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HIGH-PURITY SPHERICAL SILICA AND PROCESS FOR
PRODUCING SAME

BACKGROUND OF THE INVENTION

Field of the Invention.

The present invention relates to high-purity spherical silica and a process for producing such silica.

The high-purity spherical silica according to the present invention has excellent surface smoothness and high sphericity and finds particularly advantageous use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts.

Hereinafter the resin compositions which contain a filler are referred to as encapsulating materials.

Description of the Related Art.

With the advancement of integrated circuits, the areal ratio of the chip in relation to its encapsulating material is increasing and the thickness of packages is decreasing. Also, demand is rising for higher quality encapsulating materials so that the chips can be well protected by a thin-section of such a material.

The encapsulating material is required to be resistant to thermal stress since thermal stress is built up due to the difference in thermal expansion coefficient between the silicon chip and the encapsulating material. In order to bring the thermal expansion coefficient of the encapsulating material as close as possible to that of the silicon chip, a method is employed in which silica with a low thermal expansion coefficient is added to resin as filler at the highest possible filling rate.

Hitherto, ground silica having irregular particle shape and sharp edges has been used as filler silica. However, the encapsulating material when filled with such ground silica to a high filling rate is increased in viscosity and therefore deteriorated in fluidity at the time

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of molding, making it difficult to obtain a homogeneous package having the desired properties. Also, the ground silica particles having sharp edges tend to cause early wear of the molding die and may break through the surface protective film of the chip to damage aluminium wiring on the chip. In view of the above, there is a demand in the industry for high-purity spherical silica having little capacity to reduce the fluidity of the encapsulating material and which is substantially free from sharp edges.

Various methods such as mentioned below have been proposed for producing high-purity spherical silica:

- (1) Powdered high-purity silica is fused in flames (for example JP-A-58-145613).
- (2) An alkyl silicate is hydrolyzed to form a sol-like solution thereof. This solution is atomized in a heated medium to form granules which are dried and then fused in flames (for example, JP-A-58-2233).
- (3) A silicon alkoxide is hydrolyzed to form a partially condensed sol. After removing alcohol from the sol, it is dispersed in water and the precipitated silica gel is collected and calcined (for example, JP-A-63-225538).

The calcination of silica produced according to the above prior art has been achieved under conditions which allow progress of perfect calcination until the pore volume became less than 0.01 ml/g, in consideration of possible change of silica into hydrophobic type, strength of calcined silica particles and other matters.

There is required further a higher purity of filler in the encapsulating material to prevent or minimise occurrence of soft errors in advanced integrated circuits and associated electronic parts.

A high-purity spherical silica adapted to meet the industry's needs would have a low content of impurities such as alkali metals, alkaline earth metals, halogens and



radioactive substances.

The above-mentioned conventional methods for producing spherical silica have the following problems:

The particles obtained according to the method (1) are low in sphericity and ineffective for improving fluidity.

According to the method (2), the silica particles produced from atomization vary in size depending on the condition of the sol solution, and it is difficult to obtain the spherical silica particles falling in the desired size range.

The spherical silica particles obtained according to the method (2) or (3) shrink greatly when calcined, forming particles with poor surface smoothness or surface unevenness. Lack of surface smoothness leads to low fluidity.

The methods (2) and (3) involve the additional problem of high cost of the material used and also necessitate disposal of waste water containing organic matter derived from the starting material.

The use of conventional spherical silica has prevented lowering of the fluidity of encapsulating materials to some extent as compared with the use of ground silica having sharp edges. This is true even when the filling rate of filler in the encapsulating materials is high. However, such improvement in encapsulating material fluidity as there is not so remarkable. Accordingly, spherical silica having high sphericity and excellent surface smoothness and suited for use as a filler for encapsulating materials has been a want in the industry.

SUMMARY OF THE INVENTION

An object of the present invention is to provide high-purity spherical silica suited for use as a filler for encapsulating materials of electronic parts, which silica,

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even when blended in a resin for encapsulating to a filling rate of 50-90 wt% based on the resin, will not cause substantial lowering of fluidity of the encapsulating material, and in which the content of radioactive and ionic impurities is significantly low. It is further an object of the invention to provide a process for producing such spherical silica.

The present inventors have pursued studies for overcoming the prior art problems such as mentioned above and, surprisingly, have found that by mixing an emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution to produce a spherical silica gel, treating the produced gel with a mineral acid to obtain hydrous spherical silica and subjecting the obtained silica to a heat treatment, it is possible to control sphericity and surface smoothness of spherical silica and to obtain high-purity spherical silica suited for use as a filler in encapsulating materials.

Accordingly, the present invention provides a process for producing high-purity, spherical silica, which comprises mixing an emulsion comprising an aqueous alkali silicate solution with an emulsion comprising an aqueous mineral acid solution to produce a silica gel comprising substantially spherical silica, treating the gel with a mineral acid to form hydrous spherical silica, and drying and then calcining the spherical silica. Preferably, the aqueous alkali silicate solution is provided in the form of a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as a disperse phase and in which the aqueous mineral acid solution is provided in the form of a water-in-oil (W/O) type emulsion, the aqueous mineral acid solution being dispersed in the form of fine particles as disperse phase.

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The invention further provides high purity spherical silica obtainable by the above process and comprising not more than 1 ppb of radioactive substances. Preferably, the electrical conductivity (at 25°C) of a solution obtained by boiling for 20 hours at 160°C a mixture of 10.0 g of the silica and 100 ml of distilled water is 10 μ S/cm or below. The high-purity spherical silica according to the invention generally comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0. The ratio of the measured value of specific surface area by the BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

Thus, in one aspect of the present invention, there is provided high-purity spherical silica which is obtainable from an aqueous alkali silicate solution and in which the content of radioactive substances is less than 1 ppb, the electric conductivity of the extract of boiling lixiviation of silica is 10 μ S/cm or below, the content of the particles with a sphericity of 0.9 to 1.0 is 90% or more, and the ratio of the measured value of specific surface area determined by BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

In a preferred embodiment of the process of the invention, the emulsions are water-in-oil (W/O) type emulsions in which an aqueous alkali silicate solution and an aqueous mineral acid solution, respectively, are dispersed in the form of fine particles as dispersed phase.

PREFERRED EMBODIMENTS OF THE INVENTION

The high-purity spherical silica according to the present invention is one which can be obtained from an aqueous alkali silicate solution and in which the content of radioactive substances is less than 1 ppb, the electrical



conductivity of the extract of boiling lixiviation of silica is 10 μ S/cm or less, the content of the particles having a sphericity of 0.9 or above is 90% or more, and the measured value of specific surface area by BET method is not higher than 3 times the theoretical value of specific surface area corresponding to the particle size.

The radioactive substances usually present in silica are U and Th. It is desirable that the content of these radioactive substances in the high-purity spherical silica of this invention is as low as possible. Specifically, the content should not exceed 1 ppb. If it exceeds 1 ppb, soft errors may be caused.

On the other hand, alkali metals such as Na, K and Li, alkaline earth metals such as Ca and Mg, and other ionic impurities such as Cl may cause corrosion of aluminium wiring, so that it is desirable that the high-purity spherical silica of this invention be substantially free of such impurities. The content of these impurities can be determined directly by appropriate analytical means, but in the present invention, the electrical conductivity of the extract of boiling lixiviation of silica was measured and given as an index of ionic impurity content. This system was employed for the following reasons:

- i) electrical conductivity can be directly adopted as a measure of quality or properties of the product;
- ii) this system is a more simple and clearer way of indication than direct analysis; and
- iii) this is a very strict method for evaluation of quality.

The electrical conductivity of the extract of boiling lixiviation of silica in the present invention is measured at 25°C with the specimen (extract) prepared by adding 10.0 g of sample silica to 100 ml of pure water and boiling the mixture at 160°C for 20 hours. In the high-

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purity spherical silica of this invention, the value of this electrical conductivity is not higher than 10 $\mu\text{S/cm}$.

The sphericity specified in the present invention is expressed by the ratio of the minimal diameter to the maximal diameter of one silica particle. The value of sphericity was determined by randomly selecting 20 particles on an electron micrograph of the silica particles, measuring the maximal diameter and the minimal diameter of each of the selected particles, and calculating the ratio of the minimal diameter to the maximal diameter of each particle.

In the high-purity spherical silica of the present invention, the content of the particles having a sphericity in a range of 0.9 to 1.0 is 90% or more. The particles with a sphericity of less than 0.9 have a wide deviation from a perfect sphere. The encapsulating material containing such silica particles as filler is poor in fluidity at the time of molding.

