
10 atmospheric pressure (1) treating a liquid material to provide a treated solid material having at least one enclosed chamber therein wherein said at least one enclosed chamber is under less than atmospheric pressure and (2) encapsulating said at least one chamber in a solid, air-
15 tight, encapsulating material of sufficient strength to maintain the integrity and the vacuum characteristic of said at least one enclosed chamber thereby providing an air-tight, encapsulated article having at least one enclosed chamber under less than atmospheric pressure.
- 20 2. A method of claim 1 wherein the liquid material in step (1) is prepared by melting a solid material.
3. A method of claim 1 wherein the liquid material is selected from the group consisting of metals, metal alloys, polymeric materials (preformed polymers), glass, glass-
25 ceramics, metallic glass, wax, concrete and mixtures thereof.

4. A method of claim 1 for preparing an article of manufacture comprising: treating a molten, encapsulating material in an environment under less than atmospheric pressure to provide a treated material having at least one
5 enclosed chamber therein under less than atmospheric pressure wherein said treated material on solidifying is air-tight thereby maintaining the vacuum characteristic of said at least one chamber and of sufficient strength to maintain the integrity of said at least one chamber,
10 thereby providing an air-tight article having at least one chamber under less than atmospheric pressure.

5. A method of claim 4 comprising: (1) treating a molten material to provide at least one chamber therein, (2) while still in the molten state introducing said
15 material with at least one chamber therein into a mold, (3) allowing said material in said mold to cool below its melting temperature thereby providing a solidified molded article and (4) removing said molded article from said mold.

20 6. A method of claim 5 wherein (1) comprises creating a multiplicity of bubbles within said molten material.

7. A method of claim 6 wherein (1) comprises agitating said molten material.

8. A method of claim 7 wherein (1) comprises aerating
25 said molten material.

9. A method of claim 4 wherein treating a molten material to provide at least one chamber therein comprises

blowing a bubble wherein the pressure within said bubble is less than atmospheric pressure and separating said bubble from the device from which it was blown thereby enclosing the chamber therein.

5 10. A method of claim 4 wherein treating a molten material to provide at least one chamber therein comprises blowing a series of bubbles joined together in a chain wherein the pressure within said bubbles is less than atmospheric pressure.

10 11. A method of claim 1 wherein (1) comprises foaming a foamable composition of (a) foamable material and (b) foaming agent to provide a multiplicity of bubbles, wherein the pressure in said bubbles is less than atmospheric pressure, in a foamed article of manufacture.

15 12. A method of claim 11 where in said foamable material is chosen from the group consisting of polymeric material and concrete.

 13. A method of claim 11 wherein said foamable material on being foamed into an article of manufacture
20 has, at least on its outer periphery, air-tight enclosure of said bubbles.

 14. A method of claim 12 wherein said foamable material on being foamed produces a foamed article of manufacture providing air-tight enclosure of at least some
25 of said bubbles.

 15. A method of claim 12 wherein said foamable material on being foamed produces a foamed article of

manufacture providing air-tight enclosure of at least the majority of said bubbles.

16. A method of claim 13 wherein said foamed article of manufacture is provided with an air-tight covering by a
5 method chosen from the group consisting of dipping, spraying and coating said foamed article.

17. A method of claim 1 comprising (1) forming a bubble or group of bubbles in a mixture of plastic in an evaporatable carrier material and (2) allowing said carrier
10 to evaporate thereby recovering a solidified plastic bubble or group of plastic bubbles.

18. An article of manufacture made by the process of claim 1.

19. An article of manufacture made by the process of
15 claim 2.

20. An article of manufacture made by the process of claim 3.

21. An article of manufacture made by the process of claim 4.

20 22. An article of manufacture made by the process of claim 5.

23. An article of manufacture made by the process of claim 9.

24. An article of manufacture made by the process of
25 claim 10.

25. An article of manufacture made by the process of claim 11.

26. An article of manufacture made by the process of claim 13.
27. An article of manufacture made by the process of claim 14.
- 5 28. An article of manufacture made by the process of claim 17.
29. An article of manufacture comprising a foamed material chosen from the group consisting of metal, metal alloys, polymeric material, glass, glass-ceramic, metallic
10 glass, wax and concrete in which bubbles formed are enclosed in air-tight encapsulation by the material foamed and in which the pressure within the encapsulated bubbles is less than atmospheric.
30. An article of manufacture comprising (1) a foamed
15 polymeric material in which the bubbles formed are enclosed by the material foamed and in which the pressure within the enclosed bubbles is less than atmospheric and (2) an air-tight covering, chosen from the group consisting of metal, metal alloys, polymeric material, glass, glass-ceramic,
20 metallic glass, and wax, encapsulating said foamed material.
31. An article of manufacture comprising a multiplicity of chambers said chambers enclosed in air-tight encapsulation by the material forming the chamber
25 walls wherein said material forming said chamber walls is of sufficient strength to maintain the integrity of the

structure of said chambers and wherein the pressure within at least some of said chambers is less than atmospheric.

