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(54) Method of altering the effective bulk density of solid material and the resulting product; hollow polymeric particles

(57) Hollow spherical particles are made by spraying a mixture of powdered solid material with a solution of a film-forming polymer in a solvent therefor into a heated chamber where the solvent evaporates. The powder is thereby captured in the wall of the hollow polymer particles formed. Such particles are used to form a suspension in a fluid material. The hollow particles are of such size and wall thickness, in relation to the bulk density of the powdered solid material, that the bulk density of each hollow spherical particle is commensurate with the density of the fluid material. The particles thereby remain in suspension over a substantial period of time with little or no agitation of the fluid.

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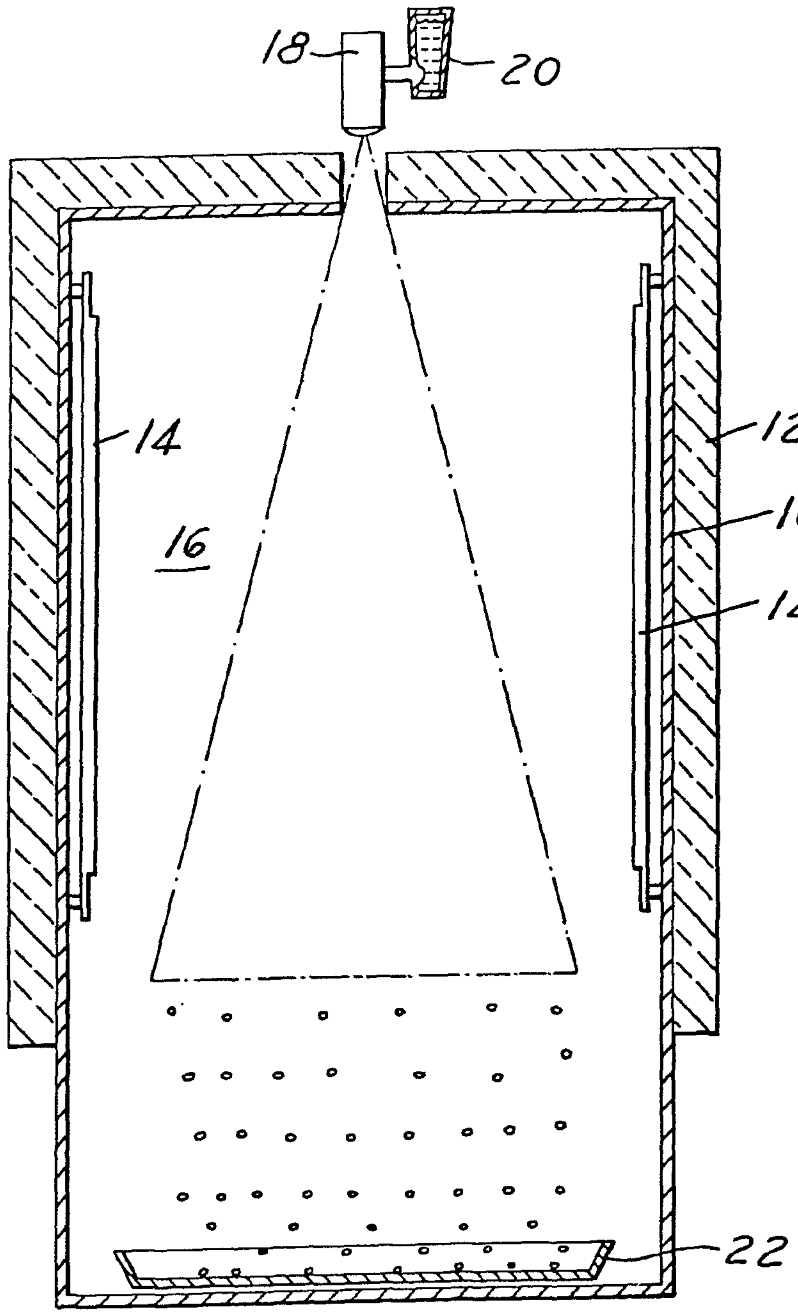

SPECIFICATION

Method of altering the effective bulk density of solid material and the resulting product

The invention relates to material processes, and more particularly to methods for altering or tailoring the bulk density of solid material and to suspensions of solid particles in fluids.