In the present invention, specific surface area is employed as a measure of particle surface smoothness of the high-purity spherical silica of this invention.

Generally, specific surface area SA of a solid (poreless) true sphere is given by the following equation (I):

$$\text{SA (m}^2/\text{g)} = 6/(d \times D) \quad (\text{I})$$

where d is diameter (μm) and D is true specific gravity.

From the equation (I), the specific surface area SA (m^2/g) of a true sphere of silica having a diameter of d (μm) and a true specific gravity of 2.2 is given by the following equation (II), so that the theoretical value of specific surface area of the silica sphere with a diameter of 10 μm is approximately 0.27 m^2/g .

$$\text{SA} = 2.73/d \quad (\text{II})$$

The spherical silica used as a filler for encapsulating materials has its pores closed usually by

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calcination, so that the surface smoothness of the silica particles can be evaluated by the amount of deviation of the measured value of specific surface area from its theoretical value. For instance, on the surface of the spherical silica particles prepared by flame fusing, there exist many microspheres or uneven sections formed by recondensation of vapors of Si evaporated by high-temperature flames, and the specific surface area of the fused particles with a diameter of 10 μm exceeds 1 m^2/g and is usually about 2 m^2/g . The encapsulating material made by using such particles as filler is still unsatisfactory in fluidity at the time of molding.

In the present invention, the specific surface area of the spherical silica is measured by the BET (Brunauer, Emmett and Teller) method which is known in the art and according to which the specific surface area of the solid is calculated from the adsorption of the monomolecular layer and the sectional area of the adsorbate by using an adsorption isotherm (BET adsorption isotherm) based on the polymolecular layer adsorption.

The specific surface area of the spherical silica of this invention is not more than 3 times the theoretical value, and the present spherical silica has excellent surface smoothness. The encapsulating material produced by using the spherical silica of this invention as filler shows quite favorable fluidity for molding.

The process for producing high-purity spherical silica according to the present invention comprises the following three steps:

Step 1: Preparation of spherical silica gel particles.

An emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution are brought into contact with each other to produce porous spherical silica gel particles.



Step 2: Extraction removal of impurities in spherical silica gel.

The spherical silica gel particles obtained in Step 1 are treated with a mineral acid for extraction removal of impurities contained in the particles to obtain hydrous high-purity porous spherical silica particles.

Step 3: Calcination of hydrous spherical silica particles.

The hydrous spherical silica particles obtained in Step 2 are calcined to afford the preferred properties specified in the present invention to the particles.

The above steps are illustrated more particularly below.

- (1) Preparation of spherical silica gel particles
(Step 1)
- (i) Preparation of emulsions

In the process of this invention, an emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution are prepared. An aqueous alkali silicate solution and an aqueous mineral acid solution are separately dispersed, in the form of fine particles as disperse phase, in respective liquids serving as external phase, which are immiscible with the above-mentioned aqueous solutions, to prepare water-in-oil (W/O) type emulsions.

An aqueous alkali silicate solution, a liquid for forming external phase and an emulsifying agent are mixed and emulsified by using an emulsifier or other appropriate means to prepare a W/O type emulsion containing an aqueous alkali silicate solution.

Similarly, an aqueous mineral acid solution, a liquid for forming external phase and an emulsifying agent are mixed and emulsified to prepare a W/O type emulsion containing an aqueous mineral acid solution.

The alkali silicates usable here include sodium



silicate, potassium silicate, lithium silicate, etc., but sodium silicate is usually used.

The concentration of silica (as SiO_2) in the aqueous alkali silicate solution is preferably in a range of 1 to 40 wt%, more preferably 15 to 30 wt%.

The mineral acids usable in the emulsion preparation include sulphuric acid, nitric acid, hydrochloric acid, etc., but sulphuric acid or nitric acid is preferably used.

The acid concentration in the solution is in a range of 1 to 30 wt%, preferably 3 to 15 wt%.

The amount of mineral acid to be used is properly decided in accordance with the amount of alkali in the aqueous alkali silicate solution forming one of the emulsions used in this invention. The amount of mineral acid is adjusted so that the mineral acid to alkali molar ratio will fall within a range of 0.1-2.

As the liquid for forming external phase, there is used a liquid which neither reacts with nor is miscible with either the aqueous alkali silicate solution or the aqueous mineral acid solution. It is recommended to use an oil having a boiling point of 100°C or above and a specific gravity of 0.9 or below.

Oils which may be used include aliphatic hydrocarbons such as n-octane, gasoline and kerosene, alicyclic hydrocarbons such as cyclononane and cyclodecane, and aromatic hydrocarbons such as toluene, xylene, ethylbenzene and tetraline.

The weight ratio of aqueous alkali silicate solution to oil and the weight ratio of aqueous mineral acid solution to oil are both in a range of from about 8 : 2 to about 2 : 8.

For emulsifying agent, it is possible to use any type of emulsifying agent provided that it acts to stabilize



the W/O type emulsions. For instance, there can be used strongly oleophilic surfactants such as polyvalent metal salts of fatty acids, cellulose ethers of limited water-solubility, and the like. It is recommended to use a nonionic surfactant.

As examples of nonionic surfactants for use in the invention there may be mentioned sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate and sorbitan monooleate; polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate and polyoxyethylene sorbitan monooleate; polyoxyethylene fatty acid esters such as polyoxyethylene monolaurate, polyoxyethylene monostearate and polyoxyethylene monooleate; and glycerol fatty acid esters such as stearic acid monoglyceride and oleic acid monoglyceride.

The amount of the emulsifying agent to be added is in a range of 0.1 to 5 wt% based on the aqueous alkali silicate solution or aqueous mineral acid solution which is to be emulsified.

(ii) Preparation of spherical silica gel particles

An emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution prepared in the manner described above are mixed with stirring. The reaction of mineral acid and alkali silicate forms a porous spherical silica gel. In the process of this invention, the porous silica gel produced at this stage may be one which is solidified only at the surface, with the inside of the particle being not sufficiently solidified because of the presence of alkali.

The order of mixing is not critical; emulsion containing an aqueous alkali silicate solution may be added



to an emulsion containing an aqueous mineral acid solution, or the latter emulsion may be added to the former emulsion, or both of said emulsions may be added simultaneously.

It is essential that an emulsion containing an aqueous mineral acid solution and an emulsion containing an aqueous alkali silicate solution are brought into contact with each other. In case an emulsion containing an aqueous alkali silicate solution is added to an aqueous mineral acid solution, there can not be obtained the spherical particles which are solid and have excellent sphericity and surface smoothness, which the present invention is intended to provide.

(iii) Demulsification

To demulsify the emulsion after the reaction, an aqueous mineral acid solution may be added to the reaction liquid, for example. The mixed liquid is then heated. According to this method, extraction removal of impurities can be accomplished concurrently with demulsification.

The demulsifying treatment is carried out usually at a temperature in a range of 60-120°C, preferably 80-100°C, for a period of from about one minute to about 5 hours, but the time and temperature are preferably decided in consideration of the operations in Step 2 described below.

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By this treatment, the emulsion-like reaction liquid is phase-separated into an oil phase and a phase of a silica gel particle-dispersed aqueous mineral acid solution. The oil phase constituting the upper layer of the liquid may be separated and recovered in the usual way for repeated use.

(2) Extraction removal of impurities in spherical silica gel particles (Step 2)

The porous spherical silica gel obtained in Step 1 is treated with a solution containing an acid.

As acid, there can be used mineral acids such as sulphuric acid, hydrochloric acid, nitric acid, etc., of which sulphuric acid or nitric acid is preferred. As the treating solution, an aqueous solution containing at least one acid such as mentioned above is preferably used. The acid concentration of the treating solution is 30 wt% or less, preferably in a range of 5 to 20 wt%.

The acid treatment in this step may be accomplished by a one-stage treating method, but it is desirable to divide the treating operation into at least two stages for extraction removal of trace amounts of impurities. It is also possible to employ a multi-stage treating system in which the treating solution is renewed for each stage. The treatment in this step is preferably carried out with stirring.

The treating temperature is not specified in this invention, but it is recommended to conduct the



extraction operation at 50°C or above. It is possible to shorten the time required for impurity extraction by conducting the treatment under pressure at a temperature higher than the boiling point of the treating solution under normal pressure. The higher the temperature, the better is the result in the case of extraction under pressure, but in view of possible corrosion of the apparatus by the acid and energy cost, it is more practical to carry out the treatment at a temperature in a range of 100 to 150°C, preferably 110 to 140°C.