32. An article of manufacture of claim 29 wherein said material forming the chamber walls is chosen from the
5 group consisting of metal, metal alloys, polymeric material, glass, glass-ceramic, metallic glass, and wax.

34. An article of manufacture comprising (1) a multiplicity of chambers said chambers enclosed by a material forming the chamber walls wherein said material
10 forming said chamber walls is of sufficient strength to maintain the integrity of the structure of said chambers and wherein the pressure within at least some of said chambers is less than atmospheric and (2) an air-tight covering enclosing said multiplicity of chambers.

15 32. An article of manufacture of claim 31 wherein said material forming the chamber walls and said air-tight covering are chosen from the group consisting of metal, metal alloys, polymeric material, glass, glass-ceramic, metallic glass, and wax.

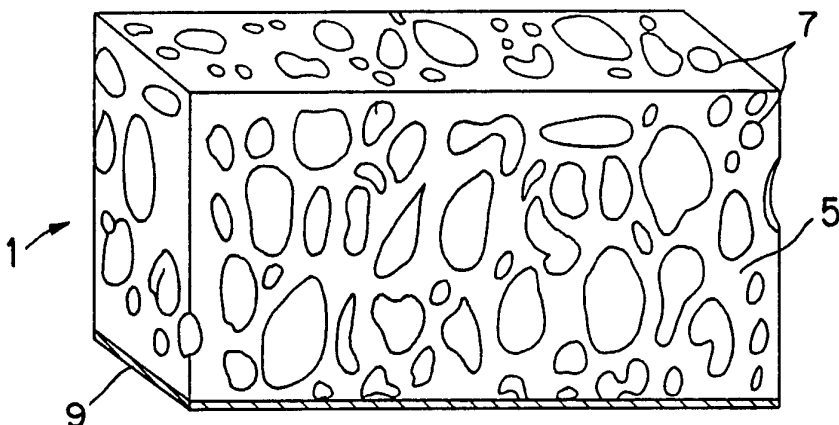


FIG. 1

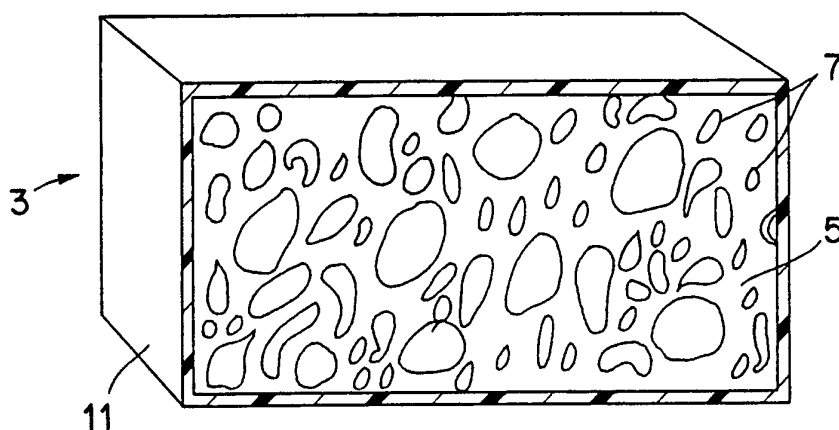


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00105

A. CLASSIFICATION OF SUBJECT MATTER IPC(5) :B32B 3/26, 5/18; C03B 19/08; B29C 65/00, 67/20; B01F 13/06 US CL :Please See Extra Sheet. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 428/312.4, 312.6, 312.8, 314.4, 319.1, 319.3, 613; 264/41, 42, 321, 344; 366/3, 139; 65/22 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,024,309 (PENDER) 17 MAY 1977. See entire document.	1-32, 34
X	US, A, 4,079,162 (METZGER) 14 MARCH 1978. See entire document.	1-32, 34
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
A	document defining the general state of the art which is not considered to be part of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E	earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 28 FEBRUARY 1994		Date of mailing of the international search report 24 MAR 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer <i>Renew Weaver for</i> BLAINE R. COPENHEAVER Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00105

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

428/312.4, 312.6, 312.8, 314.4, 319.1, 319.3, 613; 264/41, 42, 321, 344; 366/3, 139; 65/22