(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 July 2010 (01.07.2010)

PCT

(10) International Publication Number
WO 2010/074873 A2

(51) International Patent Classification:
C03B 5/00 (2006.01) *C03C 3/062* (2006.01) *C03C 3/064* (2006.01) *C03C 3/12* (2006.01) *C03C 3/19* (2006.01)

(21) International Application Number: PCT/US2009/065647

(22) International Filing Date: 24 November 2009 (24.11.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/140,333 23 December 2008 (23.12.2008) US

(71) Applicant *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LENIUS, Steven J.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **ROSENFLANZ, Anatoly Z.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **BARNES, Amy S.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) Agents: **PASTIRIK, Daniel R.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

(54) Title: MOLDABLE ARTICLES, METHOD OF MAKING SAME AND METHOD OF MOLDING

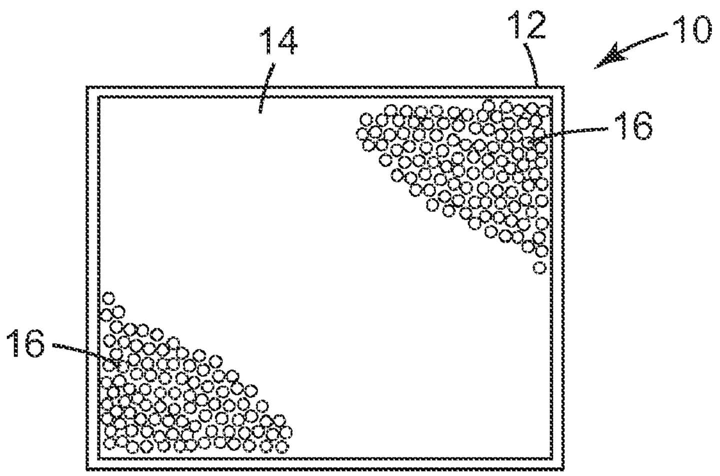

Fig. 1

(57) Abstract: A moldable article, including at least a container made of a barrier material, the container providing an interior space within which a plurality of glass particles are contained. The glass has a glass transition temperature and a crystallization onset temperature, the difference between the glass transition temperature and the crystallization onset temperature is at least about 5°K, and the glass is composed of at least two metal oxides, from 0 to less than 20% by weight SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5. The moldable article protects the glass particles by keeping them clean and moisture free prior to a molding operation. A method of making a moldable article includes: removing entrapped moisture from a plurality of glass particles, placing glass particles in a receptacle, and sealing the receptacle to form the article. The moldable article may be placed in a mold and, during the molding process, the barrier material essentially burns off while the glass particles coalesce into a molded article.

WO 2010/074873 A2

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

MOLDABLE ARTICLES, METHOD OF MAKING SAME AND METHOD OF MOLDING

The present invention relates to moldable articles for the molding of glass particles, to methods of preparing the moldable articles and to methods of molding the moldable articles.

Background

Glass compositions have been used to provide large articles and/or complex shapes. Such articles are often made by coalescing particles of glass. Recently, such articles and complex shapes have been made using microparticles of non-traditional glass materials.

The manufacture of molded glass articles is accomplished in a molding process in which glass particles are heated above the glass transition temperature of the material. The melting particles coalesce and, upon cooling, assume a solidified shape to form the article. The molding process typically involves the application of pressure on the melting particles to aid in shaping the molten glass into the form dictated by the particular mold design.

In the utilization of molding techniques to make glass articles, small glass particles (e.g., microparticles) are known to collect moisture and/or static charge. This is especially true in the manufacture of articles from microparticles of non-traditional glass materials. As a result, glass particles are difficult to handle during the molding process.

Summary

The present invention addresses problems encountered in the molding of glass materials. In one aspect, the invention provides a moldable article, comprising:

A first container comprising a first barrier, the first barrier comprised of a first material, and an interior space within the first barrier;

A plurality of first glass particles contained within the interior space and comprising a first glass, the plurality of first glass particles being moldable at a first molding temperature, the first glass having a first glass transition temperature and a first crystallization onset temperature, the difference between the first glass transition temperature and the first crystallization onset temperature being at least about 5°K, the first glass having a composition comprising at least two metal oxides, from 0 to less than 20% by weight SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5; and

Wherein, the first material has a first decomposition temperature less than the first molding temperature.

In some embodiments, the interior space of the foregoing article is divided into multiple spaces, including a first interior space and a second interior space with the plurality of first glass particles contained within the first interior space and a plurality of second glass particles contained within the second interior space, the second glass particles comprising a second glass having a composition different than the composition of the first glass.

In other embodiments, the moldable article further comprises:

A second container comprising a second barrier, the second barrier comprised of a second material, and a second interior space within the second barrier, the second container being wholly within the interior space of the first container; and

A plurality of second glass particles contained within the second interior space so that the plurality of second glass particles and the plurality of first glass particles are separated from one another, the plurality of second glass particles comprising a second glass, the plurality of second glass particles being moldable at a second molding temperature.

In another aspect, the invention provides a method of making a moldable article, the method comprising:

Placing a plurality of first glass particles in a first receptacle, the plurality of first glass particles being moldable at a first molding temperature, the first glass having a first glass transition temperature and a first crystallization onset temperature, the difference between the first glass transition temperature and the first crystallization onset temperature being at least about 5°K, the first glass having a composition comprising at least two metal oxides;

Removing entrapped moisture from the first glass particles; and

Sealing the first receptacle to form a first container comprising a first barrier, the first barrier defining an interior space, the plurality of first microparticles occupying at least a portion of the interior space, wherein the interior space is substantially free of water, and wherein the first barrier comprises a first material having a first decomposition temperature lower than the first molding temperature.

In some embodiments of the foregoing method, the method further comprises:

Placing a plurality of second glass particles in a second receptacle, the plurality of second glass particles comprising a second glass that is moldable at a second molding temperature;

Removing entrapped moisture from the second glass particles; and

Sealing the second receptacle to form a second container comprising a second barrier, the second barrier defining a second interior space, the plurality of second glass particles occupying at least a portion of the second interior space, wherein the second barrier comprises a second material having a second decomposition temperature lower than the second molding temperature; and

Placing the second container within the first receptacle prior to the step of sealing the first receptacle.

In still other embodiments of the foregoing method, the first receptacle comprises a plurality of chambers, and the step of placing the plurality of first glass particles in the first receptacle comprises placing the particles in a first chamber; the method further comprising placing a second plurality of glass particles in a second chamber, wherein the step of sealing the first receptacle forms the first container so that the interior space forms a plurality of sealed chambers with the first plurality of glass particles sealed within a first interior space and the second plurality of glass particles sealed within a second interior space.

In still another aspect, the invention provides a method for molding an article, comprising:

Placing one or more of the foregoing moldable articles in a mold cavity; and

Heating the mold cavity to decompose the first material and coalesce the glass particles to provide a molded article.

In general, terms used in the description of the embodiments of the present invention shall be understood as having the common meaning given to them, as understood by the person of ordinary skill in the art. However, certain terms shall have the meaning set forth herein.

"Amorphous material" refers to material derived from a melt and/or a vapor phase that lacks any long range crystal structure as determined by X-ray diffraction and/or has an exothermic peak corresponding to the crystallization of the amorphous material as determined by a Differential Thermal Analysis.

"Ceramic" includes amorphous material, glass, crystalline ceramic, glass-ceramic, and combinations thereof.

"Glass" refers to amorphous material exhibiting a glass transition temperature.

"Glass-ceramic" refers to ceramic comprising crystals formed by heat-treating amorphous material.

"Inert gas" refers to helium, neon, krypton, argon, xenon, nitrogen and combinations of two or more of the foregoing.