The time required for the acid treatment is about 30 minutes to about 20 hours in the case of batchwise operation and about 30 seconds to about 20 hours in the case of continuous operation.

The hydrous spherical silica particles which have undergone the acid treatment are then washed with water of a suitable temperature and, if necessary, further subjected to deacidification and dehydration treatments which may involve filtration.

The acid used in the process of this invention is preferably a refined or high-purity product called "electronic grade". Also, the water used for dilution of the materials and the acid used in the process or for washing of silica is preferably pure water with few impurities.

By the treatment in this step, the content of impurities including radioactive elements in the silica particles is remarkably lowered. Specifically, the



content of each element of alkali metals such as Na and K and alkaline earth metals such as Mg and Ca is reduced to less than 1 ppm, and the content of radioactive elements such as U and Th is reduced to less than 1 ppb.

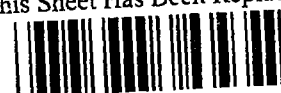
5 Also, electrical conductivity of the extract of boiling lixiviation of silica can be reduced to lower than 10 μ S/cm.

(3) Drying and calcination of hydrous spherical silica particles (Step 3)

10 Water is still retained in the hydrous spherical silica particles which have been subjected to extraction removal of impurities in Step 2. This water can be categorised into two types: adherent water and bound water. Usually adherent water can be easily
15 removed by heating to a temperature of around 100°C, but bound water is hard to remove perfectly even if heated to a temperature above 400°C.

The hydrous spherical silica particles are subjected to a drying treatment for removing adherent
20 water and further subjected to a calcining treatment for removing bound water and compacting the silica particles.

The silica particles obtained according to the process of this invention are the fine spherical particles having a particle size distribution in a range
5 of 1 to 100 μ m and an average particle size (diameter) of about 10 to 15 μ m, but as they have high sphericity and excellent surface smoothness, they can be subjected to a drying treatment without agglomerating with each



other even if left stationary.

The temperature used for the drying treatment for removing adherent water is preferably 50 to 500°C, practically 100 to 300°C, and the treating time may be properly selected from a range of one minute to 40 hours in consideration of the drying temperature used.

A drying system operated in a reduced pressure or a fluid-bed drying system may be employed for the drying treatment.

10
11 Silanol groups (Si-OH) reside on the surfaces of the silica particles obtained from the wet process, and these silanol groups are combined with water in the atmosphere to form the bound water. These silanol groups can be removed by calcining the silica
15 obtained in Step 2 at a temperature of or above 1,000°C. This treatment gives the compact spherical silica particles with a small specific surface area.

For obtaining the silica particles low in hygroscopicity, large in bulk density and small in
20 specific surface area, calcination is preferably carried out at a temperature of 1,000°C or above, more preferably 1,050 to 1,200°C. The calcination time is properly selected from a range of one minute to 20 hours in conformity to the calcination temperature.

25 The atmosphere for calcination may be oxygen or carbon dioxide gas. If necessary, an inert gas such as nitrogen or argon gas may be used. Air is also recommended for practical reasons.



The silica particles obtained according to the process of this invention have high sphericity and excellent surface smoothness, so that they can be calcined without causing sintering of the particles even
5 if the particles are not kept in a fluid state during the calcining treatment, and for carrying out such treatment, there can be used a firing furnace in which the silica particles are treated in a stationary state.

It is of course possible to use an apparatus
10 in which calcination of the silica particles is performed by keeping the particles in a fluid state, such as fluid firing furnace, rotary kiln, flame firing furnace and the like.

Electric heat or combustion gas may be
15 utilized as heating source for the calcination treatment.

According to the process of the present invention, it is possible to obtain the high-purity spherical silica particles having excellent surface
20 smoothness, a high sphericity and a very low content of impurities including radioactive elements such as uranium by using an aqueous alkali silicate solution as starting material.

The high-purity spherical silica particles
25 produced according to the process of the present invention are notably high in purity, excellent in surface smoothness and also high in sphericity as compared with the silica particles obtained with the



prior art, so that the silica particles of this invention find particularly effective use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts.

5 The present invention is further illustrated below with reference to the examples and comparative examples. The following examples, however, should not be construed to limit the scope of the present invention thereto.

10 Example 1

(1) Preparation of spherical silica gel particles

(i) Preparation of emulsions

 A nonionic surfactant (REECOL SP-010, sorbitan monoleate produced by Kao Corp.) as emulsify-
15 ing agent, an oil (ISOSOL 400, a saturated C16 hydrocarbon (isoparaffin) produced by Nippon Sekiyu KK) and water glass (equivalent to JIS K-1408 #3) were mixed in a weight ratio of 1 : 44 : 55 and stirred by an emulsifier at 18,000 r.p.m. for one minute to prepare 268 g of
20 a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution.

 Meanwhile, the surfactant, the oil and a 5 wt% aqueous sulphuric acid solution were mixed in a weight ratio of 1 : 44 : 55 and treated by an emulsifier under
25 the same conditions as described above to prepare 842 g of a W/O type emulsion containing the aqueous sulphuric acid solution.

(ii) Preparation of spherical silica gel particles and demulsification

The water glass emulsion was added to the sulphuric acid solution emulsion with stirring. After addition was completed, stirring was further continued at room temperature for one hour. Then 1,000 g of a 16 wt% aqueous sulfuric acid solution was added to the reaction liquid and the mixed liquid was heated to 100°C and stirred for one hour. By this treatment, the emulsion-like reaction liquid was separated into an oil phase (upper layer) and an aqueous phase (lower layer).

The oil phase was removed and the silica gel particles in the aqueous phase were filtered and washed in the usual way.

(2) Extraction of impurities of spherical silica gel particles

The thus obtained silica gel particles were immersed in a freshly prepared 16 wt% aqueous sulphuric acid solution, stirred at 100°C for one hour to extract impurities and then washed twice with pure water of an amount 10 times the weight of silica gel. After repeating the above extracting and washing operations twice, the obtained silica gel particles were washed with pure water until pH of the washings became 4 and then dehydrated by using a Nutsche funnel to obtain hydrous spherical silica particles.

(3) Calcination of hydrous spherical silica particles



The thus obtained hydrous silica particles were dried overnight at 120°C to obtain 70 g of dry silica particles. These dry silica particles were placed in a quartz-made beaker (one litre) and calcined
5 at 1,100°C for 30 minutes.

Analysis of the resulting silica particles showed that the concentrations of the elements of alkali metals such as Na, K and Li, alkaline earth metals such as Ca and Mg and transition metals such as Cr, Fe and Cu
10 were all below 1 ppm and the total concentration of radioactive elements U and Th was below 1 ppb.

Electrical conductivity of the extract of boiling lixiviation of silica particles, determined in the manner described before, was 1.8 μ S/cm.

15 The average particle size (diameter) of the obtained silica particles was 11.5 μ m and their specific gravity was 2.20.

The specific surface area of the particles as measured by BET method was 0.5 m²/g, which was 2.1 times
20 the theoretical value.

Also, the obtained spherical silica particles were those in which the content of the particles with a sphericity of 0.9 or above was more than 90%, and both sphericity and smoothness as judged from the electron
25 micrographs of the particles were excellent.

According to the sectional observation of the particles by electron micrographs, all of the spherical



particles were solid and there was admitted no hollow sphere.

Example 2

The procedure of Example 1 was followed except
5 for the use of the aqueous solutions of water glass prepared by diluting #3 water glass with pure water so that the silica concentration (as SiO_2) would become 20, 15 and 10 wt%, respectively, for preparation of emulsion containing an aqueous alkali silicate, to obtain the
10 spherical silica particles.

The results of measurements and observations conducted on the obtained silica particles were as shown below.

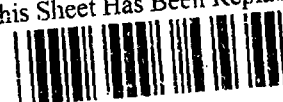
Example 3

15 The procedure of Example 1 was followed except for use of the aqueous sulfuric acid solutions prepared to the sulphuric acid concentration of 15, 10 and 3 wt%, respectively, for preparation of emulsion containing an aqueous sulphuric acid solution, to obtain the spherical
20 silica particles. The results of measurements and observations of the obtained silica particles were as shown below.

Example 4

The procedure of Example 1 was followed except
25 that the method of addition of the emulsions was

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changed, that is, an emulsion containing an aqueous sulphuric acid solution was added to an emulsion containing an aqueous water glass solution to obtain the spherical silica particles. The results of measurements and observations of the obtained silica particles were as shown below.

