

**INJECTION MOLDING OF STRUCTURAL
ZIRCONIA-BASED MATERIALS BY AN AQUEOUS PROCESS**

BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates to a process for shaping ceramic parts from powder and to molding compositions used therein. More particularly, the invention is directed to molding processes and molding compositions that form high quality, net shape and near netshape complex parts of structural ZrO_2 based materials which can be fired to full density and high strength.

2. Description Of The Prior Art

Upon cooling from elevated, usually sintering, temperatures, ZrO_2 undergoes a martensitic transformation from a tetragonal crystal structure to a monoclinic crystal structure. The transformation results in a volume and anisotropic shape change. Under controlled conditions, the tetragonal phase is maintained at room temperature, and is only transformed when a crack intersects with the grain. The subsequent transformation puts a closure force on the crack, thereby increasing the crack resistance of the material.

The addition of small amounts of stabilizers, such as Y_2O_3 , can have profound effects on the stability of the tetragonal phase. For instance, pure yttrium-stabilized tetragonal polycrystalline zirconia (Y-TZP) materials can be sintered to high strength or fracture toughness, depending on the Y_2O_3 concentration, grain size, and sintering treatments (e.g. pressureless vs. HIP'ing). A fine grain size in Y-TZP materials provides the high strength materials, while the instability of the tetragonal phase (depending on the Y_2O_3 concentration) determines the toughness. Such materials are disclosed by Masaki & Shingo in US 4,742,030, Cassidy et al. in US 4,866,014 and Ghoshid et al. in US 5,336,282.

One of the main drawbacks of Y-TZP materials is their environmental degradation. Upon exposure to especially humid environments and especially in the temperature regime of 150-300 °C, the tetragonal phase transforms spontaneously to monoclinic, drastically reducing the strength. A detailed review of this behavior is presented by S. Lawson in the J. Europ. Ceram. Soc., Vol. 15, pp. 485-502 (1995) titled Environmental Degradation of Zirconia

Ceramics. The addition of alumina particulates to Y-TZP increases both the strength and the environmental stability of Y-TZP materials. Similarly, a heat treatment at elevated temperatures also improves the environmental stability.

5 Applications for ZrO₂ based ceramics are widespread and include metal forming tools, automotive applications, textile applications, and consumer applications such as knives, scissors, golf clubs and the like. The ceramic components utilized in most of these applications are manufactured using powder pressing or slip cast forming techniques.

One objective of any forming method is to produce articles in the unfired state with a certain density and particle packing (hereinafter called "green" parts, forming, density, etc.)
10 which can be sintered to a shape that is reproducible to close dimensional tolerances and is free from defects. During green-forming and sintering, cracks, distortions and other defects can arise due to the shrinkage associated with the particle consolidation processes. It is generally recognized that these defect-producing processes are mitigated by producing homogeneous green bodies having adequate green strength

15 Another objective of shape-forming methods is to produce articles having net shape, eliminating or minimizing the need for downstream operations, such as machining, to obtain final part dimensions. Dry pressing involves compaction of powder in a die. Among the various shape-forming methods dry pressing, in particular, requires additional downstream processing in the form of machining and diamond grinding to attain intricate shapes, non-symmetrical geometrical formats and close tolerances. In slip casting a liquid suspension of
20 ceramic powder is "de-watered" in a porous mold, producing a powder cake in the shape dictated by the mold. Although slip casting has the attribute of producing net shape parts, the method is considered to be relatively slow for the manufacture of complex parts in high volume.

25 Injection molding is recognized as a premier forming method for complex, ceramic shapes. It affords significant advantages over other forming methods, by being capable of rapidly producing net shape, complex parts in high volume. Initially, injection molding comprised the step of mixing ceramic powder with a dispersant and a thermoplastic organic binder of variable composition. The molten powder/binder mixture was heated during the
30 injection molding process and injected into a relatively cold mold. After solidification, the part was ejected in a manner similar to plastic parts. Subsequently, the binder was removed and the part was densified by a high temperature heat treatment. There were a number of