The various features of the disclosed embodiments will be further understood by those skilled in the art upon consideration of the remainder of the disclosure, including the Detailed Description, the non-limiting Examples and the appended Claims.

Brief Description of the Figures

In describing the embodiments of the invention, reference is made to the various Figures. It will be appreciated that the Figures are not to scale but are provided as an aid in describing the embodiments. The various features of the embodiments are identified with reference numerals wherein like numerals generally indicate like features, and wherein:

Figure 1 is a plan view of a moldable article according to an embodiment of the invention;

Figure 2 is a side view of the moldable article of Figure 1;

Figure 3 is a schematic representation of a process for the manufacture of the moldable article of Figure 1 and also illustrating the subsequent molding thereof;

Figure 4 is a plan view of a moldable article according to another embodiment of the invention;

Figure 5 is a schematic representation of a process for the manufacture of the moldable article of Figure 4 and also illustrating the subsequent molding thereof;

Figure 6 is a plan view of a moldable article according to another embodiment of the invention;

Figure 7 is a perspective view of a moldable article according to still another embodiment of the invention;

Figure 8 is a perspective view of a molded article according to still another embodiment of the invention;

Figure 9 is a perspective of a molded article according to still another embodiment of the invention;

Figure 10 is a perspective of a molded article according to still another embodiment of the invention; and

Figure 11 is a perspective of a molded article according to still another embodiment of the invention.

Detailed Description

The invention provides for the handling of glass, including non-traditional glass, wherein the glass is initially in the form of particles (spherical particles, fibers, microspheres, etc..). The embodiments of the invention provide moldable articles comprising glass particles, processes for the preparation of moldable articles and processes for molding. In the various embodiments, moldable articles are provided in the form of a sealed container or package containing glass particles in a moisture-free, controlled and/or treated atmosphere. The moldable articles described herein may be inserted directly into a mold cavity. A molding operation is performed by the application of heat/pressure to the moldable article without removing the glass particles from the package. The molding process is carried out at temperatures above the decomposition temperature of the packaging material so that the packaging essentially burns off during the molding operation. The glass typically has a molding temperature (e.g., a temperature at which the glass particles begin to coalesce) significantly higher than the decomposition temperature of the packaging material. At or above the molding temperature for the glass, the glass particles coalesce and, upon cooling, provide a molded article.

Referring now to the Figures, Figures 1 and 2 provide different views of a moldable article 10 according to an embodiment of the invention. The moldable article 10 is provided in the form of a first package having a first barrier 12 defining a first interior space 14 containing a predetermined amount (e.g., a plurality) of glass particles 16. The first barrier 12 is sealed, and the first interior space typically has an atmosphere different than the atmosphere surrounding the article 10. In some embodiments, the first interior space 14 has an atmosphere substantially free of water vapor. In some embodiments, the first interior space 14 has an atmosphere of inert gas. In other embodiments, the atmosphere in first interior space 14 is at least partially evacuated to a reduced pressure (e.g., vacuum or near vacuum).

First barrier 12 is made of a flexible first material that is substantially gas impermeable in order to maintain a substantially constant atmosphere within the first interior space 14. While the article 10 remains sealed, glass particles 16 and first interior space 14 remain substantially dry or water-free.

Suitable flexible first materials include paper as well as various flexible polymer materials. As used herein, the term “flexible” refers to a property, and materials having such a property typically lack rigidity or stiffness under ambient conditions. In other embodiments, first barrier may be made of a more rigid first material. As used herein, the term “rigid” refers to a property, and a material having such a property tends to maintain a given shape at ambient temperatures in the absence of excess heat or external forces exerted on the material. However, a rigid material need not be entirely inflexible and, in fact, some rigid materials may be bent or otherwise deformed when heated, handled or the like. It will be appreciated that the differences between a rigid material and a flexible material may be accounted for, in some instances, by the use of different materials or by variations in the thickness of the same or similar material (e.g., increasing the thickness of a material can provide rigidity).

Polymers suitable for use as the first material include those selected from the group consisting of polyamide, poly methyl methacrylate, polyisobutylene, polycarbonate, polyethylene carbonate, polypropylene carbonate, polybutylene terephthalate, polyetheretherketone, polyethylene, polypropylene, polyphenylene oxide, polystyrene aromatic polyesters, and combinations of two or more of the foregoing. Suitable polyamides include nylon 6 and nylon 66 and combinations thereof. Suitable polyethylenes can be selected from low density polyethylene, high density polyethylene, medium density polyethylene and combinations of two or more of the foregoing. In specific embodiments, the first barrier is made with low density polyethylene. The first material has a first decomposition temperature at which the material decomposes.

Glass particles 16 occupy the first interior space 14. In embodiments of the invention, the particles 16 are microparticles comprising a first glass material that is a non-traditional glass material such as those described in patents and patent applications that include U.S. Serial Nos. 09/922,527, 09/922,528, and 09/922,530, filed August 2, 2001; U.S. 2003/0115805 A1 (Rosenflanz et al.); U.S. 2003/0110707 A1 (Rosenflanz et al.); U.S. 7,168,267 (Rosenflanz et al.); U.S. 2003/0126802 A1 (Rosenflanz); U.S. 7,147,544 (Rosenflanz et al.); and U.S. 7,101,819 (Rosenflanz et al.), the disclosures of which are incorporated herein by reference.

The aforementioned non-traditional glass materials have a first glass transition temperature and a first crystallization onset temperature. The difference between the first glass transition temperature and the first crystallization onset temperature is at least about 5°K (or even, at least 10°K, at least 15°K, at least 20°K, at least 25°K, at least 30°K, or at least 35°K). The first glass material comprises at least two metal oxides (i.e., the metal oxides do not have the same cation(s)), from 0 to less than 20% by weight SiO_2 (e.g., less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), from 0 to less than 20% by weight B_2O_3 (e.g., less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and from 0 to less than 40% by weight P_2O_5 (e.g., less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). The foregoing glass materials are moldable at or above a first molding temperature at which the microparticles begin to coalesce. In the embodiments of the invention described herein, the first decomposition temperature of the first material is lower than the first molding temperature of the first glass.

Referring to Figure 3, a process for the preparation of moldable article 10 is schematically shown along with a molding process involving the article. A measured quantity of glass particles 16 are heated within a container 20 at a heating station (not shown) such as an oven, a heating mantle or the like. The particles 16 are heated to an elevated temperature below the T_g of the glass for a sufficient time to remove water. In some embodiments, the particles are held at a temperature near the boiling point of water (e.g., 100°C). In some embodiments, a suitable temperature is in the range from about 101°C to about 150°C, from about 110°C to about 140°C, and from about 120°C to about 135°C. In some embodiments, a suitable temperature is about 130°C. The amount of time the particles are heated can depend on the volume of particles being used as well as the amount of moisture present. In various embodiments, heating for several hours is desired to ensure the particles are adequately dry, and the particles can be heated for up to about 24 hours at a temperature in one of the foregoing ranges.

Once dried, container 20 may be sealed (not shown) and the glass particles 16 are allowed to cool before being transferred from container 20 into sealable flexible container 26. Funnel 28 is shown as an optional means to facilitate the transfer of the particles 16. Following transfer of the glass particles, sealable container 26 is filled with a quantity of dried particles, and the container 26 can be sealed along its opened end 30 to provide moldable article 10 with an interior space 14 that is substantially moisture-free. In some embodiments, sealable container 26 is purged with inert gas prior to sealing. In some embodiments, the container 26 is sealed to have a reduced pressure within first interior space 14. In some embodiments, container 26 is sealed to provide a vacuum or near vacuum conditions within interior space 14.