Comparative Example 1

The procedure of Example 1 was followed except that an emulsion containing an aqueous water glass solution was added to the non-emulsified aqueous sulphuric acid solutions with the sulfuric acid concentrations of 3, 5 and 10 wt%, respectively, to obtain the silica particles. The results of measurements and observations of the obtained particles were as shown below.

The results of measurement of impurity content, electrical conductivity of the extract of boiling lixiviation, average particle size (diameter) and specific surface area and the results of observation of the electron micrographs for determining sphericity and solidity of the silica particles obtained in Examples 2-4 and Comparative Example 1 were as follows.

As a result of analysis of the obtained spherical particles, the concentrations of the contained elements Na, K, Li, Ca, Mg, Cr and Cu were all below 0.1 ppm, with Fe being 0.8 ppm in the examples and



comparative example. Also, the concentration of U was less than 0.1 ppb in each case, while the concentration of Th was in a range of 0.4-0.6 ppb, presenting no significant difference among the examples.

5 The electrical conductivity of the extract of boiling lixiviation of the silica particles, as determined by the above-described method, was in a range of 1.7-2.2 μ S/cm, indicating no significant difference among the examples.

10 As regards sphericity and solidity as determined by electron micrographical observation of the obtained silica particles, the spherical silica particles obtained in Examples 2-4 were those in which the content of the particles with a sphericity of 0.9 or
15 above was more than 90%, and thus they were excellent in both sphericity and surface smoothness. Also, these spherical particles are all solid, and there was admitted presence of no hollow sphere.

 In the case of the silica particles obtained
20 in Comparative Example 1, the content of the particles with a sphericity of 0.9 or above was less than 90% in each run, and many hollow spheres were admitted.

 The average size (diameter) of the obtained silica particles, the measured value of specific surface
25 area by BET method, and the ratio of the measured value of specific surface area to the theoretical value calculated from the above-shown equation were as shown in Tables 1 and 2.



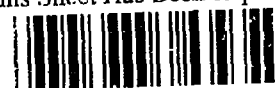
The specific gravity of the obtained silica particles was 2.20 in all cases.

Table 1

Example	Run No.	SiO ₂ concentration in water glass for emulsion (wt%)	Silica particles			Ratio of measured value of specific surface area to theoretical value
			Average diameter (μm)	Specific surface area (m ² /g)		
				Measured value	Theoretical value	
Example	2-1	20	6.5	0.8	0.420	1.9
2	2-2	15	2.0	2.5	1.365	1.8
	2-3	10	1.7	2.8	1.606	1.7

Table 2

Example	Run No.	Sulfuric acid concentration in aqueous sulfuric acid solution for emulsion (wt%)	Silica particles			Ratio of measured value of specific surface area to theoretical value
			Average diameter (μm)	Specific surface area (m ² /g)		
				Measured value	Theoretical value	
Example 3	3-1	15	12.5	0.5	0.218	2.3
	3-2	10	11.3	0.5	0.242	2.1
	3-3	3	9.5	0.7	0.287	2.4
Example 4	4-1	5	11.2	0.5	0.244	2.1
Comp. Example 1	1-1	3	10.1	1.4	0.270	5.2
	1-2	5	10.8	1.5	0.253	5.9
	1-3	10	11.2	1.9	0.244	7.8

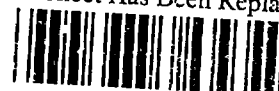




CLAIMS:

1. A process for producing high-purity, spherical silica, which comprises mixing an emulsion comprising an aqueous alkali silicate solution with an emulsion comprising an aqueous mineral acid solution to produce a silica gel comprising substantially spherical silica, treating the gel with a mineral acid to form hydrous spherical silica, and drying and then calcining the spherical silica.
2. A process according to claim 1, in which the aqueous alkali silicate solution is provided in the form of a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as a disperse phase and in which the aqueous mineral acid solution is provided in the form of a water-in-oil (W/O) type emulsion, the aqueous mineral acid solution being dispersed in the form of fine particles as disperse phase.
3. A process for producing high-purity spherical silica, which comprises mixing a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as disperse phase and a water-in-oil (W/O) type emulsion, containing an aqueous mineral acid solution dispersed in the form of fine particles as disperse phase to produce a spherical silica gel, treating the obtained spherical silica gel with a mineral acid to obtain hydrous spherical silica, and drying and then calcining said hydrous spherical silica.
4. A process for producing high-purity spherical silica conducted substantially as described herein in accordance with any one of Examples 1 to 4.
5. High-purity spherical silica obtainable by a process according to any one of claims 1 to 4 which silica comprises not more than 1 ppb of radioactive substances.
6. High-purity spherical silica obtained by a process

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according to any one of claims 1 to 4 which silica comprises not more than 1 ppb of radioactive substance.

7. High-purity silica according to claim 5 or claim 6, the electrical conductivity (at 25°C) of a solution obtained by boiling for 20 hours at 160°C a mixture of 10.0 g of the silica and 100 ml of distilled water being 10 μ S/cm or below.

8. High-purity silica according to any one of claims 5 to 7, which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

9. High-purity spherical silica obtainable by a process according to any one of claims 1 to 4 which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

10. High-purity spherical silica obtained by a process according to any one of claims 1 to 4 which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

11. High-purity silica according to any one of claims 5 to 10, in which the ratio of the measured value of specific surface area by the BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

12. High-purity spherical silica obtained from an aqueous alkali silicate solution, having content of radioactive substance less than 1 ppb, a electrical conductivity of an extract of boiling lixiviation of the silica of 10 μ S/cm or below, a content of the particles with a sphericity of 0.9 to 1.0 of 90% or more, and a ratio of the measured value of specific surface area by BET method to the theoretical value of specific surface area corresponding to the particle size being 3 or less.

13. High purity spherical silica substantially as





described herein and in accordance with any one of Examples
1 to 4.

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ABSTRACT

HIGH-PURITY SPHERICAL SILICA AND PROCESS FOR PRODUCING SAME

An emulsion containing an aqueous alkali silicate solution dispersed therein and an emulsion containing an aqueous mineral acid solution dispersed therein, both in the form of fine particles as dispersed phase, are mixed to produce a spherical silica gel. This spherical silica gel is treated with a mineral acid to obtain hydrous spherical silica, and this hydrous spherical silica is dehydrated and then calcined to obtain high-purity spherical silica. The content of radioactive substance is less than 1 ppb, the electrical conductivity of the extract of boiling lixiviation of silica is 10 μ S/cm or below, the content of the particles with a sphericity of 0.9 or above is 90% or more, and the ratio of the measured value of specific surface area by BET method to the theoretical value of specific surface area corresponding to particle size is 3 or less. By using an aqueous alkali silicate solution, there can be obtained high-purity spherical silica particles in which the content of impurities including radioactive substances is very low, and which have excellent surface smoothness and high sphericity and is suited for use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts.

REPLACEMENT SHEET

19 JAN 1998



REPLACEMENT SHEETS

- ☐ Description : paged to paged
☒ Claim(s) : paged 2 to paged 2
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

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CLAIMS:

1. A process for producing high-purity, spherical silica, which comprises mixing an emulsion comprising an aqueous alkali silicate solution with an emulsion comprising an aqueous mineral acid solution to produce a silica gel comprising substantially spherical silica, treating the gel with a mineral acid to form hydrous spherical silica, and drying and then calcining the spherical silica.
2. A process according to claim 1, in which the aqueous alkali silicate solution is provided in the form of a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as a disperse phase and in which the aqueous mineral acid solution is provided in the form of a water-in-oil (W/O) type emulsion, the aqueous mineral acid solution being dispersed in the form of fine particles as disperse phase.
3. A process for producing high-purity spherical silica, which comprises mixing a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as disperse phase and a water-in-oil (W/O) type emulsion, containing an aqueous mineral acid solution dispersed in the form of fine particles as disperse phase to produce a spherical silica gel, treating the obtained spherical silica gel with a mineral acid to obtain hydrous spherical silica, and drying and then calcining said hydrous spherical silica.
4. A process for producing high-purity spherical silica conducted substantially as described herein in accordance with any one of Examples 1 to 4.
5. High-purity spherical silica obtained by a process

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according to any one of claims 1 to 4 which silica comprises not more than 1 ppb of radioactive substance.

6. High-purity silica according to claim 4 or claim 5, the electrical conductivity (at 25°C) of a solution obtained by boiling for 20 hours at 160°C a mixture of 10.0 g of the silica and 100 ml of distilled water being 10 μ S/cm or below.

