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(54) METHOD OF FORMING A MASTER AND A MOLD BY PROMOTING THE SOLUBILITY OF A POLYMERIC MATERIAL

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(57) **ABSTRACT**

This invention involves a method of promoting solubility of a polymeric material of a master for separating the master from a mold in contact therewith to form a desired geometry on the mold. The method comprises providing a mixture of a non-polymeric organic material and polymeric material, and providing a molten material and a supercritical fluid. The non-polymeric organic material represents about 25% to 75% of the weight of the master. The polymeric material represents the balance of the weight of the master. The method further includes forming a master from the mixture. It has a predetermined shape on a contact surface thereof. The method further includes forming a mold in contact with the contact surface of the master, wherein the master and mold have relative mating surfaces to form the desired geometry on the mold. The method further includes separating the master from the mold by exposing the master to the supercritical fluid.

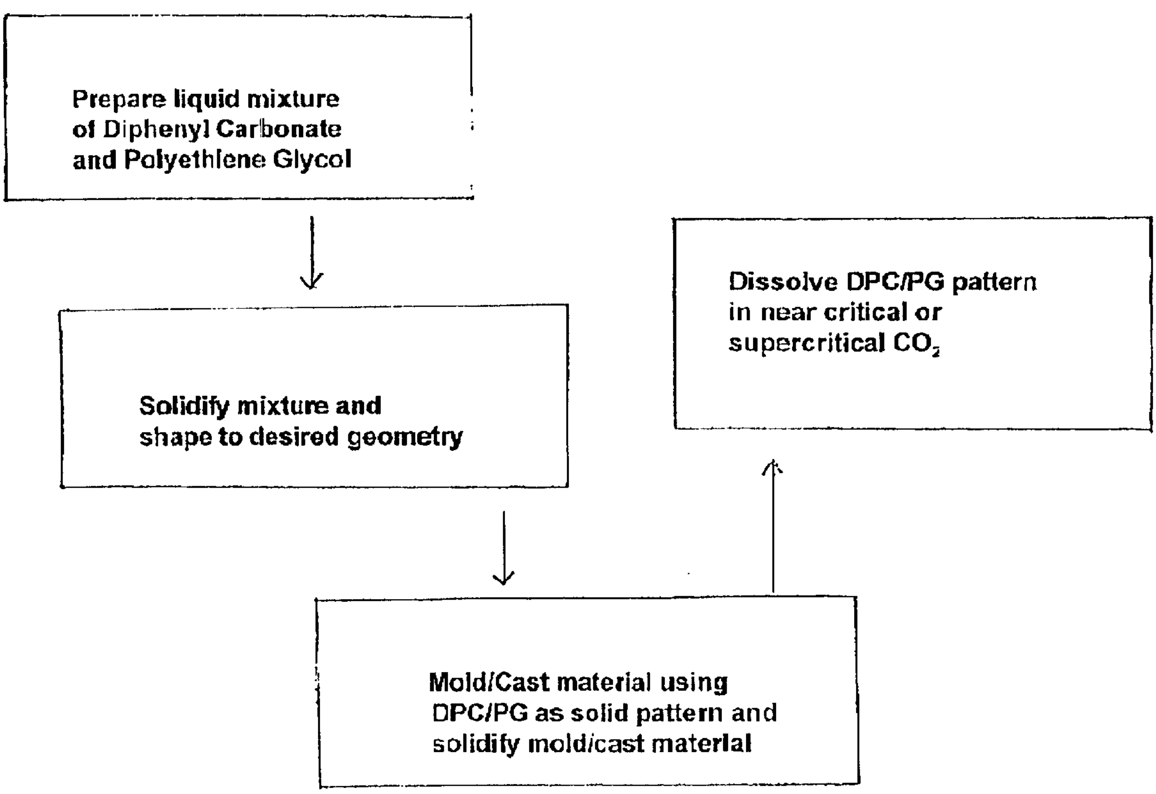


FIGURE 1

FIGURE 2

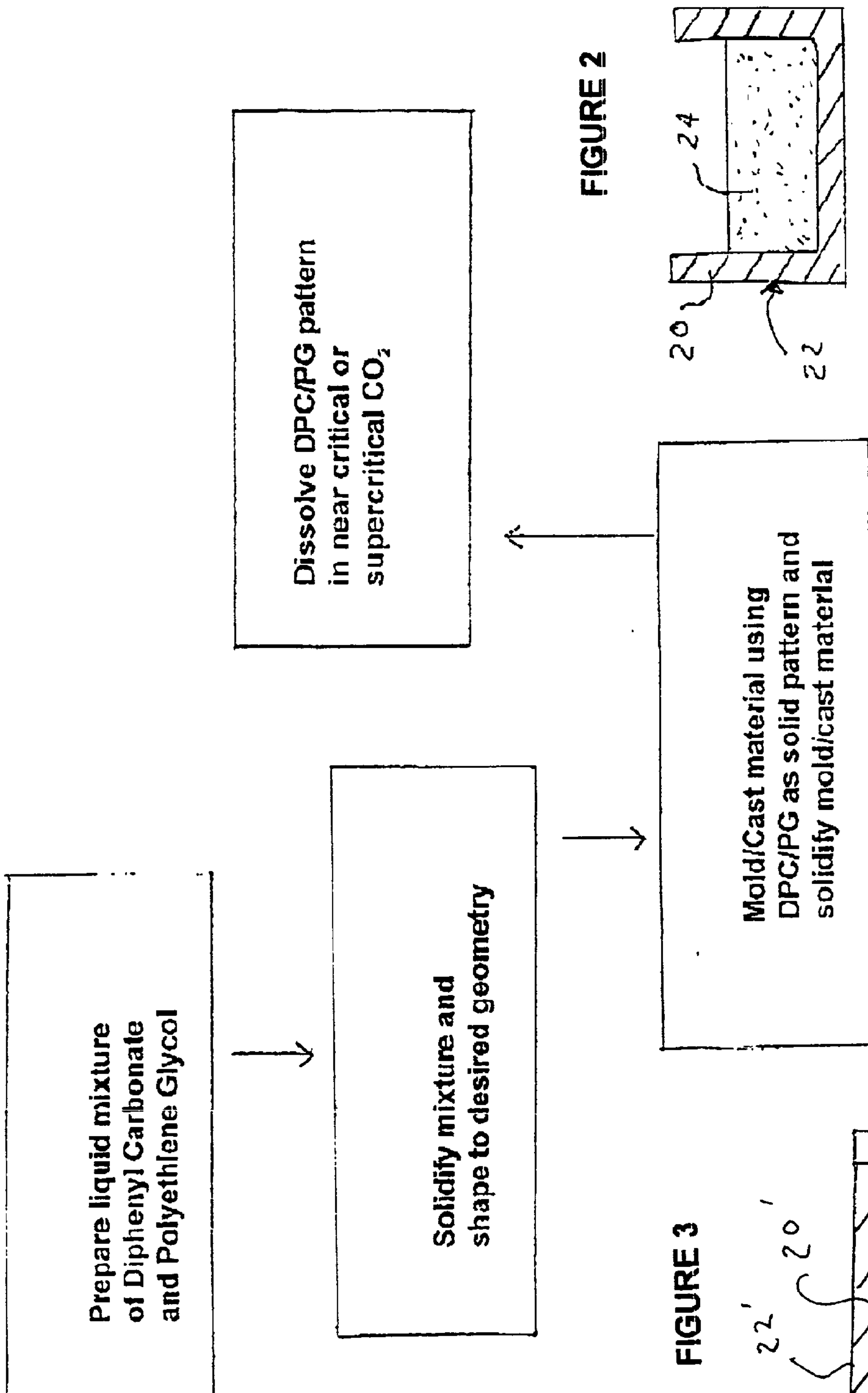


FIGURE 3

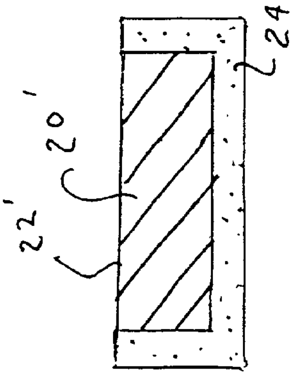


FIGURE 4

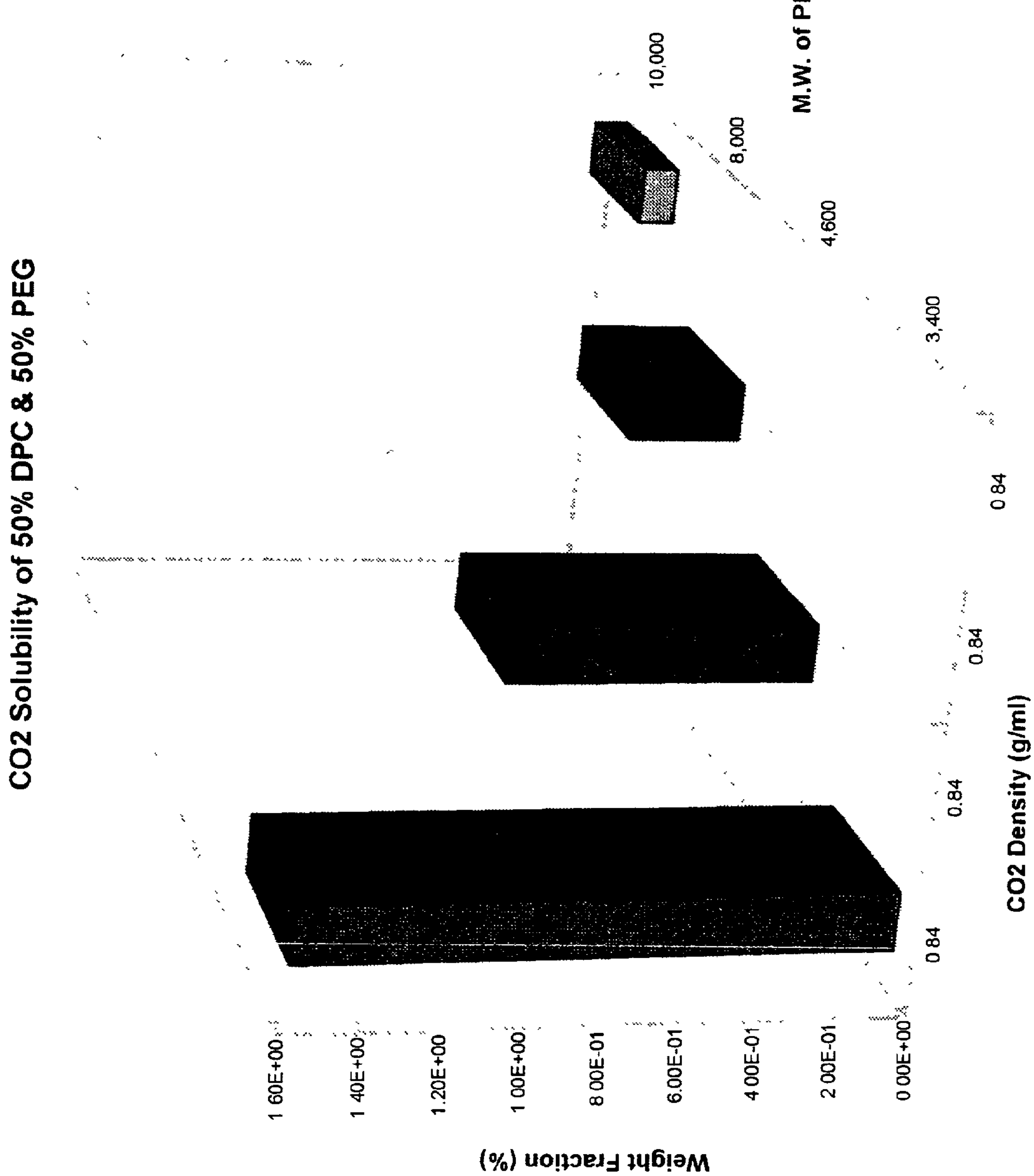

CO2 Solubility of 50% DPC & 50% PEG
Weight Fraction (%)
1 60E+00
1 40E+00
1.20E+00
1 00E+00
8 00E-01
6.00E-01
4 00E-01
2 00E-01
0 00E+00
0 84
0.84
0.84
0 84
CO2 Density (g/ml)
3,400
4,600
8,000
10,000
M.W. of PEG