The moldable article 10 is suitable for use in a molding process to mold the glass particles 16 into a molded article. In embodiments in which the glass particles 16 are in the form of microparticles, they may be of an average diameter measured in micrometers, and in some embodiments in the range from about 10 μm to about 250 μm. In any event, the glass particles 16 are moldable at a first molding temperature at or above about 300°C, at or above about 400°C, at or above about 500°C, at or above about 700°C or at or above about 900°C. In the molding process, moldable article 10 is placed in mold cavity 34 of mold 32. In the embodiment of Figure 3, the depicted molding process is compression molding, and cavity 34 is equipped to be heated to an elevated temperature. With moldable article 10 in the cavity 34, mold 32 is closed with a top or plug member 36 dimensioned to fit within the cavity 34 to apply pressure to the material within the mold.

The mold 32 is heated to a first molding temperature and the mold is pressurized by the compression exerted by plug member 36. In the various embodiments of the invention, the first barrier of the moldable article 10 comprises a first material (e.g., polyethylene) having a decomposition temperature lower than the first molding temperature of the glass particles so that the first material of barrier 12 decomposes during the molding process and typically before the particles 16 begin to soften and coalesce. In some embodiments, decomposition of the first barrier 12 removes substantially all of the first material of the barrier. As the temperature within mold 32 continues to rise to the first molding temperature, the glass particles begin to soften, coalesce and assume a shape that is consistent with the interior configuration of cavity 34. The mold 32 is then cooled to form the molded article 38 which may then be removed from the cavity 34.

In embodiments, the non-traditional glass particles are coalesced and are at least partially crystallized to provide a glass-ceramic article or a ceramic article. In some embodiments, the glass is heat treated to increase the crystallinity of the glass and provide glass-ceramic or ceramic material. Those skilled in the art will appreciate that the molded article 38 may comprise glass, glass-ceramic and/or ceramic material.

In embodiments of the invention, the surfaces of the molded article 38 are of optical quality without further processing. In such embodiments, the surfaces of the article 38 assume the topography imparted by the interior surfaces of the mold 32. As used herein, “optical quality” refers to the suitability of a surface or article for use in applications in the optics field.

In some embodiments, the first material may not completely decompose during the molding process, and the surfaces of the molded article 38 may be polished and/or further treated (e.g., with solvent) to remove remaining residue.

Referring to Figure 4, another embodiment of a moldable article 110 is shown. Article 110 includes first barrier 112 defining an interior space divided into a first interior space 114a and a second interior space 114b. Interior spaces 114a, 114b are depicted as substantially equal in their interior capacity or volume, with the two spaces being separated by a single partition 113. As previously described for the article 10 of Figure 1, the atmospheres in each of the interior spaces 114a and 114b may be different than the atmosphere surrounding the moldable article 110, and it will be appreciated that interior spaces 114a, 114b may have inner atmospheres that are the same as one another or they may be different from one another. The atmospheres in interior spaces 114a and/or 114b are substantially free of moisture, and in some embodiments, the interior spaces comprise inert gas. In some embodiments, interior spaces 114a and/or 114b have been evacuated to provide a vacuum or near vacuum state.

A volume of first glass particles 116a comprising a first glass are included within the first interior space 114a. Likewise, a predetermined amount of second glass particles 116b are included within the second interior space 114b. The amount of first particles 116a in interior space 114a may be the same as or different than the amount of second particles 116b within interior space 114b. Second particles 116b comprise a second glass. At least one of the first glass or the second glass comprise non-traditional glass materials, as previously described. First glass and second glass may be the same glass material or they may be different.

In some embodiments of the invention, second glass particles 116b are identical to first glass particles 116a in that the first glass is of the same composition as the second glass. In other embodiments, the first glass is of a different composition than that of the second glass.

In embodiments wherein both first and second glasses are non-traditional glasses, at least one of the glasses may comprise less than 40 percent (or less than 35%, 30%, 25%, 20%, 15%, 10%, 5% or even 0%) by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass. The plurality of second particles are moldable at a second molding temperature in that they will begin to soften and coalesce (e.g., during a molding operation) at or above the second molding temperature, and the second molding temperature may be the same as or different than the first molding temperature. In the various embodiments, the first decomposition temperature is less than both the first molding temperature and the second molding temperature.

First barrier 112 is made from materials as previously described with reference to the moldable article 10 (Figure 1). Partition 113 is typically made from the same material as first barrier 112, although some embodiments may include a partition made from material different than that used for barrier 112.

Referring to Figure 5, a schematic illustration of a process is shown for the manufacture of the moldable article 110 and for its subsequent use in a molding process to provide a molded glass article 138. A measured quantity of first glass particles 116a are initially heated within a container 120 to remove water, and a measured quantity of second glass particles 116b are heated in a second container 121, also to remove water. The containers 120, 121 may be heated at a separate heating station (not shown) which can include an oven, a heating mantle or the like.

Following heating to remove moisture, the containers 120 and 121 may be sealed to prevent moisture from returning to the particles as they are allowed to cool. First glass particles 116a are transferred from container 120 into the first interior space 114a of sealable container 126. Funnel 128 is shown as an optional means to facilitate the transfer of the glass particles 116a. Second glass particles 116b are transferred from container 121 into the second interior space 114b of sealable container 126. Funnel 129 is shown as an optional means to facilitate the transfer of the particles 116b. Following transfer of the glass particles, sealable container 126 is sealed along its opened side 130 to provide moldable article 110.

In some embodiments of the invention, the sealable container 126 is purged with inert gas prior to sealing. In other embodiments, interior spaces 114a and 114b are sealed following evacuation to provide a reduced pressure (e.g., vacuum or near vacuum conditions) within the interior spaces.

The moldable article 110 is suitable for use in a molding process in which the article is placed in an opened mold cavity 134 of mold 132 with the respective interior spaces 114a and 114b oriented with respect to one another so that one of the interior spaces and its contents (e.g., the glass particles 116a or 116b) lay on top of the other interior space and its contents. In this orientation, particles 116a and 116b form two layers of glass material, stacked one on top of the other. In the compression molding process of Figure 5, cavity 134 is initially opened to receive the article 110 and is configured to be heated to an elevated temperature. With moldable article 110 disposed within cavity 134, the mold 132 is closed and is heated to a predetermined temperature. Pressure is applied to the article 110 with plug member 136 to compress the glass particles within the cavity 134.

In the various embodiments of the invention, the first barrier 112 of the moldable article 110 will substantially decompose at or above a characteristic decomposition temperature. In some embodiments, decomposition of the first barrier 112 removes substantially all of the first material of the barrier. Thereafter, the temperature of the mold 132 is increased to heat the glass particles 116a and 116b to a molding temperature at which the particles will soften and coalesce. The mold 132 is cooled and the resulting molded article 138 may be removed from the cavity 134. Molded article 138 is a two layered composite with a first layer 138a resulting from molding of the first particles 116a and the second layer 138b resulting from the second particles 116b. In some embodiments, the first material of first barrier 112 may not completely decompose during the molding process so that the surfaces of the molded article 138 may require polishing and/or another treatment (e.g., cleaning with a solvent) to remove any remaining residue. At least one of the layers 138a or 138b comprise a material derived from a non-traditional glass, as described herein.

In still other embodiments, molded articles similar to molded article 138 may be made by stacking individual moldable articles (e.g., similar to article 10, Figure 1) in a mold cavity and molding the moldable articles in the same manner as previously described. Multilayered articles similar to article 138 may be particularly useful as optical lenses, for example. In such embodiments, molded layers 138a and 138b may each have one or more different properties such as different refractive indexes or the like. In various embodiments, molded article 138 may comprise glass, ceramic and/or glass-ceramic material resulting from the molding of non-traditional glass. In some embodiments, the non-traditional glass particles are coalesced and are at least partially crystallized. In some embodiments, the glass is heat treated in a manner that increases the crystallinity of the glass and provides glass-ceramic or ceramic material.