7. High-purity silica according to any one of claims 4 to 6, which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

8. High-purity spherical silica obtained by a process according to any one of claims 1 to 4 which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

9. High-purity silica according to any one of claims 5 to 8, in which the ratio of the measured value of specific surface area by the BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

10. High-purity spherical silica obtained from an aqueous alkali silicate solution, having content of radioactive substance less than 1 ppb, a electrical conductivity of an extract of boiling lixiviation of the silica of 10 μ S/cm or below, a content of the particles with a sphericity of 0.9 to 1.0 of 90% or more, and a ratio of the measured value of specific surface area by BET method to the theoretical value of specific surface area corresponding to the particle size being 3 or less.

11. High purity spherical silica substantially as described herein and in accordance with any one of Examples 1 to 4.

REPLACEMENT SHEETS		SG
☒	Description : paged 1. to paged 38.	
☒	Claim(s) : paged 25. to paged 27.	
☐	Drawing(s) : paged to paged	
☒	Abstract : paged 4. to paged 5.	
DATE OF RECEIPT ... 24/6/96		

Substitute sheet - 24 June 1996

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**HIGH-PURITY SPHERICAL SILICA AND PROCESS FOR
PRODUCING SAME**

BACKGROUND OF THE INVENTION**Field of the Invention.**

The present invention relates to high-purity spherical silica and a process for producing such silica.

The high-purity spherical silica according to the present invention has excellent surface smoothness and high sphericity and finds particularly advantageous use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts. Hereinafter the resin compositions which contain a filler are referred to as encapsulating materials.

Description of the Related Art.

With the advancement of integrated circuits, the areal ratio of the chip in relation to its encapsulating material is increasing and the thickness of packages is decreasing. Also, demand is rising for higher quality encapsulating materials so that the chips can be well protected by a thin-section of such a material.

The encapsulating material is required to be resistant to thermal stress since thermal stress is built up due to the difference in thermal expansion coefficient between the silicon chip and the encapsulating material. In order to bring the thermal expansion coefficient of the encapsulating material as close as possible to that of the silicon chip, a method is employed in which silica with a low thermal expansion coefficient is added to resin as filler at the highest possible filling rate.

Hitherto, ground silica having irregular particle shape and sharp edges has been used as filler silica. However, the encapsulating material when filled with such ground silica to a high filling rate is increased in viscosity and therefore deteriorated in fluidity at the time

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of molding, making it difficult to obtain a homogeneous package having the desired properties. Also, the ground silica particles having sharp edges tend to cause early wear of the molding die and may break through the surface protective film of the chip to damage aluminium wiring on the chip. In view of the above, there is a demand in the industry for high-purity spherical silica having little capacity to reduce the fluidity of the encapsulating material and which is substantially free from sharp edges.

Various methods such as mentioned below have been proposed for producing high-purity spherical silica:

- (1) Powdered high-purity silica is fused in flames (for example JP-A-58-145613).
- (2) An alkyl silicate is hydrolyzed to form a sol-like solution thereof. This solution is atomized in a heated medium to form granules which are dried and then fused in flames (for example, JP-A-58-2233).
- (3) A silicon alkoxide is hydrolyzed to form a partially condensed sol. After removing alcohol from the sol, it is dispersed in water and the precipitated silica gel is collected and calcined (for example, JP-A-63-225538).

The calcination of silica produced according to the above prior art has been achieved under conditions which allow progress of perfect calcination until the pore volume became less than 0.01 ml/g, in consideration of possible change of silica into hydrophobic type, strength of calcined silica particles and other matters.

There is required further a higher purity of filler in the encapsulating material to prevent or minimise occurrence of soft errors in advanced integrated circuits and associated electronic parts.

A high-purity spherical silica adapted to meet the industry's needs would have a low content of impurities such as alkali metals, alkaline earth metals, halogens and

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radioactive substances.

The above-mentioned conventional methods for producing spherical silica have the following problems:

The particles obtained according to the method (1) are low in sphericity and ineffective for improving fluidity.

According to the method (2), the silica particles produced from atomization vary in size depending on the condition of the sol solution, and it is difficult to obtain the spherical silica particles falling in the desired size range.

The spherical silica particles obtained according to the method (2) or (3) shrink greatly when calcined, forming particles with poor surface smoothness or surface unevenness. Lack of surface smoothness leads to low fluidity.

The methods (2) and (3) involve the additional problem of high cost of the material used and also necessitate disposal of waste water containing organic matter derived from the starting material.

The use of conventional spherical silica has prevented lowering of the fluidity of encapsulating materials to some extent as compared with the use of ground silica having sharp edges. This is true even when the filling rate of filler in the encapsulating materials is high. However, such improvement in encapsulating material fluidity as there is not so remarkable. Accordingly, spherical silica having high sphericity and excellent surface smoothness and suited for use as a filler for encapsulating materials has been a want in the industry.

SUMMARY OF THE INVENTION

An object of the present invention is to provide high-purity spherical silica suited for use as a filler for encapsulating materials of electronic parts, which silica,

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even when blended in a resin for encapsulating to a filling rate of 60-90 wt% based on the resin, will not cause substantial lowering of fluidity of the encapsulating material, and in which the content of radioactive and ionic impurities is significantly low. It is further an object of the invention to provide a process for producing such spherical silica.

The present inventors have pursued studies for overcoming the prior art problems such as mentioned above and, surprisingly, have found that by mixing an emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution to produce a spherical silica gel, treating the produced gel with a mineral acid to obtain hydrous spherical silica and subjecting the obtained silica to a heat treatment, it is possible to control sphericity and surface smoothness of spherical silica and to obtain high-purity spherical silica suited for use as a filler in encapsulating materials.

Accordingly, the present invention provides a process for producing high-purity, spherical silica, which comprises mixing an emulsion comprising an aqueous alkali silicate solution with an emulsion comprising an aqueous mineral acid solution to produce a silica gel comprising substantially spherical silica, treating the gel with a mineral acid to form hydrous spherical silica, and drying and then calcining the spherical silica. Preferably, the aqueous alkali silicate solution is provided in the form of a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as a disperse phase and in which the aqueous mineral acid solution is provided in the form of a water-in-oil (W/O) type emulsion, the aqueous mineral acid solution being dispersed in the form of fine particles as disperse phase.

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The invention further provides high purity spherical silica obtainable by the above process and comprising not more than 1 ppb of radioactive substances. Preferably, the electrical conductivity (at 25°C) of a solution obtained by boiling for 20 hours at 160°C a mixture of 10.0 g of the silica and 100 ml of distilled water is 10 μ S/cm or below. The high-purity spherical silica according to the invention generally comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0. The ratio of the measured value of specific surface area by the BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

Thus, in one aspect of the present invention, there is provided high-purity spherical silica which is obtainable from an aqueous alkali silicate solution and in which the content of radioactive substances is less than 1 ppb, the electric conductivity of the extract of boiling lixiviation of silica is 10 μ S/cm or below, the content of the particles with a sphericity of 0.9 to 1.0 is 90% or more, and the ratio of the measured value of specific surface area determined by BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

In a preferred embodiment of the process of the invention, the emulsions are water-in-oil (W/O) type emulsions in which an aqueous alkali silicate solution and an aqueous mineral acid solution, respectively, are dispersed in the form of fine particles as dispersed phase.

PREFERRED EMBODIMENTS OF THE INVENTION

The high-purity spherical silica according to the present invention is one which can be obtained from an aqueous alkali silicate solution and in which the content of radioactive substances is less than 1 ppb, the electrical

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conductivity of the extract of boiling lixiviation of silica is $10 \mu\text{S}/\text{cm}$ or less, the content of the particles having a sphericity of 0.9 or above is 90% or more, and the measured value of specific surface area by BET method is not higher than 3 times the theoretical value of specific surface area corresponding to the particle size.

The radioactive substances usually present in silica are U and Th. It is desirable that the content of these radioactive substances in the high-purity spherical silica of this invention is as low as possible. Specifically, the content should not exceed 1 ppb. If it exceeds 1 ppb, soft errors may be caused.

On the other hand, alkali metals such as Na, K and Li, alkaline earth metals such as Ca and Mg, and other ionic impurities such as Cl may cause corrosion of aluminium wiring, so that it is desirable that the high-purity spherical silica of this invention be substantially free of such impurities. The content of these impurities can be determined directly by appropriate analytical means, but in the present invention, the electrical conductivity of the extract of boiling lixiviation of silica was measured and given as an index of ionic impurity content. This system was employed for the following reasons:

- i) electrical conductivity can be directly adopted as a measure of quality or properties of the product;
- ii) this system is a more simple and clearer way of indication than direct analysis; and
- iii) this is a very strict method for evaluation of quality.