FIGURE 5

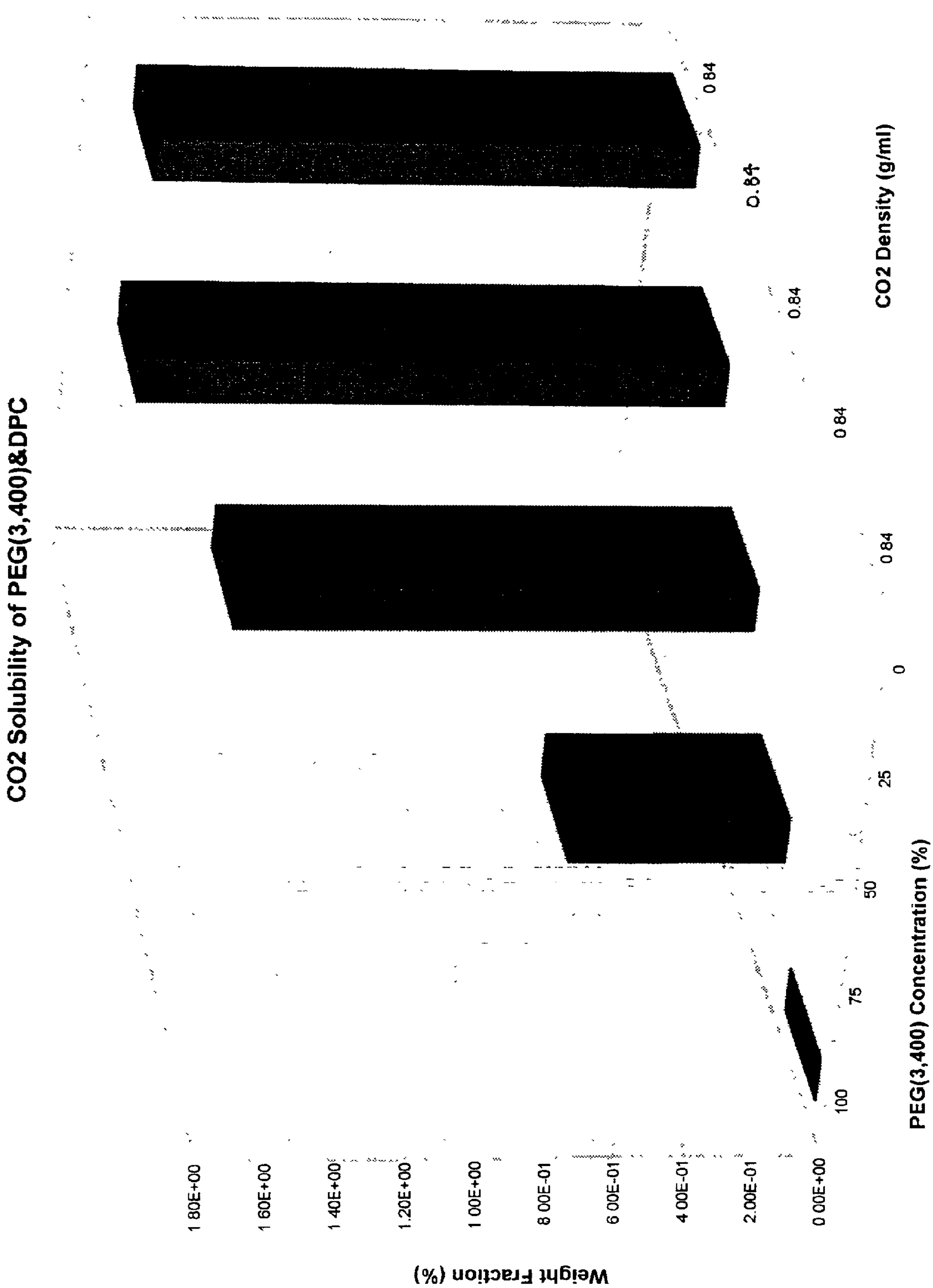

CO2 Solubility of PEG(3,400)&DPC
Weight Fraction (%)
1 80E+00
1 60E+00
1 40E+00
1.20E+00
1 00E+00
8 00E-01
6 00E-01
4 00E-01
2.00E-01
