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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018090 A1

(51) International Patent Classification⁷: **B01J 13/04**, C04B 18/08

(21) International Application Number: PCT/AU2003/001067

(22) International Filing Date: 21 August 2003 (21.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/405,790 23 August 2002 (23.08.2002) US
60/471,400 16 May 2003 (16.05.2003) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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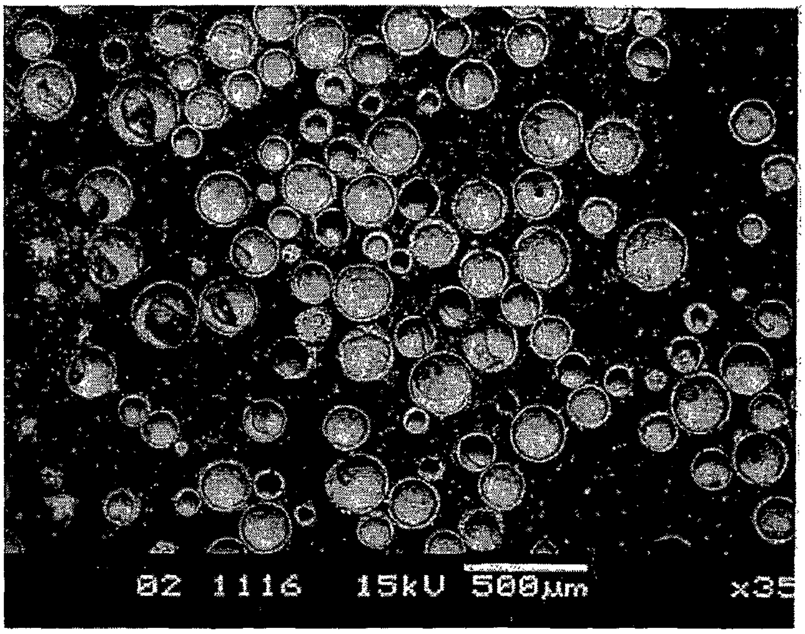
(54) Title: SYNTHETIC HOLLOW MICROSPHERES



(57) Abstract: This invention relates to a method of forming a synthetic hollow microsphere comprising the steps of preparing an agglomerate precursor, said agglomerate precursor including a primary component and a blowing agent; and firing the precursor at a predetermined temperature profile sufficient to seal the surface of the precursor and activate the blowing agent thereby forming a synthetic hollow microsphere, wherein the primary component comprises at least one aluminosilicate material. Synthetic hollow microspheres made by this method and uses thereof are also described.

WO 2004/018090 A1

(84) Designated States *(regional)***:** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SYNTHETIC HOLLOW MICROSPHERES

Technical Field

This invention relates to a process for manufacturing synthetic hollow microspheres and synthetic hollow microspheres made by this process. It has been developed primarily to provide a cost-effective alternative to commercially available cenospheres.

Background of the Invention

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

Cenospheres are spherical inorganic hollow microparticles (microspheres) found in fly ash, which is produced as a by-product in coal-fired power stations. Cenospheres typically make up around 1-2% of the fly ash and "harvested" cenospheres are widely commercially available. The composition, form, size, shape and density of cenospheres provide particular benefits in the formulation and manufacture of many low-density products.

One of the characterizing features of cenospheres is their exceptionally high chemical durability. This exceptionally high chemical durability is understood to be due to the very low content of alkali metal oxides, particularly sodium oxide, in their composition. Accordingly, low-density composites produced from harvested cenospheres have the desirable properties of high strength to weight ratio and chemical inertness. Chemical inertness is especially important in Portland cement applications, where relative chemical inertness plays an important role in achieving highly durable cementitious products. Thus, harvested cenospheres have proven to be especially useful ain building products and in general applications where they may come into contact with corrosive environments where high chemical durability is desirable.

Despite the known utility of harvested cenospheres, their widespread use has been limited to a large extent by their cost and availability. The recovery of cenospheres in large quantities from fly ash is a labour intensive and expensive process. Although it is possible to increase the recovery of cenospheres from fly ash by modifying the collection process, the cost of improved recovery does not make this economically viable.

It may also be possible to alter combustion conditions in power stations to increase the yield of cenospheres in fly ash. However, combustion conditions in power stations are optimised for coal-burning rather than cenosphere production. It is not economically viable to increase the yield of cenosphere production at the expense of a coal-burning efficiency.

Several methods for producing microspheres are described in the prior art. Early methods for manufacturing hollow glass microspheres involved combining sodium silicate and borax with a suitable foaming agent, drying and crushing the mixture, adjusting the size of the crushed particles and subsequently firing the particles. However, this method suffers from the use of expensive starting materials (*e.g.* borax). Hence, the resulting microspheres are necessarily expensive. In addition, the product has poor chemical durability due to a high percentage of sodium oxide in the resulting glass composition.

US 3,752,685 describes a method of producing glass microspheres from Shirasu, a naturally occurring volcanic rock. Upon heating at 800 to 1000°C, finely divided Shirasu forms hollow glass microspheres. However, this method relies on the provision of Shirasu, which is not a widely available starting material.

US 3,365,315 describes a method of producing glass microspheres from glass beads by heating in the presence of water vapour at a temperature of about 1200°C. This method requires the exclusive use of pre-formed amorphous glasses as the starting raw materials.

US 2,978,340 describes a method of forming glass microspheres from discrete, solid particles consisting essentially of an alkali metal silicate. The microspheres are formed by heating the alkali metal silicate at a temperature in the range of 1000-2500°F in the presence of a gasifying agent, such as urea or Na_2CO_3. Again, the alkali silicate product suffers from poor chemical durability due to a high percentage of alkali metal oxides.

US 2,676,892 describes a method of forming microspheres from a Macquoketa clay shale by heating particles of the shale to a temperature of 2500-3500°F. The resulting product undesirably has an open pore structure leading to a relatively high water absorption in an aqueous cementitious environment.

US Patent Application No. 2001/0043996 (equivalent of EP-A-1156021) describes a spray combustion process for forming hollow microspheres having a diameter of from 1 to 20 microns. However, this process is unsuitable for making hollow microspheres having a diameter similar to that of known cenospheres (*i.e.* about 200 microns). In spray combustion processes, rapid steam explosion ruptures larger particles, thereby preventing formation of hollow microspheres greater than about 20 microns in diameter.

US Patent Application No. 2002/0025436 describes a process for forming solid microspheres from fly ash. The process is said to improve the spheroidal uniformity of fly ash particles and provides fly ash spheroids having a density of about 1.8 g/cm^3.

It would be desirable to produce microspheres with acceptable chemical durability in a low-cost, high yield process from commonly available raw materials, thereby allowing such materials to be used more widely in fibre cement and other products.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Summary of the Invention

Accordingly, in a first aspect the present invention provides a method of forming a synthetic hollow microsphere comprising the steps of:

(a) preparing an agglomerate precursor, said agglomerate precursor including a primary component and a blowing agent; and

(b) firing the precursor at a predetermined temperature profile sufficient to seal the surface of the precursor and activate the blowing agent thereby forming a synthetic hollow microsphere,

wherein the primary component comprises at least one aluminosilicate material.

Unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

As used herein, the term “synthetic hollow microsphere” or “synthetic microsphere” means a hollow microsphere synthesized as a primary target product of a synthetic process. The term does not include, for example, harvested cenospheres which are merely a by-product of burning coal in coal-fired power stations.

Although the term "microsphere" is used throughout the specification, it will be appreciated that this term is intended to include any substantially spherical discrete microparticle, including microparticles that are not true geometric spheres.

As used herein, the term "preparing an agglomerate precursor" means a synthetic preparation of an agglomerate precursor by combining the various constituents, for example, by a method described below.

As used herein, the term "primary component" means that this component is the major constituent of the agglomerate precursor, in the sense that the amount of primary component exceeds the amounts of the other constituents.

The preferred method of the present invention advantageously provides a means for producing microspheres in excellent yield from widely available and inexpensive starting materials, such as fly ash, natural rocks and minerals. Hence, the method, in its preferred form, reduces the overall cost of producing microspheres, and consequently increases the scope for their use, especially in the building industry where the use of presently available cenospheres is relatively limited due to their prohibitive cost and low availability. Hitherto, it was not believed that hollow microspheres could be formed from waste aluminosilicate materials, such as fly ash.

A further advantage of the present invention, in its preferred form, is that the microspheres produced may be tailor-made to suit a particular purpose. For example, the size, density and composition of the microspheres may be modified, as required, by modifying the relative amounts of ingredients and/or the temperature profile/exposure time during formation.

Still a further advantage of the present invention, in its preferred form, is that the microspheres produced have acceptably high chemical durability and can withstand, for example, a highly caustic environment of pH 12-14 for up to 48 hours. Thus, microspheres produced according to the preferred form of the present invention can withstand aqueous cementitious environments, such as Portland cement paste.

Moreover, in most cases, fibre cement products are cured for up to 24 hours in an autoclave kept at temperatures as high as 250°C. Microspheres produced according to the preferred form of the present invention lose minimal amount of mass to dissolution (*e.g.* by leaching of silica), retain their shape, and continue to have high mechanical strength in fibre cement products, even after exposure to harsh autoclaving conditions.

In a second aspect, the present invention provides a synthetic hollow microsphere obtained or obtainable by the method described above.

In a third aspect, the present invention provides a synthetic hollow microsphere comprising an aluminosilicate material, wherein the average particle size of said microsphere is in the range of 30 to 1000 microns, and the total alkali metal oxide content of said microsphere is in the range of 3 to 10 wt.%, based on the total weight of the microsphere.

In a fourth aspect, the present invention provides the use of a synthetic hollow microsphere as described above in filler applications, modifier applications, containment applications and substrate applications.

In a fifth aspect, the present invention provides a fibre cement building product comprising synthetic hollow microspheres as described above.

In a sixth aspect, the present invention provides an agglomerate precursor suitable for preparing a synthetic hollow microsphere, the agglomerate precursor comprising a primary component and a blowing agent, wherein the primary component comprises at least one aluminosilicate material.

In a seventh aspect, the present invention provides a method of preparing an agglomerate precursor, said agglomerate precursor being suitable for forming a synthetic hollow microsphere therefrom, comprising the steps of:

(a) providing a primary component of a predetermined size, said primary component comprising at least one aluminosilicate material;
(b) mixing the primary component with a blowing agent in water; and
(c) drying the mixture.

Preferred features of all aspects of the present invention are described in more detail below.

Agglomerate Precursor

The agglomerate precursor is generally a substantially solid agglomerate mixture of its constituent materials.

Preferably, the amount of primary component comprises at least 40 wt.% based on the total weight of the agglomerate precursor, more preferably at least 50 wt.%, more preferably at least 70 wt.%, more preferably at least 80 wt.% and more preferably at least 90 wt.%.

Preferably, the amount of blowing agent is in the range of 0.05 to 10 wt.% based on the total weight of the agglomerate precursor, more preferably 0.1 to 6 wt.%, more preferably 0.2 to 4 wt.%. The exact amount of blowing agent will depend on the composition of the primary component, the type of blowing agent and the required density of the final microsphere.

The preferred ratio of primary component to blowing agent will vary, depending on the composition of each of these ingredients. Typically, the ratio of primary component to blowing agent will be in the range of 1000:1 to 10:1, more preferably, 700:1 to 15:1, and more preferably 500:1 to 20:1.

Preferably, the agglomerate precursor has a water content of less than about 14 wt.%, more preferably less than about 10 wt.%, more preferably less than about 5 wt.%, and more preferably about 3 wt.% or less. It was found that with 14 wt.% water or more in the agglomerate precursor, the agglomerate tends to burst into fines during firing. It is understood by the present inventors that this bursting is caused by rapid steam explosion in the presence of too much water.

Hence, the agglomerate precursor is essentially dry, although a small amount of residual moisture may be present in the agglomerate precursor after a solution-based process for forming the precursor (*e.g.* the solution-based processes for forming an agglomerate precursor described below). Indeed, a small amount of water may help to bind particles in the agglomerate together, especially in cases where particles in the agglomerate precursor are water-reactive. Furthermore, a small amount of water may also act as a partial blowing agent by release of some H_2O gas during firing.

Preferably, the agglomerate precursor has a total alkali metal oxide content of up to about 10 wt.%, and typically in the range of 2 to 10 wt.%, 3 to 10 wt.%, 4 to 10 wt.% or 5 to 10 wt.%. A total alkali metal oxide content of less than about 10 wt.% is advantageous, because microspheres formed from such agglomerate precursors will still have acceptably high chemical durability suitable for most applications.

Preferably, the agglomerate is particulate, having an average agglomerate particle size in the range of 10 to 1000 microns, more preferably 30 to 1000 microns, and more preferably 40 to 500 microns.

