

## BARIUM TITANATE DISPERSIONS

### BACKGROUND OF THE INVENTION

The present invention relates to barium titanate dispersions and, more particularly, to barium titanate dispersions in non-aqueous media.

5        The high dielectric constant of barium titanate-based materials make them suitable for multilayer ceramic capacitors, commonly referred to as "MLC's." MLC's comprise alternating layers of dielectric and electrical conductor materials. Examples of MLC's are disclosed in U.S. Patent Nos. 3,612,963 and 4,435,738. Palladium, silver, palladium-silver alloys, copper, and nickel are common electrical conductor materials used in MLC's. The dielectric layers of an MLC are usually prepared from a high solids dispersion, known in the art as a "slip." Such slips typically comprise powdered barium titanate-based material and a polymeric binder in an aqueous or non-aqueous solvent. Films of binder-stabilized powder made by casting or coating with a slip are dried to provide a "green" layer of ceramic dielectric. Green layers are coated with conductor materials in a pattern and are then stacked to provide a laminate of alternating layers of green ceramic dielectric and conductor. The stacks are diced into MLC-sized cubes, which are heated to burn off organic materials such as binder and dispersant and then fired to sinter the particles of barium titanate-based material to form a capacitor structure with laminated, dense ceramic dielectric and conductor layers. Sintering temperatures are typically in the range of about 1000°C and 1500°C. During sintering increased ceramic dielectric density is achieved as a result of the fusion and consolidation of the particles to form grains. Even with the use of grain growth inhibitors, ceramic grain size in an MLC dielectric layer is typically larger, for example, by a factor of 3 to 5, than the size of the original primary particles. Moreover, not all porosity is removed during the sintering process. Typically, between about 2% and 10% porosity remains in MLC dielectric layers. These pores, or hole defects, in the dielectric layer, tend to be larger in larger

grain size ceramics. Certain critical capacitor properties such as break down voltage and DC leakage are influenced by dielectric thickness, grain size and pore defects. For instance, it is believed that effective dielectric layers need to be several grains thick, for example at least 3 to 5 grains thick. Because a defect in any one of the layers of an MLC can be fatal to its performance, MLC's are manufactured with a sufficient thickness of dielectric layer to effectively reduce the impact of ceramic defects which can be caused by random large grains or pores, adversely affect the properties of the MLC.

With the market demand for miniaturization in the design of electronic devices there is a need in the MLC industry for ceramic materials that will allow thinner dielectric layers without incurring the catastrophic effects of large grain and pore size relative to dielectric thickness.

Barium titanate powders produced by known processes, for example calcination or hydrothermal processes, have large particles and/or strongly-agglomerated fine particles of a size substantially larger than 1  $\mu\text{m}$ . Such particles and agglomerates are not readily amenable to the production of MLC's with fine grained, ultrathin dielectric layers, for example of less than 4-5  $\mu\text{m}$ . Thus, it would represent an advance in the art to provide a barium titanate-based material, and dispersion, that would be suitable for making MLC's with thinner dielectric ceramic layers of, for example less than 4  $\mu\text{m}$ , with acceptable or exceptional electrical properties including DC leakage and breakdown voltage without the need for extended ball milling.

### SUMMARY OF THE INVENTION

In one aspect, the invention provides a slurry, dispersion, or slip including barium titanate-based particles dispersed in a non-aqueous medium. The particles include a coating comprising a metal oxide, metal hydrous oxide, metal hydroxide or organic acid salt of a metal other than barium or titanium, wherein at least 90 percent of the particles have a particle size of less than 0.9 micrometer when dispersed by high shear mixing.

As used herein the term "barium titanate-based" refers to barium titanate, barium titanate having another metal oxide coating, and other oxides based on barium and titanate having the general structure  $\text{ABO}_3$ , where A represents one or more divalent metals such as barium, calcium, lead, strontium, magnesium and zinc, and B represents one or more tetravalent metals such as titanium, tin, zirconium and hafnium.

In another aspect, this invention provides a method of forming a slurry, dispersion, or slip. The method includes the step of dispersing barium titanate-based particles in a non-aqueous medium by high shear mixing until 90 percent of the particles have a particle size of less than 0.9 micrometer. The particles have a coating comprising a metal oxide, metal  
5 hydrous oxide, metal hydroxide or organic acid salt of a metal other than barium or titanium.

In another aspect, the invention provides another method of forming a slurry, dispersion, or slip. The method includes forming a slurry of barium titanate-based particles in an aqueous medium by a hydrothermal process. The method further includes forming a coating on the particles including a metal oxide, metal hydrous oxide, metal hydroxide or  
10 organic acid salt of a metal other than barium or titanium. The method further includes replacing the aqueous medium with a non-aqueous medium, and dispersing barium titanate-based particles in a non-aqueous medium by high shear mixing.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 FIGS. 1A, 1B, and 1C are graphs of the particle size distribution of one embodiment of the barium titanate particles of the present invention, after high shear mixing for 45 minutes, after an additional mixing in a horizontal media mill for 30 minutes, and after an additional mixing in a horizontal media mill for 45 minutes; and

20 FIGS. 2A, and 2B are graphs of the particle size distribution of another embodiment of the barium titanate particles of the present invention, after high shear mixing for 10 minutes, and after high shear mixing for 30 minutes.

Other novel features and aspects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying figures, and from the claims.

#### DETAILED DESCRIPTION OF THE INVENTION

25 The present invention is directed to slurries, dispersions, or slips of barium titanate-based particles dispersed in a non-aqueous medium. The particles include a coating on at least a portion of the particle surface. The coating comprising a metal oxide, metal hydrous oxide, metal hydroxide, or organic acid salt of a metal other than barium or titanium, or mixtures  
30 thereof. The coated particles have a particle size less than 0.9 micrometer when dispersed by high shear mixing.

The barium titanate-based particles are dispersible, without the need for ball milling, into submicron dispersions in non-aqueous media that are advantageous in the manufacture of MLC's with thin dielectric layers having submicron grain size and high breakdown voltage. High shear mixing is effective in reducing the size of agglomerates of barium titanate-based particles, and involves de-agglomeration or separation of agglomerates into smaller coated particles without ball milling, which includes impacting the particles with hard, ball milling media such as rods, balls or zirconia particles, and the like. Since ball milling can split particles into smaller than the primary particle size resulting in non-equiaxed particles with exposed, uncoated, surface(s), in a preferred embodiment the particles of this invention are not ball milled and the particles have a major portion of the surface covered by the coating. In another aspect of the invention, unmilled particles are equiaxed or spherical.

The barium titanate-based particles are useful in providing monolithic capacitors comprising a ceramic body having a grain size of less than 0.3 micrometers. Preferred MLC's exhibit an X7R or a Y5V temperature coefficient of capacitance, and have a dielectric thickness of less than 5  $\mu\text{m}$  and a dielectric strength of at least 50 volts per  $\mu\text{m}$ .

The primary particle size of the barium titanate-based particles may be determined by methods known to those skilled in the art. Examples of such methods are by using scanning electron microscopy (SEM) or transmission electron microscopy (TEM). While it is understood that the barium titanate-based particles may comprise primary particles of varying sizes, the coated, barium titanate-based particles have an average primary particle size of less than 0.6  $\mu\text{m}$ . Preferably, the particles have a primary particle size of less than 0.5  $\mu\text{m}$ ; more preferably, less than 0.4  $\mu\text{m}$ ; and more preferably, the particles have a primary particle size of less than 0.3  $\mu\text{m}$ ; most preferably, the particles have a primary particle size of less than 0.2  $\mu\text{m}$ .

The barium titanate-based particles may exist in forms other than primary particles, for example as aggregates of primary particles, and/or agglomerates of aggregates of primary particles. SEM and TEM are not effective in distinguishing the size distribution among primary particles, aggregates of primary particles, and agglomerates of aggregates of primary particles. Particle size distribution analysis, for example by light scattering techniques, is a preferred method for characterizing the particle size of the barium titanate-based particles, provided that the preparation for analysis does not include treatment that would change the distribution of aggregated or agglomerated particles, such as by deagglomeration due to

ultrasonic treatment, high shear mixing, or milling. One such automated light scattering technique employs a HORIBA LA-910™ laser light scattering particle size analyzer or similar device. Such analysis typically presents the volume fraction, normalized for frequency, of discrete sizes of particles including primary particles, aggregates and agglomerates in ten groupings or deciles. Thus, as used herein the term "particle size" refers to individual particles in the powder and may include primary particles, aggregates of primary particles, agglomerates of aggregates, and mixtures thereof. In one aspect of this invention, at least 90 percent of the metal oxide-coated, barium titanate-based particles in a barium titanate-based particle dispersion have a particle size less than 0.8  $\mu\text{m}$ ; preferably, less than 0.7  $\mu\text{m}$ ; more preferably, less than 0.6  $\mu\text{m}$ . In more preferred aspects of this invention, at least 90 percent of the particles in a barium titanate dispersion have a particle size less than 0.5  $\mu\text{m}$ ; preferably, less than 0.4  $\mu\text{m}$ ; and more preferably, less than 0.3  $\mu\text{m}$ .