0 00E+00
PEG(3,400) Concentration (%)
100
75
50
25
0
CO2 Density (g/ml)
0.84
0 84
0 84
0.84
0 84

FIGURE 6

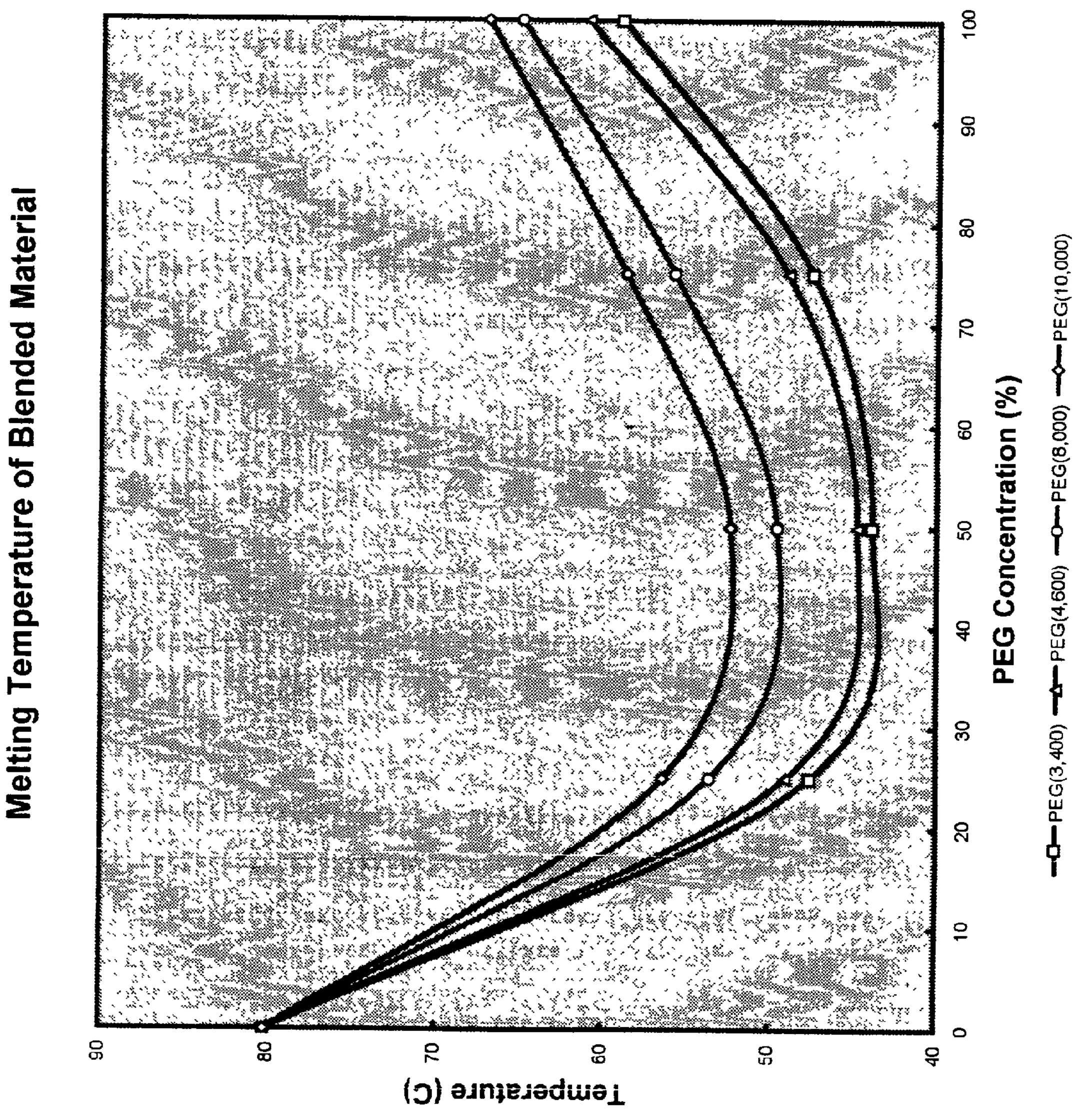
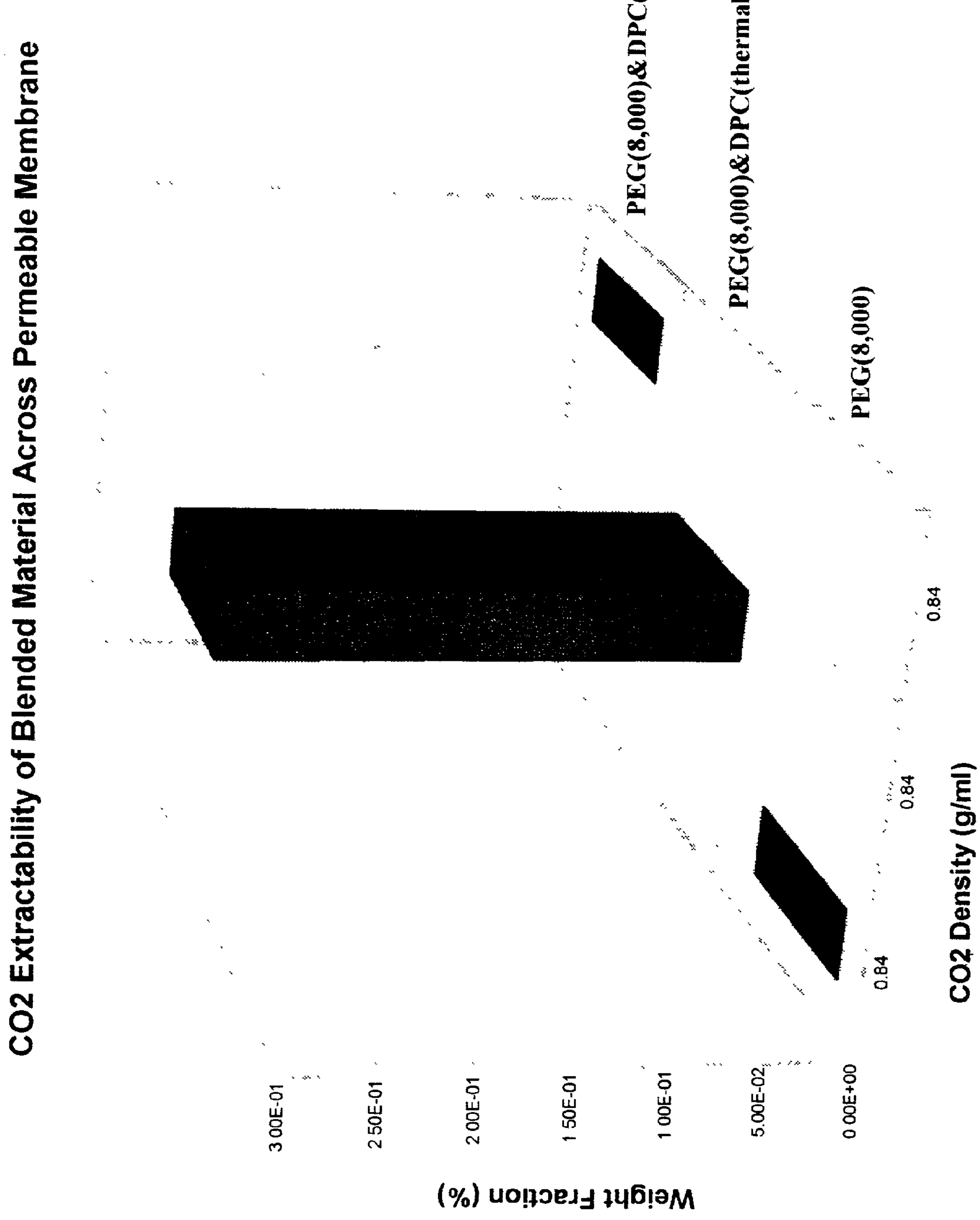