Primary Component

Preferably, the primary component is a low alkali material. By "low alkali material", it is meant a material having an alkali metal oxide content of less than 10 wt.%, more preferably less than 8 wt.%, and more preferably less than 5 wt.%. In this preferred form of the present invention, relatively high alkali materials may still be included in the primary component. Accordingly, waste glass powders, such as soda lime glasses (sometimes referred to as cullet) having an alkali content of up to about 15 wt.% may be included in the primary component. However, when combined with other low alkali primary component(s), the overall alkali concentration of the primary component should be less than 10 wt.% in this preferred form of the invention.

Hitherto, it was believed that relatively large amounts of alkali metal oxides were required to act as a fluxing agent in forming glass microspheres from alkali metal silicates (see, for example, US 3,365,315). However, the present inventors have found that using the method of the present invention, synthetic microspheres may be formed from commonly available sources of low alkali content aluminosilicate raw materials without the need for large quantities of additional alkali metal oxides. This will be described in more detail below.

Aluminosilicate materials are well known to the person skilled the art. Generally, these are materials having a large component (*i.e.* greater than about 50% wt.%, preferably greater than about 60 wt.%) of silica (SiO_2) and alumina (Al_2O_3). However, the skilled person will readily understand those materials classed as "aluminosilicates".

The amounts of silica and alumina in the aluminosilicate material will vary depending on the source and may even vary within the same source. Fly ash, for example, will contain varying amounts of silica and alumina depending on the type of coal used and combustion conditions. Preferably, the mass ratio of silica (SiO_2) to alumina (Al_2O_3) is greater than about 1 in the aluminosilicate materials used in the present invention.

Typically, aluminosilicate materials for use in the present invention have a composition of 30 to 85 wt.% SiO_2; 2 to 45 wt.% (preferably 6 to 45 to wt.%) Al_2O_3; up to about 30 wt.% (preferably up to about 15 wt.%) divalent metal oxides (*e.g.* MgO, CaO, SrO, BaO); up to about 10 wt.% monovalent metal oxides (*e.g.* Li_2O, Na_2O, K_2O); and up to about 20 wt.% of other metal oxides, including metal oxides which exist in multiple oxidation states (*e.g.* TiO_2, Fe_2O_3 *etc.*).

The method of the present invention is not limited to any particular source of aluminosilicate material. However, the primary component preferably comprises at least one aluminosilicate material selected from fly ash (*e.g.* Type F fly ash, Type C fly ash *etc.*), bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, aluminosilicate clays (*e.g.* kaolinite clay, illite clay, bedalite clay, bentonite clay, china, fire clays *etc.*), bauxite, obsidian, volcanic ash, volcanic rocks, volcanic glasses, geopolymers or combinations thereof. More preferably, the primary component comprises fly ash, andesitic rock, basaltic rock and/or an aluminosilicate clay.

The aluminosilicate material may be either calcined or non-calcined. The term "calcined" means that the aluminosilicate material has been heated in air to a predetermined calcination temperature for a predetermined duration so as to either oxidise or pre-react certain component(s) of the aluminosilicate material. Calcination of the aluminosilicate material may be advantageous in the present invention since the blowing (expansion) process can be sensitive to the redox state of multivalent oxide(s) present in the aluminosilicate material. Without wishing to be bound by theory, it is believed that activation of the blowing agent is influenced by the release of oxygen from the multivalent oxide(s) present in the aluminosilicate material (*e.g.* by redox reaction). As an example, a carbonaceous blowing agent may be oxidised to CO_2 by ferric oxide (Fe_2O_3), which is in turn reduced to ferrous oxide (FeO). The release of CO_2 from the blowing agent expands the microsphere. Hence, by pre-calcinating the aluminosilicate material in air, the relative amount of ferric oxide is increased, which is then used as a source of oxygen for blowing agents to produce more gas, thereby lowering the density of the microspheres.

In addition, calcination can promote pre-reaction of oxide components and/or cause partial vitrification in the aluminosilicate material, which may be beneficial in the production of high quality microspheres.

Fly ash is a particularly preferred aluminosilicate primary component due to its low cost and wide availability. In one preferred form of the invention, the primary component comprises at least 5 wt.% fly ash, and more preferably at least 10 wt.% fly ash, based on the total amount of primary component. In another preferred form, the primary component comprises at least 50 wt.% fly ash, more preferably at least 70 wt.% fly ash, and more preferably at least 90 wt.% fly ash, based on the total amount of primary component. In some embodiments of the present invention, the primary component may be substantially all fly ash.

Fly ash may also be used in the form of a fly ash geopolymer, which is formed when fly ash is contacted with an aqueous solution of a metal hydroxide (*e.g.* NaOH or KOH). Fly ash geopolymers are well known in the art.

Preferably, the at least one aluminosilicate material comprises an amorphous phase and is either partially or wholly amorphous.

Preferably, the at least one aluminosilicate material has an average primary particle size in the range of 0.01 to 100 microns, more preferably 0.05 to 50 microns, more preferably 0.1 to 25 microns, and more preferably 0.2 to 10 microns. Preferred particle sizes may be achieved by appropriate grinding and classification. All types of grinding, milling, and overall size reduction techniques that are used in ceramic industry can be used in the present invention. Without limiting to other methods of size reduction used for brittle solids, preferred methods according to the present invention are ball milling (wet and dry), high energy centrifugal milling, jet milling, and attrition milling. If more than one aluminosilicate material is to be used, then the multitude of ingredients can be co-ground together. In one method of the present invention, the blowing agent and, optionally the binding agent, are added to the aluminosilicate material before the milling process. For example, all the ingredients can be co-ground together (*e.g.* in a wet ball mill), which then eliminates the aqueous mixing.

Typically, the majority of the primary component is the at least one aluminosilicate material. It is generally preferred the amount of the aluminosilicate material(s) is at least 50 wt.%, more preferably at least 70 wt.%, and more preferably at least 90 wt.%, based on the total weight of the primary component. In some cases, the primary component comprises substantially all aluminosilicate material(s).

However, in an alternative embodiment of the present invention, the primary component may include waste material(s) and/or other glass-forming material(s) in addition to the at least one aluminosilicate material. Typical waste materials or other glass-forming material which may be used in this alternative embodiment are waste glasses (*e.g.* soda lime glasses, borosilicate glasses or other waste glasses), waste ceramics, kiln dust, waste fibre cement, concrete, incineration ash, diatomaceous earth, silica sand, silica fume or combinations thereof. The total amount of waste material and/or other glass-forming material may be up to about 50 wt.% (*e.g.* up to about 40 wt.%, up to about 30 wt.%, or up to about 20 wt.%), based on the weight of the primary component. As stated above, it is preferred that the total amount of alkali metal oxide in primary component mixtures of this type is still less than about 10 wt.%.

Blowing Agent

The blowing agent used in the present invention is a substance which, when heated, liberates a blowing gas by one or more of combustion, evaporation, sublimation, thermal decomposition, gasification or diffusion. The blowing gas may be, for example, CO_2, CO, O_2, H_2O, N_2, N_2O, NO, NO_2, SO_2, SO_3 or mixtures thereof. Preferably, the blowing gas comprises CO_2 and/or CO.

Preferably, the blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates (*e.g.* sugar, starch *etc.*), PVA (polyvinyl alcohol), carbonates, carbides (*e.g.* silicon carbide, aluminium carbide, boron carbide *etc.*), sulfates, sulfides, nitrides (*e.g.* silicon nitride, aluminium nitride, boron nitride *etc.*), nitrates, amines, polyols, glycols or glycerine. Carbon black, powdered coal, sugar and silicon carbide are particularly preferred blowing agents.

Preferably, and particularly if the blowing is non-water soluble, the blowing agent has an average particle size in the range of 0.01 to 10 microns, more preferably 0.5 to 8 microns, and more preferably 1 to 5 microns.

Binding Agent

In a preferred embodiment of the present invention, the agglomerate precursor further includes a binding agent (or binder). The primary function of the binding agent is to intimately bind the particles in the agglomerate together.

In some instances, the binding agent may act initially to bind particles of the agglomerate together during formation of the agglomerate precursor, and then act as a blowing agent during subsequent firing.

In general, any chemical substance that is reactive and/or adheres with the aluminosilicate primary component can be used as the binding agent. The binder may be any commercially available material used as a binder in the ceramic industry.

Preferably, the binding agent is selected from alkali metal silicates (*e.g.* sodium silicate), alkali metal aluminosilicates, alkali metal borates (*e.g.* sodium tetraborate), alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides (*e.g.* NaOH, KOH or $Ca(OH)_2$), carbohydrates (*e.g.* sugar, starch *etc.*), colloidal silica, inorganic silicate cements, Portland cement, alumina cement, lime-based cement, phosphate-based cement, organic polymers (*e.g.* polyacrylates) or combinations thereof. In some cases, fly ash, such as ultrafine, Type C or Type F fly ash, can also act as a binding agent.

The binding agent and blowing agent are typically different from each other, although in some cases (*e.g.* sugar, starch *etc.*) the same substance may have dual blowing/binding agent properties.

The term “binder” or “binding agent”, as used herein, includes all binding agents mentioned above, as well as the *in situ* reaction products of these binding agents with other components in the agglomerate. For example, an alkali metal hydroxide (*e.g.* NaOH) will react *in situ* with at least part of the aluminosilicate material to produce an alkali metal aluminosilicate. Sodium hydroxide may also form sodium carbonate when exposed to ambient air containing CO_2, the rate of this process increasing at higher temperatures (*e.g.* 400°C). The resulting sodium carbonate can react with the aluminosilicate material to form sodium aluminosilicate.

Preferably, the amount of binding agent is in the range of 0.1 to 50 wt.% based on the total weight of the agglomerate precursor, more preferably 0.5 to 40 wt.% and more preferably 1 to 30 wt.%.

It has been unexpectedly found that the properties of the binder, and in particular its melting point, affect the properties of the resulting microspheres. Without wishing to be bound by theory, it is understood by the present inventors that the binder is responsible for forming a molten skin around the agglomerate precursor during or prior to activation of the blowing agent in the firing step (b). Hence, in a preferred form of the present invention, the binding agent has a melting point which is lower than the melting point of the whole agglomerate precursor. Preferably, the binding agent has a melting point which is less than 1200°C, more preferably less than 1100°C, and more preferably less than 1000°C (*e.g.* 700 to 1000°C).

It has also been unexpectedly found that the degree of crystallinity in the binder phase can have a pronounced effect on the formation kinetics of the molten skin. The degree of crystallinity at a given temperature may be readily determined from the phase diagram of oxides present in the mixture. In a simple binary system of SiO_2 and Na_2O, there are three eutectic points, with the lowest one having a liquidus temperature of about 790°C and a SiO_2 to Na_2O ratio of about 3. As sodium oxide concentration is increased, the liquidus temperature increases sharply, to about 1089°C at a SiO_2:Na_2O ratio of 1:1. This can be seen from the phase diagram of SiO_2-Na_2O in Figure 1. Other alkali metal oxides behave similarly to sodium oxide. For example, the K_2O-SiO_2 system has also several eutectics points, with the lowest at about 750°C occurring at a SiO_2 to K_2O ratio of about 2.1. Similarly Li_2O has several eutectics with one at 1028°C and a ratio of about 4.5.

In standard glass technology, sodium oxide is known to be a strong fluxing agent. Its addition to silicate glasses lowers the melting point and viscosity of the glass. For example, in a typical soda lime glass composition, there is about 15 wt.% sodium oxide, which lowers the melting temperature of SiO_2 from 1700°C to less than 1400°C. However, in melting commercial glasses, enough time is given for the melt to reach the equilibrium concentration throughout the glass mass, normally in the order of hours or longer. Thus, in standard glass technology, sufficient sodium oxide and/or other fluxing agents are added so that the *whole* melt has the requisite viscosity-temperature characteristics.

However, without wishing to be bound by theory, it is understood by the present inventors that, under the fast reaction kinetics of firing (with a temperature increase as fast as 2000°C/second), the critical requirement for rapid formation a molten skin around the agglomerate precursor is rapid melting of the *binder* component. Hence, it is preferred that the binder (present as, for example, sodium silicate or sodium aluminosilicate) has a eutectic or near eutectic composition. Preferably, the binder is sodium silicate having a SiO_2:Na_2O ratio in the range of 5:1 to 1:1, more preferably 4:1 to 1.5:1, more preferably 3.5:1 to 2:1. It will be appreciated that other alkali metal oxides (*e.g.* Li_2O, K_2O) can have the same effect in the binder. However, Na_2O is preferred due to its low cost.