It is often desirable to suspend solid materials in a liquid medium having a bulk density which is substantially lower than that of the solid. For example, it is known that the conductivity of the plasma in magnetohydrodynamic power generators is improved substantially if a material such as cesium or a cesium compound is injected into the plasma. However, difficulties are encountered in attempts to suspend cesium carbonate having a bulk density of 4.6 grams per cubic centimeter (g/cc) in toluene, the plasma fuel, having a density of 0.866 g/cc. The cesium or cesium compound settles from suspension and clogs fuel passages.

An object of the present invention is to provide a method of altering or tailoring the effective density of a solid material, such as cesium or a cesium compound, so as to be readily suspensible in a medium of lesser density, such as toluene. A related object of the invention is to provide a particulate product which includes said solid material and which possesses a bulk density which is tailored as desired.

One aspect of the invention is a method of forming hollow bulk particles comprising the steps of

(a) mixing a solid material in powdered form with a film-forming polymer and a solvent in which the polymer is soluble, and

(b) forming said mixture into droplets at a temperature at which said solvent evaporates such that said polymer solidifies into hollow particles having a particle wall in which said solid material is captured.

Another aspect of the invention is a method of tailoring the bulk density of a selected solid material comprising the steps of

(a) forming a mixture at preselected concentration comprising said solid material, a film-forming polymer and a volatile solvent in which said polymer is soluble,

(b) forming said mixture into droplets of predetermined size, and

(c) heating said droplets to a preselected temperature to evaporate said solvent and thereby form a hollow shell of said polymeric material having said solid material captured therein and having a bulk density which is a function of said concentration, droplet size and temperature.

A further aspect of the invention is a method of suspending a solid material having a predetermined first bulk density in a carrier fluid having a second bulk density substantially less than said first bulk density comprising the steps of:

(a) forming a solution at preselected concentrations comprising said solid material in powdered form, a film-forming polymer and a solvent in which said polymer is soluble,

(b) forming said solution into droplets of predetermined nominal size,

(c) forming said droplets into hollow spherical shells having a bulk density which is substantially equal to said second bulk density by spraying said solution in droplet form into the upper portion of a zone heated at atmospheric pressure to a preselected temperature such that said solvent evaporates as said droplets fall by gravity through said zone and said film-forming polymer forms said hollow spherical shells each having a shell wall in which said solid material is captured and having a said shell bulk density which is a function of said preselected concentration, said predetermined nominal droplet size and said preselected temperature, and then

(d) suspending said spherical shells with said solid material captured in said shell walls in said carrier fluid.

The invention includes a hollow particle comprising a hollow substantially spherical shell of a polymer and powdered solid material captured in the wall of said shell.

The invention also includes a suspension of such particles in a carrier fluid.

The invention is further described, by way of example, with reference to the drawing, which is not to scale, and which illustrates one presently preferred embodiment of an apparatus for practicing the invention.

It has been known heretofore that hollow spherical shells or particles may be formed by dissolving a film-forming polymer in a suitable volatile solvent and then spraying the mixture into the upper portion of a heated chamber to form atomized droplets. As the droplets fall by gravity within the heated chamber, the solvent rapidly evaporates and a polymer skin or shell is formed. The U.S. patent to Veatch et al 2 797 201 discloses such a process and an apparatus for practicing such process. The Veatch et al patent additionally describes how polymer/solvent concentration, drying temperature and droplet size may be varied to yield shells of predetermined (nominal) size and density.

The drawing illustrates a modified chamber utilized in practice of the invention as comprising a four-foot square hollow rectangular chamber 10 of galvanized steel. Chamber 10 is preferably 3.660 mm high, such height being sufficient to permit particle solidification over a size range of interest. Chamber 10 is insulated externally by 100 mm of glass fibre 12 and has a plurality of sixteen 1500 mm long electrical resistance heaters 14 distributed at regular intervals around the inner chamber wall to provide uniform heating of the enclosed zone 16. An atomization nozzle 18 is disposed to feed droplets into an upper portion of zone 16 and preferably consists of a model A-CUADF Automatic Airbrush manufactured by Paasche Airbrush Company of 1809 Diversey Parkway, Chicago, Illinois 60614. This atomizer employs a high velocity jet of gas, preferably air, to impart a shearing force to solution received from a reservoir 20 to form droplets as the solution expands through the atomization orifice.