Melting Temperature of Blended Material
Temperature (C)
90
80
70
60
50
40
0
10
20
30
40
50
60
70
80
90
100
PEG Concentration (%)
PEG(3,400)
PEG(4,600)
PEG(8,000)
PEG(10,000)

FIGURE 7


CO2 Extractability of Blended Material Across Permeable Membrane
Weight Fraction (%)
3 00E-01
2 50E-01
2 00E-01
1 50E-01
1 00E-01
5.00E-02
0 00E+00
0.84
0.84
0.84
CO2 Density (g/ml)
PEG(8,000)&DPC(without blending)
PEG(8,000)&DPC(thermally blended)
PEG(8,000)

METHOD OF FORMING A MASTER AND A MOLD BY PROMOTING THE SOLUBILITY OF A POLYMERIC MATERIAL

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a division of a U.S. application Ser. No. 09/246,741, filed Feb. 8, 1999.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates generally to materials used as masters or templates in molding/casting processes to form cavities in the mold. More specifically, the present invention relates to such materials which are removed from the mold through the use of near critical and supercritical solvents.

[0004] 2. Background Art

[0005] In a number of molding/casting applications a cavity or void must be created in the cast article. In one such process known as the "lost wax" method, a three dimensional body (master) made from wax or the like is used to form a cavity in a mold. Upon application of heat, the wax body is liquefied to extract it from the mold. In addition to wax, a number of synthetic polymeric materials have been used to form three dimensional templates (masters) in similar thermal extraction methods. In many instances, however, it may be undesirable to apply heat sufficient to melt the master. In addition, many prior art materials leave an undesirable residue on the surface of the mold after thermal extraction. This residue must typically be removed by combustion or the like, requiring an additional step.