It was unexpectedly found that when sodium silicate with a 1:1 ratio of SiO_2:Na_2O was used as binder to formulate the agglomerate precursor, relatively dense microspheres with a particle density of about 1.0 g/cm^3 resulted. However, sodium silicate binder with a SiO_2:Na_2O ratio of about 3:1 resulted in microspheres having a lower density of about 0.7 g/cm^3. In both cases, the overall concentration of Na_2O

relative to the agglomerate was the same. Under the principles of traditional glass-making technology, it would have been expected there would be little or no difference in the final products when using the same amount of fluxing agent. However, the present inventors have found that using a eutectic or near eutectic composition in the *binder*, a molten skin is formed rapidly during firing, and low density microspheres result, irrespective of the *total* amount of fluxing agent in the agglomerate.

Equally unexpected, it was found that sodium hydroxide showed the same trend. Sodium oxide, when used as a binder, reacts with silica present in aluminosilicate powders to a form a compound of sodium silicate. As more sodium hydroxide is added, the ratio of silica to sodium oxide is lowered, resulting in binders with progressively higher melting temperatures.

Furthermore, the properties of the synthetic microspheres may also be dependent on the drying temperature of the agglomerate, and to some extent, the pressure. For example, a high drying temperature favours formation of sodium silicate having a lower SiO_2:Na_2O ratio, thereby giving a binder having a higher melting temperature. For example, about 5 wt.% of NaOH was found to be an appropriate amount of binder for forming low density microspheres when the agglomerate was dried at about 50°C. However, an identical formulation resulted in higher density microspheres when the agglomerate was dried at 400°C. It was surprisingly found that, when the agglomerate was dried at 400°C, a lower concentration of NaOH (*e.g.* 2-3 wt.%) was required to produce low density microspheres.

Traditionally, it was believed that a relatively high amount (*e.g.* 15 wt.%) of sodium oxide was necessary in glass-making technology to act as a fluxing agent. However, in the present invention, it was surprisingly found that relatively high amounts of sodium oxide are less preferred.

The agglomerate precursor may also include surfactants, which assist in dispersion of the agglomerate precursor components into an aqueous solution or paste. The surfactants may be anionic, cationic or non-ionic surfactants.

Firing Conditions

Preferably, the temperature profile used in the present invention fuses the precursor into a melt, reduces the viscosity of the melt, seals the surface of the precursor and promotes expansive formation of gas within the melt to form bubbles. The temperature profile should also preferably maintain the melt at a temperature and time sufficient to allow gas bubbles to coalesce and form a single primary void. After foaming, the newly expanded particles are rapidly cooled, thus forming hollow glassy microspheres. Accordingly, the temperature profile is preferably provided by a furnace having one or more temperature zones, such as a drop tube furnace, a vortex type furnace, a fluidised bed furnace or a fuel fired furnace, with upward or downward draft air streams. A fuel fired furnace used in the method of present invention includes furnace types in which agglomerated precursors are introduced directly into one or a multitude of combustion zones, to cause expansion or blowing of the particles. This is a preferred type of furnace, since the particles benefit by direct rapid heating to high temperatures, which is desirable. The heat source may be electric or provided by burning fossil fuels, such as natural gas or fuel oil. However, the preferred method of heating is by combustion of natural gas, since this is more economical than electric heating and cleaner than burning fuel oil.

Typically, the peak firing temperature in firing step (b) is in the range of 600 to 2500°C, more preferably 800 to 2000°C, more preferably 1000 to 1500°C, and more preferably 1100 to 1400°C. However, it will be appreciated that the requisite temperature profile will depend on the type of aluminosilicate primary component and blowing agent used.

Preferably, the exposure time to the peak firing temperature described above will be for a period of 0.05 to 20 seconds, more preferably 0.1 to 10 seconds.

Synthetic Hollow Microspheres

The present invention provides a synthetic hollow microsphere comprising an aluminosilicate material, wherein the average particle size of said microsphere is in the range of 30 to 1000 microns, and the total alkali metal oxide content of said microsphere is in the range of 2 to 10 wt.%, based on the total weight of the microsphere.

The synthetic hollow microspheres of the present invention may contain several alkali metal oxides, typically a combination of Na_2O and K_2O, which make up the total alkali metal oxide content. Preferably, the total alkali metal oxide content is in the range of 3 to 9 wt.%, and more preferably 4 to 8 wt.%, based on the total weight of the microsphere. In some embodiments, the total alkali metal oxide content of the synthetic microspheres is in the range of 4 to 6 wt.% or 5 to 8 wt.%, based on the total weight of the microsphere.

Preferably, the amount of sodium oxide in the synthetic hollow microspheres is in the range of 1 to 10 wt.%, more preferably 2 to 10 wt.%, more preferably, 3 to 9 wt.%, more preferably 4 to 8 wt.% and more preferably 4 to 7 wt.%, based on the total weight of the microsphere. A portion of sodium oxide in the synthetic hollow microspheres is typically derived from the binding agent containing sodium compounds, such as sodium silicate or sodium hydroxide.

The synthetic microspheres of the present invention have several advantages over microspheres known in the art. Firstly, the microspheres comprise an aluminosilicate material. Aluminosilicates are inexpensive and widely available throughout the world, for example from a large variety of rocks, clays and minerals and also from waste by-products, particularly bottom ash and fly ash. It is particularly advantageous that the synthetic hollow microspheres of the present invention can be prepared from fly ash. Secondly, the presence of moderate quantities of alkali metal oxide enables microspheres with consistent properties to be produced synthetically from waste materials, such as fly ash. Thirdly, the presence of only moderate quantities of alkali metal oxide means that the microspheres have acceptably high chemical durability and can be used in the same situations as known cenospheres. It has been recognised by the present inventors that the extremely low levels of alkali metal oxide, and consequent very high chemical durability of harvested cenospheres, are not essential for most applications of cenospheres. Synthetic hollow microspheres according to the preferred forms of the present invention can withstand highly caustic environments and harsh autoclaving conditions. By contrast, synthetic microspheres produced according to methods known in the prior art generally contain high amounts of alkali metal oxides and have unacceptably low chemical durability.

Furthermore, an average particle size of between 30 and 1000 microns is advantageous, because such particles are not considered to be respirable dusts.

Synthetic hollow microspheres according to the present invention typically comprise a substantially spherical wall with a closed shell (void) structure. The synthetic hollow microspheres preferably have one or more of the following characteristics, which are also generally characteristics of harvested cenospheres:

(i) an aspect ratio of between about 0.8 and 1.

(ii) a void volume of between about 30 and 95%, based on the total volume of the microsphere;

(iii) a wall thickness of between about 5 and 30% of the microsphere radius;

(iv) a composition of 30 to 85 wt.% SiO_2, 2 to 45 wt.% (preferably 6 to 40 wt.%) Al_2O_3, up to about 30 wt.% divalent metal oxides (*e.g.* MgO, CaO, SrO, BaO), 2 to 10 wt.% monovalent metal oxides (*e.g.* Na_2O, K_2O), and up to about 20 wt.% of other metal oxides, including metal oxides which exist in multiple oxidation states (*e.g.* TiO_2, Fe_2O_3 *etc.*);

(v) a silica to alumina ratio which is greater than about 1;

(vi) an average diameter of between 30 and 1000 microns, more preferably between 40 and 500 microns;

(vii) an outer wall thickness of between 1 and 100 microns, preferably between 1 and 70 microns, more preferably between 2.5 and 20 microns;

(viii) a particle density of between 0.1 and 2.0 g/cm^3, more preferably between 0.2 and 1.5 g/cm^3, and more preferably between 0.4 and 1.0 g/cm^3; or

(ix) a bulk density of less than about 1.4 g/cm^3, preferably less than about 1.0 g/cm^3.

Use of Synthetic Hollow Microspheres

The synthetic hollow microspheres according to the present invention may be used in a wide variety of applications, for example, in filler applications, modifier applications, containment applications or substrate applications. The scope of applications is much greater than that of harvested cenospheres due to the low cost and consistent properties of synthetic microspheres.

Synthetic microspheres according to the present invention may be used as fillers in composite materials, where they impart properties of cost reduction, weight reduction, improved processing, performance enhancement, improved machinability and/or improved workability. More specifically, the synthetic microspheres may be used as fillers in polymers (including thermoset, thermoplastic, and inorganic geopolymers), inorganic cementitious materials (including material comprising Portland cement, lime cement, alumina-based cements, plaster, phosphate-based cements, magnesia-based cements and other hydraulically settable binders), concrete systems (including precise concrete structures, tilt up concrete panels, columns, suspended concrete structures etc.), putties (*e.g.* for void filling and patching applications), wood composites (including particleboards, fibreboards, wood/polymer composites and other composite wood structures), clays, and ceramics. One particularly preferred use of the microspheres according to the present invention is in fibre cement building products.

The synthetic microspheres may also be used as modifiers in combination with other materials. By appropriate selection of size and geometry, the microspheres may be combined with certain materials to provide unique characteristics, such as increased film thickness, improved distribution, improved flowability *etc.* Typical modifier applications include light reflecting applications (*e.g.* highway markers and signs), industrial explosives, blast energy absorbing structures (*e.g.* for absorbing the energy of bombs and explosives), paints and powder coating applications, grinding and blasting applications, earth drilling applications (*e.g.* cements for oil well drilling), adhesive formulations and acoustic or thermal insulating applications.

The synthetic microspheres may also be used to contain and/or store other materials. Typical containment applications include medical and medicinal applications (e.g. microcontainers for drugs), micro-containment for radioactive or toxic materials, and micro-containment for gases and liquids.

The synthetic microspheres may also be used in to provide specific surface activities in various applications where surface reactions are used (*i.e.* substrate applications). Surface activities may be further improved by subjecting the synthetic microspheres to secondary treatments, such as metal or ceramic coating, acid leaching *etc.* Typical substrate applications include ion exchange applications (for removing contaminants from a fluid), catalytic applications (in which the surface of the microsphere is treated to serve as a catalyst in synthetic, conversion or decomposition reactions), filtration (where contaminants are removed from gas or liquid streams), conductive fillers or RF shielding fillers for polymer composites, and medical imaging.

Method of Forming Agglomerate Precursor

As described above, the present invention also provides a method of preparing an agglomerate precursor.

Preferably, the amount of primary component is greater than about 40 wt.% based on the total dry weight of the agglomerate precursor. Preferably, the amount of blowing agent is less than about 10 wt.% based on the total dry weight of the agglomerate precursor. Further preferred forms of the primary component and blowing agent are described above.

Preferably, a binding agent is additionally mixed with the primary component and the blowing agent in mixing step (b). Preferably, the amount of binding agent is in the range of 0.1 to 50 wt.%, based on the total dry weight of the agglomerate precursor. Further preferred forms of the binding agent are described above.

Other additives (*e.g.* surfactants) may be added in mixing step (b), as appropriate. Surfactants may used to assist with mixing, suspending and dispersing the particles.

Typically, the mixing step (b) provides an aqueous dispersion or paste, which is dried in step (c). Mixing can be performed by any conventional means used to blend ceramic powders. Examples of preferred mixing techniques include, but are not limited to, agitated tanks, ball mills, single and twin screw mixers, and attrition mills.

Drying may be performed at a temperature in the range of 30 to 600°C and may occur over a period of up to about 48 hours, depending on the drying technique employed. Any type of dryer customarily used in industry to dry slurries and pastes may be used in the present invention. Drying may be performed in a batch process using, for example, a stationary dish or container. Alternatively, drying may be performed in a fluid bed dryer, rotary dryer, rotating tray dryer, spray dryer or flash dryer. Alternatively, drying may be performed using a microwave oven. It will be readily appreciated that the optimum drying period will depend on the type of drying method employed.

When drying is performed in a stationary dish or container, it is preferred that the drying temperature is initially not set too high in order to avoid water boiling violently and thus spewing solids out of the drying container. In this case, the drying temperature, at least initially, is preferably in the range of 30 to 100°C, and more preferably 40 to 80°C to avoid initial, rapid boiling of water. However, after initial evaporation of water, the drying temperature may be increased to temperatures up to about 350°C, which completes the drying process more speedily.

Preferably, the method of forming the agglomerate precursor comprises the further step of (d) comminuting the dried mixture from step (c) to form agglomerate precursor particles of a predetermined particle size range. The drying and comminuting may be performed in a single step.

Preferably, the dried mixture is comminuted to provide agglomerate precursor particles having an average particle size in the range of 10 to 1000 microns, more preferably 30 to 1000 microns, more preferably 40 to 500 microns, and more preferably 50 to 300 microns.

The particle size of the agglomerate precursor will be related to the particle size of the resultant synthetic hollow microsphere, although the degree of correspondence will, of course, only be approximate.