Referring now to Figure 8, a multilayered molded article 168 is shown. The article 168 may be made according to an embodiment of the invention. Molded layers 168a, 168b, and 168c occupy discrete positions within the stacked arrangement. In some embodiments, each of the molded layers 168a, 168b, and 168c is made from a different glass composition to provide a molded layer with a refractive index that is different than the refractive index of either of the other two layers. In embodiments in which the article 168 is a gradient index lens, for example, layers 168a and 168c may comprise a high refractive index glass while the middle layer 168b may be made of a low refractive index glass. At least one of the layers 168a, 168b, and/or 168c is the molded product of a non-traditional glass, as previously described, and molding of the non-traditional glass may result in glass, ceramic and/or glass-ceramic materials in one or more of the layers 168a, 168b or 168c of molded article 168. The article 168 may be made from a moldable article comprising three different interior spaces, for example, each interior space containing a separate set of glass particles. Alternatively, the article 168 may be made by simultaneously molding three moldable articles stacked on top of one another within a mold cavity, each moldable article containing its own separate set of glass particles. Through the molding process, as previously described, each of the moldable articles would result in the creation of a layer in the finished article 168.

Figure 6 depicts a moldable article 210 configured according to still another embodiment of the invention. Article 210 is a container having a first barrier 212 and an interior space divided into a first interior space 214a and a second interior space 214b. Interior spaces 214a, 214b each have inner atmospheres as previously described with respect to the embodiments of Figures 1 and 4. A predetermined amount of first glass particles 216a are included within the first interior space 214a, and a predetermined amount of second glass particles 216b are included within second interior space 214b. In the depicted embodiment, interior space 214a is larger than interior space 214b, and the amount of first particles 216a in first interior space 214a is greater than the amount of second particles 216b within second interior space 214b. As in the previous embodiments, the particles 216a are of a first glass composition which may be different than the second glass composition of particles 216b. In general, first and second glass particles may be selected to provide different properties to the final molded article such as different refractive indexes, for example. At least one of the first glass particles 216a or the second glass particles 216b comprise non-traditional glass, as previously described.

Moldable article 210 may be made using a combination of individual containers wherein first barrier 212 is made of a flexible material such as a polymeric material, as already described. In such an embodiment, the single container is a ‘bag’ or a flexible-walled container with a single opened end leading into its interior space. Second interior space 214b may be created by providing heat sealed edges 215a, 215b, 215c to form three sides of the second interior space 214b. A fourth heat sealed edge 215d is formed after the interior space 214b is filled with glass particles 216b. In Figure 6, second interior space 214b is positioned in the center of first interior space 214b. Alternatively, the second interior space may be positioned elsewhere within the larger first interior space 214b, depending on the configuration desired for the final molded article. It will also be appreciated that, in some embodiments, more than two interior spaces (e.g., a third interior space, a fourth interior space and the like) may be associated with the same moldable article, each such interior space containing a volume of glass particles with at least one of the volumes of glass particles comprising a non-traditional glass, as previously described.

Moldable article 210 may be used in a molding process, as previously described with respect to the embodiments of Figures 1-5. The resulting molded article will include at least two different molded portions, one of the molded portions resulting from processing of the first glass particles 214a and another molded portion made from processing of the second glass particles 214b.

Molded article 238, shown in Figure 9, is of the type obtained from a molding process involving moldable article 210 of Figure 6. Article 238 includes a first or outer molded portion 238a and a second or inner molded portion 238b nested within and affixed to the outer portion 238a. It will be appreciated that the depicted shapes of molded portions 238a, 238b are merely illustrative, and that other shapes are within the scope of this disclosure and may be readily obtained merely by altering the design of the mold used to make the molded articles, for example. At least one of the layers of the molded article 238 results from the molding of non-traditional glass materials, as previously described, so that such a layer may comprise glass, ceramic and/or glass-ceramic materials.

Other embodiments are contemplated wherein the moldable article is similar to the article 210 in Figure 6, but wherein the second interior space (e.g., comparable to space 114b) is actually comprised of a separate moldable article placed within the interior space of a larger moldable article (e.g., comparable to interior space 214a). In other words, embodiments of the invention include those wherein separate moldable articles are included in the interior space of another moldable article. Each of the separate interior spaces of each moldable article include a volume of glass particles. At least one of the volumes of glass particles comprise a non-traditional glass, as previously described.

In still other embodiments, molded articles may be made according to the present invention wherein the articles include both glass and non-glass portions affixed to one another. Article 338 is depicted in Figure 10 and includes two components, molded glass portion 338b placed within a circular, non-glass, first portion 338a (e.g., a frame). Molded glass portion 338b comprises a non-traditional glass as previously described. The circular non-glass portion 338a may be made from any of a variety of other materials including polymeric materials, metallic materials or the like. Prior to forming the finished molded article 338, the non-glass portion 338a may be pre-formed and placed within a mold cavity. In the molding operation, the non-glass portion 338a is placed in the mold and a moldable article (as described herein) is positioned in the center of the non-glass portion 338a within the mold. A molding process may be performed to form article 338 having molded glass portion 338b positioned within the center of portion 338a. During the molding operation, glass particles in the moldable article coalesce while also bonding to the non-glass portion to form a finished article 338 with portions 338a and 338b affixed to one another.

The person of ordinary skill in the art will appreciate that other multi-component articles may also be made using the moldable articles of the present invention. Such multi-component molded articles can include glass and non-glass portions arranged as needed or desired. Another such multi-component molded article 448 is depicted in Figure 11. The article 448 includes three components 448a, 448b, and 448c. At least one of the molded components comprises a material derived from a non-traditional glass, as previously described. Article 448 results from molding at least one moldable article, as described herein.

In still another embodiment, a moldable article 310 is depicted in Figure 7. As in the previously described embodiments, article 310 is a container having a first barrier 312. Instead of being flexible, however, first barrier 312 is made of a shaped, more rigid, material. In Figure 7, the molded article 310 has a hemispherical shape with a concave center portion 311 (e.g., it is cup-shaped). A plurality of glass particles 316 occupy interior space 314 within the article 310, and the interior space 314 has a substantially moisture-free inner atmosphere, as previously described. First barrier 312 comprises a first material that will decompose as the mold is heated and pressurized during a molding operation. Decomposition of the barrier 312 occurs at a decomposition temperature substantially less than the molding temperature of the glass particles 316. Moldable article 310 is shaped to nest within the mold cavity 334, with center portion 311 dimensioned to receive the mold's plug member 336 therein. Molding the cup-shaped article 310 results in a similarly shaped molded article. While the shape of article 310 has been somewhat exaggerated for the purposes of describing this embodiment, it will be appreciated that shape of the moldable article will facilitate the formation of a similarly shaped molded article such as a concave optical lens, for example.

Use of a rigid first material for the barrier 312 serves to hold the plurality of glass particles 316 in a predetermined cup-shaped configuration. In the compression molding process, cavity 334 is heated to an elevated temperature and pressure is applied to the article 310 with plug member 336 extending from the mold top 335 into concave center portion 311. As the mold reaches the decomposition temperature of the first material, the barrier 312 will decompose and the glass particles 316 will soften and coalesce. As the temperature continues to rise to the first molding temperature, the particles 316 begin to soften and to coalesce into a molded form. Upon cooling, the glass will solidify and the molded article can be removed from the mold cavity 334. The resulting molded article may comprise glass, glass-ceramic and/or ceramic material.