[0006] In a similar process, the master is formed of a material which can be extracted from the mold through the use of a solvent or the like. Again, the master is used to form a cavity or insert in the mold. The mold with the master still in place is contacted with an appropriate liquid solvent, often an organic solvent. The solvent dissolves the master. As will be appreciated by those skilled in the art, however, the use of organic solvents may be undesirable from an environmental standpoint.

[0007] In still another approach, the solvent which is used to remove the master template is a supercritical or near supercritical fluid. For example in copending U.S. patent application Ser. No. 09/047,187, filed on Mar. 6, 1998, and entitled "METHOD OF MAKING A MOLD FOR METAL CASTINGS", the entire disclosure of which is incorporated herein by reference, materials are disclosed which are used to form molding/casting patterns that are easily removed with carbon dioxide, in one embodiment as supercritical CO_2.

[0008] In U.S. Pat. No. 5,409,650, entitled "MOLDING FINELY DIVIDED SINTERABLE MATERIAL" there is disclosed a method of forming a molded product by preparing a dispersion of a sinterable powder and a binder. The preferred binder which is employed contains polystyrene, which forms the predominant weight proportion of the binder and, in a lower proportion, an organic compound. Diphenyl carbonate is stated therein to be an acceptable organic compound. After the part is formed, the diphenyl carbonate is removed either by vaporization at low temperature or by solvent dissolution. The polystyrene part of the binder is then removed by heat at high temperatures. Once the binder is removed the part is solidified by sintering.

[0009] It is an object of the present invention to provide industrial grade materials suitable for use in forming extractable masters, templates or temporary casting patterns in molding/casting processes. It is a further object of the invention to provide a single-step extraction process using such materials.

[0010] It is a further objective of the invention that the template/casting-pattern materials be extractable into a near critical or supercritical fluid.

SUMMARY OF THE INVENTION

[0011] In one aspect the present invention provides a material for use in molding/casting. A solid body, to serve as a master for making a mold, formed of a homogeneous mixture of a non-polymeric organic material and a polymeric material is provided in a desired shape. The non-polymeric material serves as a solubilizer for the polymeric material in solid "solution". In the process of use, a second body (a mold) is then formed in contact with this master by molding or casting. That is, the first body (master) is used as a template on which the molding/casting material is applied. Accordingly, the second body (mold) takes on a shape which is defined by or corresponds to the contact surface of the master (first body). The master is then removed through the use of an agent which in essence dissolves or disperses the master.

[0012] In another aspect, the master is formed by liquefying the non-polymeric organic material and the polymeric material and then solidifying the resultant liquid mixture (which itself may be formed to the desired shape). In one aspect the non-polymeric organic material is, diphenyl carbonate and the polymeric material is polyethylene glycol.

[0013] In one aspect the master is dissolved through the use of a near supercritical or supercritical fluid. It has been found that near supercritical or supercritical carbon dioxide is a preferred solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1** is a flow chart illustrating the steps of the present invention.

[0015] **FIG. 2** is a cross-section of a cast article and template in accordance with the present invention.

[0016] **FIG. 3** is a cross-section of a part being formed in accordance with another embodiment of the invention.

[0017] **FIG. 4** illustrates CO_2 solubility of a 50% DPC and 50% PEG blend template.

[0018] **FIG. 5** illustrates CO_2 solubility of PEG (3,400) and DPC.

[0019] **FIG. 6** illustrates melting temperatures of the blended material based on PEG concentration and molecular weight.

[0020] **FIG. 7** illustrates CO_2 solubility of blended material with thermal vs. mechanical blending.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The composition of the present invention comprises a mixture of a non-polymeric organic compound and a polymeric material. The non-polymeric material acts as a solubilizer for the polymer in both solid and liquid phases of the mixture. When the organic-polymer mixture is contacted by a supercritical fluid, the organic compound acts as a co-solvent to promote dissolution of the polymeric material. By "non-polymeric" it is meant that the molecule does not comprise a series of repeating chemical structures commonly referred to as mers.

[0022] The non-polymeric organic compound preferably has a molecular weight of less than about 400 (most preferably between about 50 and 250) and in the solid state can be dissolved in supercritical or near supercritical fluid. The most preferred non-polymeric organic compound is diphenyl carbonate. Additional preferred non-polymeric organic compounds are naphthalene, benzophenone and combinations thereof.

[0023] The preferred polymer has a weight average molecular weight of between about 1,000 and about 20,000. Most preferably, the polymer molecular weight is less than its entanglement weight. The most preferred polymeric material is polyethylene glycol having a weight average molecular weight of between about 2,000 and about 20,000. Another preferred polymeric material for use in the present invention is low molecular weight polystyrene (molecular weight of about 1,000 to about 5,000). Additional preferred polymeric materials (within the same molecular weight range) are polymethyl methacrylate and combinations thereof, including copolymers.