The electrical conductivity of the extract of boiling lixiviation of silica in the present invention is measured at 25°C with the specimen (extract) prepared by adding 10.0 g of sample silica to 100 ml of pure water and boiling the mixture at 160°C for 20 hours. In the high-

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purity spherical silica of this invention, the value of this electrical conductivity is not higher than $10 \mu\text{S/cm}$.

The sphericity specified in the present invention is expressed by the ratio of the minimal diameter to the maximal diameter of one silica particle. The value of sphericity was determined by randomly selecting 20 particles on an electron micrograph of the silica particles, measuring the maximal diameter and the minimal diameter of each of the selected particles, and calculating the ratio of the minimal diameter to the maximal diameter of each particle.

In the high-purity spherical silica of the present invention, the content of the particles having a sphericity in a range of 0.9 to 1.0 is 90% or more. The particles with a sphericity of less than 0.9 have a wide deviation from a perfect sphere. The encapsulating material containing such silica particles as filler is poor in fluidity at the time of molding.

In the present invention, specific surface area is employed as a measure of particle surface smoothness of the high-purity spherical silica of this invention.

Generally, specific surface area SA of a solid (poreless) true sphere is given by the following equation (I):

$$\text{SA (m}^2\text{/g)} = 6 / (d \times D) \quad (\text{I})$$

where d is diameter (μm) and D is true specific gravity.

From the equation (I), the specific surface area SA ($\text{m}^2\text{/g}$) of a true sphere of silica having a diameter of d (μm) and a true specific gravity of 2.2 is given by the following equation (II), so that the theoretical value of specific surface area of the silica sphere with a diameter of $10 \mu\text{m}$ is approximately $0.27 \text{ m}^2\text{/g}$.

$$\text{SA} = 2.73/d \quad (\text{II})$$

The spherical silica used as a filler for encapsulating materials has its pores closed usually by

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calcination, so that the surface smoothness of the silica particles can be evaluated by the amount of deviation of the measured value of specific surface area from its theoretical value. For instance, on the surface of the spherical silica particles prepared by flame fusing, there exist many microspheres or uneven sections formed by recondensation of vapors of Si evaporated by high-temperature flames, and the specific surface area of the fused particles with a diameter of 10 μm exceeds 1 m^2/g and is usually about 2 m^2/g . The encapsulating material made by using such particles as filler is still unsatisfactory in fluidity at the time of molding.

In the present invention, the specific surface area of the spherical silica is measured by the BET (Brunauer, Emmett and Teller) method which is known in the art and according to which the specific surface area of the solid is calculated from the adsorption of the monomolecular layer and the sectional area of the adsorbate by using an adsorption isotherm (BET adsorption isotherm) based on the polymolecular layer adsorption.

The specific surface area of the spherical silica of this invention is not more than 3 times the theoretical value, and the present spherical silica has excellent surface smoothness. The encapsulating material produced by using the spherical silica of this invention as filler shows quite favorable fluidity for molding.

The process for producing high-purity spherical silica according to the present invention comprises the following three steps:

Step 1: Preparation of spherical silica gel particles.

An emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution are brought into contact with each other to produce porous spherical silica gel particles.

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Step 2: Extraction removal of impurities in spherical silica gel.

The spherical silica gel particles obtained in Step 1 are treated with a mineral acid for extraction removal of impurities contained in the particles to obtain hydrous high-purity porous spherical silica particles.

Step 3: Calcination of hydrous spherical silica particles.

The hydrous spherical silica particles obtained in Step 2 are calcined to afford the preferred properties specified in the present invention to the particles.

The above steps are illustrated more particularly below.

(1) Preparation of spherical silica gel particles
(Step 1)

(i) Preparation of emulsions

In the process of this invention, an emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution are prepared. An aqueous alkali silicate solution and an aqueous mineral acid solution are separately dispersed, in the form of fine particles as disperse phase, in respective liquids serving as external phase, which are immiscible with the above-mentioned aqueous solutions, to prepare water-in-oil (W/O) type emulsions.

An aqueous alkali silicate solution, a liquid for forming external phase and an emulsifying agent are mixed and emulsified by using an emulsifier or other appropriate means to prepare a W/O type emulsion containing an aqueous alkali silicate solution.

Similarly, an aqueous mineral acid solution, a liquid for forming external phase and an emulsifying agent are mixed and emulsified to prepare a W/O type emulsion containing an aqueous mineral acid solution.

The alkali silicates usable here include sodium

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silicate, potassium silicate, lithium silicate, etc., but sodium silicate is usually used.

The concentration of silica (as SiO_2) in the aqueous alkali silicate solution is preferably in a range of 1 to 40 wt%, more preferably 15 to 30 wt%.

The mineral acids usable in the emulsion preparation include sulphuric acid, nitric acid, hydrochloric acid, etc., but sulphuric acid or nitric acid is preferably used.

The acid concentration in the solution is in a range of 1 to 30 wt%, preferably 3 to 15 wt%.

The amount of mineral acid to be used is properly decided in accordance with the amount of alkali in the aqueous alkali silicate solution forming one of the emulsions used in this invention. The amount of mineral acid is adjusted so that the mineral acid to alkali molar ratio will fall within a range of 0.1-2.

As the liquid for forming external phase, there is used a liquid which neither reacts with nor is miscible with either the aqueous alkali silicate solution or the aqueous mineral acid solution. It is recommended to use an oil having a boiling point of 100°C or above and a specific gravity of 0.9 or below.

Oils which may be used include aliphatic hydrocarbons such as n-octane, gasoline and kerosene, alicyclic hydrocarbons such as cyclononane and cyclodecane, and aromatic hydrocarbons such as toluene, xylene, ethylbenzene and tetraline.

The weight ratio of aqueous alkali silicate solution to oil and the weight ratio of aqueous mineral acid solution to oil are both in a range of from about 8 : 2 to about 2 : 8.

For emulsifying agent, it is possible to use any type of emulsifying agent provided that it acts to stabilize

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the W/O type emulsions. For instance, there can be used strongly oleophilic surfactants such as polyvalent metal salts of fatty acids, cellulose ethers of limited water-solubility, and the like. It is recommended to use a nonionic surfactant.

As examples of nonionic surfactants for use in the invention there may be mentioned sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate and sorbitan monooleate; polyoxyethylene sorbitan fatty acid esters such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate and polyoxyethylene sorbitan monooleate; polyoxyethylene fatty acid esters such as polyoxyethylene monolaurate, polyoxyethylene monostearate and polyoxyethylene monooleate; and glycerol fatty acid esters such as stearic acid monoglyceride and oleic acid monoglyceride.

The amount of the emulsifying agent to be added is in a range of 0.1 to 5 wt% based on the aqueous alkali silicate solution or aqueous mineral acid solution which is to be emulsified.

(ii) Preparation of spherical silica gel particles

An emulsion containing an aqueous alkali silicate solution and an emulsion containing an aqueous mineral acid solution prepared in the manner described above are mixed with stirring. The reaction of mineral acid and alkali silicate forms a porous spherical silica gel. In the process of this invention, the porous silica gel produced at this stage may be one which is solidified only at the surface, with the inside of the particle being not sufficiently solidified because of the presence of alkali.

The order of mixing is not critical; emulsion containing an aqueous alkali silicate solution may be added

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to an emulsion containing an aqueous mineral acid solution, or the latter emulsion may be added to the former emulsion, or both of said emulsions may be added simultaneously.

It is essential that an emulsion containing an aqueous mineral acid solution and an emulsion containing an aqueous alkali silicate solution are brought into contact with each other. In case an emulsion containing an aqueous alkali silicate solution is added to an aqueous mineral acid solution, there can not be obtained the spherical particles which are solid and have excellent sphericity and surface smoothness, which the present invention is intended to provide.

(iii) Demulsification

To demulsify the emulsion after the reaction, an aqueous mineral acid solution may be added to the reaction liquid, for example. The mixed liquid is then heated. According to this method, extraction removal of impurities can be accomplished concurrently with demulsification.

The demulsifying treatment is carried out usually at a temperature in a range of 60-120°C, preferably 80-100°C, for a period of from about one minute to about 5 hours, but the time and temperature are preferably decided in consideration of the operations in Step 2 described below.