It is preferred that the present invention provides synthetic hollow microspheres having a controlled particle size distribution. Accordingly, the comminuted agglomerate precursor may be classified to a predetermined particle size distribution. Alternatively, a controlled particle size distribution in the agglomerate precursor may be achieved by the use of spray dryer in the drying step. Spray drying has the additional advantage of allowing a high throughput of material and fast drying times. Hence, in a preferred embodiment of the present invention, the drying step (c) is performed using a spray dryer. Spray dryers are described in a number of standard textbooks (*e.g. Industrial Drying Equipment*, C.M. van't Land; *Handbook of Industrial Drying 2nd Edition*, Arun S. Mujumbar) and will be well known to the skilled person. The use of a spray dryer in the present invention has been found to substantially eliminate the need for any sizing/classification of the agglomerate precursor.

Preferably, the aqueous slurry feeding the spray dryer comprises 20 to 80 wt.% solids, more preferably 25 to 75 wt.% solids, and more preferably 50 to 70 wt.% solids.

In addition to the agglomerate ingredients described above, the slurry may contain further processing aids or additives to improve mixing, flowability or droplet formation in the spray dryer. Suitable additives are well known in the spray drying art. Examples of such additives are sulphonates, glycol ethers, hydrocarbons, cellulose ethers and the like. These may be contained in the aqueous slurry in an amount ranging from 0 to 5 wt.%.

In the spray drying process, the aqueous slurry is typically pumped to an atomizer at a predetermined pressure and temperature to form slurry droplets. The atomizer may be, for example, an atomizer based on a rotating disc (centrifugal atomization), a pressure nozzle (hydraulic atomization), or a two-fluid pressure nozzle wherein the slurry is mixed with another fluid (pneumatic atomization). The atomizer may also be subjected to cyclic mechanical or sonic pulses.

The atomization may be performed from the top or from the bottom of the dryer chamber. The hot drying gas may be injected into the dryer co-current or counter-current to the direction of the spraying.

The atomized droplets of slurry are dried in the spray dryer for a predetermined residence time. Typically, the residence time in the spray dryer is in the range of 0.1 to 10 seconds, with relatively long residence times of greater than 2 seconds being generally more preferred.

Preferably, the inlet temperature in the spray dryer is in the range of 300 to 600°C and the outlet temperature is in the range of 100 to 220°C.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to the following drawings in which:

Figure 1 is a phase equilibrium diagram for binary system Na_2O-SiO_2, the composition being expressed as a weight percentage of SiO_2.

Figure 2 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 1 (Sample 1).

Figure 3 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 1 (Sample 2).

Figure 4 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 1 (Sample 3).

Figure 5 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 2 (Sample 4).

Figure 6 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 2 (Sample 5).

Figure 7 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 2 (Sample 6).

Figure 8 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 3 (Sample 7).

Figure 9 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 4 (Sample 12).

Figure 10 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 4 (Sample 13).

Figure 11 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 5.

Figure 12 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 5.

Figure 13 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 5.

Figure 14 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 6.

Figure 15 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 6.

Figure 16 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 8 (Sample 14).

Figure 17 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 8 (Sample 15).

Figure 18 is a scanning electron micrograph of synthetic hollow microspheres obtained from Example 8 (Sample 16).

Figure 19 is a schematic representation of an agglomerate precursor.

Detailed Description of Preferred Embodiments

EXAMPLE 1

This example illustrates a method of making synthetic microspheres from formulations consisting of fly ash, sodium silicate, and sugar.

Three samples were made by mixing a type F fly ash (ground to an average size of 5.4 microns) with a commercial grade sodium silicate solution (SiO_2/Na_2O is 3.22, 40% solid content), a commercial grade sugar, and water. The amounts of ingredients are given in Table 1. The composition of fly ash is given in Table 2. The mixtures were blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting products were further dried at about 50°C for about 20 hours, after which they were ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, for each sample, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace was 1 litre of air plus 3 litres of nitrogen per minute.

The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately a few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (apparent density), percent of water flotation, and approximate particle size distribution. The results for various firing temperatures and residence times are summarized in Table 3. Figures 2 to 4 show the cross sections of the products obtained from Samples 1, 2 and 3 respectively.

Table 1.

Sample No.	Fly ash	Sodium silicate solution	Sugar	Water
1	93.1	58.0	3.6	7.0
2	104.8	29.1	3.6	19.2
3	108.0	21.0	3.6	21.0

All masses are in grams

Table 2.

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Mn_2O_3	P_2O_5	Tota
0.39	50.63	21.14	7.62	12.39	3.61	0.66	0.63	1.27	1.30	0.17	0.14	99.9

All amounts are in percentage of weight

Table 3.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
1	1300	0.6-1.1	0.64	81	100-275
1	1300	0.8-1.5	0.78		
2	1300	0.6-1.1	0.87	55	110-240
3	1300	0.6-1.1	1.05		75-225

Apparent density and particle density are the same.

EXAMPLE 2

This example illustrates a method of making synthetic microspheres from formulations consisting of fly ash, sodium silicate, and carbon black.

Three samples were made by mixing a type F fly ash (ground to an average size of 5.4 microns) with a commercial grade sodium silicate solution (SiO_2/Na_2O is 3.22, 40% solid content), a commercial grade carbon black, and water. The amounts of ingredients are given in Table 4. The composition of fly ash is given in Table 2. Each mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting products were further dried at about 50°C for about 20 hours, after which they were ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, for each sample, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately a few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (e.g. apparent density), percent of water floatation, and approximate particle size distribution. The results for various firing temperatures and residence times are summarized in Table 5. Figures 5 to 7 show the cross sections of the products obtained from Samples 4, 5 and 6 respectively.

Table 4.

Sample No.	Fly ash	Sodium silicate solution	Carbon black	Water
4	95.0	59.0	1.2	7.1
5	100.8	45.0	1.2	18.4
6	106.8	30.0	1.2	30.1

All masses are in grams

Table 5.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
4	1300	0.6-1.1	0.87	70	100-275
5	1300	0.6-1.1	0.75	71	100-275
6	1300	0.6-1.1	0.86	67	110-260

EXAMPLE 3

This example illustrates a method of making synthetic microspheres form formulations consisting of fly ash, sodium hydroxide, and carbon black.

Three samples were made by mixing a type F fly ash (ground to an average size of 5.4 microns) with a commercial grade solid sodium hydroxide (flakes), a commercial grade carbon black, and water. The amounts of ingredients are given in Table 6. The composition of fly ash is given in Table 2. Each mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting products were further dried at about 50°C for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (e.g. apparent density), percent of water floatation, and approximate particle size distribution. The results are summarized in Table 7. Figure 8 shows the cross section of the product obtained from Sample 7.

Table 6.

Sample No.	Fly ash	Sodium hydroxide	Carbon black	Water
7	112.8	6.0	1.2	39.5
8	116.4	2.4	1.2	46.6
9	117.6	1.2	1.2	47.0

All masses are in grams

Table 7.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
7	1300	0.6-1.1	0.65	77	85-290
8	1300	0.6-1.1	0.76		
9	1300	0.6-1.1	0.78	66	

<u>*EXAMPLE 4*</u>

This example illustrates a method to make synthetic microspheres form formulations consisting of fly ash, basalt, sodium hydroxide, and carbon black.

94 grams of a type F fly ash and basalt co-ground to an average size of 3.7 microns were mixed with 5 grams of solid sodium hydroxide (flakes), 1 gram of a commercial grade carbon black, and 38 ml of water. Several samples were made by changing the proportions of basalt to fly ash as shown in Table 8. The compositions of fly ash and basalt are given in Tables 2 and 9 respectively. Each mixture was blended into an homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting product was further dried at about 50°C for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen

positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (e.g. apparent density), percent of water floatation, and approximate particle size distribution. The results are summarized in Table 10. Figures 9 and 10 show the cross section of the products of Samples 12 and 13 respectively.

Table 8.

Sample No.	Fly ash	Basalt	Sodium hydroxide	Carbon black	Water
10	75.2	18.8	5.0	1.0	38.0
11	56.4	37.6	5.0	1.0	38.0
12	37.6	56.4	5.0	1.0	38.0
13	18.8	75.2	5.0	1.0	38.0

All masses are in grams

Table 9.

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Mn_2O_3	P_2O_5	Tota
0	46.13	15.81	9.50	9.50	9.60	0	2.78	1.53	2.38	0.25	0.59	98.0

All amounts are in percentage of weight

Table 10.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
10	1300	0.8-1.5	0.76	62	
11	1300	0.8-1.5	0.77	63	
12	1300	0.8-1.5	0.76	65	100-250
13	1300	0.8-1.5	1.00	44	100-225

EXAMPLE 5

This example illustrates a method to make synthetic microspheres form a formulation consisting of basalt, sodium hydroxide, and silicon carbide.

93.5 grams of basalt ground to an average size of 3.7 microns was mixed with 5 grams of a commercial grade solid sodium hydroxide (flakes), 1.5 grams of a commercial grade silicon carbide, and 37.4 ml of water. The composition of basalt is given in table 9. The mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting product was further dried at about 50°C for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (e.g. apparent density), percent of water floatation, and approximate particle size distribution. The results for various firing temperatures and residence times are summarized in Table 11. Figures 11-13 show the cross section of the products obtained at 1300°C, 1250°C and 1200°C respectively.

Table 11.

Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
1300	0.6-1.1	0.61		
1250	0.6-1.1	0.56	86	130-260
1200	0.6-1.1	0.59		85-195
1150	0.6-1.1	1.21		105-240

EXAMPLE 6

This example illustrates a method to make synthetic microspheres form a formulation consisting of fly ash, sodium hydroxide, and silicon carbide.

93.5 grams of a type F fly ash ground to an average size of 3.2 microns was mixed with 5 grams of solid sodium hydroxide (flakes), 1.5 grams of a commercial grade silicon carbide, and 37.4 ml of water. The composition of the fly ash is given in Table 12. The mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting product was further dried at about 50°C for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (e.g. apparent density), percent of water floatation, and approximate particle size distribution. The results for various firing temperatures and residence times are summarized in Table 13. Figures 14 and 15 show the cross section of the products obtained at 1300°C and 1250°C respectively.

Table 12

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Mn_2O_3	P_2O_5	Total
0.40	61.53	17.91	4.72	7.30	2.91	0.40	2.16	1.39	0.86	0.08	0.28	99.94

All amounts are in percentage of weight

Table 13

Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
1400	0.6-1.1	0.52	83	
1300	0.6-1.1	0.49	96	130-280
1250	0.6-1.1	0.58		105-220

EXAMPLE 7

This example illustrates a method of making synthetic microspheres from a formulation consisting of fly ash, sodium hydroxide and carbon black.

A sample was prepared by mixing 94 grams of a type F fly ash (ground to an average particle size of 5.4 microns) with 5 grams of solid sodium hydroxide (flakes), 1 gram of a commercial grade carbon black, and 38 mL of water. The composition of fly ash is given in Table 2. The mixture was blended into homogeneous slurry, poured onto a concave watchglass that was then immediately placed inside a household microwave and covered with a larger watchglass. The slurry was dried in the microwave for four minutes using an intermittent power-on / power-off heating program, controlled to avoid excessive heating of the slurry. The resulting product was suitable for grinding and further sample preparation, however if necessary it could be held in an oven at about 50 degrees Celsius. After drying, the mixture was ground and sieved to obtain a powder within a size range of 106 to 180 microns. In the next step, the powder was fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace is 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace could be adjusted to provide residence times from less than a second to approximately a few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (apparent density) and approximate particle size distribution. The results of this sample (MW) are compared to those of sample 7 that is made of the same formulation but was dried at 50°C using a convection oven. Results are summarized in Tables 14 and 15.

Table 14.

Sample No.	Fly ash	Sodium hydroxide	Carbon black	Water
MW	112.8	6.0	1.2	39.5
7	112.8	6.0	1.2	39.5

Table 15.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Water float (%)	Size of microspheres (micron)
MW	1300	0.6-1.1	0.72		
7	1300	0.6-1.1	0.65	77	85-290

EXAMPLE 8

This example illustrates a method to make synthetic microspheres form a formulation consisting of green illite, sodium hydroxide, and carbon black.

112.86 grams of a green illite ground to an average size of 2 microns was mixed with 5.94 grams of solid sodium hydroxide (flakes), 1.2 grams of a commercial grade carbon black, and 86.8 ml of water. The composition of green illite is given in table 16. The mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for about 5 minutes. The resulting product was further dried at about 50 degree C for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 grams/min. The gas flow inside the tube furnace was 1 litre of air plus 3 litres of nitrogen per minute. The constant temperature zone of the furnace was adjusted to provide residence times from less than a second to approximately few seconds at the peak firing temperatures. The foamed microspheres were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom part of the furnace. A mild suction was applied to the end of funnel to aid in collecting the microspheres. The products were characterized for particle density (apparent density) and approximate particle size distribution. The results for various firing temperatures and residence times are summarized in Table 17. Figures 16, 17 and 18 show the cross sections of the products from Samples 14, 15 and 16 respectively.

Table 16.