The method described in the Veatch et al patent is modified and utilized to tailor the bulk density of desired solid materials by forming hollow spherical shells of polymeric material having the solid material captured within the shell walls. The size and weight of the ultimate shell may be tailored by varying polymer/solid/solvent concentration, droplet size and drying temperature.

The method of the invention is carried out by first forming a mixture comprising, and preferably consisting essentially of, the desired solid material, a film-forming polymer and a suitable volatile solvent in which the polymer is soluble. The solid material, which may be in elemental or compound form, may be reduced to powdered form having a particle size in the range of 5μm to 0.1μm, preferably 0.5μm. Droplet size and shell wall thickness place an upper limit on particle size of the solid material.

A wide variety of film-forming polymers are identified in the above-referenced Veatch et al patent. Polymers preferred in accordance with the present invention are selected from the group consisting of poly (vinyl alcohol), poly (methyl methacrylate), sodium carboxymethyl cellulose, poly (vinyl alcohol-co-vinyl butyral), polystyrene, polystyrene-co-allyl alcohol, poly (vinyl formal), poly (2-hydroxpropyl methacrylate) and ABS. Any solvent in which the selected polymer is soluble and which will evaporate at the desired chamber temperature would be suitable. The solvent essentially acts only as a polymer/solid carrier and plays no substantial role in the structure of the ultimate product. The mixture or solution in reservoir 20 is formed to possess a preselected solid/polymer concentration and a viscosity in the range of 1 to 500 cp. The solid material may be either soluble or suspendable in the polymer, solution or suspension being facilitated by an ultra-sonic bath where desired.

The solid/polymer/solvent mixture is then sprayed as small atomized droplets of preselected (nominal) size into chamber 10 which is preheated to a predetermined temperature. The droplets may be anywhere from 5μm to 500μm in size, with a diameter in the range of 20μm to 200μm being preferred. Drying temperature may be in the range of 20°C to 500°C, with the range of 50°C to 200°C being preferred. The relationship of mixture concentration, droplet size and drying temperature to ultimate shell density will be set forth hereinafter. The droplets are heated as they fall and the solvent vaporizes to form hollow shells having the suspended or soluble solid material captured in the shell walls. The chamber preferably encloses heated air at atmospheric pressure. The product shells, which may be collected in a tray 22 on the chamber floor, enclose air and solvent at a pressure at or slightly above atmospheric depending upon variations in shell permeability with temperature. The contained solvent will be liquid or vapor (or solid) depending upon shell temperature and resultant pressure.

The density of the product shells are primarily affected by adjustment of shell diameter and wall thickness, and of polymer/solid concentration. Shell density d is given by the equation

$$d = pd_s\left(\frac{D_2}{D_1}\right)3$$

where p equals weight fraction of polymer in the polymer/solid mixture, d_s is the polymer/solid density, D_1 is shell diameter and D_2 is droplet diameter. The relationship of shell diameter and wall thickness to drying temperature, droplet size and concentration, may be determined empirically. Generally speaking, smaller droplets produce smaller shells, higher concentrations produce shells with thicker walls, and higher temperatures produce larger shells having thinner walls.

In a specific working example of the invention mentioned in the background above, it is desired to produce shells which include cesium and which may be suspended in toluene. Cesium carbonate and polyvinyl alcohol are materials of choice as the solid and polymer respectively. Water may be used as solvent. An ultimate shell composition by weight of 50% cesium carbonate and 50% polyvinyl alcohol is selected arbitrarily. Calcium carbonate possesses a density of 4.6 g/ml and polyvinyl alcohol a density of 1.3 g/ml. A desired shell radius of 10μm is selected, which translates into a total shell volume V_s of $4.19 \times 10^3 \mu m^3$. Solution density d_s is 2.95 g/ml, while that of toluene is 0.866 g/cc. Thus, an effective density reduction factor f of 3.4 is required. Shell wall volume V_w is given by the equation

$$V_w = \frac{V_s}{f} = 1.23 \times 10^3 \mu m^3.$$

This implies a wall thickness of 1.09μm.