critical stages in this process, which included the initial mixing of the powder and binder, the injection of the mixture into the mold, and the removal of the organic matrix material. One of the main disadvantages of the initial powder injection molding (PIM) process is the removal of the organic vehicle. At present, with the PIM process the cross section limit for fine particle sizes is 0.5-0.75 inch. If the particle sizes exceed that limit, the binder removal process will lead to defects, pinholes, cracks, blisters etc. Binder removal takes place by slow heat treatments that can take up to several weeks. During debinding at elevated temperatures, the binder becomes a liquid which can result in distortion of the green part due to capillary forces. Another disadvantage of the initial PIM process is the tendency for the relatively high molecular weight organic to decompose throughout the green body, causing internal or external defects. The use of solvent extraction, wherein a part of the organic is removed using an organic or supercritical liquid, sometimes minimizes defect formation. Solvent extraction encounters difficulties because the remainder still needs to be removed at elevated temperatures. However, the solvent extraction process allows for the formation of porosity throughout the part, with the result that removal of the remaining organic is facilitated. During binder removal, part slumping can pose problems, especially for the larger particle sizes if the green density/strength is not high enough.

As such, PIM offers certain advantages for high volume automation of net shape, high dimensional control and complex parts, but the limitation of part size and the very long binder removal times combined with their environmental impact has not resulted in the expected growth of the use of this technique.

Some improvements, such as the use of water based binder systems, have been made to the initial PIM process. Hens et al. developed a water leachable binder system.[US Patent 5,332,537] The injection molding feed-stock is made with a tailored particle size distribution (to control the rheology), a PVA based majority binder, and a coating on each of the binder particles. During molding, these coatings form necks which give the part rigidity. After injection molding there is a water de-bind that lasts several hours. After the remaining binder is cross-linked by either UV or chemical methods, the part undergoes a thermal de-bind, which takes 8-12 hours for a part such as a golf club head. Other aqueous-based binders contain either polyethylene glycols, PVA copolymers, or COOH-containing polymers. BASF has developed a polyacetal based system that is molded at moderately high temperatures after which the binder is removed by a heat treatment with gaseous formic or

nitric acid. The low temperature excludes the formation of a liquid phase and thus distortion of the green part due to viscous flow. The gaseous catalyst does not penetrate the polymer and the decomposition only takes place at the interface of the gas and binder, thereby preventing the formation of internal defects. These improvements are limited by the requirement for separate binder removal furnaces and times, depending on the part size.

There remains a need in the powder injection molding art for ready moldable feedstocks that contain the ceramic powders in correct proportion and the necessary binder, liquid carrier and other additives in a form for immediate use in commercially available injection molding machines.

SUMMARY OF THE INVENTION

The present invention provides an aqueous, zirconia-based molding compound and a method for compounding its constituent materials into a homogeneous mixture and format that is useful for low cost manufacture of ceramic articles by injection molding. As used herein, the term "zirconia-based" means compositions containing 50 - 100 wt% zirconium oxide in the fired ceramic. The molding compounds of the present invention advantageously contain, as a homogeneous mixture, ingredients which (i) are essential for shape-forming parts by injection molding, and (ii) yield zirconia-based ceramic materials after firing. Generally stated, there is provided, in accordance with the invention, a molding compound comprising essentially the ceramic precursors, zirconium oxide, yttrium oxide and alumina in a form that is suitable for fabricating articles by injection molding.

Advantageously, the ready moldable zirconia-based compound of the invention obviates the need for high molding pressures and special de-binding furnaces. The molding compound of the invention uses water as the liquid carrier and can be molded at low machine pressure below about 1,000 psi. Furthermore molded parts are dried before sintering by evaporation of the water, and the lengthy and complex de-binding step, typical of polymer-based molding systems, is eliminated. After firing, a ZrO_2 material is obtained having full density and high strength.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred
5 embodiments of the invention and the accompanying drawing, wherein Fig. 1 is a schematic representation depicting the basic steps of one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