Characteristics of particle size distribution include  $D_{90}$ , which is the smallest particle size in the decile of largest particles;  $D_{50}$ , which represents the median diameter; and  $D_{10}$ , which is the largest particle size in the decile of smallest particles. The ratio of  $D_{90}/D_{10}$  is a convenient characteristic for identifying the width of the particle size distribution curve. In various aspects of this invention the particle size distribution is narrow, preferably having a ratio of  $D_{90}/D_{10}$  of less than 4; more preferably, the ratio of  $D_{90}/D_{10}$  is less than 3; and more preferably the ratio of  $D_{90}/D_{10}$  is less than 2.5.

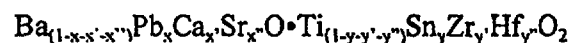
As used herein the term "dispersion" refers to two phase systems of solid particles suspended in a non-aqueous medium. In a preferred embodiment, the stability of the dispersion, or the resistance of the suspended solid particles to settling, can be enhanced by the use of a dispersing agent.

Except where the context is clear that a metal oxide only is meant, as used herein the term "metal oxide" is used to describe coatings of metal oxides, metal hydroxides, hydrous metal oxides, and organic acid salts of a metal. Such organic acid salt can be converted to an oxide or hydroxide, for example by thermal decomposition that occurs during heating for ceramic binder burnout and/or ceramic sintering.

As used herein the term "high shear mixing" means mixing in a liquid medium that imparts sufficient energy to separate agglomerates of the coated particles into smaller particles without the impact of a solid agent such as rods, cylinders, or hard spherical media, such as zirconia spheres. Hard media is used in certain high shear mixing equipment where small

sized media is used to create shear without impacting. Although high shear mixing can be effected by various equipment as described below, it is difficult to precisely define the force applied to separate agglomerates in high shear mixing.

As defined above, "barium titanate-based" refers to barium titanate, barium titanate having another metal oxide coating, and other oxides based on barium and titanate having the general structure  $ABO_3$ , where A represents one or more divalent metals such as barium, calcium, lead, strontium, magnesium and zinc, and B represents one or more tetravalent metals such as titanium, tin, zirconium and hafnium. A preferred barium titanate-based material which typically can be used in Y5V applications has the structure  $Ba_{(1-x)}A_xO \cdot Ti_{(1-y)}B_yO_2$ , where x and y can be in the range of 0 to 1, where A represents one or more divalent metals other than barium such as lead, calcium or strontium, and B represents one or more tetravalent metals other than titanium such as tin, zirconium and hafnium. Where the other metals are present as impurities, the value of x and y will be small, for example less than 0.1. In other cases, other metal or metals can be introduced to provide a significantly identifiable compound such as barium-calcium titanate, barium-strontium titanate, barium titanate-zirconate, and the like. In still other cases where x or y is 1, barium or titanium can be replaced by the other metal of appropriate valence to provide a compound such as lead titanate or barium zirconate. In still other cases, the compound can have multiple partial substitutions of barium or titanium. An example of such multiply partial substituted composition is represented by the structural formula



where x, x', x'', y, y', and y'' are each  $\geq 0$ , and  $(x + x' + x'')$  is  $< 1$ , and  $(y + y' + y'')$  is  $< 1$ . In many cases, the barium titanate-based material will be disposed with a perovskite crystal structure, and it is preferred that the barium titanate material have a perovskite structure.

While hydrothermally-produced, barium titanate particles are conventionally dried into powders, the particles form into relatively strongly-agglomerated particles that are not effectively deagglomerated by simple high shear mixing. Dispersions made from such dry, agglomerated, barium titanate-based particles, which have a submicron primary particle size require a substantially long duration of impact milling to provide particles in the micron range, and longer more intense milling for submicron particles. In contrast, agglomerated metal oxide-coated, barium titanate-based particles having a submicron primary particle size

may be deagglomerated to the submicron size range of the coated particles by the moderate action of high shear mixing of slurries, dispersions, or slips comprising such particles in non-aqueous media.

The non-aqueous slurries, dispersions, or slips of barium titanate-based particles of the present invention can be prepared from barium titanate-based particles produced hydrothermally are maintained in an aqueous environment, such as an aqueous slurry, at least until the particles are provided with a coating, after which the aqueous phase is replaced with a non-aqueous phase as described further below.

A slurry of submicron barium titanate-based particles can be prepared by a hydrothermal process, for example as disclosed in U.S. Patent Nos. 4,832,939; 4,829,033; and 4,863,833. In such hydrothermal processes, an excess amount, up to about 20 mole percent excess, of barium hydroxide solution is typically added to a hydrous titanium oxide slurry and heated, typically to a temperature in the range of between about 100°C and 200°C, to create submicron particles with perovskite crystalline structure. The particle size and particle size distribution can be manipulated by controlling various process variables, such as temperatures of slurry and solutions, addition rate, and heating rate to and cooling rate from the perovskite forming temperature. The selection of process variables for a desired particle product can be readily determined by those skilled in the art following general principles of crystallization. For instance, larger particles can be prepared by adding barium hydroxide relatively slowly to a slurry maintained at a relatively low temperature, for example about 35°C; while smaller particles can be prepared by adding barium hydroxide relatively quickly to a slurry maintained at a relatively high temperature, for example about 95°C. Good agitation is important for preparing uniform particles.

After the perovskite structure is imparted to barium titanate particles by thermal treatment of a slurry, the particles are preferably washed to remove unreacted metal species such as barium ions. Washing can be effected with ammoniated de-ionized water at pH 10 to prevent barium from dissolving from the particles. The wash water can be removed by filtration or decanting from settled particles. The number of wash cycles will be determined by the purity desired in the aqueous phase, such as to provide a slurry with a low ionic strength having a conductivity less than 5 milliSiemens, preferably less than 1 milliSiemens. Four to five washing cycles has been found to be adequate to reduce the ion content of the

water phase to a low level characterized by a conductivity of not more than about 100 microSiemens.

The barium titanate particles may be maintained in an aqueous state until after the coating process. As discussed above, the barium titanate-based particles may include a coating comprising an oxide, hydrous oxide, hydroxide or organic acid salt of at least one metal other than barium and titanium. The coatings can be provided by adding to an agitated slurry of barium titanate-based particles an aqueous solution(s) of salts, such as nitrates, borates, oxalates, and the like, of metals corresponding to the desired coating. Precipitation to the coating is promoted by an appropriate pH. Salt solutions can be added either as one mixture of salt to form a single layer homogenous coating, or separately and sequentially to form individual oxide, hydrous oxide, hydroxide or organic acid salt layers. In the case of metals of relatively higher solubility, such as cobalt and nickel, oxide coatings tend to be more difficult to apply and maintain without resolubilization. Therefore, it is often preferred to apply oxide coatings of these more soluble metals as a top coating over more readily deposited metal oxide layers. An alkaline environment also minimizes solubilization of barium, and readily provides particles with a barium- and titanium-free coatings. Coatings of particles intended for ceramic capacitor application typically have a thickness less than 10 percent of the diameter of the particle, often less than 20 nm thick, and preferably not more than between 5 nm and 10 nm thick.

Useful organic acid salt coatings include those which are organic salts of metals that have a low solubility. Examples of such organic acid salt coatings are metal salts of oxalic acid (for example, niobium oxalate), citric acid, tartaric acid and palmitic acid. It is believed that the organic acid salt will be converted to a metal oxide during binder burnout. The selection of metal is made on the basis of enhancement imparted to the processing or properties of MLC's. The metal in coatings is typically selected from among bismuth, lithium, magnesium, calcium, strontium, scandium, zirconium, hafnium, vanadium, niobium, tantalum, tungsten, manganese, cobalt, nickel, zinc, boron, silicon, antimony, tin, yttrium, lanthanum, lead, and the Lanthanide elements. Preferably, the barium titanate particles have a barium- and titanium-free metal oxide coating. When ceramic capacitors with X7R dielectric properties are desired, it is useful to provide the barium titanate particles with dopants such as niobium oxide, tantalum oxide, or neodymium oxide, in combination with nickel oxide, or cobalt oxide. When it is desired to provide ceramic capacitors that are sintered at relatively

low temperatures, for example in the range of about 1000°C and 1200°C, as compared to about 1300°C and 1600°C, it is useful to provide the barium titanate particles with a dopant that promotes low temperature sintering. Such low temperature sintering aids include bismuth oxide, zinc oxide, zinc borate, zinc vanadate, lithium borate, and combinations thereof.

5 Dielectric-modifying and sintering temperature-lowering metal oxides can be effectively added to the barium titanate-based particles after the particles have been washed and prior to formation of dispersible wet cake.