It will also be appreciated by the person of ordinary skill that variations to the rigid moldable article 310 are obtainable and are entirely within the scope of the invention. For example, the molded article may be provided in a different shape and/or with multiple chambers, each chamber including a separate plurality of glass particles therein, with at least one of the chambers containing a plurality microparticles comprising non-traditional glass materials as previously described. All such embodiments are within the scope of the invention.

The use of a moldable article according to an embodiment of the invention, provides an improved molding process for glass particles, and especially for glass microspheres. The various embodiments of the invention provide a means to initially prepare a plurality of glass particles for a molding process and thereafter preserve the particles in a ready-state for an undetermined period of time. Moisture as well as carbon and dirt are known contaminants in the molding of small particles such as microspheres. Such contaminants may be picked up by handling the particles, during placement of the particles into a mold cavity, and/or during pressurization of the mold cavity.

Contamination can be problematic because it can cause structural defects in the final molded glass article. In the molding of optical lenses, for example, structural defects can result in undesirable optical properties in the finished lens. In addition to contamination caused be dirt or the like, small particles (e.g., microparticles) can pick up static charge that further complicates the handling of the particles, especially during placement of the particles into a mold cavity, for example.

The moldable articles of the invention facilitate the molding process by allowing for the easy deposition of glass particles into a mold cavity without concern for retained moisture and without the difficulties of handling particles that are statically charged. A maker of glass particles, for example, can utilize the invention to prepare the particles for a molding operation that may be performed by an outside vendor, a customer or the like. Vendors and customers using the glass particles in a molding process are thus assured of the purity and cleanliness of the packaged particles. Moreover, any of a variety of molded articles may be provided including, for example, single layered articles as well as multilayered articles.

Examples

The following non-limiting Examples further illustrate the embodiments of the present invention.

Example 1

Twenty grams of glass microparticles were deposited in a glass jar and dried in an oven for 16 hours at 130°C. The microparticles were made of a non-traditional glass having a composition represented as La_2O_3 Al_2O_3 ZrO_2 Gd_2O_3. The jar was sealed and allowed to cool. The microparticles were poured into a flexible container (e.g., an envelope) made of 2 mil (0.051mm) polyethylene film and the envelope was heat sealed. The envelope was positioned in a mold cavity. The mold was heated to ~900°C and pressurized, burning off the polyethylene film and reshaping the spherical microparticles into a consolidated article with the shape of the mold cavity. The mold was cooled and the glass article was removed and the surfaces were polished. A clear molded glass article was produced.

Example 2

Five hundred grams of La_2O_3 Al_2O_3 ZrO_2 Gd_2O_3 spherical glass microparticles were dried, placed in a flexible polyethylene envelope and heat sealed to provide a moldable article made of 4 mil (0.102 mm) thick polyethylene film. Carbon plates were used to construct a mold cavity having the dimensions of 5 in. x 5 in. x ~3/8 in. (12.7 cm x 12.7 cm x 0.95 cm). The moldable article was positioned in this mold cavity and the cavity was covered and sealed with additional carbon plates. The mold was heated to 870°C and pressurized, compressing the microparticles into a solid molded article. The polyethylene film was burned off during the heating process.

While various embodiments have been described and exemplified herein, the person of ordinary skill in the art will appreciate that changes and modifications may be made to the described embodiments without departing from the spirit and scope of the invention.

What is claimed:

1. A moldable article, comprising:

A first container comprising a first barrier, the first barrier comprised of a first material, and an interior space within the first barrier;

A plurality of first glass particles contained within the interior space and comprising a first glass, the plurality of first glass particles being moldable at a first molding temperature, the first glass having a first glass transition temperature and a first crystallization onset temperature, the difference between the first glass transition temperature and the first crystallization onset temperature being at least about $5^{o}K$, the first glass having a composition comprising at least two metal oxides, from 0 to less than 20% by weight SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5; and

Wherein, the first material has a first decomposition temperature less than the first molding temperature.

2. The article according to claim 1 wherein the first glass particles comprise microparticles.

3. The article according to claim 1 wherein the first material comprises a polymer.

4. The article according to claim 3 wherein the polymer is selected from the group consisting of polyamide, poly methyl methacrylate, polyisobutylene, polycarbonate, polyethylene carbonate, polypropylene carbonate, polybutylene terephthalate, polyetheretherketone, polyethylene, polypropylene, polyphenylene oxide, polystyrene aromatic polyesters, and combinations of two or more of the foregoing.

5. The article according to claim 4 wherein the polyamide is selected from the group consisting of nylon 6, nylon 66 and combinations thereof.

6. The article according to claim 4 wherein the polyethylene is selected from the group consisting of low density polyethylene, high density polyethylene, medium density polyethylene and combinations of two or more of the foregoing.

7. The article according to claim 4 wherein the polyethylene is low density polyethylene.

8. The article according to claim 1 wherein the first material is flexible.

9. The article according to claim 1 wherein the first material is rigid.

10. The article according to claim 1 wherein the first material is paper.

11. The article according to claim 1 wherein the interior space is substantially free of water vapor.

12. The article according to claim 1 wherein the interior space has an atmosphere comprising an inert gas selected from the group consisting of helium, neon, krypton, argon, xenon, nitrogen and combinations of two or more of the foregoing.

13. The article according to claim 1 wherein the interior space is divided into at least a first interior space and a second interior space with the plurality of first glass particles contained within the first interior space and a plurality of second glass particles contained within the second interior space, the second glass particles comprising a second glass having a composition different than the composition of the first glass.

14. The article according to claim 13 wherein the second glass particles comprise microparticles, the second glass having a second glass transition temperature and a second crystallization onset temperature, the difference between the second glass transition temperature and the second crystallization onset temperature is at least about 5^{o}K, the second glass comprising at least two metal oxides, from 0 to less than 20% by weight

SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5.

15. The article according to claim 1 further comprising:

A second container comprising a second barrier, the second barrier comprised of a second material, and a second interior space within the second barrier, the second container being wholly within the interior space of the first container;

A plurality of second glass particles contained within the second interior space so that the plurality of second glass particles and the plurality of first glass particles are separated from one another, the plurality of second glass particles comprising a second glass, the plurality of second glass particles being moldable at a second molding temperature.

16. The article according to claim 15 wherein the second glass has a second glass transition temperature and a second crystallization onset temperature, the difference between the second glass transition temperature and the second crystallization onset temperature is at least about 5°K, the second glass having a composition different than the composition of the first glass and comprising at least two metal oxides, from 0 to less than 20% by weight SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5.

17. The article according to claim 15 wherein the second material has a second decomposition temperature less than the second molding temperature.

18. The article according to claim 15 wherein the second material is the same as the first material.

19. The article according to claim 1 wherein the first molding temperature is about 300°C or greater.

20. A method of making a moldable article, the method comprising:

Placing a plurality of first glass particles in a first receptacle, the plurality of first glass particles being moldable at a first molding temperature, the first glass having a first glass transition temperature and a first crystallization onset temperature, the difference between the first glass transition temperature and the first crystallization onset temperature being at least about 5°K, the first glass having a composition comprising at least two metal oxides;

Removing entrapped moisture from the first glass particles; and

Sealing the first receptacle to form a first container comprising a first barrier, the first barrier defining an interior space, the plurality of first microparticles occupying at least a portion of the interior space, wherein the interior space is substantially free of water, and wherein the first barrier comprises a first material having a first decomposition temperature lower than the first molding temperature.

21. The method according to claim 20 wherein the first glass particles are microparticles, the first glass further comprising from 0 to less than 20% by weight SiO_2, from 0 to less than 20% by weight B_2O_3, and from 0 to less than 40% by weight P_2O_5.