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By this treatment, the emulsion-like reaction liquid is phase-separated into an oil phase and a phase of a silica gel particle-dispersed aqueous mineral acid solution. The oil phase constituting the upper layer of the liquid may be separated and recovered in the usual way for repeated use.

(2) Extraction removal of impurities in spherical silica gel particles (Step 2)

The porous spherical silica gel obtained in Step 1 is treated with a solution containing an acid.

As acid, there can be used mineral acids, such as sulphuric acid, hydrochloric acid, nitric acid, etc., of which sulphuric acid or nitric acid is preferred. As the treating solution, an aqueous solution containing at least one acid such as mentioned above is preferably used. The acid concentration of the treating solution is 30 wt% or less, preferably in a range of 5 to 20 wt%.

The acid treatment in this step may be accomplished by a one-stage treating method, but it is desirable to divide the treating operation into at least two stages for extraction removal of trace amounts of impurities. It is also possible to employ a multi-stage treating system in which the treating solution is renewed for each stage. The treatment in this step is preferably carried out with stirring.

The treating temperature is not specified in this invention, but it is recommended to conduct the

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extraction operation at 50°C or above. It is possible to shorten the time required for impurity extraction by conducting the treatment under pressure at a temperature higher than the boiling point of the treating solution under normal pressure. The higher the temperature, the better is the result in the case of extraction under pressure, but in view of possible corrosion of the apparatus by the acid and energy cost, it is more practical to carry out the treatment at a temperature in a range of 100 to 150°C, preferably 110 to 140°C.

The time required for the acid treatment is about 30 minutes to about 20 hours in the case of batchwise operation and about 30 seconds to about 20 hours in the case of continuous operation.

The hydrous spherical silica particles which have undergone the acid treatment are then washed with water of a suitable temperature and, if necessary, further subjected to deacidification and dehydration treatments which may involve filtration.

The acid used in the process of this invention is preferably a refined or high-purity product called "electronic grade". Also, the water used for dilution of the materials and the acid used in the process or for washing of silica is preferably pure water with few impurities.

By the treatment in this step, the content of impurities including radioactive elements in the silica particles is remarkably lowered. Specifically, the

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content of each element of alkali metals such as Na and K and alkaline earth metals such as Mg and Ca is reduced to less than 1 ppm, and the content of radioactive elements such as U and Th is reduced to less than 1 ppb.

5 Also, electrical conductivity of the extract of boiling lixiviation of silica can be reduced to lower than 10 $\mu\text{S}/\text{cm}$.

(3) Drying and calcination of hydrous spherical silica particles (Step 3)

10 Water is still retained in the hydrous spherical silica particles which have been subjected to extraction removal of impurities in Step 2. This water can be categorised into two types: adherent water and bound water. Usually adherent water can be easily
15 removed by heating to a temperature of around 100°C, but bound water is hard to remove perfectly even if heated to a temperature above 400°C.

The hydrous spherical silica particles are subjected to a drying treatment for removing adherent
20 water and further subjected to a calcining treatment for removing bound water and compacting the silica particles.

The silica particles obtained according to the process of this invention are the fine spherical particles having a particle size distribution in a range
25 of 1 to 100 μm and an average particle size (diameter) of about 10 to 15 μm , but as they have high sphericity and excellent surface smoothness, they can be subjected to a drying treatment without agglomerating with each

other even if left stationary.

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The temperature used for the drying treatment for removing adherent water is preferably 50 to 500°C, practically 100 to 300°C, and the treating time may be properly selected from a range of one minute to 40 hours in consideration of the drying temperature used.

A drying system operated in a reduced pressure or a fluid-bed drying system may be employed for the drying treatment.

10

Silanol groups ($\equiv\text{Si-OH}$) reside on the surfaces of the silica particles obtained from the wet process, and these silanol groups are combined with water in the atmosphere to form the bound water. These silanol groups can be removed by calcining the silica obtained in Step 2 at a temperature of or above 1,000°C. This treatment gives the compact spherical silica particles with a small specific surface area.

15

For obtaining the silica particles low in hygroscopicity, large in bulk density and small in specific surface area, calcination is preferably carried out at a temperature of 1,000°C or above, more preferably 1,050 to 1,200°C. The calcination time is properly selected from a range of one minute to 20 hours in conformity to the calcination temperature.

20

The atmosphere for calcination may be oxygen or carbon dioxide gas. If necessary, an inert gas such as nitrogen or argon gas may be used. Air is also recommended for practical reasons.

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The silica particles obtained according to the process of this invention have high sphericity and excellent surface smoothness, so that they can be calcined without causing sintering of the particles even
5 if the particles are not kept in a fluid state during the calcining treatment, and for carrying out such treatment, there can be used a firing furnace in which the silica particles are treated in a stationary state.

It is of course possible to use an apparatus
10 in which calcination of the silica particles is performed by keeping the particles in a fluid state, such as fluid firing furnace, rotary kiln, flame firing furnace and the like.

Electric heat or combustion gas may be
15 utilized as heating source for the calcination treatment.

According to the process of the present invention, it is possible to obtain the high-purity spherical silica particles having excellent surface
20 smoothness, a high sphericity and a very low content of impurities including radioactive elements such as uranium by using an aqueous alkali silicate solution as starting material.

The high-purity spherical silica particles
25 produced according to the process of the present invention are notably high in purity, excellent in surface smoothness and also high in sphericity as compared with the silica particles obtained with the

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prior art, so that the silica particles of this invention find particularly effective use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts.

5 The present invention is further illustrated below with reference to the examples and comparative examples. The following examples, however, should not be construed to limit the scope of the present invention thereto.

10 Example 1

(1) Preparation of spherical silica gel particles

(i) Preparation of emulsions

 A nonionic surfactant (RHEODOL SP-010, sorbitan monooleate produced by Kao Corp.) as emulsifying agent, an oil (ISOSOL 400, a saturated C16 hydrocarbon (isoparaffin) produced by Nippon Sekiyu KK) and water glass (equivalent to JIS K-1408 #3) were mixed in a weight ratio of 1 : 44 : 55 and stirred by an emulsifier at 18,000 r.p.m. for one minute to prepare 268 g of
15 a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution.

 Meanwhile, the surfactant, the oil and a 5 wt% aqueous sulphuric acid solution were mixed in a weight ratio of 1 : 44 : 55 and treated by an emulsifier under
20 the same conditions as described above to prepare 842 g of a W/O type emulsion containing the aqueous sulphuric acid solution.

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(ii) Preparation of spherical silica gel particles and demulsification

The water glass emulsion was added to the sulphuric acid solution emulsion with stirring. After
5 addition was completed, stirring was further continued at room temperature for one hour. Then 1,000 g of a 16 wt% aqueous sulfuric acid solution was added to the reaction liquid and the mixed liquid was heated to 100°C and stirred for one hour. By this treatment, the
10 emulsion-like reaction liquid was separated into an oil phase (upper layer) and an aqueous phase (lower layer).

The oil phase was removed and the silica gel particles in the aqueous phase were filtered and washed in the usual way.

15 (2) Extraction of impurities of spherical silica gel particles

The thus obtained silica gel particles were immersed in a freshly prepared 16 wt% aqueous sulphuric acid solution, stirred at 100°C for one hour to extract
20 impurities and then washed twice with pure water of an amount 10 times the weight of silica gel. After repeating the above extracting and washing operations twice, the obtained silica gel particles were washed with pure water until pH of the washings became 4 and
25 then dehydrated by using a Nutsche funnel to obtain hydrous spherical silica particles.

(3) Calcination of hydrous spherical silica particles

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The thus obtained hydrous silica particles were dried overnight at 120°C to obtain 70 g of dry silica particles. These dry silica particles were placed in a quartz-made beaker (one litre) and calcined
5 at 1,100°C for 30 minutes.

Analysis of the resulting silica particles showed that the concentrations of the elements of alkali metals such as Na, K and Li, alkaline earth metals such as Ca and Mg and transition metals such as Cr, Fe and Cu
10 were all below 1 ppm and the total concentration of radioactive elements U and Th was below 1 ppb.

Electrical conductivity of the extract of boiling lixiviation of silica particles, determined in the manner described before, was 1.8 $\mu\text{S}/\text{cm}$.

15 The average particle size (diameter) of the obtained silica particles was 11.5 μm and their specific gravity was 2.20.

The specific surface area of the particles as measured by BET method was 0.5 m^2/g , which was 2.1 times
20 the theoretical value.

Also, the obtained spherical silica particles were those in which the content of the particles with a sphericity of 0.9 or above was more than 90%, and both sphericity and smoothness as judged from the electron
25 micrographs of the particles were excellent.

According to the sectional observation of the particles by electron micrographs, all of the spherical

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particles were solid and there was admitted no hollow sphere.

Example 2

The procedure of Example 1 was followed except
5 for the use of the aqueous solutions of water glass prepared by diluting #3 water glass with pure water so that the silica concentration (as SiO_2) would become 20, 15 and 10 wt%, respectively, for preparation of emulsion containing an aqueous alkali silicate, to obtain the
10 spherical silica particles.

The results of measurements and observations conducted on the obtained silica particles were as shown below.

Example 3

15 The procedure of Example 1 was followed except for use of the aqueous sulfuric acid solutions prepared to the sulphuric acid concentration of 15, 10 and 3 wt%, respectively, for preparation of emulsion containing an aqueous sulphuric acid solution, to obtain the spherical
20 silica particles. The results of measurements and observations of the obtained silica particles were as shown below.

Example 4

The procedure of Example 1 was followed except
25 that the method of addition of the emulsions was

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changed, that is, an emulsion containing an aqueous sulphuric acid solution was added to an emulsion containing an aqueous water glass solution to obtain the spherical silica particles. The results of measurements and observations of the obtained silica particles were as shown below.

Comparative Example 1

The procedure of Example 1 was followed except that an emulsion containing an aqueous water glass solution was added to the non-emulsified aqueous sulphuric acid solutions with the sulfuric acid concentrations of 3, 5 and 10 wt%, respectively, to obtain the silica particles. The results of measurements and observations of the obtained particles were as shown below.

The results of measurement of impurity content, electrical conductivity of the extract of boiling lixiviation, average particle size (diameter) and specific surface area and the results of observation of the electron micrographs for determining sphericity and solidity of the silica particles obtained in Examples 2-4 and Comparative Example 1 were as follows.

As a result of analysis of the obtained spherical particles, the concentrations of the contained elements Na, K, Li, Ca, Mg, Cr and Cu were all below 0.1 ppm, with Fe being 0.8 ppm in the examples and

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arative example. Also, the concentration of U was less than 0.1 ppb in each case, while the concentration of Th was in a range of 0.4-0.6 ppb, presenting no significant difference among the examples.

5 The electrical conductivity of the extract of boiling lixiviation of the silica particles, as determined by the above-described method, was in a range of 1.7-2.2 $\mu\text{S}/\text{cm}$, indicating no significant difference among the examples.

10 As regards sphericity and solidity as determined by electron micrographical observation of the obtained silica particles, the spherical silica particles obtained in Examples 2-4 were those in which the content of the particles with a sphericity of 0.9 or
15 above was more than 90%, and thus they were excellent in both sphericity and surface smoothness. Also, these spherical particles are all solid, and there was admitted presence of no hollow sphere.

 In the case of the silica particles obtained
20 in Comparative Example 1, the content of the particles with a sphericity of 0.9 or above was less than 90% in each run, and many hollow spheres were admitted.

 The average size (diameter) of the obtained silica particles, the measured value of specific surface
25 area by BET method, and the ratio of the measured value of specific surface area to the theoretical value calculated from the above-shown equation were as shown in Tables 1 and 2.

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The specific gravity of the obtained silica particles was 2.20 in all cases.

Table 1

Example	Run No.	SiO ₂ concentration in water glass for emulsion (wt%)	Silica particles			Ratio of measured value of specific surface area to theoretical value
			Average diameter (μm)	Specific surface area (m ² /g)		
				Measured value	Theoretical value	
Example 1	2-1	20	6.5	0.8	0.420	1.9
2	2-2	15	2.0	2.5	1.365	1.8
	2-3	10	1.7	2.8	1.606	1.7

Table 2

Example	Run No.	Sulfuric acid concentration in aqueous sulfuric acid solution for emulsion (wt%)	Silica particles		Ratio of measured value of specific surface area to theoretical value	
			Average diameter (μm)	Specific surface area (m ² /g)		
				Measured value		Theoretical value
Example 3	3-1	15	12.5	0.5	0.218	2.3
	3-2	10	11.3	0.5	0.242	2.1
	3-3	3	9.5	0.7	0.287	2.4
Example 4	4-1	5	11.2	0.5	0.244	2.1
Comp. Example 1	1-1	3	10.1	1.4	0.270	5.2
	1-2	5	10.8	1.5	0.253	5.9
	1-3	10	11.2	1.9	0.244	7.8



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CLAIMS:

1. A process for producing high-purity, spherical silica, which comprises mixing an emulsion comprising an aqueous alkali silicate solution with an emulsion comprising an aqueous mineral acid solution to produce a silica gel comprising substantially spherical silica, treating the gel with a mineral acid to form hydrous spherical silica, and drying and then calcining the spherical silica.
2. A process according to claim 1, in which the aqueous alkali silicate solution is provided in the form of a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as a disperse phase and in which the aqueous mineral acid solution is provided in the form of a water-in-oil (W/O) type emulsion, the aqueous mineral acid solution being dispersed in the form of fine particles as disperse phase.
3. A process for producing high-purity spherical silica, which comprises mixing a water-in-oil (W/O) type emulsion containing an aqueous alkali silicate solution dispersed in the form of fine particles as disperse phase and a water-in-oil (W/O) type emulsion, containing an aqueous mineral acid solution dispersed in the form of fine particles as disperse phase to produce a spherical silica gel, treating the obtained spherical silica gel with a mineral acid to obtain hydrous spherical silica, and drying and then calcining said hydrous spherical silica.
4. A process for producing high-purity spherical silica conducted substantially as described herein in accordance with any one of Examples 1 to 4.
5. High-purity spherical silica obtainable by a process according to any one of claims 1 to 4 which silica comprises not more than 1 ppb of radioactive substances.
6. High-purity spherical silica obtained by a process

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according to any one of claims 1 to 4 which silica comprises not more than 1 ppb of radioactive substance.

7. High-purity silica according to claim 5 or claim 6, the electrical conductivity (at 25°C) of a solution obtained by boiling for 20 hours at 160°C a mixture of 10.0 g of the silica and 100 ml of distilled water being 10 μ S/cm or below.

8. High-purity silica according to any one of claims 5 to 7, which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

9. High-purity spherical silica obtainable by a process according to any one of claims 1 to 4 which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

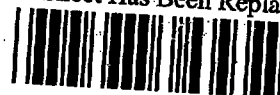
10. High-purity spherical silica obtained by a process according to any one of claims 1 to 4 which comprises about 90% by weight or more of particles having a sphericity of from about 0.9 to about 1.0.

11. High-purity silica according to any one of claims 5 to 10, in which the ratio of the measured value of specific surface area by the BET method to the theoretical value of specific surface area corresponding to the particle size is 3 or less.

12. High-purity spherical silica obtained from an aqueous alkali silicate solution, having content of radioactive substance less than 1 ppb, a electrical conductivity of an extract of boiling lixiviation of the silica of 10 μ S/cm or below, a content of the particles with a sphericity of 0.9 to 1.0 of 90% or more, and a ratio of the measured value of specific surface area by BET method to the theoretical value of specific surface area corresponding to the particle size being 3 or less.

13. High purity spherical silica substantially as

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described herein and in accordance with any one of Examples
1 to 4.

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HIGH-PURITY SPHERICAL SILICA AND PROCESS
FOR PRODUCING SAME

ABSTRACT

An emulsion containing an aqueous alkali silicate solution dispersed therein and an emulsion containing an aqueous mineral acid solution dispersed therein, both in the form of fine particles as dispersed phase, are mixed to produce a spherical silica gel. This spherical silica gel is treated with a mineral acid to obtain hydrous spherical silica, and this hydrous spherical silica is dehydrated and then calcined to obtain high-purity spherical silica. The content of radioactive substance is less than 1 ppb, the electrical conductivity of the extract of boiling lixiviation of silica is 10 μ S/cm or below, the content of the particles with a sphericity of 0.9 or above is 90% or more, and the ratio of the measured value of specific surface area by BET method to the theoretical value of specific surface area corresponding to particle size is 3 or less. By using an aqueous alkali silicate solution, there can be obtained high-purity spherical silica particles in which the content of impurities including radioactive substances is very low, and which have excellent surface smoothness and high sphericity and is suited for use as a filler in resin compositions for encapsulating advanced integrated circuits and associated electronic parts.