After a coating is applied to hydrothermally-produced barium titanate-based particles, the slurry can be washed and the water content of the slurry can be reduced to provide a  
10 concentrated slurry, wet cake or powder. Moreover, the slurry, wet cake or powder can be treated with a dispersing agent to provide a dispersion, and further treated with a binder and other additives to provide a slip. Water is preferably removed by means that avoids or at least minimizes formation of strongly-agglomerated particles, such as in calcination. Because they are not calcined or dried, certain metal oxide coatings may tend to remain in the form of a  
15 hydrated metal oxide, which can be soluble if not maintained at a pH near that for minimum solubility for that metal oxide. For instance, nickel oxide or cobalt oxides tend to be somewhat soluble if not maintained at a pH near 10. Thus, to maintain a properly coated particle, the pH of an aqueous component are preferably maintained in the range of 9 to 11. Slurries of metal oxide-coated, barium titanate-based particles are conveniently produced at a  
20 relatively low level of solids, for example less than 30 wt% barium titanate-based particles. A higher levels of solids is typically preferred for the production of MLC's. Thus, in the case where a slurry of this invention is to be used directly in the manufacture of MLC's, it is useful to concentrate the slurry, for example by removing water such as by filtration, to at least 40 wt% solids; preferably, at least 50 wt% solids; more preferably, at least 55 wt% solids; and  
25 even more preferably, in the range of at least about 60 or 75 wt% solids. A dispersing agent and binder can be added to concentrated slurry to provide a slip or a stable dispersion of the barium titanate-based particles.

As noted above, after the barium titanate based particles have been coated, the aqueous phase can be replaced with a non-aqueous phase. The aqueous phase may be replaced with an  
30 organic liquid phase by solvent exchange or distillation. In the solvent exchange process a filtration device can be used. In a preferred embodiment, the filtration device is a Funda™ filter that includes flat trays, lined with an ultra-filtration membrane, which are mounted on a

central standpipe. Liquid flows through the FUNDA™ filter, and is removed through this central standpipe. Once the filtration operation is complete, the filter cake is spun off of the trays using centrifugal force. The solids then drop through a valve to the next processing step. Ultrafiltration membrane material is utilized due to the sub-micron particle size of hydrothermal barium titanate.

In operation, the solvent exchange process first involves pumping an aqueous slurry of barium titanate particles into the filter device. Water is removed through the ultrafiltration membrane. After most of the water is removed, an anhydrous water-miscible organic solvent, such as methylethyleketone (MEK) or toluene (described below), is introduced into the filter device. This water-miscible solvent is added and removed from the filter device through the ultrafiltration membrane material until the water content of the barium titanate filter cake decreases to a desired value. Once water has been removed from the filter cake using the water-soluble solvent, a water insoluble solvent is then added. Enough of the water insoluble solvent is added and removed through the ultrafiltration material to dilute the concentration of the water-soluble solvent to a desired value. The barium titanate is then spun off the ultrafiltration material, and it is dropped into a mixing tank positioned below the filter device.

Once the barium titanate enters the mixing tank located below the filter device, a dispersant is added and the vessel contents are mixed until a homogeneous slurry is obtained. Desiccants, such as activated alumina, can be added if a low water content is desired. The dispersed slurry is then pumped to milling and packaging.

Another method to accomplish solvent exchange is through a distillation process. This process involves a mixed batch distillation vessel, a condensing heat exchanger, and a phase separation tank. In operation, the aqueous barium titanate slurry is pumped into the distillation tank, and the desired organic solvent is added. If the desired organic solvent is not miscible in water, a small amount of a water-miscible solvent, such as a high molecular weight alcohol can be added. The components are then mixed to an emulsion and heated. The distillation process is preferably used with high molecular weight solvents, which have a higher boiling point than water. The heating of the mixture selectively drives off water, leaving the barium titanate dispersed in the organic media. The phase separation tank, located downstream of a condenser unit, separates the water from any solvent, which would also be removed during the distillation. The solvent is then pumped back into the distillation vessel, and water is pumped to waste. A vacuum could also be used with the phase separation tank to

force the distillation to occur at a lower temperature. During the distillation process dispersant can be added to prevent the slurry from solidifying in the distillation vessel. Once the desired water content is achieved, solvent is no longer recycled, and the mixture is then concentrated via distillation to achieve the desired percent solids.

5           Similar to the ultrafiltration process described above, if a low water content is desired, the mixture in the distillation tank can be fed through a bed containing a desiccant, such as activated silica, or activated alumina. It is also noted that the thermodynamic efficiency of the distillation process can be improved by adding ultrafiltration modules upstream to feed the aqueous barium titanate slurry into the distillation vessel. These ultrafiltration modules would  
10           remove most of the water from the aqueous barium titanate slurry before it is introduced to the distillation process.

          A non-aqueous slurry can also be concentrated, for example by filtration, to provide a solid wet cake, which is a non-flowing solid comprising metal oxide-coated, barium titanate-based particles and liquid. A non-aqueous wet cake can be in a solid state with about 60 wt%  
15           solids mixed with a non-aqueous solution. More preferably, wet cake will comprise at least 65 wt% solids; and more preferably, at least 70 wt% solids. Wet cake can comprise up to about 85 wt% solids. In non-aqueous wet cake the non-aqueous solution should have a pH greater than 8 to inhibit metal dissolution. A preferred pH range is between about 8 and 12; more preferably, the pH range is between about 9 and 11. Wet cake of barium titanate-based  
20           particles is a colloidal dispersion precursor. That is, the wet cake can be dispersed, for example by admixture with a dispersing agent. Little, if any, additional liquid medium is required to transform a wet cake from a solid state into a fluid dispersion.

          At least in the case of non-aqueous wet cake, the particles in the cake will remain weakly-agglomerated for a relatively long time as long as the cake is maintained with a liquid  
25           content of at least 15 wt%; more preferably, as long as the cake is maintained with a liquid content of at least 20 wt%; and more preferably, as long as the cake is maintained with a liquid content of at least 25 wt%.

          Preferably the wet cake is encapsulated in a moisture barrier to inhibit loss of water content that could promote formation of strongly agglomerated particles which are not readily  
30           deagglomerated. Such moisture barrier, such as polyethylene bags or polyethylene-coated fiber drums, can provide an extended shelf life of at least one day or more; preferably, an extended shelf life of at least 3 days; more preferably, an extended shelf life of at least 30

days; and most preferably, an extended shelf life of at least 90 days. Such characteristics facilitate storage and transportation of the wet cake embodiment of the invention.

The wet cake is readily transformed into a fluid dispersion by incorporating into the cake a dispersing agent without a significant addition of fluid. Although fluid can be added to the cake, the amount of dispersing agent required to transform a solid cake into a fluid dispersion is remarkably small, for example typically less than 2 wt%, based on weight of the barium titanate-based material. In some cases no additional fluid other than the fluid volume of the dispersing agent is required to transform a wet cake into a fluid dispersion. Contemplated dispersing agents are polyelectrolytes which include organic polymers with anionic or cationic functional groups. Anionically functionalized polymers include carboxylic acid polymers such as polystyrene sulfonic acid and polyacrylic acid; cationically functionalized polymers include polyimides such as polyetherimide and polyethyleneimine. Polyacrylic acids are preferred for many applications. While polymeric acid groups can be protonated, it is preferable that such acid groups have a counter cation that will avoid reduction of dispersion pH to a level that will promote dissolution of barium or other metal species, such as might be present in dopant coatings. For capacitor applications a preferred cation is the ammonium ion. In some cases, it may be feasible to employ dopant metals as the counter cation for the polymeric acid dispersant. Regardless of the dispersing agent selected the appropriate amount of dispersing agent can be readily determined by those skilled in the art through a process of titration. When the amount of dispersing agent selected is that amount which provides the lowest viscosity for the dispersion, the concentration of dispersing agent can be reduced on use of the dispersion, such as by dilution or interaction with additives, to cause the viscosity to rise to an undesirably high level. Thus, for many applications it is desirable to employ a "viscosity minimizing amount" of dispersing agent.

A preferred dispersing agent for use in colloidal dispersions intended for capacitor applications and for such testing has been found to be an ammoniated polyacrylic acid having a number average molecular weight of about 8000. For instance, 0.75 wt% of such ammoniated polyacrylic acid (as a 40 wt% aqueous solution) has been found to be useful for transforming wet cake into a liquid dispersion. The incorporation of dispersing agent can be done by convenient means such as mechanically blending dispersant into the wet cake. When high shear mixing is employed, excess dispersing agent is consumed by new particle surface area exposed by deagglomeration. Thus, it may be convenient to add dispersing agent

incrementally in the course of high shear mixing.

Wet cake is distinguished from slurries, dispersions, slips, and dry powders in that wet cake is a non-flowing solid, while slurries, dispersions and slips are fluid liquids, and dry powders are flowing solids. Moist powders may or may not flow depending on the amount of liquid present. As more liquid is removed moist powder becomes progressively drier. It is understood, however, that dry powder is not necessarily totally dehydrated. Spray drying, freeze drying and low temperature vacuum-assisted drying are preferred methods for providing dry powders of coated, barium titanate-based particles which remain dispersible merely by mixing into dispersing agent-containing solution, for example with high shear mixing. Thus, dry powders of coated, barium titanate-based particles are surprisingly dispersible into dispersions of submicron particles without the need for long duration, impact milling. Unlike known materials, high energy milling for several hours is not required to reduce the particle size to a point where dispersions or slips of the coated, barium titanate-based particles can be used to make capacitors with fine grained, thin dielectric layers and high breakdown voltage.