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Mn_2O_3	P_2O_5	Tota

13.14	50.49	13.88	5.16	9.02	2.38	1.05	0.21	3.63	0.75	0.10	0.14	100

Table 17.

Sample No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm^3)	Size of microspheres (micron)
14	1200	0.8-1.5	1.50	120-240
15	1300	0.8-1.5	1.51	110-210
16	1400	0.8-1.5	1.51	90-200

EXAMPLE 9

The compositions (percentage of weight) of synthetic microspheres (“A” and “B”) according to the present invention were compared with a sample of commercially available harvested cenospheres. The results are shown in Table 18.

Table 18

Major Oxides	Harvested Cenosphere	Synthetic Microsphere “A”	Synthetic Microsphere “B”
SiO_2	62.5	58.9	65.8
Al_2O_3	25.2	17.1	12.8
Fe_2O_3	3.7	4.5	3.3
CaO	1.1	7.0	5.2
MgO	1.7	2.8	2.0
Na_2O	1.1	5.2	6.8
K_2O	1.9	1.3	1.0
SO_3	0.5	0.4	0.3
Others	2.3	2.8	2.8

EXAMPLE 10

This example shows typical spray drying conditions used to produce agglomerate precursors in the present invention.

Dryer:	Bowen Engineering, Inc. No 1 Ceramic Dryer fitted with a two-fluid nozzle type 59-BS
Air nozzle pressure:	about 20 psi
Cyclone vacuum:	about 4.5
Inlet/Outlet temperature:	about 550°C/120°C
Chamber vacuum:	about 1.6
Slurry solids:	about 50%

Agglomerate precursors produced using these spray drying conditions had a average particle size and particle size distribution suitable for forming synthetic hollow microspheres therefrom. Figure 19 shows schematically an agglomerate precursor having a primary component 1, a blowing agent 2, and a binder 3.

It will be appreciated that the present invention has been described by way of example only and the modifications of detail within the scope of the invention will be readily apparent to those skilled in the art.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of forming a synthetic hollow microsphere comprising the steps of:
   (a) preparing an agglomerate precursor, said agglomerate precursor including a primary component and a blowing agent; and
   (b) firing the precursor at a predetermined temperature profile sufficient to seal the surface of the precursor and activate the blowing agent thereby forming a synthetic hollow microsphere,

wherein the primary component comprises at least one aluminosilicate material.

2. The method of claim 1, wherein the amount of primary component is at least 40 wt.%, based on the total weight of the agglomerate precursor

3. The method of claim 1 or claim 2, wherein the amount of blowing agent is in the range of 0.05 to 10 wt.%, based on the total weight of the agglomerate precursor.

4. The method of any one of the preceding claims wherein the ratio of primary component to blowing agent is in the range of 1000:1 to 10:1

5. The method of any one of the preceding claims, wherein the agglomerate precursor has a water content of less than about 14 wt.%.

6. The method of any one of the preceding claims, wherein the agglomerate precursor is particulate, having an average agglomerate particle size in the range of 30 to 1000 microns.

7. The method of any one of the preceding claims, wherein the agglomerate precursor has a total alkali metal oxide content of up to about 10 wt.%.

8. The method of any one of the preceding claims, wherein the primary component comprises at least one aluminosilicate material selected from fly ash, bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, aluminosilicate clays,

bauxite, obsidian, volcanic ash, volcanic rocks, volcanic glasses, geopolymers or combinations thereof.

9. The method of any one of the preceding claims, wherein the at least one aluminosilicate material is fly ash.

10. The method of any one of the preceding claims, wherein the at least one aluminosilicate material is calcined.

11. The method of any one of the preceding claims, wherein the mass ratio of silica to alumina in the at least one aluminosilicate material is greater than about 1.

12. The method of any one of the preceding claims wherein the at least one aluminosilicate material comprises an amorphous phase.

13. The method of any one of the preceding claims, wherein the at least one aluminosilicate material has an average primary particle size in the range of 0.01 to 100 microns.

14. The method of the any one of the preceding claims, wherein the primary component further comprises at least one waste material and/or other glass-forming material.

15. The method of claim 14, wherein the at least one waste material and/or other glass-forming material is selected from waste glasses, waste ceramics, kiln dust, waste fibre cement, concrete, incineration ash, diatomaceous earth, silica sand, silica fume or combinations thereof.

16. The method of any one of the preceding claims, wherein the blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

17. The method of any one of the preceding claims, wherein the blowing agent is selected from silicon carbide, powdered coal, carbon black or sugar.

18. The method of any one of the preceding claims, wherein the blowing agent has an average particle size in the range of 0.01 to 10 microns.

19. The method of any one of the preceding claims, wherein the agglomerate precursor further includes a binding agent.

20. The method of claim 19, wherein the binding agent is selected from alkali metal silicates, alkali metal aluminosilicates, alkali metal borates, alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides, carbohydrates, colloidal silica, ultrafine fly ash, Type C fly ash, Type F fly ash, inorganic silicate cements, Portland cement, alumina cement, lime-based cement, phosphate-based cement, organic polymers or combinations thereof.

21. The method of claims 19 or 20, wherein the binding agent has a melting point which is lower than the melting point of the agglomerate precursor as a whole.

22. The method of any one of claims 19 or 21, wherein the binding agent has a melting point in the range of 700 to 1000°C.

23. The method according to any one claims 19 to 22, wherein the binding agent has a eutectic or near eutectic composition.

24. The method of claim 23, wherein the binding agent has a ratio of SiO_2 to Na_2O in the range of 5:1 to 1:1.

25. The method of any one of claims 19 to 24, wherein the binding agent is sodium silicate.

26. The method of any one of claims 19 to 23, wherein the binding agent is an alkali metal aluminosilicate generated by *in situ* reaction of an alkali metal hydroxide and the aluminosilicate material.

27. The method of any one of claims 19 to 26, wherein the amount of binding agent is in the range of 0.1 to 50 wt.%, based on the total weight of the agglomerate precursor.

28. The method of any one of the preceding claims, wherein the primary component, the blowing agent and, optionally the binding agent, are co-ground together such that the agglomerate precursor constituents all have a substantially equal average particle size.

29. The method of any one of the preceding claims, wherein the firing step (b) is performed at a temperature in the range of 600 to 2500°C for a period of 0.05 to 20 seconds.

30. The method of any one of the preceding claims, wherein a molten skin is formed around the precursor in the firing step (b).

31. The method of claim 30, wherein the blowing agent is activated during and/or after formation of the molten skin.

32. The method of claim 30 or 31, wherein a blowing gas is trapped inside the molten skin.

33. The method of any one of the preceding claims, wherein the firing step is performed in a fluidised bed reactor, a vortex furnace, heated vertical pipe or fuel fired furnace.

34. A synthetic hollow microsphere obtained or obtainable by a method according to any one of the preceding claims.

35. A synthetic hollow microsphere comprising an aluminosilicate material, wherein the average particle size of said microsphere is in the range of 30 to 1000 microns, and the total alkali metal oxide content of said microsphere is in the range of 2 to 10 wt.%, based on the total weight of the microsphere.

36. The synthetic hollow microsphere of claim 35, wherein the microsphere comprises sodium oxide in amount ranging from 1 to 10 wt.%.

37. The synthetic hollow microsphere of any one of claims 34 to 36 having one or more of the following characteristics:

(i) an aspect ratio of between about 0.8 and 1.

(ii) a void volume of between about 30 and 95%, based on the total volume of the microsphere;

(iii) a wall thickness of between about 5 and 30% of the microsphere radius;

(iv) a composition of 30 to 85 wt.% SiO_2, 2 to 45 wt.% Al_2O_3, up to about 30 wt.% divalent metal oxides, 2 to 10 wt.% alkali metal oxides, and up to about 20 wt.% of other metal oxides, including metal oxides which exist in multiple oxidation states;

(v) a silica to alumina ratio which is greater than about 1;

(vi) an average diameter of between 30 and 1000 microns;

(vii) an outer wall thickness of between 1 and 50 microns;

(viii) a particle density of between 0.1 and 2.0 g/cm^3; or

(ix) a bulk density of less than about 1.4 g/cm^3.

38. Use of a synthetic hollow microsphere according to any one of claims 34 to 37 in a filler application, a modifier application, a containment application or a substrate application.

39. Use according to claim 38, wherein the filler application is a filler in a composite material selected from polymers, inorganic cementitious materials, concrete systems putties, wood composites, clays, and ceramics.

40. Use according to claim 38, wherein the modifier application is selected from light reflecting applications, industrial explosives, blast energy absorbing structures, paints and powder coating applications, grinding and blasting applications, earth drilling applications, adhesive formulations and acoustic or thermal insulating applications.

41. Use according to claim 38, wherein the containment application is selected from medical and medicinal applications, micro-containment for radioactive or toxic materials, and micro-containment for gases and liquids.

42. Use according to claim 38, wherein the substrate application is selected from ion exchange applications, catalytic applications, filtration, conductive fillers or RF shielding fillers for polymer composites, and medical imaging.

43. Use according to claim 42, wherein the synthetic hollow microspheres have a secondary surface treatment.

44. A fibre cement building product comprising a synthetic hollow microsphere according to any one of claims 34 to 37.

45. An agglomerate precursor suitable for preparing a synthetic hollow microsphere, said agglomerate precursor comprising a primary component and a blowing agent, wherein the primary component comprises at least one aluminosilicate material.

46. The agglomerate precursor of claim 45, which is as defined in any one of claims 2 to 7.

47. The agglomerate precursor of claim 45 or 46, wherein the primary component is as defined in any one of claims 8 to 15.

48. The agglomerate precursor of any one of claims 45 to 47, wherein the blowing agent is as defined in any one of claims 16 to 18.

49. The agglomerate precursor of any one of claim 45 to 48, further comprising a binding agent.

50. The agglomerate precursor of claim 49, wherein the binding agent is as defined in any one of claims 19 to 27.

51. A method of preparing an agglomerate precursor, said agglomerate precursor being suitable for forming a synthetic hollow microsphere therefrom, comprising the steps of:

(a) providing a primary component of a predetermined size, said primary component comprising at least one aluminosilicate material;
(b) mixing the primary component with a blowing agent in water; and
(c) drying the mixture.

52. The method of claim 51, wherein the amount of primary component is greater than about 40 wt.% based on the total dry weight of the agglomerate precursor.

53. The method of claim 51 or 52, wherein the amount of blowing agent is less than about 10 wt.% based on the total dry weight of the agglomerate precursor.

54. The method of any one of claims 51 to 53, wherein the primary component is as defined in any one of claims 8 to 15.

55. The method of any one of claims 51 to 54, wherein the blowing agent is as defined in any one of claims 16 to 18.

56. The method of any one of claims 51 to 55, wherein a binding agent is additionally mixed with the primary component and the blowing agent in step (b).

57. The method of claim 56, wherein the binding agent is as defined in any one of claims 19 to 27.

58. The method of any one of claims 51 to 57, wherein the drying step (c) comprises drying at a temperature in the range of 30 to 600°C.

59. The method of any one of claim 51 to 58, further comprising the step of:

(d) comminuting the dried mixture from step (c) to form agglomerate precursor particles of a predetermined particle size.

60. The method of claim 59, wherein the dried mixture is comminuted to provide agglomerate precursor particles having an average particle size in the range of 10 to 1000 microns.

61. The method of claim 59 or claim 60, wherein drying and comminuting are performed in a single step.

62. The method of any one of claims 59 to 61, further comprising the step of (e) classifying the agglomerate precursor particles to provide agglomerate precursor particles of a predetermined particle size distribution.