According to the process of our invention, the ceramic powders are initially mixed
10 with a gel-forming powder and a solvent for the gel-forming material. In normal practice zirconia ceramics require a stabilizing additive to prevent catastrophic destruction of the article due to the occurrence of a monoclinic phase transition upon cooling from the sintering temperature. Any of the stabilizers known to those skilled in the art of fabricating zirconia ceramics can be used in the process. Common stabilizers comprise oxides of the elements Y,
15 Ce, Ca, and Mg or compounds such as carbonates, nitrates, oxylates and the like, which produce oxides of those elements during high temperature processing. The amount of stabilizer can be chosen to produce the tetragonal, cubic or monoclinic or a mixture of phases. Yttria is the preferred stabilizer. The presence of alumina produces certain desired effects, such as an improvement in the environmental stability. For the purpose of densifying
20 the material to full density and obtaining high strengths, the average particle size should be below 1 μm . Preferably, the average particle size ranges from about 0.1-0.9 μm , and more preferably from about 0.3-0.5 μm . As used herein, the term 'particle size' means equivalent spherical diameter.

The invention provides a ceramic molding compound consisting essentially of
25 zirconium oxide as the major phase with lesser amounts of other metal inorganic compounds, water, binder (selected from class of polysaccharides) and minor amounts of other additives that improve the processability of the molding feed-stocks. The invention further provides a method for producing a ready-moldable feed-stock from the constituent ceramic powders, binder, carrier and other processing aids. It is customary to represent the ceramic
30 constituents of a fired ceramic body in terms of the constituent metal oxide compounds irrespective of the actual phases present after firing. Using this convention the ceramic

constituents of the molding compounds disclosed herein may be represented by the formula $[\text{ZrO}_2]_a[\text{Y}_2\text{O}_3]_b[\text{Al}_2\text{O}_3]_c$, wherein a ranges from about 50 -95 wt and b ranges from about 4 to 6 wt. % and c ranges from about 0-45 wt. %. In the present invention, one preferred molding compound in terms of the constituent metal oxides is composed of a = about 85.8 wt %, and b = about 4.3 wt. % and c = about 14.3 wt. %. An example of a second preferred molding compound in terms of starting ceramic powders contains about 95 wt. % zirconium oxide and 5 wt. % yttrium oxide.

Generally, the amount of powder in the mixture is between about 50 and about 95 percent by weight of the mixture. Preferably, the powders constitute between about 75 and about 90 percent by weight of the mixture, and most preferably constitute between about 83 and about 86 percent by weight of the mixture. The preferred and most preferred amounts are quite useful in producing net and near net shape injection molded parts.

The molding compound provides a binder which provides the mechanism for allowing the fluid material to set in a mold and be removed as a self-supporting structure. In the present invention this role is served by a compound derived from the category of polysaccharides known as agaroids. An agaroid has been defined as a gum resembling agar but not meeting all of the characteristics thereof (See H.H. Selby et al., "Agar", *Industrial Gums*, Academic Press, New York, NY, 2nd ed., 1973, Chapter 3, p. 29). As used herein, however, agaroid not only refers to any gums resembling agar, but also to agar and derivatives thereof such as agarose. An agaroid is employed because it exhibits rapid gelation within a narrow temperature range, a factor which can dramatically increase the rate of production of articles. The preferred gel-forming materials are those which are water soluble and comprise agar, agarose, or carrageenan, and the most preferred gel-forming materials consist of agar, agarose, and mixtures thereof.

The gel-forming materials are present in an amount between 0.2 wt.% and about 6 wt.% based upon the solids in the mixture. More than about 6 wt.% of the gel-forming material may be employed in the mixture. Higher amounts are not believed to have any adverse impact on the process, although such amounts may begin to reduced some of the advantages produced by our novel composition. Most preferably, the gel-forming material comprises between about 1 percent and about 4 percent by weight of solids in the mixture.

The molding compound also provides a liquid carrier to facilitate transport of the molding compound along the barrel of an injection molding machine to a mold. Water is the

most preferred liquid carrier in the molding compounds because it ideally serves the dual purpose of being a solvent for the gel forming binder and liquid carrier for the solid constituents in the mixture. In addition, because of its low boiling point, water is easily removed from the molded part prior to and/or during firing. The amount of water is chosen to confer the molding compounds with the essential rheological characteristics for proper behavior in the injection molding machine. The proper amount of water is between about 10 wt. % and 30 wt. % of the mixture with amounts between about 15 wt. % and 20 wt. % being preferred.

The molding compound may also contain a variety of additives which can serve any number of useful purposes. Additives that have been found to be very useful in the present molding compounds comprise dispersants, pH control agents, biocides and gel strength enhancing agents (e.g., metal borate compounds such as calcium borate, magnesium borate and zinc borate). Biocides may be used to inhibit bacterial growth in the molding compounds, especially if they are to be stored for long periods of time.

It is well-known that use of dispersants and pH control can greatly improve the rheology and processability of ceramic suspensions. In the present case dispersants based on polyacrylate and polymethylmethacrylate polymer backbones have been found useful in improving the processability of the aluminum oxide-based compositions, the amount of dispersant in the molding compound being about 0.2 wt. % to 1 wt. % and preferably 0.2 wt. % to 0.8 wt. % based on the ceramic powders. Similarly, tetramethylammonium hydroxide has been found useful for controlling the pH of the suspensions, the useful pH range being about 8.8 to 11 and preferably 9.5 to 10.5.

The molding compounds of the present invention combine the ceramic powders, liquid carrier, binder and processing aids in a ready-moldable form. A preferred composition in terms of the constituent compounds is 66.90 wt. % Zirconium oxide, 4 wt. % yttrium oxide, 11.7 wt. % aluminum oxide, 2.5 wt. % Agar, 0.33 wt. % dispersant, 0.53 wt. % tetramethylammonium hydroxide, 0.02 wt. % biocide and 14 wt. % water (where the dispersant is added as a 40 % aqueous solution and the TMA as a 25 % aqueous solution).

The invention also provides a method for combining all of the various constituents of the molding compounds into a homogeneous mixture which will produce homogeneous molded bodies that can be fired free of cracks and other defects. Raw material ceramic powders are frequently highly agglomerated and require deagglomeration before they can be

manufactured into useful ceramic articles, free of cracks, distortions and other defects. Of the various available methods ball milling has been found convenient and useful for producing the aqueous-based molding compounds disclosed herein, the powders being simultaneously deagglomerated and homogenized in the aqueous medium. The useful concentration range for ball milling the ceramic powders is 50 wt. % to 85 wt. %, the preferable range being between 65 wt. % and 80 wt. %.

Compounding of the ceramic suspension with the binder can be done in any number of efficient mixers, e.g., a sigma mixer or planetary-type mixer. The biocide may be blended into the composition at the compounding stage of the process or optionally near the end of the ball milling cycle. During compounding the blend is heated in the range 75°C to 95°C and preferably between 80°C and 90°C for a period of about 15 min to 120 min and preferably between 30 min and 60 min.

The molding compound must be in a suitable form for charging an injection molding machine. In the present invention the compounded, homogeneous mixture is allowed to cool below the gel point of the gel-forming agent (<37°C) and removed from the blender. Thereafter it is shredded into a particulate format using a rotating cutter blade typically used in food processing. The shredded format can be fed directly into the hopper of an injection molding machine. The shredded feed-stock may be dried to a particular molding solids by evaporation, by exposure of the material to the atmosphere, until the desired moisture level is obtained. The useful solids levels in the molding compounds are in the range 75 wt. % to 88 wt% and preferably between 83 wt. % and 86 wt. %.

A very wide range of molding pressures may be employed. Generally, the molding pressure is between 20 psi and about 3500 psi. Most preferably, the molding pressure is in the range of 40 psi to about 1500 psi. The mold temperature must of course be at below the gel point of the gel forming material in order to produce a self supporting body. The appropriate mold temperature can be achieved before, during or after the mixture is supplied to the mold. Ordinarily, the mold temperature is maintained at less than 40°C, and preferably between about 15 °C an about 25 °C.

After the part is molded and cooled to a temperature below the gel point of the gel-forming material, the body is removed from the mold. The green body is typically sufficiently

self supporting that it requires no special handling during removal from the mold. After removal from the mold, the part is dried. Similar to the drying of slip-cast parts, care needs to be taken to control the drying behavior. Depending on part size and complexity, fast drying may result in cracking. In such a case, the part may be dried in a controlled humidity environment.

After the part is are dried, the body is sintered at an elevated temperature to produce the final product. The sintering time and temperature is regulated according to the powdered material employed to form the part. Preferably, the elevated temperature at which the body is sintered is at least 1250°C, and more preferably ranges from 1300 to 1550 °C, and most preferably ranges from 1350 °C to 1500 °C. Preferably, the sintering time at maximum temperature is less than 4 hrs., more preferably from 1-3 hrs, and most preferably from 1-2 hrs.

The present invention can thus be used to form complex and thick net-shape or near net-shape bodies of zirconia based materials which have excellent strength properties and environmental stability. The physical properties of the densified ceramic from one preferred molding compound containing 20 vol.% alumina, referred to AS280, have been found excellent for a variety of structural applications, as summarized in Table I.

Table I. Injection Molded AS280 Alumina-Zirconia Properties

PROPERTY	UNITS	TEST	VALUE
Color	-	-	OFF-WHITE
Density	g/cm ³	ASTM C20-83	5.63
Flexural strength	MPa (ksi)	3-point	970 (140)
Flexural strength	MPa (ksi)	4-point	820 (118)
Hardness	kg/mm ²	Knoop (100 g.)	1518
Fracture Toughness	MPa.m ^{1/2}	Indentation	5.6
Elastic Modulus	GPa (10 ⁶ psi)	ASTM C623	239 (34.7)
Shear Modulus	GPa (10 ⁶ psi)	ASTM C623	92 (13.4)
Poisson's Ratio	-	ASTM C623	0.3
CTE	ppm/°C	ASTM E 228 (Theta dilatometer)	
50 °C			8.9
250 °C			9.42
500 °C			9.98
750 °C			10.31
1000 °C			10.5

- 5 The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of the invention.

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Example 1

- 2314.27 g. of HSY-3 zirconia powder and 384.74 g. of Alcan C-901 alumina powder were weighed in a 1.6 gallon Abbethane ball-mill jar. 10.6 kg of 3/8" zirconia media was added. A mixture was made by weighing off 889.2 g. of deionized water, 10.8 g. of Darvan 821A ammonium polyacrylate (40 % solution Vanderbilt Laboratories) and 17.5 g. of TMA (25 wt. % solution, Alfa Inorganics). The slip was ball-milled for 24 hrs. and 3200 g. was recovered and transferred to a sigma mixer. During agitation in the sigma mixer, 72 g. of Agar (S-100, Frutarom Meer Corp.), 0.62 g. methyl-p-hydroxy benzoate (Penta Mfg) and 0.45 g. propyl-p-hydroxy benzoate (Penta Mfg.) were added incrementally. The sigma mixer

was heated to 190 F for 45 min, after which the temperature was reduced to 170 F and mixing continued for another 45 min. After the material was allowed to cool to room temperature, it was shredded using a food processor (Kitchen Aid KSM90) and sieved using a #5 sieve to remove any large and fine shards.

- 5 Before being molded, the shredded feed-stock was dried to a desired solids level by exposing a loose bed of material to the atmosphere. Solids loadings were determined using a moisture balance (Ohaus Corp.).

Plates were molded on both a Boy 15s and 22M. The plates were dried slowly on the bench for several hours after which they were dried in a vacuum oven @ 100°C. After
10 the plates were dry, they were densified @ 1450°C for 2 hrs. Standard 3- and 4-point bars were cut (Military type B) and the bending strength was determined to be 0.97 and 0.82 GPa, respectively.

Example 2

15 A molding feed-stock was prepared as in Example 1, and was used to mold a variety of shapes, such as "3-hole sensors". The fired parts were cylindrical in shape, nominally 0.85" in length with 3 holes, nominally 0.1" in diameter running lengthwise. A step divided each part into a larger diameter shoulder, 0.45" OD x 0.35" length and a smaller diameter
20 shoulder, 0.35" OD x 0.5" length. Molding was performed at 85 wt. %, after which the parts were dried under ambient conditions and fired at 1450°C for 2 hrs. After firing, the average density was $5.59 \pm 0.012 \text{ g/cm}^3$. Their average dimensions were $0.407'' \pm 0.001''$ for the larger diameter, $0.358'' \pm 0.0011''$ for the smaller diameter and $0.7404 \pm 0.002''$ for the length. The average shrinkages for the three dimensions were $21.6 \pm 0.2\%$, $22.2 \pm 0.2\%$, and $19.7 \pm 0.2 \%$, respectively.