Another aspect of this invention provides methods of making a dispersion of submicron, coated, barium titanate-based particles in a solution by deagglomerating a dispersion of large (greater than 1  $\mu\text{m}$ ), weakly-agglomerated metal oxide-coated, barium titanate-based particles until substantially all of the particles are less than 1  $\mu\text{m}$ . In a preferred method of this invention high solids dispersions, comprising between about 30 wt% and 75 wt% particles, are deagglomerated by high shear mixing with a dispersing agent. The optimal time for high shear mixing is readily determined by routine experimentation. High shear mixing can be effected in a centrifugal pumping deagglomerating mill, commercially available, for example, from Silverson Machine Inc. (East Longmeadow, MA). Other apparatus useful for providing the deagglomerated dispersions include what is known as supermills, colloid mills, and cavitation mills. Supermills have a media-filled milling chamber with high speed rotating discs on a central shaft, and are commercially available, for example, from Premier Mill (Reading, PA). Colloid mills have a grinding gap between extended surfaces of a high speed rotor and a fixed stator, and are also commercially available, for example, from Premier Mill. In cavitation mills, which are commercially available, for example, from Arde Barinco Inc. (Norwood, NJ), fluid is pumped through a series of rapidly opening and closing chambers that rapidly compress and decompress the

fluid imparting a high frequency shearing effect that can deagglomerate particles. It is expected that concentrated slurry, dispersions, wet cake, moist powder, or dry powder will perform equally well in providing slips for manufacture of high performance capacitors, depending on unique capacitor manufacturing facilities or methods.

5           A test to determine the effective amount of dispersing agent for weakly agglomerated coated barium titanate-based particles comprises using a high shear mixer, such as a Silverson Model L4R high shear laboratory mixer, equipped with a square hole high shear screen to high shear mix a 500 g sample of a dispersion comprising 70 wt% of the coated particles in an alkaline non-aqueous solution at a temperature range of between 25°C and 30°C, a pH at  
10       which the coating will not dissolve, and containing an effective amount of dispersing agent for an effective time for deagglomerating coated particles. An effective amount of dispersing agent is sufficient to maintain separated agglomerates and aggregates in the smaller particle sizes without reagglomeration. An effective amount of dispersing agent will vary depending on factors such as the size of particles, the nature of the coating and the power of the  
15       dispersing agent. An effective amount of dispersing agent and effective time can be readily determined with a few routine experiments by those skilled in the art observing the effect of variables, such as concentration of dispersing agent and high shear mixing time, on reducing the magnitude of particle size distribution. An effective amount of those variables will allow a particle size analysis that reflects the true effect of high shear mixing on deagglomeration.  
20       For many cases it had been found that an effective amount of ammoniated polyacrylic acid dispersing agent (number average molecular weight of about 8000) is about 1 wt% dispersing agent per total weight of particles and dispersing agent, and an effective high shear mixing time is about 1 minute.

          The coated, barium titanate-based particles prepared by hydrothermal processes are  
25       substantially spherical, and equiaxed in appearance. Such particles remain substantially spherical even after size reduction by high shear mixing. Occasionally, substantially spherical particles may be twinned. The occurrence of twinned particles is desirably rare. The use of spherical particles, as compared to non-spherical milled powders, provides powders characterized with exceptionally high surface area, having a BET surface area of at least about  
30       4 m<sup>2</sup>/g; preferably, the spherical particles have a BET surface area of at least about 8 m<sup>2</sup>/g, more preferably, the spherical particles have a BET surface area of at least about 12 m<sup>2</sup>/g.

          Submicron, coated, barium titanate particles are suspendable with a wide variety of

binders, dispersants, and release agents using non-aqueous solvents to provide ceramic casting slips.

The barium titanate-based particles are dispersed in an organic solvent containing dissolved polymeric binder and, optionally, other dissolved materials such as plasticizers, release agents, dispersing agents, stripping agents, antifouling agents and wetting agents. Useful organic solvents have low boiling points and include benzene, methyl ethyl ketone, acetone, xylene, methanol, ethanol, propanol, 1,1,1-trichloroethane, tetrachloroethylene, amyl acetate, 2,2,4-triethyl pentanediol-1,3-monoisobutyrate, toluene, methylene chloride, turpentine, ethyl alcohol, bromochloromethane, butanol, diacetone, methyl isobutyl ketone, cyclohexanone, methyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, n-octyl alcohol, benzyl alcohol, glycerol, ethylene glycol, benzaldehyde, propionic acid, n-octanoic acid, ethylacetate, butylbutyrate, n-hexane, and the like, and including mixtures thereof, and mixtures with water such as methanol/water mixtures. In addition, several azeotropic organic solvent mixtures have low boiling points and can be used as a carrier vehicle. The solvent mixtures can include, for example, 72% trichloroethylene/28% ethyl alcohol, 66% methyl ethyl ketone/34% ethyl alcohol, 70% methyl ethyl ketone/30% ethyl alcohol, 59% methyl ethyl ketone/41% ethyl alcohol, 50% methyl ethyl ketone/50% ethyl alcohol, 80% toluene/20% ethanol, 80% toluene/20% ethyl alcohol, 70% toluene/30% ethyl alcohol, 60% toluene/40% ethyl alcohol, 70% isopropyl alcohol/30% methyl ethyl ketone, 40% methyl ethyl ketone/60% ethyl alcohol, and mixtures thereof.

In addition to those disclosed above, dispersants (deflocculants/wetting agents) useful in non-aqueous dispersions of submicron, metal oxide-coated, barium titanate particles include, for example, phosphate ester, glycol trioleate, ethoxylate, 2-amino-2-methyl-1-propanol, tall oil hydroxyethylimidazoline, oleic hydroxyethylimidazoline, fatty acids such as glycerol trioleate, lanolin fatty acids, poly(vinyl butyral), sodium bis(tridecyl) sulfosuccinate, diisobutyl sodium sulfosuccinate, sodium dioctyl sulfosuccinate, ethoxylated alkylguanidine amine, sodium dihexylsulfosuccinate, sodium diisobutylsulfosuccinate, benzenesulfonic acid, oil soluble sulfonates, alkyl ether of poly(ethylene glycol), oleic acid ethylene oxide adduct, sorbitan trioleate, steric acid amide ethylene oxide adduct, alkylaryl polyether alcohols, ethyl ether of poly(ethylene glycol), ethyl phenyl glycol, polyoxyethylene acetate, polyoxyethylene ester, and the like. Preferred dispersing agents for organic solvent suspensions and slips include menhadden oil, corn oil, polyethyleneimine, and ammoniated polyacrylic acid.

Among the polymeric binder materials useful in non-aqueous slips, for example, are poly(vinyl butyral), poly(vinyl acetate), poly(vinyl alcohol), cellulosic polymers such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, methylhydroxyethyl cellulose, cellulose acetate butyrate, nitrocellulose, polypropylene, polyethylene, silicon polymers such as poly(methyl siloxane) and poly(methylphenyl siloxane), polystyrene, butadiene/styrene copolymer, poly(vinyl pyrrolidone), polyamides, polyethers, poly(ethylene oxide-propylene oxide), polyacrylamides, and acrylic polymers such as sodium polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polyacrylate esters, and copolymers, such as copolymers of ethyl methacrylate and methyl acrylate, poly(vinyl alcohol), poly(vinyl chloride), vinyl chloride acetate, poly(tetrafluoroethylene), poly( $\alpha$ -methylstyrene), and the like. Polymeric binders are typically useful in the range of between about 5 to 20 wt%. A preferred commercially available polymer is ACRYLOID™ B-7 acrylate polymer (Rohm & Haas Co., Philadelphia, PA).

Frequently, the organic medium will also contain a small amount of a plasticizer to lower the glass transition temperature ( $T_g$ ) of the binder polymer. The choice of plasticizers is determined primarily by the polymer which must be modified and can include phthalate esters (and mixed phthalate esters) such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, butyl benzyl phthalate, alkyl phosphates, poly(alkylene glycol), polyethylene glycol, glycerol, poly(ethylene oxides), hydroxyethylated alkyl phenol, dialkyl dithiophosphonate, poly(isobutylene), butyl stearate, methyl abietate, tricresyl phosphate, dipropylglycol dibenzoate, and the like.

In one embodiment an organic solvent-based slip of the invention comprises, per 100 parts by weight of barium titanate-based particles:

- 25 to 40 parts of organic solvent,
- 2 to 5 parts of dispersing agent,
- 5 to 20 parts of polymeric binder, and
- 0 to 15 parts of plasticizer.

The dispersion of the barium titanate-based particles in various non-aqueous solvents can be promoted with the application of various coatings, such as coupling agents, to the surface of the particles. The wide range of available silane coupling agents in particular provides a means to tailor the particle surface to the carrier vehicle of choice. Coating of the

hydrothermally derived barium titanate-based particles with a silane coupling agent could be useful not only for dried powders, but also particles remaining in solution. Although silane coupling agents can be applied to the surface of the powders with or without drying, the coupling agent preferably would be applied after drying of the particles to aid in their dispersion in the carrier vehicle. Moreover, drying of the powders provides an easy mechanism to determine whether a complete coating is achieved by attempting to disperse the treated powder in water. Uncoated or partially coated powders will partially or fully disperse in water, whereas fully coated particles will float on top of the water even with agitation.