22. The method according to claim 20 wherein the step of removing entrapped moisture comprises heating the first glass particles.

23. The method according to claim 22 wherein the step of removing entrapped moisture further comprises purging the first receptacle with inert gas before the step of sealing the first receptacle, the inert gas selected from the group consisting of helium, neon, krypton, argon, xenon, nitrogen and combinations of two or more of the foregoing.

24. The method according to claim 20 wherein the step of removing entrapped moisture comprises at least partially evacuating the first container to provide a reduced atmospheric pressure in the first container.

25. The method according to claim 20 wherein the first material comprises a polymer selected from the group consisting of polyamide, poly methyl methacrylate, polyisobutylene, polycarbonate, polyethylene carbonate, polypropylene carbonate,

polybutylene terephthalate, polyetheretherketone, polyethylene, polypropylene, polyphenylene oxide, polystyrene aromatic polyesters, and combinations of two or more of the foregoing.

26. The method according to claim 25 wherein the polyamide is selected from the group consisting of nylon 6, nylon 66 and combinations thereof.

27. The method according to claim 25 wherein the polyethylene is selected from the group consisting of low density polyethylene, high density polyethylene, medium density polyethylene and combinations of two or more of the foregoing.

28. The method according to claim 27 wherein the polyethylene is low density polyethylene.

29. The method according to claim 20 further comprising:

Placing a plurality of second glass particles in a second receptacle, the plurality of second glass particles comprising a second glass that is moldable at a second molding temperature;

Removing entrapped moisture from the second glass particles; and

Sealing the second receptacle to form a second container comprising a second barrier, the second barrier defining a second interior space, the plurality of second glass particles occupying at least a portion of the second interior space, wherein the second barrier comprises a second material having a second decomposition temperature lower than the second molding temperature; and

Placing the second container within the first receptacle prior to the step of sealing the first receptacle.

30. The method according to claim 29 wherein the second glass particles comprise microparticles and the second glass has a second glass transition temperature and a second crystallization onset temperature, the difference between the second glass transition temperature and the second crystallization onset temperature being at least about 5°K, the

second glass having a composition comprising at least two metal oxides, from 0 to 20% by weight SiO_2, from 0 to 20% by weight B_2O_3, and from 0 to 40% by weight P_2O_5.

31. The method according to claim 21 wherein the first receptacle comprises a plurality of chambers, and the step of placing the plurality of first glass particles in the first receptacle comprises placing the particles in a first chamber; the method further comprising placing a second plurality of glass particles in a second chamber, wherein the step of sealing the first receptacle forms the first container so that the interior space forms a plurality of sealed chambers with the first plurality of glass particles sealed within a first interior space and the second plurality of glass particles sealed within a second interior space.

32. The method according to claim 31 wherein the second glass particles comprise microparticles, the second glass having a second glass transition temperature and a second crystallization onset temperature, the difference between the second glass transition temperature and the second crystallization onset temperature is at least about 5^{o}K, the second glass comprising at least two metal oxides, from 0 to 20% by weight SiO_2, from 0 to 20% by weight B_2O_3, and from 0 to 40% by weight P_2O_5.

33. A method for molding an article, comprising:

Placing one or more of the moldable articles of claim 1 in a mold cavity;

Heating the mold cavity to a temperature above the first decomposition temperature and above the first glass transition temperature to decompose the first material and coalesce the first glass particles to provide a molded article comprising the first glass.

34. The method according to claim 33 further comprising treating the molded article as needed to remove residue of the first material from the surfaces of the molded article.

35. The method according to claim 34 wherein the step of treating the molded article as needed to remove residue comprises polishing the surfaces of the molded article.

36. The method according to claim 34 wherein the step of treating the molded article as needed to remove residue comprises chemically treating the surfaces of the molded article.

37. The method according to claim 34 wherein the step of placing one or more of the moldable articles of claim 1 in a mold cavity further comprises placing a premolded part into the mold cavity so that the molded article comprises the premolded part affixed to the first glass.

38. A method for molding an article, comprising:

Placing one or more of the moldable articles of claim 13 in a mold cavity; and

Heating the mold cavity to a temperature above the first decomposition temperature to decompose the first material and coalesce the first plurality of glass particles and the second plurality of glass particles to provide a molded article comprising a first molded portion and a second molded portion, the first molded portion affixed to the second molded portion.

39. A method for molding an article, comprising:

Placing one or more of the moldable articles of claim 15 in a mold cavity;

Heating the mold cavity to decompose the first material and the second material and to coalesce the first plurality of glass particles and the second plurality of glass particles to provide a molded article comprising a first molded portion affixed to a second molded portion.