25 Another batch of parts, hereinafter called "half shell" parts were molded. The parts were half cylindrical in shape with several steps and grooves on the flat side. Molding was performed at 86 wt. %, after which the parts were dried under ambient conditions and fired at 1450°C for 2 hrs. After firing, the average density of the parts was $5.6 \pm 0.01 \text{ g/cm}^3$. The fired length was nominally 0.9" with a width of 0.4". Within a sample of 84 green parts, the
30 average length was $0.949 \pm 0.005''$ and the average diameter was $0.496 \pm 0.003''$. After firing, the average shrinkage was $21.1 \pm 0.5 \%$ and $21.4 \pm 0.5 \%$, for the length and diameter respectively.

Example 3

This example represents a scale-up of the molding compound preparation described in Example 1. A slip was prepared from 38.4 kg HSY-3 zirconia/yttria, 6.24 kg aluminum oxide, 14.62 kg D.I. water, 0.179 kg ammonium polyacrylate and adjusted to pH 11 with TMA. After ball milling, 55 kg of slip was transferred to a planetary type blender where it was blended (in three separate runs) with 1.24 kg agar, 0.011 kg methyl-p-hydroxy benzoate and 0.0077 kg propyl-p-benzoate while being agitated and heated. Mixing was continued for 1h after the blender reached a final temperature of 95°C. The material was put into feed-stock form by shredding.

Having thus described the invention in rather full detail it will be understood that such detail need not be strictly adhered to but that various changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.



What is claimed is:

1. A molding composition for forming net-shape or near net-shape articles from zirconia-based materials, consisting essentially of about 50 to 100 wt.% $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ and 0 to about 50 wt.% Al_2O_3 .
2. A molding composition as recited by claim 1, consisting essentially of about 95 wt.% ZrO_2 and about 5 wt.% Y_2O_3 .
3. A molding composition as recited by claim 1, consisting essentially of about 14 wt.% Al_2O_3 and about 4.3 wt.% Y_2O_3 , the remainder being ZrO_2 .
4. A molding compound as recited by claim 1, further including from about 0.2 wt.% to 1 wt.% of a dispersant based on a polyacrylate or polymethylmethacrylate polymer backbone.
5. A molding compound as recited by claim 1, further including an additive selected from the group consisting of dispersants, pH control agents, biocides, gel strength enhancing agents and mixtures thereof.
6. A method for blending constituents of a molding compound into a homogeneous mixture, comprising the steps of:
 - a: Mixing together ceramic powders to produce a composition defined essentially by the formula $[\text{ZrO}_2]_a[\text{Y}_2\text{O}_3]_b[\text{Al}_2\text{O}_3]_c$ wherein a ranges from about 50 -95 wt. %, b ranges from about 4 to 6 wt. % and c ranges from about 0-45 wt. %; and
 - b: ball milling the ceramic powders in the presence of an aqueous medium to produce a ceramic suspension, the ceramic powders comprising about 50 to 85 wt.% of the medium.
7. A method as recited by claim 6, further comprising the step of compounding the ceramic suspension with a binder and, optionally, a biocide to produce a compounded homogeneous mixture.

8. A method, as recited by claim 7, wherein during compounding said suspension is heated to a temperature ranging from 75°C to 95°C for a time period ranging from about 15 to 120 min.

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9. A method a recited by claim 8, wherein said temperature rages from about 80 C to 90°C and said item ranges from about 30 to 60 min.

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10. A method as recited by claim 6, wherein said mixture includes a gel-forming agent, and said method further comprising the step of cooling said mixture to a temperature below the gel point of the gel-forming agent and removing said mixture from the blender.

11. A method as recited by claim 10, further comprising the step of shredding said mixture to form a particulate material.

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12. A method as recited by claim 11, further comprising the step of drying said particulate material until it exhibits a solids level ranging from 75 to 88 wt. %

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13. A method as recited by claim 12, wherein said particulate material is dried until it exhibits a solids level ranging from about 84-86 wt. %