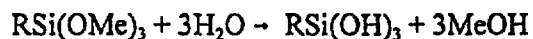
Particles can be coated in one carrier vehicle and then transferred to another carrier vehicle via solvent exchange processing (as described above), or distillation processing. Although silane coupling agents can be applied to the surface of the powders before or after a solvent exchange, it is preferred to apply the coating after the solvent exchange processing. Silane coupling agents can be attached to a particle surface to aid dispersion in a desired carrier vehicle, and to help in passivating the particle surface.

The general formula of an organosilane,  $R_nSiX_{(4-n)}$ , shows two classes of functionality. The X group is involved in the reaction with the inorganic substrate. The bond between X and the silicon atom in coupling agents is replaced by a bond between the inorganic substrate and the silicon atom. X is a hydrolyzable group, typically, alkoxy, acyloxy, amine, or chlorine. The most common alkox groups are methoxy and ethoxy, which give methanol and ethanol as byproducts during coupling reactions. Since chlorosilanes generate hydrogen chloride as a byproduct during coupling reactions, they are generally utilized less than alkoxysilanes. R is a nonhydrolyzable organic radical that possesses a functionality that enables the coupling agent to bond with organic resins and polymers. Most of the widely used organosilanes have one organic substituent. In most cases the silane is subjected to hydrolysis prior to the surface treatment. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, iron, and carbon. Alkali metal oxides and carbonates do not form stable bonds with Si-O-.

Water for hydrolysis may come from several sources. It may be added, it may be present on the substrate surface, or it may come from the atmosphere. Reaction of these

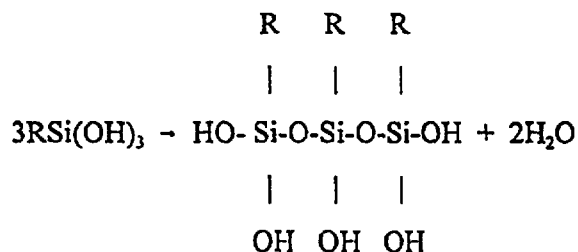
silanes involves four steps demonstrated below with a trimethoxy hydrolyzable X group.

- Initially, hydrolysis of the three liable X groups attached to silicon occurs.



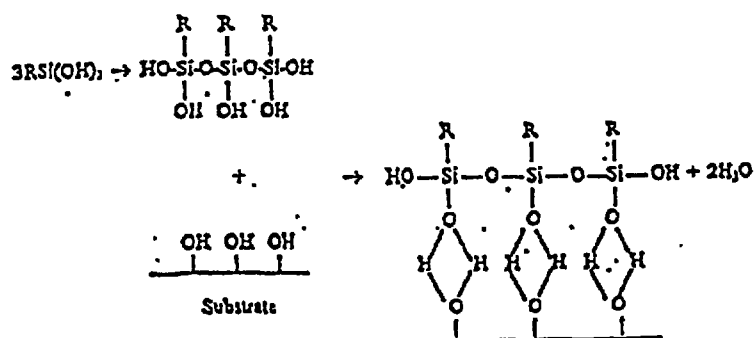
- Condensation to oligomers follows:

5

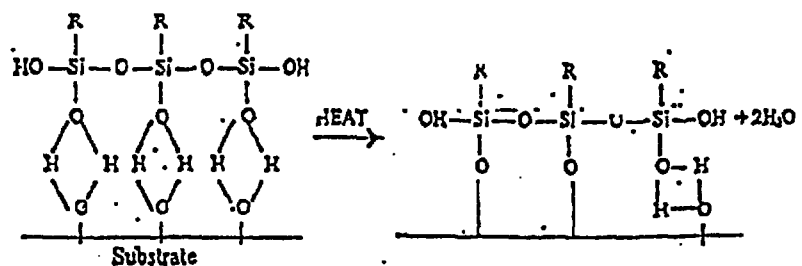


10

- The oligomers then hydrogen bond with OH groups of the substrate:



- Finally, during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water.



At the interface, there is usually only one bond from each silicon of the organosilane to the

substrate surface. The two remaining silanol groups are present either bonded to other coupling agent silicon atoms or in free form.

With organic solvent-based slips, green tapes can be formed onto carrier surfaces by methods known to the skilled artisan. See, for example, J.C. Williams at page 173-197 of Ceramic Fabrication Processes, Volume 9 of Treatise on Materials Science and Technology, Academic Press (1976), and U.S. Patent Nos. 3,717,487 and 4,640,905, both of which are incorporated herein by reference.

Moreover, there exists a variety of techniques for converting slips into thin films, green layers and fired ceramics. It is believed that the dispersions of this invention will find application, with minor modification, for example selection of preferred suspension medium and binder, dilution to a desired fluid viscosity, etc., in the various ceramic processes for making dielectric layers for MLC's. Slips can be formed into films by spraying, layering onto a moving sheet from a waterfall or die (such as a doctor blade) and other methods used in the MLC industry. When sufficient non-aqueous liquid is removed from the film, a cohesive, solid "green" film is provided which can be coated in a registered pattern on one or both sides with a conductor material or conductive material precursor, such as ink containing fine particles of palladium, silver, nickel or alloys of palladium and silver. Such conductive inks can contain fine particles of the metal and ceramic. Sheets of green film are typically stacked, for example up to 250 layers or more, and diced into MLC-sized cubes which are fired to burn out polymeric binder and dispersant and sintered to form a dense multilayer capacitor structure with fine grain structure dielectric layers. Conductive metal applied to the ends can connect the alternating conductive interlayers forming the MLC.

The unique particle size properties of barium titanate-based particles of this invention are expected to allow the production of novel MLC's having ultrathin layers of dielectric ceramic having submicron grains. Such dielectric materials should facilitate significant increases in volumetric capacitance. Moreover, it is expected that MLC's will have unexpectedly high breakdown voltage. The absence of large, for example greater than 1  $\mu\text{m}$ , particles should allow for the commercial production at high yields, for example greater than 98 %, of MLC's comprising multiple, for example greater than 40, dielectric layers. The particles of this invention are expected to be preferably used to produce MLC's having a dielectric ceramic layer with a maximum grain size is 0.9  $\mu\text{m}$  or less; more preferably, the maximum grain size is less than 0.8  $\mu\text{m}$ ; most preferably, the grain size is 0.7  $\mu\text{m}$  or less.

Other aspects of this invention provide X7R or Y5V capacitors comprising more than 20 dielectric layers of barium titanate-based material sintered into ceramic structure wherein said layers are less than 5  $\mu\text{m}$  thick, for example in the range of 2 to 4  $\mu\text{m}$  thick. A higher number of dielectric layers, for example 250 or 500, may be preferred depending on MLC design.

5 Thin dielectric layers allow MLC's with an increased number of dielectric layers to be used in a standard sized MLC or MLC's with a fixed number of layers to fit in a smaller sized package. The result is that the capacitance of standard sized MLC package can be readily increased by a factor of 5 to 10 or more.

For providing monolithic X7R MLC's the particles used to make the dielectric are preferably coated with oxides of niobium, cobalt, nickel and manganese. For low fire capability, for example sintering at below 1200°C, a preferred metal oxide coating can also contain bismuth oxide. To achieve ultrathin dielectric layers with a thickness less than 4 micrometers, the particles preferably have a primary particle size less than 0.3 micrometers, most preferably in the range of 0.1 to 0.2 micrometers. A uniform, fine grain size, for example less than 0.3 micrometers, in ultrathin dielectric layers provides superior dielectric strength in excess of 100 volts per micrometer and low dissipation factor. These properties provide increased reliability for high capacitance, high voltage ceramic capacitors. The ability to provide thin dielectric layers has allowed the production of capacitors having 5 to 10 times the capacitance for a standard case size. Such MLC's preferably comprise a monolithic ceramic body, for example, of metal oxide-doped barium titanate, two groups of interdigitated electrodes buried in said body and extending respectively to opposites ends of said body, and two conductive terminations contacting said two groups respectively at said opposite ends. MLC's with X7R characteristics have a temperature coefficient of capacitance over a temperature range of -55°C to 125°C which does not vary by more than  $\pm 15\%$  from the capacitance at 25°C. In a preferred aspect of this invention the ceramic in an X7R MLC has a grain size of less than 0.3 micrometers and comprises 93 to 98 weight percent of the barium titanate-based ceramic and 2 to 7 weight percent of other metal oxides.

The following examples are not intended as setting forth limitations to the scope of this invention.

30

#### EXAMPLE 1

To determine the effectiveness of dispersing barium titanate-based particles in a non-

aqueous solvent, hydrothermally derived, low fire X7R particles after drying were dispersed in a 80 toluene/20 ethanol solution with a phosphate ester dispersant.

An X7R formulated hydrothermally derived barium titanate wet cake, containing 72 weight percent solids and 28 weight percent water, was dried at 200°C in a rotating drying unit with applied vacuum.