63. The method of any one of claims 51 to 58, wherein the drying step (c) is performed using a spray dryer.

64. An agglomerate precursor obtained or obtainable by a method according to any one of claims 51 to 63.

Figure 1

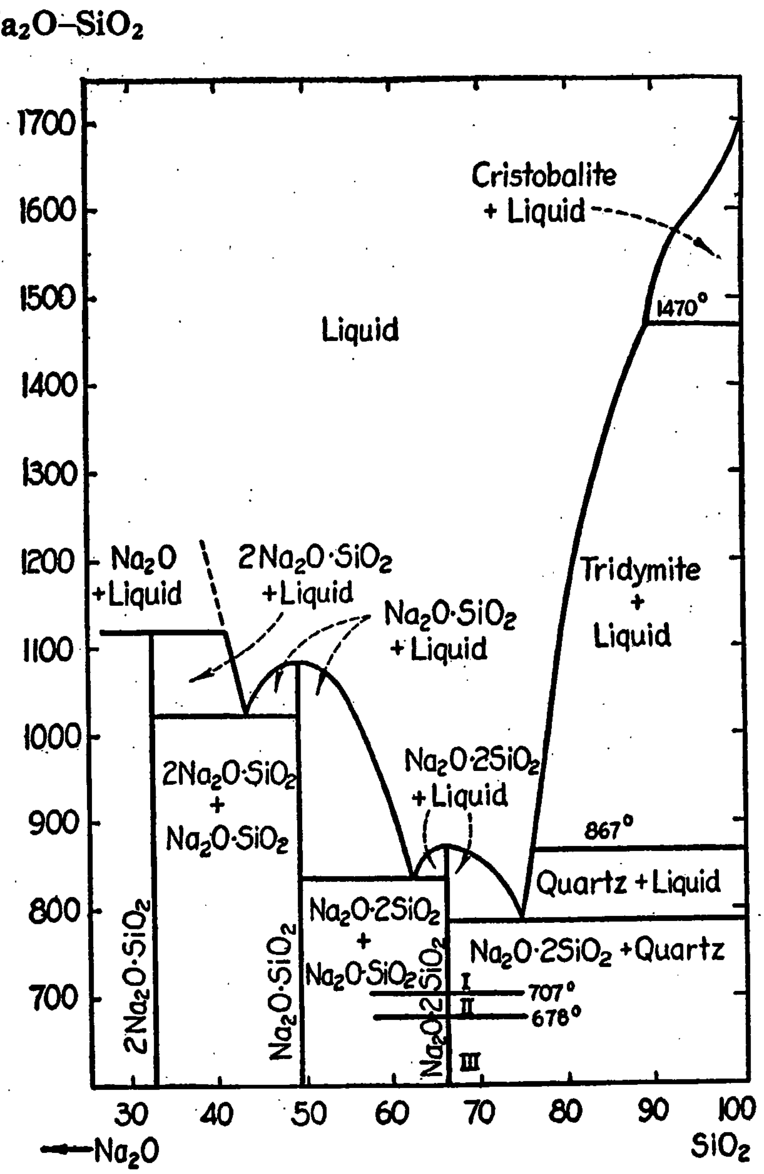
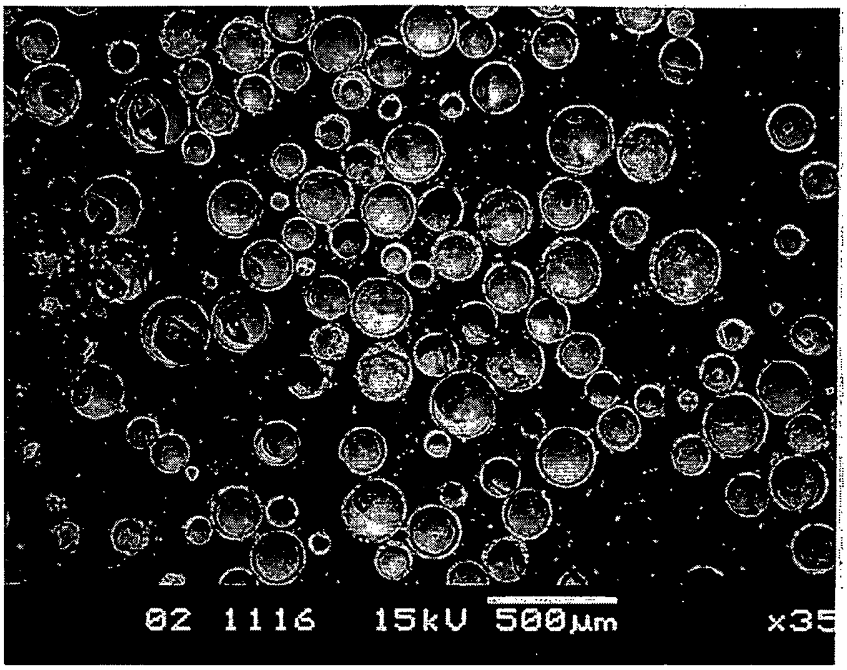


FIG. 192.—System SiO_2–$2Na_2O·SiO_2$.

F. C. Kracek, *J. Phys. Chem.*, **34**, 1588 (1930); *J. Am. Chem. Soc.*, **61**, 2869 (1939).

Figure 2



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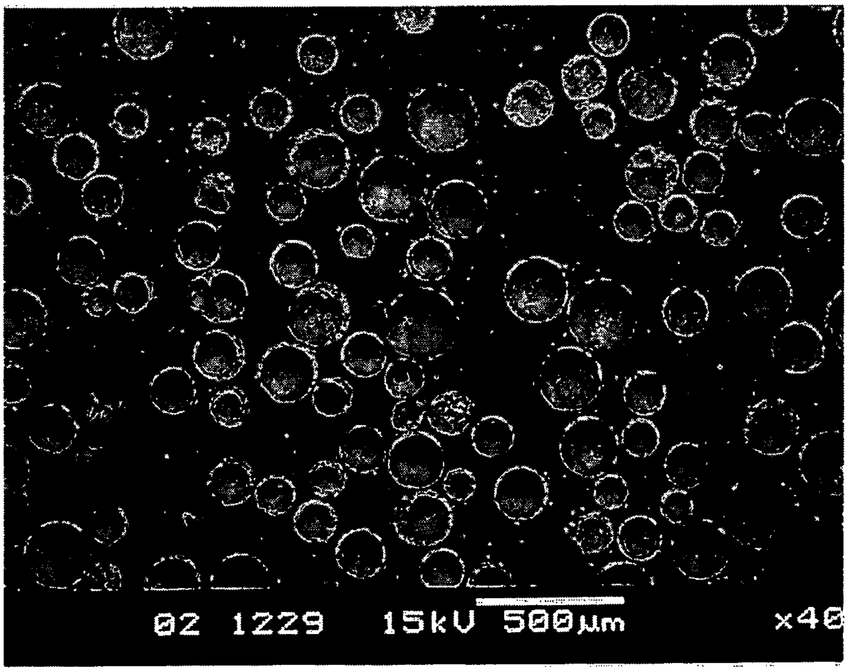

Figure 4

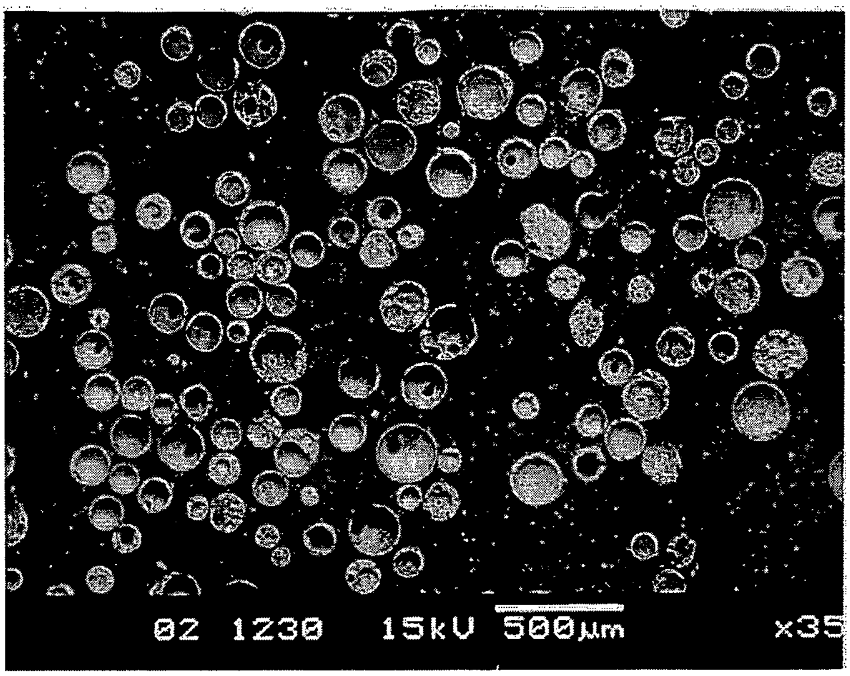

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Figure 5

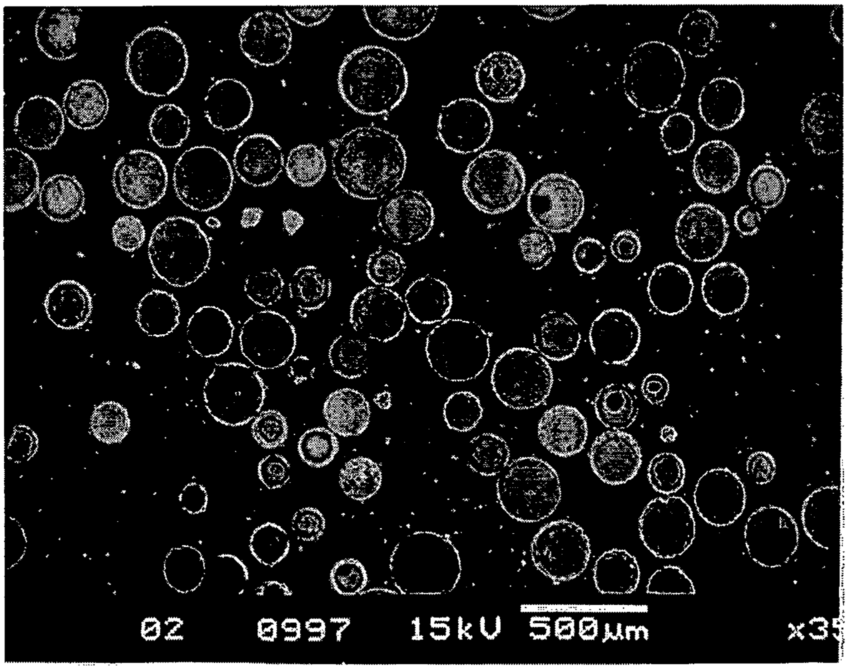
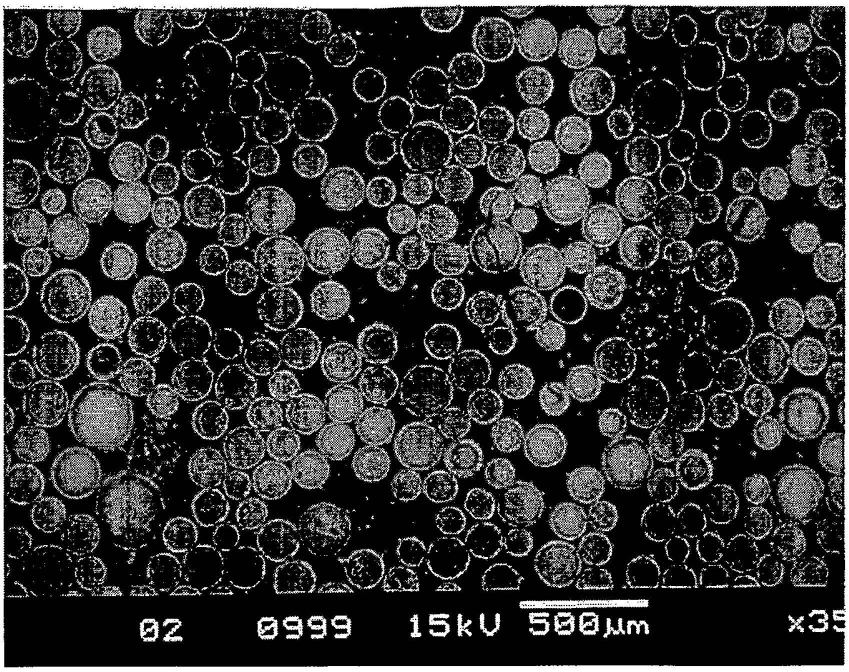


Figure 6



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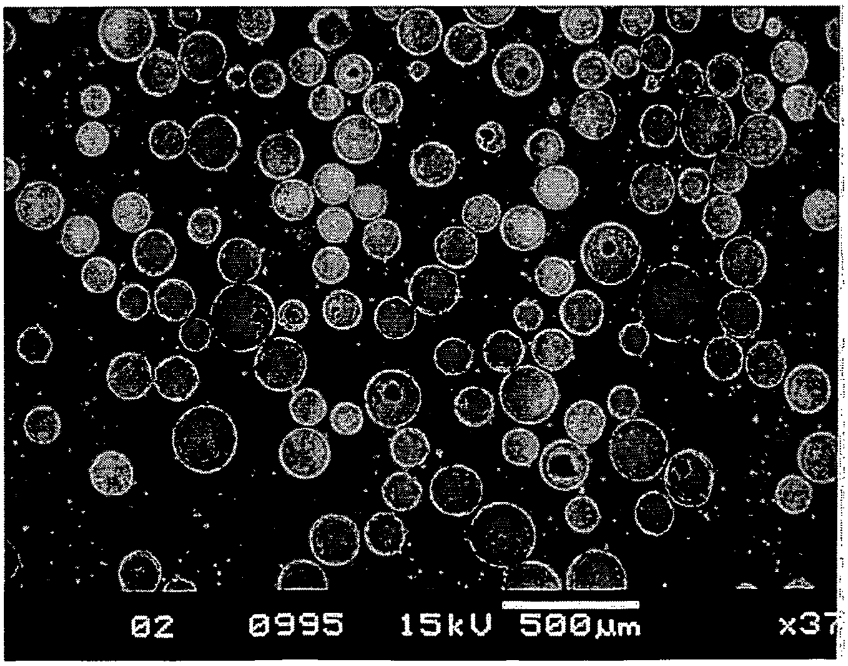