[0024] Generally, diphenyl carbonate and/or naphthalene comprises from about 25 to about 75 weight percent of the two-part composition and polyethylene glycol and/or polystyrene comprises from about 25 to about 75 weight percent of the combination. Most preferably, diphenyl carbonate and the polyethylene glycol are present in a ratio of about one-to-one by weight (all percentages herein are by weight percent unless otherwise indicated).

[0025] Referring now to **FIG. 1** of the drawings, the overall sequence of preferred steps in the present invention is illustrated. In step one, a liquid mixture of a non-polymeric organic compound and polymeric material is prepared (diphenyl carbonate and polyethylene glycol.

[0026] The non-polymeric organic compound and the polymer which are combined to form the master generally have melting points of between about 50° C. and about 250° C. and are thermally blended. That is, the materials may be individually liquefied with heat and then combined or combined as powders or the like and subsequently heated to form the liquid mixture. In liquid admixture they form a homogeneous fluid.

[0027] In step two, the liquid master is cooled to form a solid body (master). The master is a homogeneous solid solution. In one preferred embodiment, the mixture is poured into a mold, such as a shell mold, having the desired geometry **13** and is then solidified in the mold. Alternatively, a near-net shape or the like is formed by solidifying the liquid and the final geometry is formed by machining the master or through a similar technique. The specific shape will of course vary widely depending upon the application. Moreover, it will be understood that the shape of the template will be three dimensional and will define the desired shape of the article to be molded/cast.

[0028] In step three, as illustrated in **FIG. 2** of the drawings, the solid solution **20** of diphenyl carbonate and polyethylene glycol is used essentially as a mold **22**. The mold **22** is preferably formed of suitable sand and a suitable binder material. That is, the material **20** which will shape the final molded/cast article **24** is placed in contact with the master formed in the previous step. In one embodiment the template is simply used to cast the mold material and thus defines a cavity into which the mold material is poured. In other applications the template may be an insert which forms a cavity in a mold or may be augmented by traditional mold parts and surfaces. Numerous materials such as metals, polymers, cellulose, ceramics and the like can be formed by molding and solidifying in accordance with the present invention.

[0029] In another embodiment, and referring now to **FIG. 3** of the drawings, the solid solution **20'** of diphenyl carbonate and polyethylene glycol is used essentially as a mold body **22'** or insert. After article **24'** is formed, the master **22'** is removed as described below.

[0030] In the final step (**FIG. 1**), the master (serving as the mold) is separated from the solidified molded/ cast article. This is carried out in the preferred embodiment by exposing the template to a near critical or supercritical fluid. The fluid is preferably comprised principally of CO_2 which acts as a solvent for the template, causing the template to dissolve or disperse. In some applications it may be suitable to use CO_2 as a true liquid or gas to remove the template. If liquid CO_2 is used, the temperatures employed during the process are preferably below 31 degrees C. If gaseous CO_2 is used, it is preferred that the phase be employed at high pressure. As used herein, the term "high pressure" generally refers to CO_2 having a pressure from about 50 to about 300 bar. Again, in the most preferred embodiment, CO_2 is used in a supercritical phase. As used herein "supercritical" means that a fluid medium is at a temperature that is sufficiently high that it cannot be liquefied by pressure. The thermodynamic properties of CO_2 are described in Hyat, J. Org. Chem. 49:5097-5101 (1984) which is incorporated herein by reference. In the preferred embodiment, the CO_2 employed may contain components other than CO_2 such as aqueous and organic liquid co-solvents the identity of which can be ascertained based on the teachings herein. Other supercritical fluids which may be useful in the present invention are ethane, ethylene, propane and butane, and refrigerants R152a and R134a.

[0031] The following examples are provided to more fully illustrate the present invention and in no manner are to be construed as limiting the full scope of the invention.

EXAMPLES

[0032] **FIG. 4** of the drawings illustrates the decrease in CO_2 solubility of the blend as the molecular weight of the polymer component increases.

[0033] **FIG. 5** illustrates changes in CO_2 solubility as a function of PEG concentration.

[0034] **FIG. 6** illustrates the melting temperature of the blended material as a function of PEG concentration and molecular weight. **FIG. 7** of the drawings illustrates the CO_2 extractability of the thermally blended materials across a permeable membrane compared with a mechanical blend and with PEG alone.

[**0035**] While particular embodiments of this invention are shown and described herein, it will be understood, of course, that the invention is not to be limited thereto since many modifications may be made, particularly by those skilled in this art, in light of this disclosure. It is contemplated, therefore, by the appended claims, to cover any such modifications as fall within the true spirit and scope of this invention.

What is claimed is:

21. (New) A method of promoting solubility of a polymeric material of a master for separating the master from a mold in contact therewith to form a desired geometry on the mold, the method comprising:

providing a mixture of a non-polymeric organic material and the polymeric material for forming the master, the non-polymeric organic material having a weight percent of from about 25% to about 75% of the weight of the master, the polymeric material having a weight percent of from about 75% to about 25% of the weight of the master;

providing a mold material for forming the mold in the desired geometry;

providing a supercritical fluid;

forming a master comprising the mixture and having a predetermined shape on a contact surface of the master;

forming a mold solid body in contact with the contact surface of the master, the master and mold having relative mating surfaces to form the desired geometry on the mold, the desired geometry of the mold complementing the predetermined shape of the master; and

separating the master from the mold by exposing the master to the supercritical fluid.