Twenty (20) pounds of the dried X7R formulated hydrothermally derived barium titanate particles were then mixed with 6.7 pounds (3041.8 grams) of a 80 toluene/20 ethanol solvent mixture to form a slurry. The slurry was then mixed with a DISPERSATOR™ high shear mixer (Premier Mill) for 45 minutes while adding 0.8 pounds (363.2 grams) of a RHODAFAC RS-410™ phosphate ester dispersant (Rhone-Poulenc). The particle size distribution of the resultant slurry (Sample 1) was then measured, and the results are presented below and are illustrated in FIG. 1A.

The slurry was then mixed in a PREMIER™ horizontal media mill for 30 minutes (Premier Mill). The particle size distribution of the resultant slurry (Sample 2) was then measured, and the results are presented below and are illustrated in FIG. 1B.

The slurry was then mixed in the PREMIER™ horizontal media mill for an additional 15 minutes (45 minutes total). The particle size distribution of the resultant slurry (Sample 3) was then measured, and the results are presented below and are illustrated in FIG. 1C. The final solids loading was determined to be 78 weight percent.

| SAMPLE                           | D <sub>10</sub> | D <sub>50</sub> | D <sub>90</sub> | D <sub>90</sub> /D <sub>10</sub> |
|----------------------------------|-----------------|-----------------|-----------------|----------------------------------|
| 1. 45 Min. High Shear Mixer      | 10.6            | 65.3            | 225.6           | 21.3                             |
| 2. 30 Min. Horizontal Media Mill | 0.136           | 0.205           | 0.347           | 2.6                              |
| 3. 45 Min. Horizontal Media Mill | 0.133           | 0.192           | 0.356           | 2.7                              |

The above experimental results illustrate that the dried hydrothermally derived X7R powder may be dispersed in a 80 toluene/20 ethanol solvent mixture, using a phosphate ester dispersant. This demonstrates the ability to create a slurry with particles possessing a ratio ( $D_{90}/D_{10}$ ) of less than 3 from hydrothermally derived X7R powder in a non-aqueous solvent with the selection of an appropriate dispersant. It is believed that alternative solvents (such as, for example, those disclosed above), with an appropriate dispersant, may be used to create slurries with particles possessing a ratio ( $D_{90}/D_{10}$ ) of less than 3.

Although the results indicate that an X7R formulated hydrothermally derived barium titanate wet cake may be dried and redispersed in a non-aqueous solvent to form a slurry with particles possessing a ratio ( $D_{90}/D_{10}$ ) of less than 3, the dried particles formed into relatively strongly-agglomerated particles that are not effectively deagglomerated by high shear mixing. Dispersions made from such dry, agglomerated, barium titanate-based particles, which have a submicron primary particle size required a substantially long duration of media milling to provide particles in the submicron range. Also, it is believed that the heating used for drying the wet cake, particularly if it is performed under a high temperature and/or long period of time, may potentially effect a coating on the barium titanate-based particle. Such potential negative effects include, for example, bonding of a hydrous oxide coating layer between particles which could become difficult to separate without peeling or spalling of the coating layer from some of the barium titanate-based particles.

## EXAMPLE 2

To determine the effectiveness of dispersing barium titanate-based particles in a non-aqueous solvent, hydrothermally derived low fire X7R particles were subjected to a solvent exchange process, followed by dispersion with a phosphate ester dispersant. The hydrothermally derived low fire X7R particles were initially in water. The water was displaced by a 80 toluene/20 ethanol solvent mixture.

One kilogram (1 kg) of an X7R formulated hydrothermally derived barium titanate wet cake, containing 72 weight percent solids and 28 weight percent water, was slurried with one kilogram (1 kg) of ethanol. The slurry was then placed in a Buchner funnel containing an ultrafiltration membrane that was then used as the filter medium. The ethanol filtered through the formed wet cake, and cracks that formed were mechanically eliminated. Once the first filtration neared completion, one kilogram (1 kg) of ethanol was poured over and filtered through the wet cake. This step was repeated once the second filtration neared completion.

After the ethanol filtration was completed, one kilogram (1 kg) of toluene was added and filtered through the wet cake. The wet cake was then allowed to dry to a solids loading of 75 weight percent.

The resultant wet cake (859.3 grams) was then mixed with a DISPERSATOR™ high shear mixer (Premier Mill) with 26.81 grams of a RHODAFAC RS-410™ phosphate ester dispersant (Rhône-Poulenc). The high shear mixer was allowed to mix the wet cake for a

period of 10 minutes (Sample 4), and a period of 30 minutes (Sample 5). The particle size distributions were then measured, and the results are presented below and are illustrated in FIG. 2A and FIG. 2B.

| SAMPLE                      | D <sub>10</sub> | D <sub>50</sub> | D <sub>90</sub> | D <sub>90</sub> /D <sub>10</sub> |
|-----------------------------|-----------------|-----------------|-----------------|----------------------------------|
| 4. 10 Min. High Shear Mixer | 0.381           | 0.869           | 1.908           | 5.0                              |
| 5. 30 Min. High Shear Mixer | 0.351           | 0.764           | 1.805           | 5.1                              |

The above experimental results illustrate that solvent exchange may be used to replace aqueous solvents with non-aqueous solvents, if desired, followed by the addition of an appropriate dispersant to achieve an acceptable ratio ( $D_{90}/D_{10}$ ). The solvent exchange process provides dispersions having much narrower particle size distributions with only high shear mixing (without horizontal media mill) in less time than dispersions resulting from dried powders (as shown in EXAMPLE 1, Sample 1). Moreover, it is believed that a ratio ( $D_{90}/D_{10}$ ) of less than 3 from hydrothermally derived X7R powder in a non-aqueous solvent (from solvent exchange) with the selection of an appropriate dispersant may be achieved with less subsequent processing in a horizontal media mill (depending on other factors such as the batch size). It is also believed that alternative solvents (such as, for example, those disclosed above), with an appropriate dispersant, may be used to create slurries with particles possessing acceptable ratios ( $D_{90}/D_{10}$ ).

In addition to the foregoing, the solvent exchange process avoids the potential negative effects on the coating layer on the barium titanate-based particle from drying the wet cake, particularly under a high temperature and/or a long period of time.

### EXAMPLE 3

To determine the effectiveness of the use of silane coupling agents to promote the dispersion of barium titanate-based particles in a non-aqueous solvent, a hydrothermally derived X7R powder was coated using methyltrimethoxysilane as the coupling agent.

The methyltrimethoxysilane provides a hydrophobic coating, and was placed on the surface of the X7R formulated hydrothermally derived BaTiO<sub>3</sub> particles as follows:

1. 95 ml of ethanol was mixed with 5 ml of deionized water. The pH of the solution was

adjusted to 4 using 0.1M HNO<sub>3</sub>. Methyltrimethoxysilane (5 grams) was added to the acidified ethanol/water solution and stirred for 5 minutes to allow hydrolysis of the three liable methoxy groups.

2. X7R formulated BaTiO<sub>3</sub> wet cake (70 weight percent solids) was diluted with 250ml of ethanol and emulsified at 7000 rpm for 1 minute.
3. The ethanol/water solution containing the hydrolyzed silane coupling agent was added to the slurry containing X7R formulated hydrothermal particles and emulsified for 30 seconds at 7000 rpm.
4. The resulting slurry was allowed to air dry for 24 hours to remove excess carrier. The resultant material was then placed in a vacuum drying oven at 80°C for 12 hours to fully dry the powder.

Dilution of the X7R formulated wet cake with ethanol resulted in a very viscous suspension upon emulsification. The resultant dried powder was tested using a sink/float test on water to determine whether a hydrophobic coating was successfully attached to the surface of the powder. The powder was ground gently in a mortar and pestle and then sprinkled on top of water contained in a beaker. The particles floated on the surface of water initially, but when agitated some of the particles went into the solution. Therefore, when the X7R formulated wet cake was initially diluted with ethanol only partial coating of the surface was achieved. This partial coating is likely a result of the high viscosity that resulted when the X7R wet cake was diluted initially with ethanol. The high viscosity resulted in coating of agglomerates which tended to break down when mixed in the sink/float test.

#### EXAMPLE 4

To determine the effectiveness of the use of silane coupling agents to promote the dispersion of barium titanate-based particles in a non-aqueous solvent, a hydrothermally derived X7R powder was coated using methyltrimethoxysilane as the coupling agent.

The methyltrimethoxysilane provides a hydrophobic coating, and was placed on the surface of the X7R formulated hydrothermally derived BaTiO<sub>3</sub> particles as follows:

1. 95 ml of methanol was mixed with 5 ml of deionized water. The pH of the solution was adjusted to 4 using 0.1M HNO<sub>3</sub>. Methyltrimethoxysilane (5 grams) was added to the

acidified methanol/water solution and stirred for 5 minutes to allow hydrolysis of the three liable methoxy groups.