Figure 8

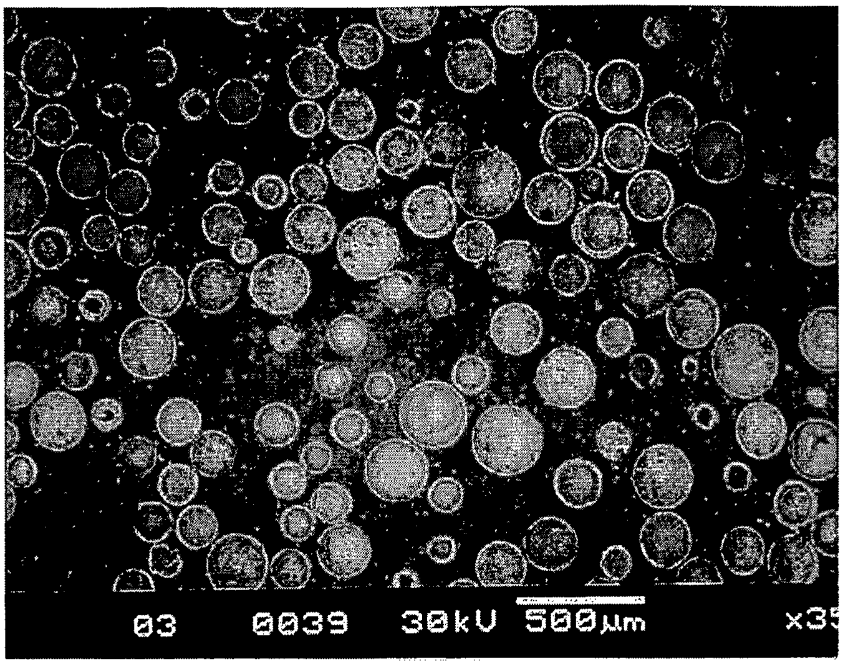


Figure 9

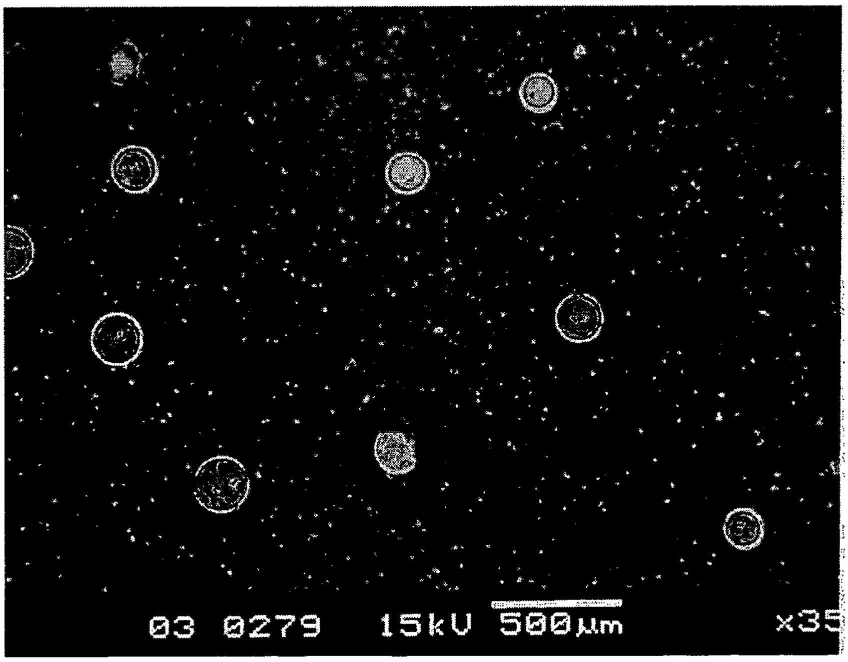


Figure 10

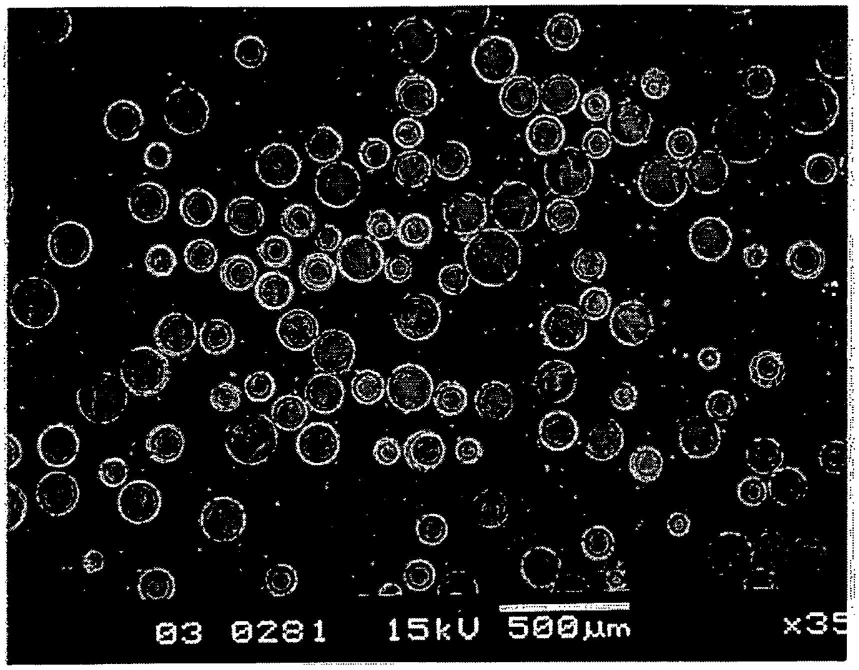


Figure 11

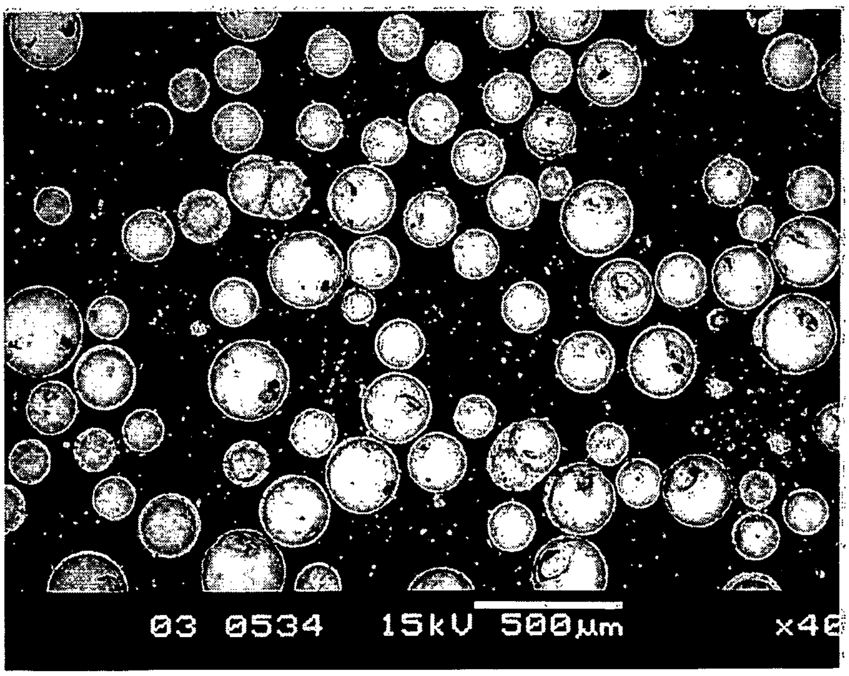


Figure 12

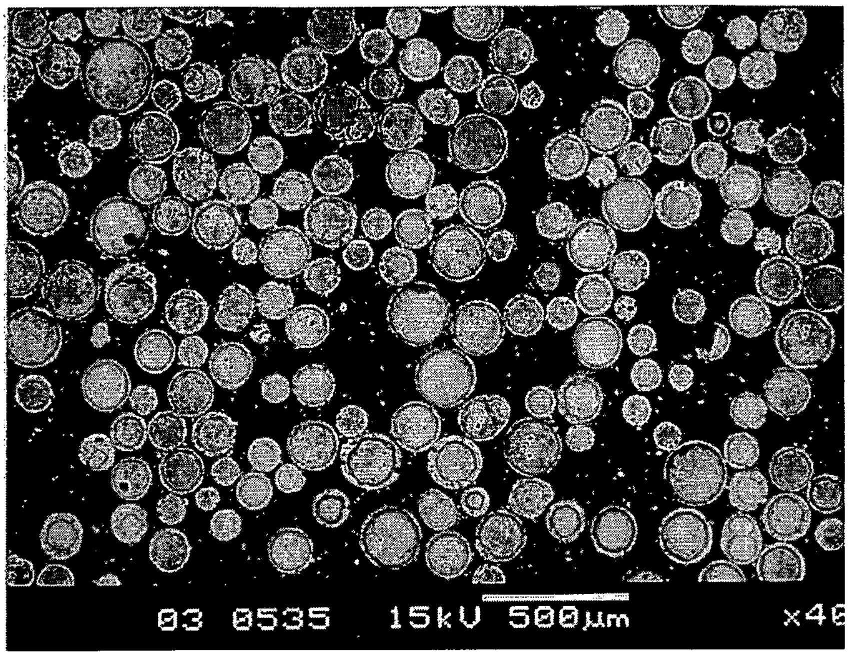


Figure 13

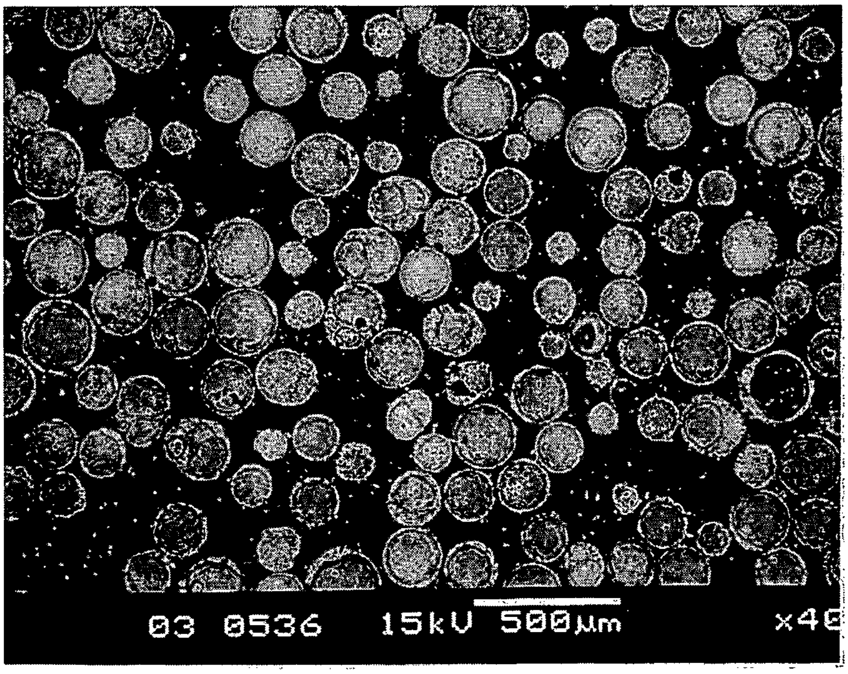


Figure 14

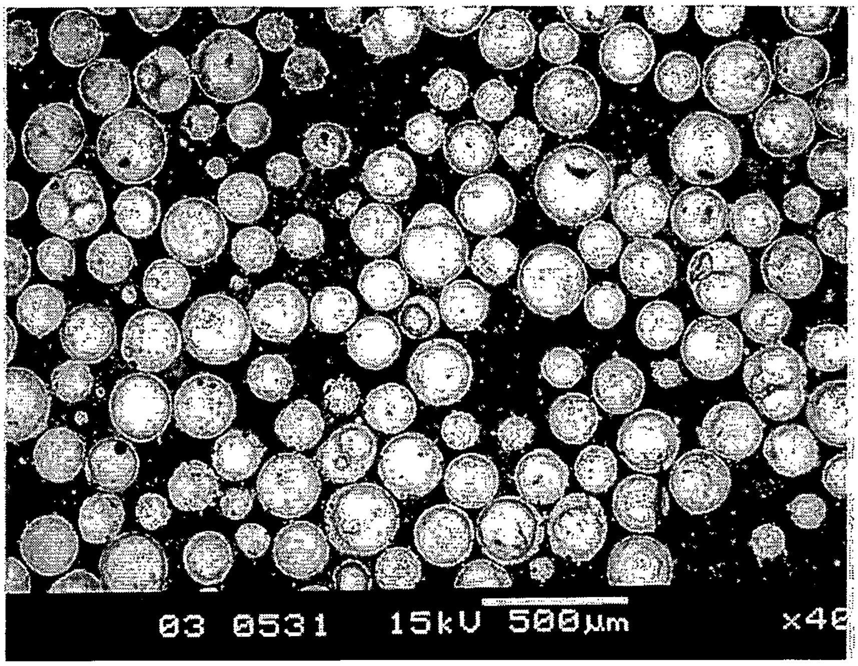


Figure 15

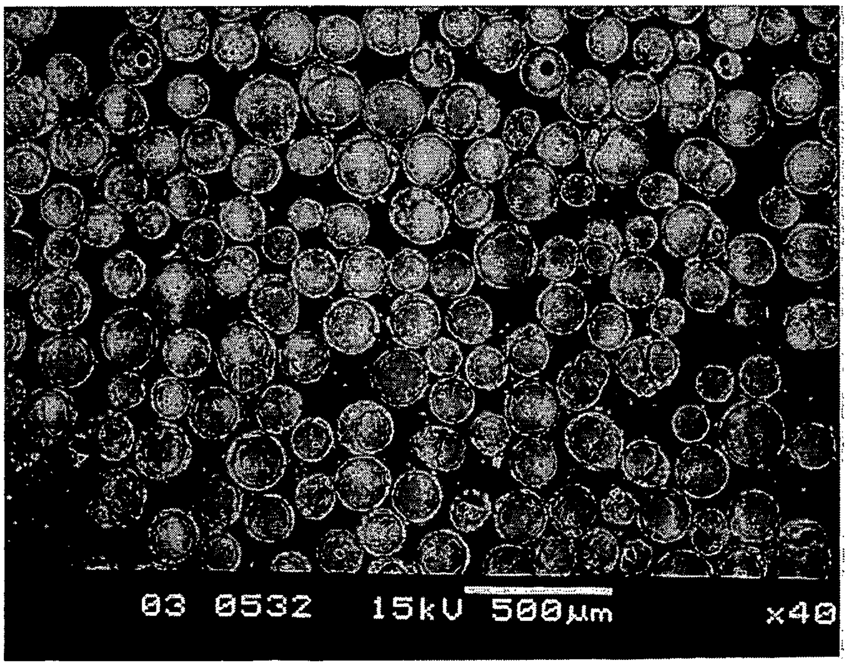


Figure 16

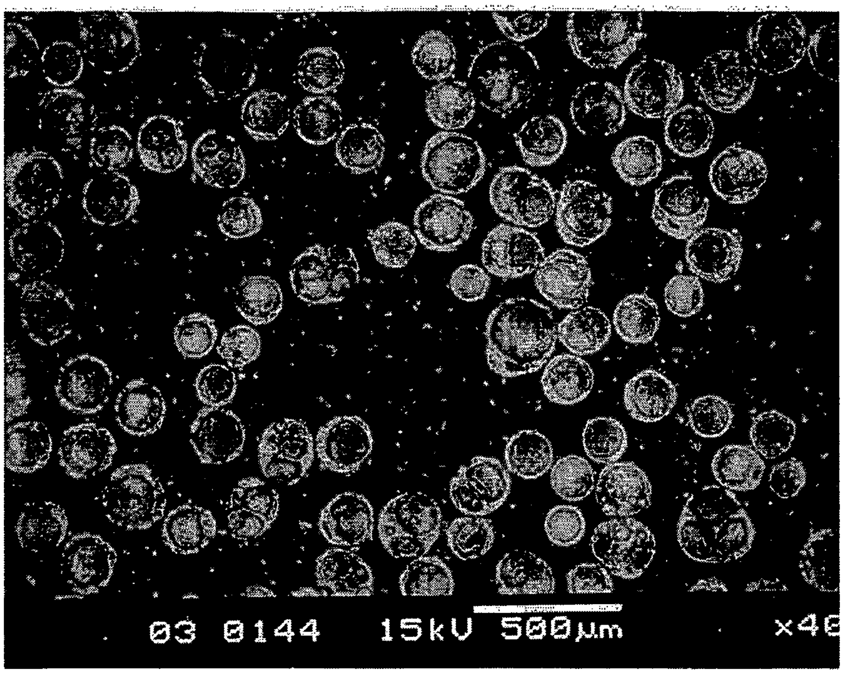


Figure 17

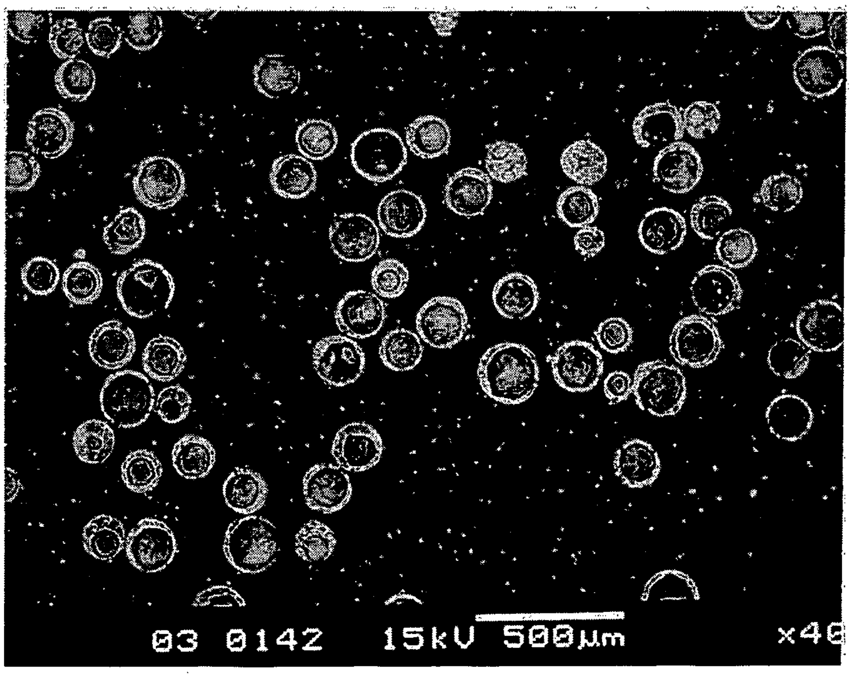


Figure 18

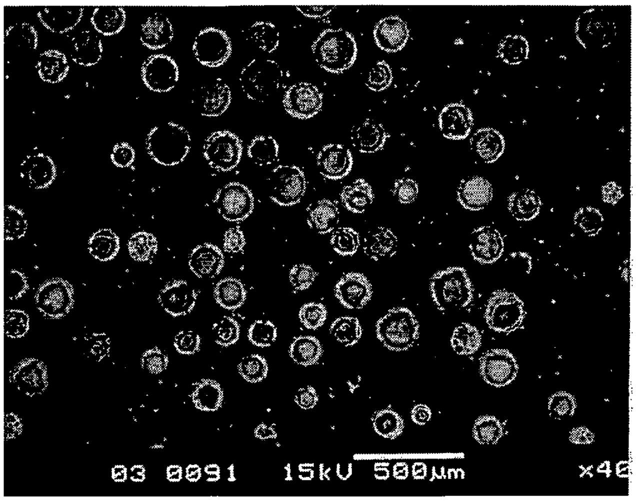
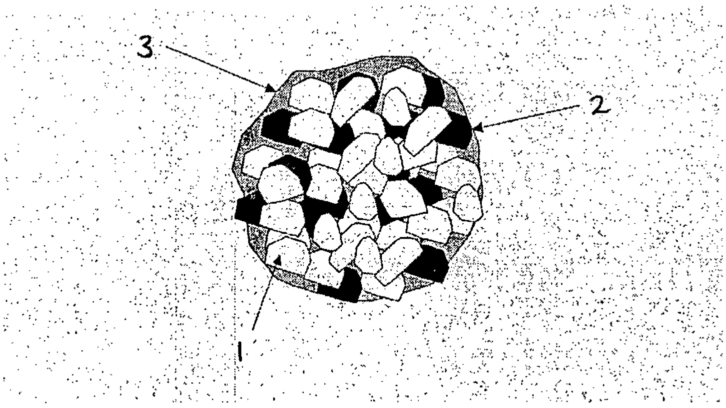


Figure 19



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/01067

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ^{7}: B01J 13/04, C04B 18/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J 13/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT, CAPLUS, JAPIO (IPC and/or keywords)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5176732 A (BLOCK) 5 January 1993. See whole document and especially abstract, claims and example 1.	1, 35, 45, 51
X	EP 359362 B1 (ECC INTERNATIONAL LIMITED) 5 April 1995. See page 3 and claims 1, 7, 8 & 11.	1, 35, 45, 51
X	EP 1160212 A (ASAHI GLASS CO) 5 December 2001. See abstract and col 6 lines 11-52.	1, 45

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 24 September 2003	Date of mailing of the international search report 02 OCT 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **JAMES DZIEDZIC** Telephone No : (02) 6283 2495

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/01067

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D, X	EP 1156021 A (ASAHI GLASS CO) 21 November 2001. See examples 1 & 2 and claim 5.	1, 45
X	US 4867931 A (COCHRAN) 19 September 1989. See claim 1, col 14 lines 30-40 and col 17 line 60 to col 19 line 3.	1, 45
X	US 4111713 A (BECK) 5 September 1978. See col 2 lines 62-65, col 5 lines 4-5 and cols 7-8.	1, 45
X	EP 801037 B1 (ASAHI GLASS COMPANY) 16 August 2000. See page 4 lines 24-34, page 6 line 54, example 11 and claim 6.	1, 35, 45
X	US 5458973 A (JEFFS) 17 October 1995. See col 10 lines 15-49 and claim 5.	1, 35, 45
D, X	US 2002/0025436 A1 (MEYER) 28 February 2002. See paras [8], [53] and [61].	1, 35, 45
X	CA 1040859 A (MATTHEWS, W) 24 October 1978. See abstract, page 3 lines 2, 20, page 8, page 9 lines 10-20, 22-23, page 23 line 27, page 25 lines 7-12 and claim 3.	1, 35, 45
X	US 4624798 A (GINDRUP) 25 November 1986. See col 2 line 30 to col 3 line 10.	35
X	US 4307142 A (BLITSTEIN) 22 December 1981. See col 2 lines 63-68.	35
X	Derwent Abstract Accession Number 96-055752/06 Class L01 JP 07315869 A (CALSEED KK) 5 December 1995.	1, 45
X	Derwent Abstract Accession Number 95-101164/14 Class A82 G01 J04 L01 JP 07024299 A (KAGOSHIMA) 27 January 1995.	1, 45
X	Esp@cenet abstract JP 9020526 A (ASAHI GLASS CO) 21 January 1997.	1, 45

International application No.
PCT/AU03/01067

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Esp@cenet abstract JP 9124327 A (ASAHI GLASS CO) 13 May 1997.	1, 45
X	Derwent Abstract Accession Number 96-358434/36 Class L02 JP 08169779 A (ONODA CEMENT CO) 2 July 1996.	45, 51
X	Derwent Abstract Accession Number 96-017764/02 Class L02 JP 07292846 A (SEKISUI CHEM IND CO LTD) 7 November 1995.	45, 51
X	Derwent Abstract Accession Number 61521 K/26 Class P35 DE 3213521 A (YTONG AG) 23 June 1983.	45, 51

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU03/01067

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	5176732	AU	89666/91	CA	2051837	EP	493734
		HK	437/96	JP	4275927	US	5069702
EP	359362	AU	37917/89	BR	8903448	CA	1331410
		GB	2220666	JP	2067341	NZ	229907
		US	5028482	US	4800103	US	5049594
		BR	8604149	CA	1281600	EP	213931
		ES	2001407	GB	2179665	JP	62096540
		JP	7173330				
EP	1160212	JP	2002087831	US	2002004111	JP	2002087832
US	4867931	AU	71287/87	CA	1321452	EP	259441
		WO	8704659				
US	4111713	BR	7600473	CA	1080924	DE	2603534
		FR	2299362	GB	1527432	JP	51100167
		JP	55023177	JP	58171469	US	4144372
EP	801037	JP	9278463	US	5849055		
US	5458973	AU	59195/90	BR	9003561	EP	410678
		EP	588374	JP	3065312	NO	903212
		NO	940295	NZ	234596	US	5188778
		ZA	9005728	CA	2021866		
US	4624798	CA	1256628	EP	162979	JP	60254514
		US	4624865	US	5786785	US	5892476
		FR	2798389	LU	87058	CA	1341340
US	4307142	US	4374874	US	4403048		

END OF ANNEX