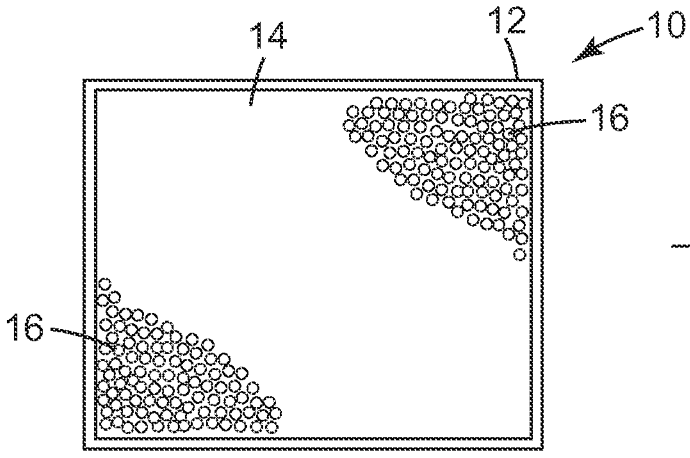

Fig. 1

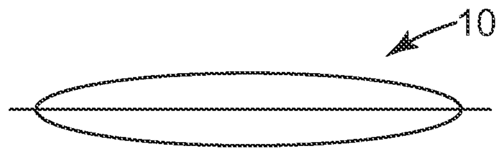

Fig. 2

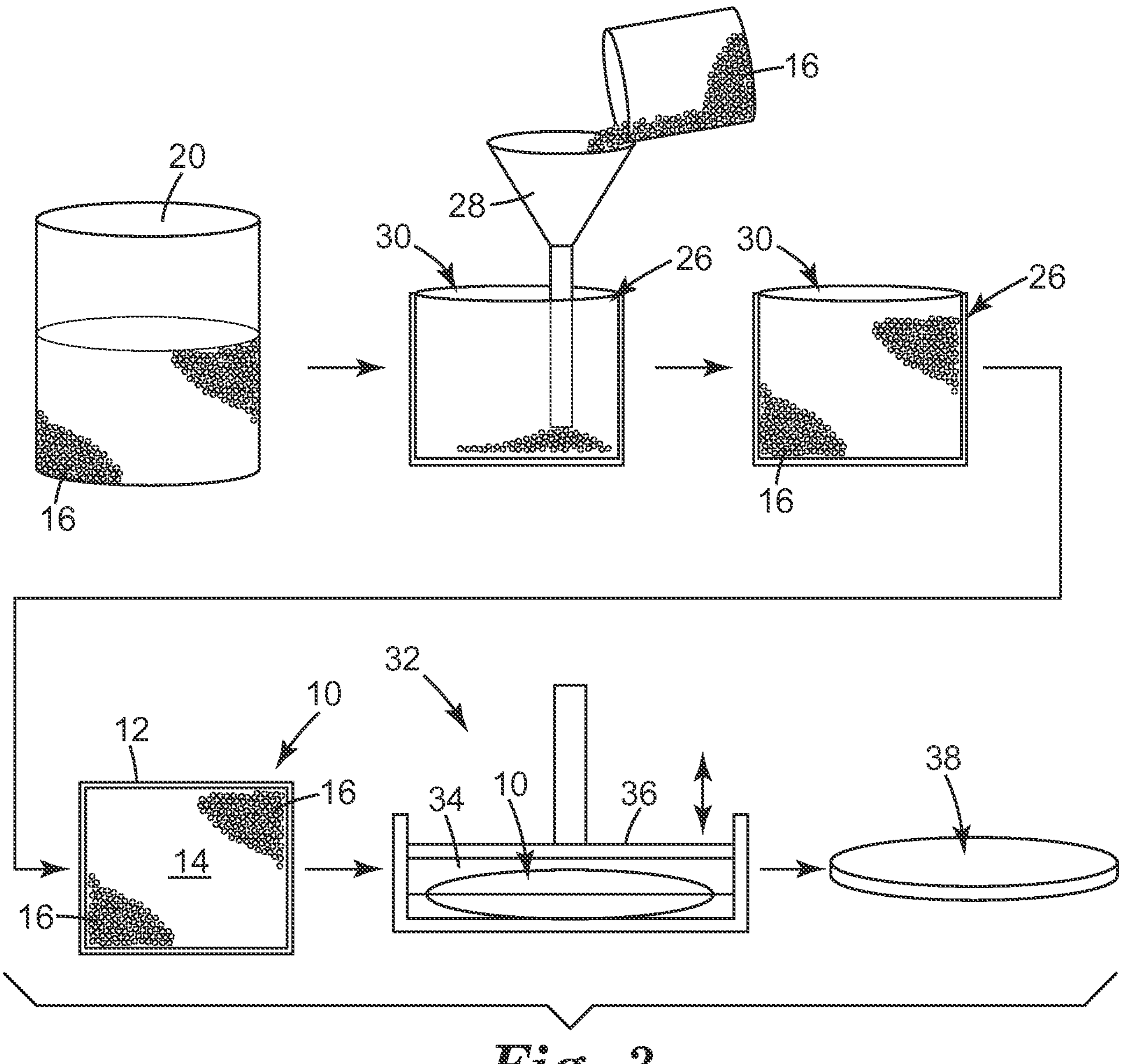

Fig. 3

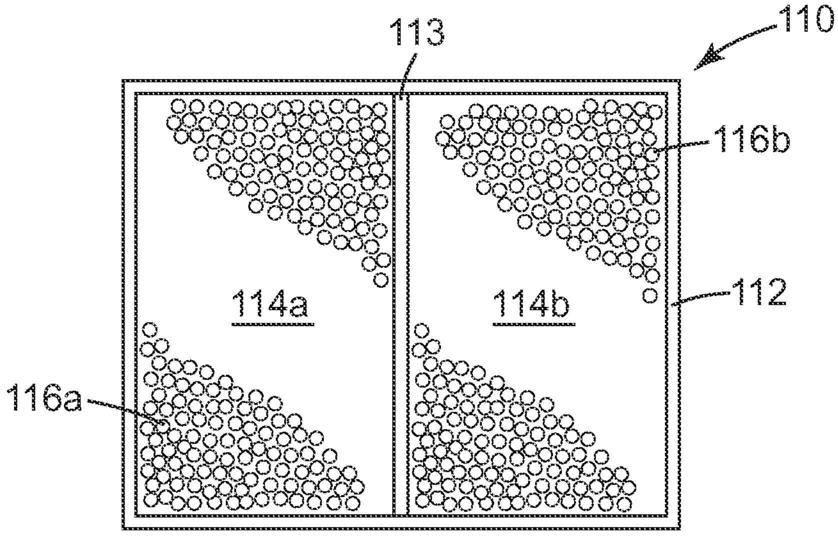
110
113
116b
114a
114b
112
116a

Fig. 4

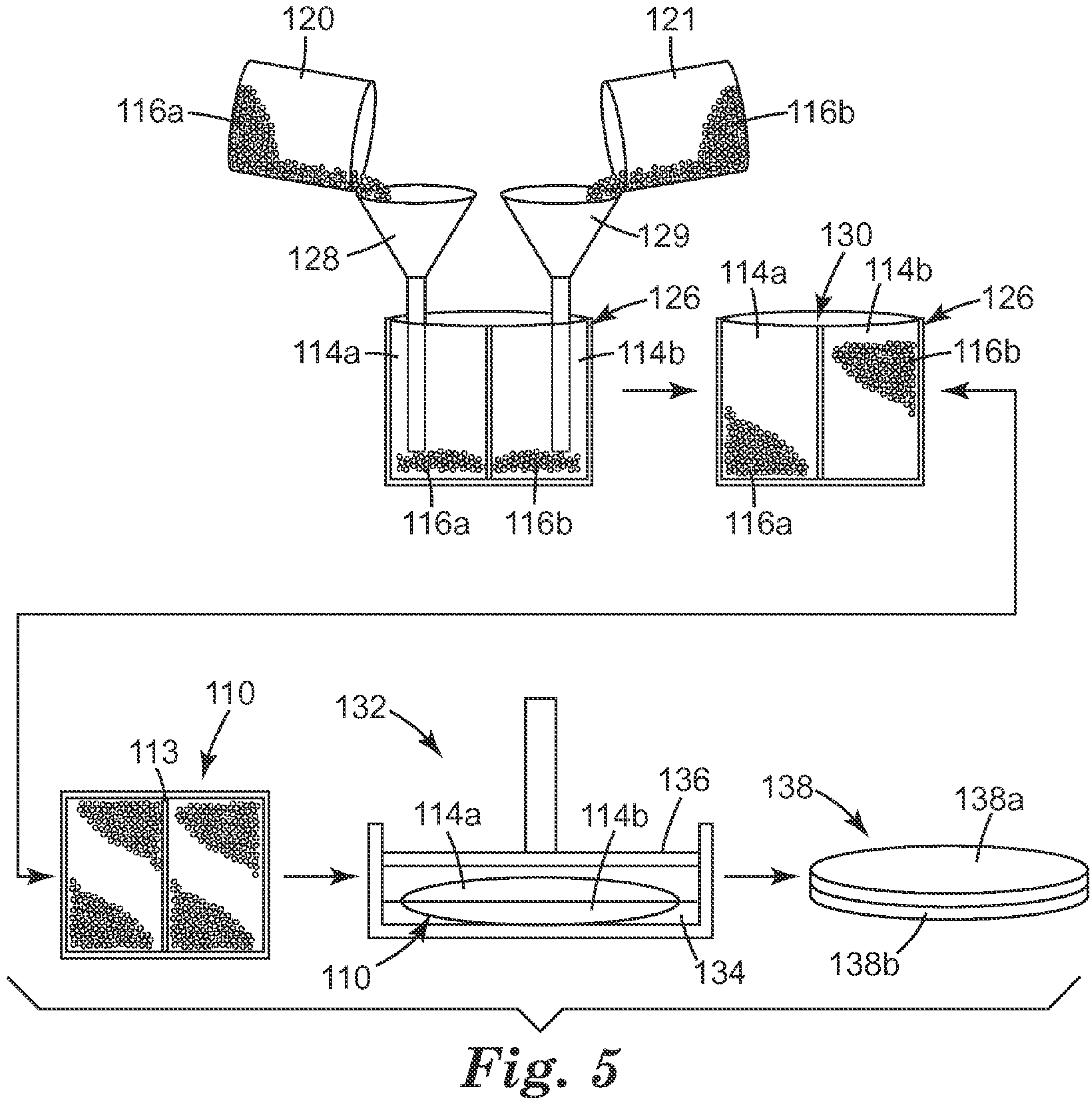
120
121
116a
116b
128
129
130
126
114a
114b
116a
116b
114a
114b
126
116b
116a
110
113
132
136
114a
114b
138
138a
110
134
138b