2. X7R formulated BaTiO<sub>3</sub> wet cake (70 weight percent solids) was diluted with 250 ml of methanol and emulsified at 7000 rpm for 1 minute.
- 5 3. The methanol/water solution containing the hydrolyzed silane coupling agent was added to the slurry containing X7R formulated hydrothermal particles and emulsified for 30 seconds at 7000 rpm.
4. The resulting slurry was allowed to air dry for 24 hours to remove excess carrier. The resultant material was then placed in a vacuum drying oven at 80°C for 12 hours to fully  
10 dry the powder.

The resultant dried powder was tested using a sink/float test on water to determine whether a hydrophobic coating was successfully attached to the surface of the powder. The powder was ground gently in a mortar and pestle and then sprinkled on top of water contained in a beaker. The particles floated on the surface of water and remained on the surface even  
15 during agitation. Therefore, when the X7R formulated wet cake was initially diluted with methanol, complete coating of the surface was achieved. Dilution of the X7R formulated wet cake with methanol resulted in a well dispersed slurry with low viscosity. This enable complete coating of the particles when the hydrolyzed silane coupling agent solution was added.

20 Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon specific application for which the methods and apparatuses of the invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced  
25 otherwise than as specifically described.

What is claimed is:

CLAIMS

1. A slurry, dispersion or slip comprising barium titanate-based particles dispersed in a non-aqueous medium, said particles having a coating comprising a metal oxide, metal  
5 hydrous oxide, metal hydroxide or organic acid salt of a metal other than barium or titanium, wherein at least 90 percent of said particles have a particle size of less than 0.9 micrometer when dispersed by high shear mixing.
2. The slurry, dispersion or slip of claim 1, wherein said particles have a particle size  
10 distribution decile ratio of  $D_{90}/D_{10}$  less than 4.
3. The slurry, dispersion or slip of claim 1, wherein said particles have a particle size distribution decile ratio of  $D_{90}/D_{10}$  less than 3.
- 15 4. The slurry, dispersion or slip of claim 1, wherein said particles have a particle size distribution decile ratio of  $D_{90}/D_{10}$  less than 2.5.
5. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.8 micrometer when said particles are dispersed by  
20 high shear mixing.
6. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.7 micrometer when said particles are dispersed by high shear mixing.  
25
7. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.6 micrometer when said particles are dispersed by high shear mixing.
- 30 8. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.5 micrometer when said particles are dispersed by high shear mixing.



9. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.4 micrometer when said particles are dispersed by high shear mixing.

5        10. The slurry, dispersion or slip of claim 1, wherein at least 90 percent of said particles have a particle size less than 0.3 micrometer when said particles are dispersed by high shear mixing.

11. The slurry, dispersion or slip of claim 1 comprising at least 50 weight percent of  
10 said particles.

12. The slurry, dispersion or slip of claim 1 comprising at least 60 weight percent of said particles.

15        13. The slurry, dispersion or slip of claim 1 comprising at least 75 weight percent of said particles.

14. The slurry, dispersion or slip of claim 1 further comprising a dispersant.

20        15. The slurry, dispersion or slip of claim 1, wherein said particles include a coupling agent coating on the surface of said particles.

16. The slurry, dispersion or slip of claim 15, wherein the coupling agent comprises an organosilane.

25

17. The slurry, dispersion or slip of claim 1 further comprising between 3 and 20 weight percent of a binder composition comprising a dissolved or suspended, film-forming, polymer.

30        18. The slurry, dispersion or slip of claim 1, wherein substantially all of said particles are equiaxed or spherical.



19. The slurry, dispersion or slip of claim 1, wherein said particles are hydrothermally-produced.

20. The slurry, dispersion or slip of claim 1, wherein said coating covers a major  
5 portion of the surface of the particles.

21. The slurry, dispersion or slip of claim 1, wherein said coating comprises at least one metal selected from the group consisting of bismuth, lithium, magnesium, calcium, strontium, scandium, zirconium, hafnium, vanadium, niobium, tantalum, tungsten,  
10 manganese, cobalt, nickel, zinc, boron, silicon, antimony, tin, yttrium, lanthanum, lead, or a Lanthanide element.

22. The slurry, dispersion or slip of claim 1, wherein the non-aqueous medium comprises an organic solvent.

15

23. The slurry, dispersion or slip of claim 22, wherein the non-aqueous medium comprises a mixture of organic solvent and water.

24. The slurry, dispersion or slip of claim 22, wherein the organic solvent is selected  
20 from the group consisting of benzene, methyl ethyl ketone, acetone, xylene, methanol, ethanol, propanol, 1,1,1-trichloroethane, tetrachloroethylene, amyl acetate, 2,2,4-triethyl pentanediol-1,3-monoisobutyrate, toluene, methylene chloride, turpentine, ethyl alcohol, bromochloromethane, butanol, diacetone, methyl isobutyl ketone, cyclohexanone, methyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, n-octyl alcohol, benzyl alcohol,  
25 glycerol, ethylene glycol, benzaldehyde, propionic acid, n-octanoic acid, ethylacetate, butylbutyrate, n-hexane, and mixtures thereof.

25. The slurry, dispersion or slip of claim 24, wherein the organic solvent is ethanol.

30 26. The slurry, dispersion or slip of claim 1, wherein the non-aqueous medium comprises a mixture of more than one organic solvent.



27. The slurry, dispersion or slip of claim 26, wherein said mixture is selected from the group consisting of 72% trichlorethylene/28% ethyl alcohol, 66% methyl ethyl ketone/34% ethyl alcohol, 70% methyl ethyl ketone/30% ethyl alcohol, 59% methyl ethyl ketone/41% ethyl alcohol, 50% methyl ethyl ketone/50% ethyl alcohol, 80% toluene/20% ethanol, 80% toluene/20% ethyl alcohol, 70% toluene/30% ethyl alcohol, 60% toluene/40% ethyl alcohol, 70% isopropyl alcohol/30% methyl ethyl ketone, 40% methyl ethyl ketone/60% ethyl alcohol, and mixtures thereof.

28. The slurry, dispersion or slip of claim 27, wherein the non-aqueous medium is 80% toluene/20% ethanol.

29. A method of forming a slurry, dispersion or slip comprising:  
forming a slurry of barium titanate-based particles in an aqueous medium by a hydrothermal process;  
forming a coating on said particles comprising a metal oxide, metal hydrous oxide, metal hydroxide or organic acid salt of a metal other than barium or titanium;  
replacing the aqueous medium with a non-aqueous medium; and  
dispersing said particles in the non-aqueous medium by high shear mixing.

30. The method of claim 29, wherein said particles are dispersed in the non-aqueous medium by high shear mixing until 90 percent of said particles have a particle size of less than 0.9 micrometer.

31. The method of claim 29, wherein replacing the aqueous medium with a non-aqueous medium comprises a solvent exchange process.

32. The method of claim 31, wherein the solvent exchange process comprises:  
filtering the slurry of barium titanate-based particles in the aqueous medium; and  
introducing the filtered particles into a non-aqueous medium.

33. The method of claim 29, wherein replacing the aqueous medium with a non-aqueous medium comprises a distillation process.



34. The method of claim 33, wherein the distillation process comprises:  
adding the non-aqueous medium to the slurry of barium titanate-based particles in the  
aqueous medium; and  
evaporating the aqueous medium.

5

35. The method of claim 29, further comprising applying a coupling agent to the  
surface of said particles after replacing the aqueous medium with a non-aqueous medium.

36. The method of claim 29, further comprising applying a coupling agent to the  
10 surface of said particles after forming a coating on said particles and prior to replacing the  
aqueous medium with a non-aqueous medium.

..