A solution of 2.5% polyvinyl alcohol and 2.5% cesium carbonate in water was prepared and atomized in drying chamber 10. Mean atomized droplet size was 65μm and chamber temperature was 150°C. The product shells had a radius of 10 to 50μm and a wall thickness on the order of 1μm. The shells could be suspended for several minutes in toluene with only slight agitation. The composition of the shells were 50% (by weight) poly (vinyl alcohol) and 50% cesium carbonate.

CLAIMS

1. A method of forming hollow bulk particles comprising the steps of

(a) mixing a solid material in powdered form with a film-forming polymer and a solvent in which the polymer is soluble, and

(b) forming said mixture into droplets at a temperature at which said solvent evaporates such that said polymer solidifies into hollow particles having a particle wall in which said solid material is captured.

2. A method as claimed in claim 1, wherein said step (b) comprises the step of spraying said mixture into an upper portion of a heated zone such that said hollow particles are formed as said droplets fall by gravity in said zone, and wherein said method includes the additional step of (c) collecting said hollow particles at the floor of said zone.

3. A method as claimed in claim 2, wherein concentration of said mixture, size of said droplets and temperature of said zone are preselected such that said particles possess a predefined bulk density less than the bulk density of said solid material.

4. A method of tailoring the bulk density of a selected solid material comprising the steps of

(a) forming a mixture at preselected concentration comprising said solid material, a film-forming polymer and a volatile solvent in which said polymer is soluble,

(b) forming said mixture into droplets of predetermined size, and

(c) heating said droplets to a preselected temperature to evaporate said solvent and thereby form a hollow shell of said polymeric material having said solid material captured therein and having a bulk density which is a function of said concentration, droplet size and temperature.

5. A method as claimed in claim 4, wherein said steps (b) and (c) are carried out by spraying said mixture into a zone heated to said preselected temperature.

6. A method as claimed in claim 5, wherein said steps (b) and (c) are carried out by spraying said mixture into an upper region of said heated zone such that said hollow shells are formed as said droplets fall by gravity through said zone.

7. A method as claimed in claim 5 or 6, wherein said mixture is formed to possess a viscosity in the range of 1 to 500 cp.

8. A method as claimed in claim 7, wherein said polymer is poly (vinyl alcohol), poly (methyl methacrylate), sodium carboxymethyl cellulose, poly (vinyl alcohol-co-vinyl butyral), polystyrene, polystyrene-co-allyl alcohol, poly (vinyl formal), poly (2-hydroxpropyl methacrylate) or ABS.

9. A method as claimed in any of claims 5 to 8, wherein said zone contains heated air at atmospheric pressure.

10. A hollow particle comprising a hollow substantially spherical shell of a polymer and powdered solid material captured in the wall of said shell.

11. A method of suspending a solid material having a predetermined first bulk density in a carrier fluid having a second bulk density substantially less than said first bulk density comprising the steps of:

(a) forming a solution at preselected concentrations comprising said solid material in powdered form, a film-forming polymer and a solvent in which said polymer is soluble.

(b) forming said solution into droplets of predetermined nominal size,

(c) forming said droplets into hollow spherical shells having a bulk density which is substantially equal to said second bulk density by spraying said solution in droplet form into the upper portion of a zone heated at atmospheric pressure to a preselected temperature such that said solvent evaporates as said droplets fall by gravity through said zone and said film-forming polymer forms said hollow spherical shells each having a shell wall in which said solid material is captured and having a said shell bulk density which is a function of said preselected concentration, said predetermined nominal droplet size and said preselected temperature, and then

(d) suspending said spherical shells with said solid material captured in said shell walls in said carrier fluid.

12. A method as claimed in claim 11, wherein said predetermined nominal droplet size is in the range of five to five hundred microns, and said preselected temperature is in the range of twenty to five hundred degrees celsius.

13. A method as claimed in claim 12, wherein said predetermined nominal droplet size is in the range of twenty to two hundred microns, and said preselected temperature is in the range of fifty to five hundred degrees celsius.

14. A suspension of hollow particles, each as claimed in claim 10, in a carrier fluid.

15. A suspension as claimed in claim 14, wherein each hollow particle has a bulk density commensurate with the density of the carrier fluid.

16. A method of forming hollow particles substantially as herein described with reference to the drawing.

17. A method of forming a suspension substantially as herein described with reference to the drawing.

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