22. (New) The method of claim **21** wherein the mixture is a homogeneous liquid mixture of the non-polymeric organic compound and the polymeric material is thermally blended to have a melting point of between about 50 to about 250 degrees Celsius.

23. (New) The method of claim **22** wherein forming the master includes:

pouring the homogeneous liquid mixture into a mold cavity having the desired geometry; and

cooling the homogeneous liquid mixture in the mold cavity to solidify the mixture to define a solidified mixture having the predetermined shaped on the contact surface.

24. (New) The method of claim **22** wherein forming the master includes:

solidifying the homogeneous liquid mixture to define a solidified mixture; and

configuring the solidified mixture so that the solidified mixture has the predetermined shape on the contact surface of the master.

25. (New) The method of claim **21** wherein forming the mold includes:

juxtaposing the mold material with the contact surface of the master; and

solidifying the mold material in contact with the contact surface to define the mold having the desired geometry.

26. (New) The method of claim **21** wherein the non-polymeric organic compound is selected from the group consisting of diphenyl carbonate, naphthalene, benzophenone and combinations thereof.

27. (New) The method of claim **21** wherein the polymeric material is selected from the group consisting of polyethylene glycol, polystyrene, polymethyl methacrylate, and copolymers and combinations thereof.

28. (New) The method of claim **21** wherein the supercritical fluid includes carbon dioxide.

29. The method of claim **21** wherein separating the master from the mold includes substantially dissolving the master from the cast by exposing the master to the supercritical fluid.

30. (New) The method of claim **21** wherein the supercritical fluid includes liquid carbon dioxide at a temperature of about 31 degrees Celsius.

31. (New) The method of claim **21** wherein the supercritical fluid includes gaseous carbon dioxide at a pressure of between about 50 to about 300 bar.

32. (New) The method of claim **21** wherein the mold is formed of sand and a binder material to define a sand-binder material.

33. (New) A method of separating an extractable master from a mold in contact therewith for forming a desired geometry on the mold, the method comprising:

providing a mixture of a non-polymeric organic material and a polymeric material, the non-polymeric organic material being diphenyl carbonate, the polymeric material being polyethylene glycol, the diphenyl carbonate comprising in weight percent from about 25% to about 75% of the weight of the master, the polyethylene glycol comprising in weight from about 25% to about 75% of the weight of the master;

providing carbon dioxide under supercritical conditions;

providing a sand-binder material for forming the mold in the desired geometry;

solidifying the mixture to form an extractable master having a predetermined shape on a contact surface of the master;

contacting the mold material on the contact surface of the master and solidifying the sand-binder material thereon to form a mold, the contact surface of the master and mold having relative mating surfaces to define the desired geometry on the mold, the desired geometry of the mold complementing the predetermined shape of the master; and

substantially dissolving the master from the mold by exposing the master to the carbon dioxide.

34. (New) The method of claim **33** wherein the mixture is a homogeneous liquid mixture of the non-polymeric organic compound and the polymeric material blended to have a melting point of between about 50 to 250 degrees Celsius.

35. (New) The method of claim **34** wherein solidifying the mixture includes:

pouring the homogeneous liquid mixture into a mold cavity having the desired geometry; and

cooling the homogeneous liquid mixture on the mold cavity to solidify the mixture to define a solidified mixture having the predetermined shaped on the contact surface.

36. (New) The method of claim **33** wherein solidifying the mixture includes:

solidifying the homogeneous liquid mixture to define a solidified mixture; and

configuring the solidified mixture so that the solidified mixture has the predetermined shaped on the contact surface of the master.

37. (New) The method of claim **33** wherein the non-polymeric organic compound is selected from the group consisting of diphenyl carbonate, naphthalene, benzophenone and combinations thereof.

38. (New) The method of claim **33** wherein the polymeric material is selected from the group consisting of polyethylene glycol, polystyrene, polymethyl methacrylate, and copolymers and combinations thereof.

39. (New) A method of forming a mold by promoting the solubility of a polymeric material of a master for separating the master from a mold in contact therewith to form a desired geometry on the mold, the method comprising:

providing a heated homogeneous fluid of a non-polymeric organic material and the polymeric material, the non-polymeric organic material being diphenyl carbonate and the polymeric material being polyethylene glycol, the diphenyl carbonate comprising in weight percent from about 25% to about 75% of the weight of the master and the polyethylene glycol comprising in weight from about 25% to about 75% of the weight of the master;

providing carbon dioxide at a pressure of between about 50 to 300 bar or at a temperature of below about 31 degree Celsius;

providing a sand-binder material for forming the mold in the desired geometry;

cooling the heated homogeneous fluid to form the master, the master being a homogeneous solid and having a predetermined shape on a contact surface thereof, the master including the non-polymeric organic material and the polymeric material;

contacting the sand-binder material on the contact surface of the master and cooling the sand-binder material for solidification thereof to define the mold in contact with the master, the master and mold having relative mating surfaces to form the desired geometry on the mold, the desired geometry on the cast complementing the predetermined shape of the master; and

substantially dissolving the master from the mold by exposing the master to the carbon dioxide, the mold sufficiently retaining the desired geometry form thereon.

* * * * *