Fig. 5

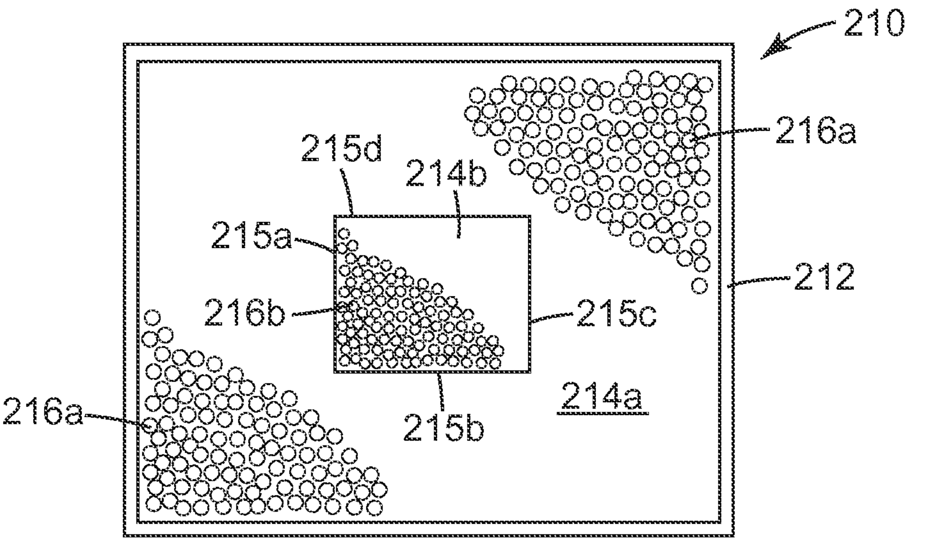

Fig. 6

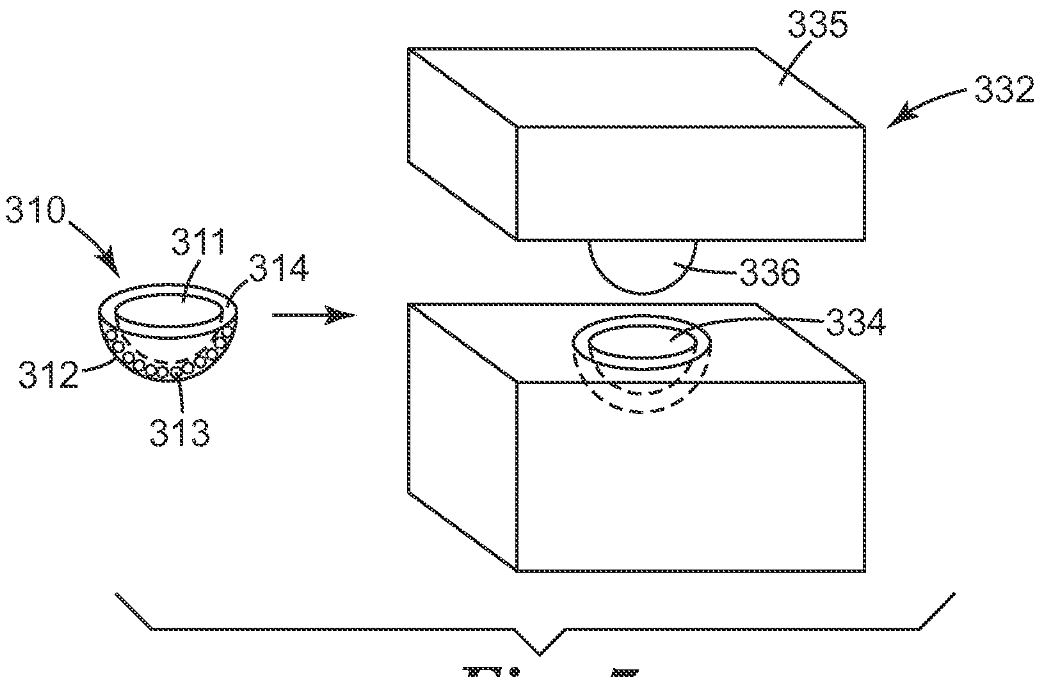

Fig. 7

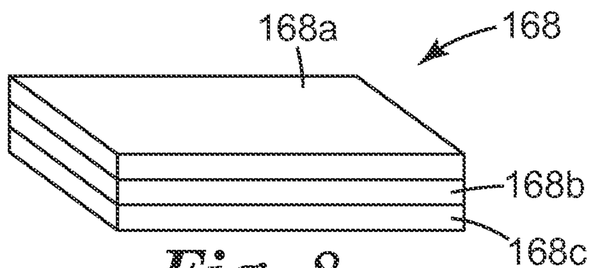

Fig. 8

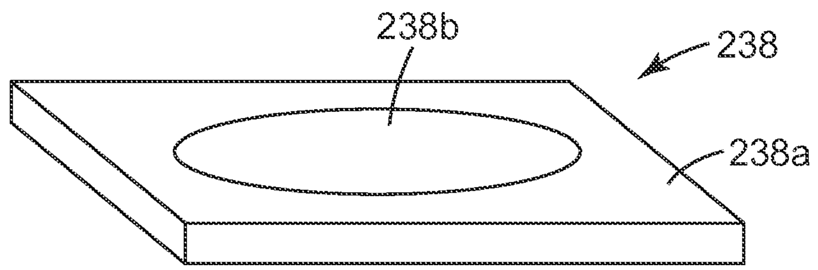

Fig. 9

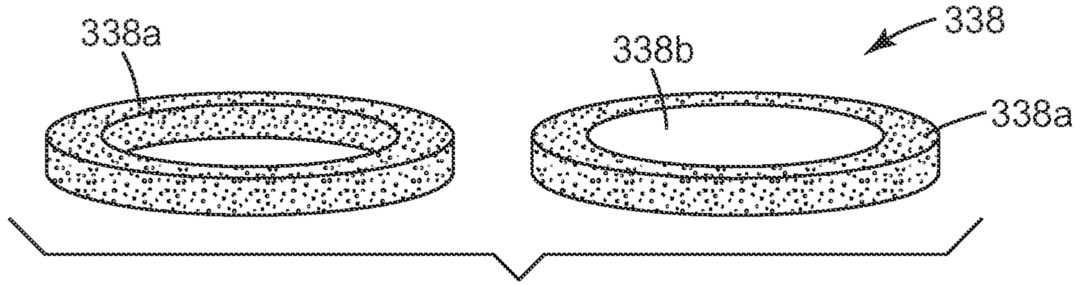

Fig. 10

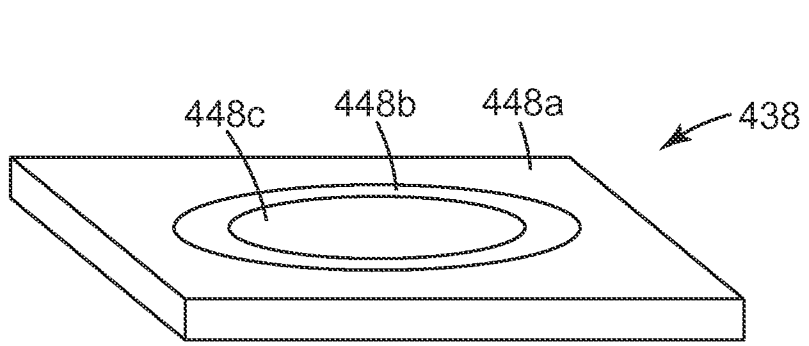

Fig. 11