37. The method of claims 35 or 36, wherein the coupling agent comprises  
organosilane.

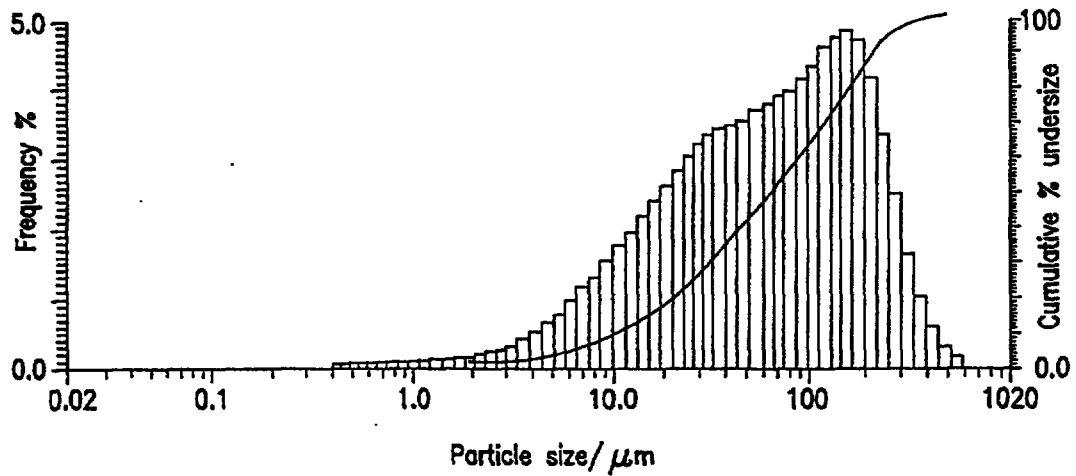
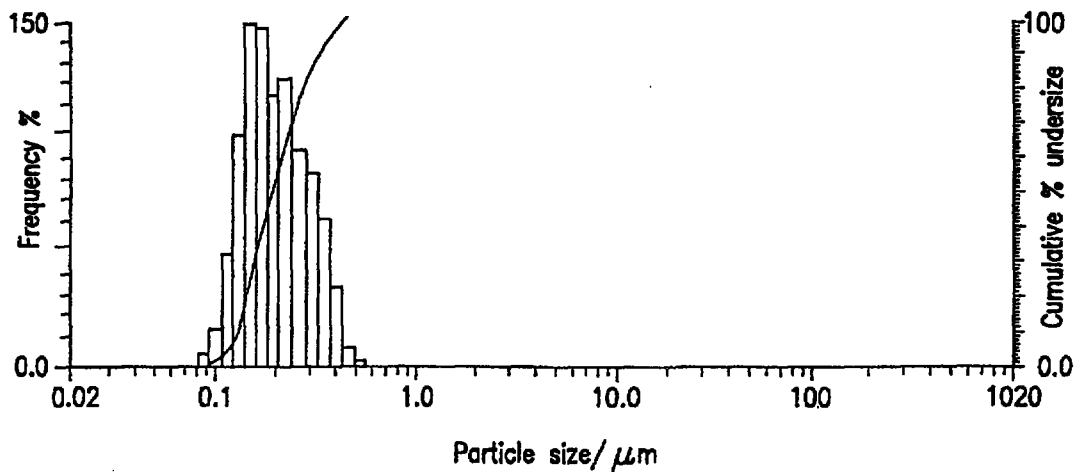
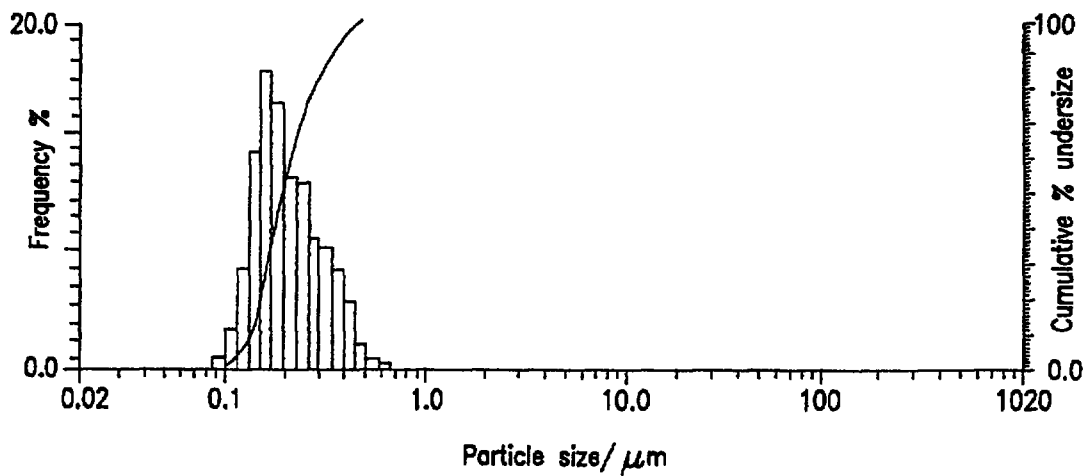
15

38. A method of forming a slurry, dispersion, or slip comprising:  
dispersing barium titanate-based particles in a non-aqueous medium by high shear  
mixing until 90 percent of said particles have a particle size of less than 0.9 micrometer, said  
particles having a coating comprising a metal oxide, metal hydrous oxide, metal hydroxide or  
20 organic acid salt of a metal other than barium or titanium.



\* C L M S \*

1 / 2

**FIG. 1A****FIG. 1B****FIG. 1C**

SUBSTITUTE SHEET (RULE 26)

2 / 2

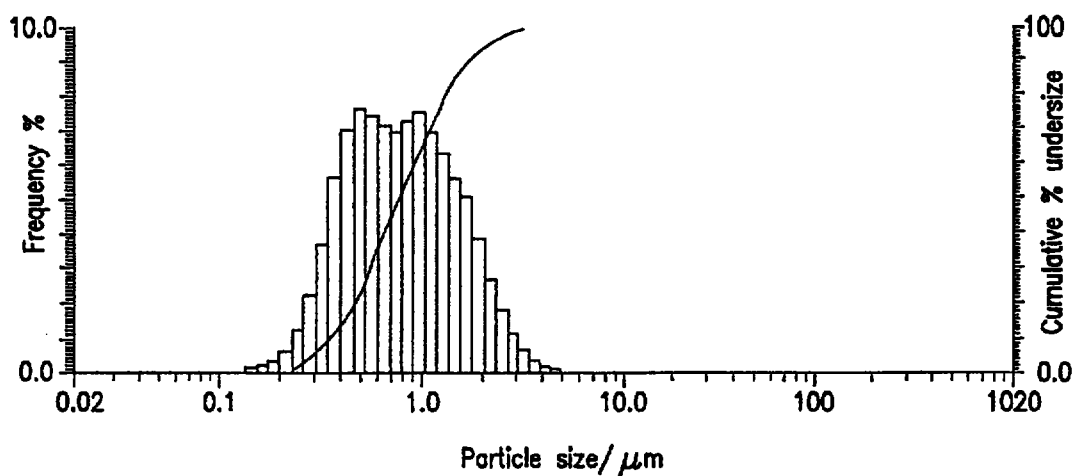


FIG. 2A

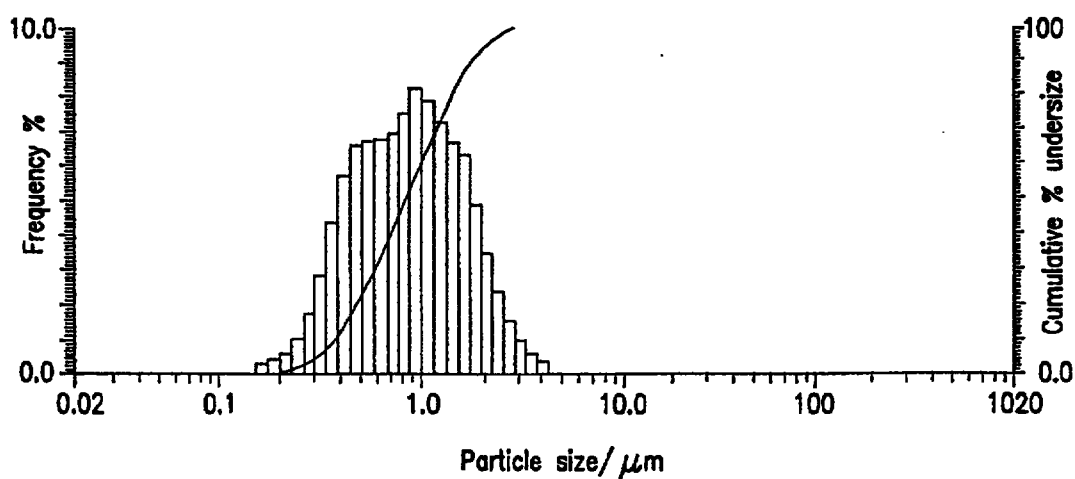


FIG. 2B

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

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

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>(51) International Patent Classification <sup>6</sup> :</b><br><b>C04B 35/628, 35/468, H01G 4/12</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 99/67189</b><br><b>(43) International Publication Date:</b> 29 December 1999 (29.12.99)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| <b>(21) International Application Number:</b> PCT/US99/13980<br><b>(22) International Filing Date:</b> 21 June 1999 (21.06.99)<br><br><b>(30) Priority Data:</b><br>60/090,408 23 June 1998 (23.06.98) US<br>60/096,668 14 August 1998 (14.08.98) US<br><br><b>(71) Applicant:</b> CABOT CORPORATION [US/US]; 75 State Street, Boston, MA 02109-1806 (US).<br><br><b>(72) Inventors:</b> MILLER, David, V.; 5787 Fresh Meadow Drive, Macungie, PA 18062 (US). VENIGALLA, Sridhar; 5354 Princeton Road, Macungie, PA 18062 (US). CLANCY, Donald, J.; 1296 Vale Circle, Pottstown, PA 19464 (US).<br><br><b>(74) Agent:</b> LANDO, Michelle, B.; Cabot Corporation, 157 Concord Road, P.O. Box 7001, Billerica, MA 01821-7001 (US). |           | <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, 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, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> BARIUM TITANATE DISPERSIONS<br><br><b>(57) Abstract</b><br><br>The invention provides slurries, dispersions, or slips of barium titanate-based particles in a non-aqueous medium and methods of their production. The particles have a coating comprising a metal oxide, metal hydrous oxide, metal hydroxide or organic acid salt of a metal other than barium or titanium. At least 90 percent of the particles have a particle size less than 0.9 micrometer when the coated particles are dispersed by high shear mixing.                                                                                                                                                                                  |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |