



TITLE OF THE INVENTION

Organic-Inorganic Composite Particles
And Production Process Therefor

BACKGROUND OF THE INVENTION

The present invention relates to organic-inorganic composite particles, to a production process therefor and to liquid crystal displays which employ the organic-inorganic composite particles.

Liquid crystal displays (LCD) typically include two opposed electrode substrates, and spacers and a liquid crystal substance interposed between the aforementioned electrode substrates. The spacers are employed in order to maintain a liquid crystal layer uniform and constant in thickness.

High speed of response, high contrast, and a wide viewing angle, etc. are among display performance characteristics cited as required in practice in liquid crystal displays. For these performance characteristics to be manifested, the thickness of the liquid crystal layers, and in the final analysis the distance separating the two electrode substrates, must be maintained strictly constant.

Spacers for liquid crystal displays which meet such a need include silica particles made by the sol-gel method (Japanese Unexamined Patent Publication (Kokai) 62-269933), the calcined product of the aforementioned silica particles



(Japanese Unexamined Patent Publication (Kokai) 1-234826), and styrene or divinylbenzene type polymer particles obtained by suspension polymerization of styrene monomers or divinylbenzene monomers, etc. (Japanese Unexamined Patent Publication (Kokai) 61-95016), etc. These are all spherical particles with a narrow particle diameter distribution and a well ordered particle diameter.

However, the above prior art has the following problems.

(A) Calcined products of silica particles made by the sol-gel method are not readily deformable and are very hard, and consequently when they are pressed in constructing liquid crystal displays they may cause physical damage to coating layers on the substrates such as vapor deposited electrodes, etc., orientating layers and color filters, etc., and cause faults in the display due to image unevenness or breakages of TFT array. There is also a large difference between the thermal expansion coefficient of these calcined silica particles and that of liquid crystals, and consequently in liquid crystal displays using such calcined silica particles the problem of so-called low-temperature bubbling is produced, so that when cooled in a low temperature environment, of -40°C for example, the particles do not shrink to the same extent as the liquid crystals; voids are produced between the liquid crystals and



the electrode substrates, and the display function becomes completely inoperative.

(B) Silica particles made by the sol-gel method are more pliant than calcined silica particles. However, because these uncalcined silica particles are weak in mechanical resilience the gap distance is prone to become uneven, producing image unevenness. Moreover, uncalcined silica particles give rise to the low-temperature bubbling problem as well as the calcined silica particles do.

(C) Since styrene or divinylbenzene type polymer particles are organic particles and are very pliant, they must be dispersed in large numbers onto an electrode substrate. This not only tends to raise manufacturing costs, but results in an increase in the area of the portion of the display screen where no image is formed. Moreover, the quality of the display is lowered due to lowering contrast and increasing image roughness, etc. due to the fact that the quantity of ionic and molecular impurities eluting from the spacers into the liquid crystal layer increases.

Accordingly, polymer particles have been proposed which are not easily deformed, formed by suspension polymerization using crosslinkable monomers such as divinylbenzene, etc., and using a large quantity of polymerization initiator (Japanese Unexamined Patent Publication (Kokai)



4-313727).

Polymer particles made by suspension polymerization of tetramethylolmethane tetraacrylate or tetramethylolmethane tetraacrylate and divinylbenzene, and then classified to regulate mean particle diameter and standard deviation of particle diameter have also been proposed (Japanese Patent Publication (Kohyo) 6-503180).

These polymer particles have the problem that they are prone to produce abnormal orientation in the liquid crystals on the surfaces of these particles. In liquid crystal displays no display is possible in spots in which the liquid crystals are abnormally orientated.

The present inventors have proposed spacers for liquid crystal displays which have a residual displacement after 10% deformation and an elastic modulus in compression at the 10% displacement of the particle diameter (an elastic modulus in 10 % compression) within specified ranges, and which includes specific organic-inorganic composite particles (Japanese Patent Application 5-288536). The fact that these spacers for liquid crystal displays are harder than prior polymer particles means that the number of the particles dispersed on the electrode substrate can be decreased. However, the decrease in numbers means that the load per particle is increased, and the fracture strength is inadequate.



Prior electrically conductive particles are inorganic particles such as silica particles, etc., or polymer particles provided with a conductive layer formed on the surface of the particles. Commonly, conductive particles are employed in the electronics field for connecting between pairs of electrodes. Thus, by pressing a pair of electrodes with conducting particles interposed between them, an electrical connection is established between the two electrodes via the conductive particles.

Conductive particles including a polymer are too pliant, and consequently when pressed the conductive layer cannot accompany the deformation of the particles, and the conductive layer may detach and fall from the particle surface, and the electrodes may become too close and short. On the other hand, conductive particles including inorganic particles are too hard, and consequently it is impossible to broaden the area of contact with the electrodes to lower contact resistance, and if unreasonable pressure is applied when deforming so as to get large contact area, the conductive layer may detach and fall away. There are also problems with the poor mechanical resilience of the conductive particles, and it becomes difficult to maintain a constant gap distance, causing poor contact.

SUMMARY OF THE INVENTION

One purpose of the present invention is to provide

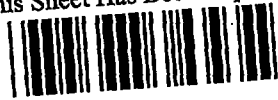


organic-inorganic composite particles which have the mechanical resilience needed in order to maintain constant the aforementioned gap distance between a pair of members placed with the proper gap, together with the hardness and fracture strength needed in order to maintain the aforementioned gap distance constant with smaller numbers of particles, and which do not readily cause physical damage to the aforementioned members.

Another purpose of the present invention is to provide a process for producing organic-inorganic composite particles which have the mechanical resilience needed to maintain a constant gap distance between a pair of spaced apart members, together with the hardness and strength needed in order to maintain the aforementioned gap distance constant with smaller numbers of particles, and which do not cause physical damage to the aforementioned members.

Another purpose of the present invention is to reduce physical damage to the electrode substrates of liquid crystal displays, and to improve picture quality of the liquid crystal displays.

An organic-inorganic composite particle according to a first embodiment of the present invention includes a particle body having an elastic modulus of $350-3000 \text{ kg/mm}^2$ in 10% compression, a residual displacement of 0-5% after 10% deformation, a mean particle diameter of $0.5-50 \mu\text{m}$ and



a coefficient of variation of 20% or less in particle diameter, the particle body including:

an organic group; and

a polysiloxane framework which has in its molecule an organosilicon containing a silicon atom directly and chemically combined with at least one carbon atom of the organic group.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a fragmentary cross-sectional diagram representing an embodiment of a liquid crystal display of the present invention.

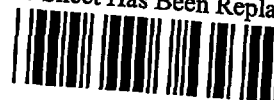
Figure 2 is a cross-sectional diagram of an embodiment of an organic-inorganic composite particle of the present invention.

Figure 3 is a cross-sectional diagram of an embodiment of an organic-inorganic composite particle of the present invention.

Figure 4 is a cross-sectional diagram of an embodiment of an organic-inorganic composite particle of the present invention.

Figure 5 is a cross-sectional diagram of an embodiment of an organic-inorganic composite particle of the present invention.

Figure 6 is a cross-sectional diagram of an embodiment of an organic-inorganic composite particle of the present



invention.

DETAILED DISCLOSURE OF THE INVENTION

An organic-inorganic composite particle according to a first embodiment of the present invention includes a particle body having an elastic modulus of $350\text{--}3000\text{ kg/mm}^2$ in 10% compression, a residual displacement of 0-5% after 10% deformation, a mean particle diameter of $0.5\text{--}50\text{ }\mu\text{m}$ and a coefficient of variation of 20% or less in particle diameter, the particle body including:

an organic group; and

a polysiloxane framework which has in its molecule an organosilicon containing a silicon atom directly and chemically combined with at least one carbon atom of the organic group.

In the first embodiment of the organic-inorganic composite particle of the present invention, for example, the organic group is at least one monovalent group selected from the group consisting of alkyl groups of 1-10 carbon atoms, aryl groups of 6-10 carbon atoms and unsaturated aliphatic residual groups of 2-14 carbon atoms. These monovalent groups may have a substituent group.

The first embodiment of the organic-inorganic composite particle of the present invention may further include a conductive layer formed on a surface of the particle body.

The first embodiment of the organic-inorganic composite particle of the present invention may further include an adhesive layer formed on a surface of the particle body.

The first embodiment of the organic-inorganic composite particle of the present invention may be colored by including in the particle body at least one selected from the group consisting of dyes and pigments.

An organic-inorganic composite particle according to a second embodiment of the present invention includes a particle body having an organic polymer framework and a polysiloxane framework. The polysiloxane framework has in its molecule an organosilicon containing a silicon atom directly and chemically combined with at least one carbon atom of the organic polymer framework. The quantity of SiO_2 which constitutes the polysiloxane framework is ≥ 25 wt% of the total weight of the particle body. The particle body has a mean particle diameter of $\geq 0.5 \mu\text{m}$.

In the second embodiment of the organic-inorganic composite particle of the present invention, the particle body may further include an organic group, and the polysiloxane framework may have a silicon atom directly and chemically combined with at least one carbon atom of the organic group. The organic group here is, for example, at least one monovalent group selected from the group



consisting of alkyl groups of 1-10 carbon atoms, aryl groups of 6-10 carbon atoms and unsaturated aliphatic residual groups of 2-14 carbon atoms. These monovalent groups may have a substituent group.

In the second embodiment of the organic-inorganic composite particle of the present invention, the particle body may further have a fracture strength which satisfies the following equation:

$$G \geq 14 \times Y^{1.75}$$

where: G indicates a fracture strength (kg); and Y indicates a particle diameter (mm).

In the second embodiment of the organic-inorganic composite particle of the present invention, the particle body may have an elastic modulus of 350-3000 kg/mm² in 10% compression, a residual displacement of 0-5% after 10% deformation, a mean particle diameter of 0.5-50 μ m, and a coefficient of variation of $\leq$ 20% in particle diameter.

The second embodiment of the organic-inorganic composite particle of the present invention may further have a conductive layer formed on a surface of the particle body.

The second embodiment of the organic-inorganic composite particle of the present invention may further have an adhesive layer formed on a surface of the particle body.

The second embodiment of the organic-inorganic composite particle of the present invention may be colored



by including in the particle body at least one selected from the group consisting of dyes and pigments.

A process for producing organic-inorganic composite particles according to the present invention includes a condensation step and a heat-treatment step.

The condensation step includes hydrolyzing and condensing a silicon compound to give condensed particles.

The silicon compound is at least one silicon compound selected from the group consisting of compounds represented by General Formula (1) below and derivatives thereof:



where:

R' indicates a monovalent group selected from the group consisting of alkyl groups of 1-10 carbon atoms, aryl groups of 6-10 carbon atoms and unsaturated aliphatic residual groups of 2-14 carbon atoms, which may have a substituent group;

R'' indicates a hydrogen atom or a monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;

m indicates an integer of 0-3;

when m is 2, the two R's may be either different from or identical with one another;

when m is 3, the three R's may differ from one another, or two or more of the R's may be identical;

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when $4-m$ is 2, the two OR"s may be either different from or identical with one another;

when $4-m$ is 3, the three OR"s may be different from each other, or two or more of the OR"s may be identical; and

when $4-m$ is 4, the four OR"s may be different from each other, or two or more of the OR"s may be identical;

with the proviso that only a compound selected from the group consisting of compounds of $m = 1$ in the Formula (1) and derivatives thereof can be employed alone as the silicon compound, and that 2 or more silicon compounds used together need to include either or both of: a compound selected from the group consisting of compounds of $m = 1$ in the Formula (1) and derivatives thereof; and a compound selected from the group consisting of compounds of $m = 0$ in the Formula (1) and derivatives thereof.

The heat-treatment step includes treating the condensed particles by heating at a temperature of $\leq 1000^{\circ}\text{C}$ to obtain particle bodies of the organic-inorganic composite particles. The heat-treatment step is performed, for example, in an atmosphere with an oxygen concentration of ≤ 10 vol%.

The process of the present invention for producing organic-inorganic composite particles may further include a conducting-layer-forming step of forming a conducting layer on a surface of the particle body.

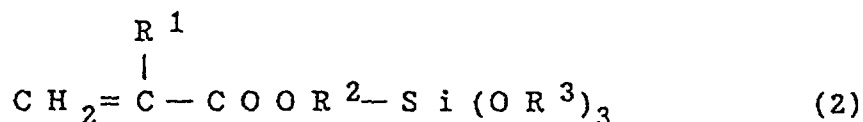


The process of the present invention for producing organic-inorganic composite particles may further include an adhesive-layer-forming step of forming an adhesive layer on a surface of the particle body.

The process of the present invention for producing organic-inorganic composite particles may further include a coloring step of coloring the produced particles during and/or after at least one step selected from the group consisting of the condensation step and the heat-treatment step.

The process of the present invention for producing organic-inorganic composite particles may further include a polymerization step, wherein the silicon compound is a first silicon compound containing a radical-polymerizable group.

The first silicon compound which contains a radical-polymerizable group is at least one selected from the group consisting of compounds represented by the following general formulae and derivatives thereof:



where:

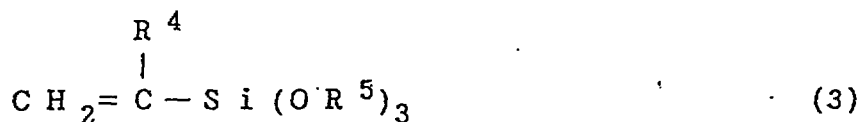
R^1 indicates a hydrogen atom or a methyl group;

R^2 indicates an alkylene group of 1-10 carbon atoms which may have a substituent group; and

R^3 indicates a hydrogen atom or at least one



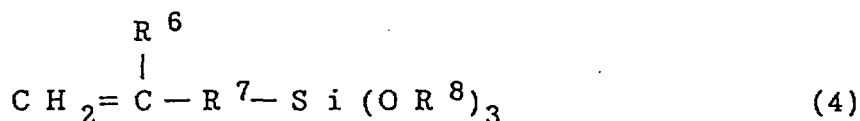
monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;



where:

R^4 indicates a hydrogen atom or a methyl group; and

R^5 indicates a hydrogen atom or at least one monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;



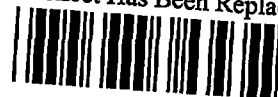
where:

R^6 indicates a hydrogen atom or a methyl group;

R^7 indicates an alkylene group of 1-10 carbon atoms, which may have a substituent group; and

R^8 indicates a hydrogen atom or at least one monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms.

The polymerization step includes subjecting the radical-polymerizable group of the silicon compound to radical polymerization to obtain polymerized particles, during and/or after the condensation step, and before the



heat-treatment step. The heat-treatment step here includes treating the polymerized particles by heating at a temperature of ≤ 800 °C to obtain particle bodies of organic-inorganic composite particles.

When the production process of the present invention further includes the polymerization step, it may still further include a coloring step of coloring the produced particles during and/or after at least one step selected from the group consisting of the condensation step, the polymerization step and the heat-treatment step.

When the production process of the present invention further includes the polymerization step, it may still further include a recondensation step of further condensing the polymerized particles between the polymerization step and the heat-treatment step; and the heat-treatment step may be a step of treating the recondensed particles by heating at a temperature of ≤ 800 °C .

When the production process of the present invention further includes the polymerization step and the recondensation step, it may still further include a coloring step of coloring the produced particles during and/or after at least one step selected from the group consisting of the condensation step, the polymerization step, the recondensation step and the heat-treatment step.

When the production process of the present invention

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further includes the polymerization step, it may still further include a conductive-layer-forming step of forming a conductive layer on a surface of the particle body.

When the production process of the present invention further includes the polymerization step, it may still further include an adhesive-layer-forming step of forming an adhesive layer on a surface of the particle body.

A liquid crystal display according to a first embodiment of the present invention includes a first electrode substrate, a second electrode substrate, a sealing material, a spacer for the liquid crystal display, and a liquid crystal. The second electrode substrate is arranged opposite to the first electrode substrate. The sealing material binds (joins) the first electrode substrate and the second electrode substrate at their respective circumferential edges. The spacer for the liquid crystal display is interposed between the first electrode substrate and the second electrode substrate, functions to maintain a gap distance between the two electrode substrates, and includes the organic-inorganic composite particles according to the first embodiment of the present invention described above. The liquid crystal is packed into space defined by the first electrode substrate, the second electrode substrate and the sealing material.

In the first embodiment of the crystal display of the

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present invention, the first embodiment of the organic-inorganic composite particles may further have an adhesive layer formed on a surface of the particle body.

In the first embodiment of the crystal display of the present invention, the first embodiment of the organic-inorganic composite particles may be colored by including in the particle body at least one selected from the group consisting of dyes and pigments.

A liquid crystal display according to a second embodiment of the present invention includes a first electrode substrate, a second electrode substrate, a sealing material, a spacer for the liquid crystal display, and a liquid crystal. The second electrode substrate is arranged opposite to the first electrode substrate. The sealing material binds (joins) the first electrode substrate and the second electrode substrate at their respective circumferencial edges. The spacer for the second embodiment of the liquid crystal display is interposed between the first electrode substrate and the second electrode substrate, functions to maintain the gap distance between the two electrode substrates, and includes the second embodiment of the organic-inorganic composite particles of the present invention described above. The liquid crystal is packed into space defined by the first electrode substrate, the second electrode substrate and the sealing

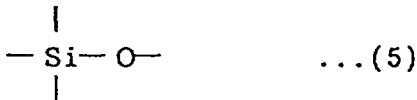


material.

In the second embodiment of the crystal display of the present invention, the second embodiment of the organic-inorganic composite particles may further have an adhesive layer formed on a surface of the particle body.

In the second embodiment of the crystal display of the present invention, the second embodiment of the organic-inorganic composite particles may be colored by including in the particle body at least one selected from the group consisting of dyes and pigments.

In the present invention, the polysiloxane is defined as a compound in which siloxane units represented by the following Formula (5)



are chemically combined with each other in sequence to constitute a 3-dimensional network.

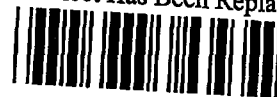
The organic group in the present invention is at least one selected from the group consisting of monovalent, divalent and trivalent groups which have 1-10, and preferably 1-5, carbon atoms and in which at least one carbon atom is directly and chemically combined with one or more hydrogen atoms. As the aforementioned organic groups, monovalent groups selected from the group consisting of alkyl groups of 1-10 carbon atoms, aryl groups of 6-10



carbon atoms and unsaturated aliphatic residual groups of 2-14 carbon atoms, which may have a substituent group, are preferred; monovalent groups selected from the group consisting of alkyl groups of 1-5 carbon atoms, and unsaturated aliphatic residual groups of 2-5 carbon atoms (e.g. vinyl groups, allyl groups, ethynyl groups, propynyl groups) are more preferred. These organic groups have the advantages that they are cheaper and more easily obtained than other organic groups, and are easier to handle, etc. Examples of the substituent groups allowable in the case of alkyl groups include glycidoxy groups, mercapto groups and amino groups, etc.; from one to all of the hydrogen atoms of the alkyl group can be substituted, but preferably 1-3 hydrogen atoms are substituted. Concrete examples of the aforementioned organic groups include methyl, ethyl, propyl, butyl, vinyl, 3-glycidoxypropyl, 3-mercaptopropyl, 3-(2-aminoethylaminopropyl) and phenyl, etc.

Organosilicon in the present invention means that at least one of the carbon atoms of an organic group is directly and chemically combined with at least one of the silicon atoms contained in the siloxane unit above. One to three organic groups can be chemically combined per silicon atom.

Because the first embodiment of the organic-inorganic



composite particles of the present invention has simultaneously both inorganic structural units represented by Formula (5) above and organosilicon, the particles are provided simultaneously with the great hardness characteristic of inorganic substances, and the high mechanical resilience characteristic of organic substances. The measures indicating the hardness and mechanical resilience referred to above are the elastic modulus in compression and the residual displacement; these will be discussed in more detail hereafter. In order to satisfy the aforementioned ranges for the elastic modulus in 10% compression and the displacement after 10% deformation; the proportion of polysiloxane in the organic-inorganic composite particles which has organosilicon in its molecule is preferably ≥ 70 wt%, and more preferably 100%. Examples of components other than polysiloxane having organosilicon in its molecule include oxides of boron, aluminum, gallium, indium, phosphorus, titanium and zirconium, etc.

The elastic modulus in 10% compression referred to in the present invention is the value determined by the method of determination below. Using a Shimadzu micro compression tester (KK Shimadzu Seisakusho MCTM-200), at room temperature (25°C) the test particles are scattered on a testing platform (material: flat SKS disk) and a load is applied to a single particle at a constant loading rate



towards the center of the particle using a round frustrum-shaped loading element (material : diamond) with 50 μ m in diameter; the particle is deformed until compression displacement is 10% of the particle diameter, and the load in kilogramme and compression displacement in millimeters at 10% deformation are found. The elastic modulus in compression calculated by substituting the load and compression displacement found and the radius of the particles into the following equation

$$E = \{3 \times F \times (1 - K^2)\} / (2^{1/2} \times S^{3/2} \times R^{1/2})$$

(where E: Elastic modulus in compression (kg/mm²)

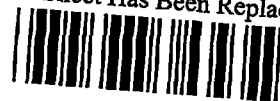
F: Compression load (kg)

K: Poisson ratio of the particle (constant
0.38)

S: Compression displacement (mm)

R: Particle radius (mm))

is the elastic modulus in 10% compression. Directly after this, the load is removed at the same rate as when applying the load, until the load becomes 0.1 g, and the extent of the residual displacement assumed by the particle to which no load is applied is found by extrapolating tangent at 0.1 g in the diagram obtained to the horizontal axis at which the load applied is zero. The residual displacement is this deformation as a percentage of particle diameter. This procedure is repeated on 3 different particles, and the mean



values for the elastic modulus in 10% compression and residual displacement of the particles are taken as the measures of the hardness and mechanical resilience of the particles.

When the elastic modulus in 10% compression of prior spacer particles were determined by the method above, the values were 4400 kg/mm^2 for calcined silica particles and 300 kg/mm^2 for styrene type polymer particles.

By contrast, with the first embodiment of the composite particles of the present invention, the particle body can be regulated to have a hardness chosen at will to give an elastic modulus in 10% compression in the range 350-3000 kg/mm^2 , and preferably in the range 550-2500 kg/mm^2 , and even more preferably in the range 550-2000 kg/mm^2 . If the elastic modulus in 10% compression falls below the aforementioned range, there are the previously mentioned problems of giving a rise in production costs due to an increase in the number of spacer particles that have to be used, lowering contrast and increasing image roughness, etc.; and if it is greater there are the previously described problems of physical damage to vapor deposited layers and coating layers on the substrates, and low-temperature bubbling, etc.

Similarly, as far as residual displacement after 10% deformation is concerned, the residual displacement of non-



calcined silica particles was 8%; but the first embodiment of the composite particles of the present invention is a composite particle with superior mechanical resilience, having a residual displacement in the range 0-5%, and preferably 0-4%. A residual displacement after 10% deformation above the aforementioned range causes the previously mentioned problem of image unevenness, etc.

An elastic modulus in 10% compression and residual displacement within the above ranges are achieved by regulating the proportion of organic groups in the particles. For example, raising the proportion of organic groups lowers the elastic modulus in 10% compression and residual displacement, and lowering the proportion of organic groups increases the elastic modulus in 10% compression and the residual displacement.

In the first embodiment of the composite particles of the present invention the proportion accounted for organic groups in the particles, representing the quantity of organic groups by the total weight of carbon atoms, is usually 5-17 wt%, and is preferably 7-17 wt%. The reason is that if there are fewer organic groups than the above range, elastic modulus in compression and residual displacement become large and the particles become too hard, or adequate mechanical resilience cannot be obtained; and if there are more, the elastic modulus in compression becomes too small



and the particles become more pliant than necessary. When the quantity of organic groups is within the aforementioned range hardness and mechanical resilience which are effective to avoid the aforementioned problems are obtained.

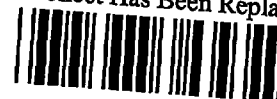
In the first embodiment of the composite particles of the present invention the mean particle diameter of the particle body can be regulated at will according to the size of the intended gap distance, but will usually be 0.5-50 μm , and is preferably 1-20 μm , and more preferably 1-15 μm . With diameter outside the aforementioned range it is impossible to achieve the gap distance of a liquid crystal display for practical use, and the particle diameter is in a range which precludes use as an ordinary spacer.

From the point of view of the uniformity of the gap distance, the coefficient of variation in the particle diameter of the particle body in the first embodiment of the composite particles of the present invention is $\leq 20\%$, preferably $\leq 10\%$, and more preferably $\leq 8\%$. When it is over the above upper limit the uniformity of gap distance is prone to be lowered, causing image unevenness. The coefficient of variation of particle diameter is defined by the following equation

Coefficient of variation in particle diameter (%) =

$$(\sigma / \bar{X}) \times 100$$

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(σ : Standard deviation of particle diameter

$\bar{X}$: Mean particle diameter).

In the present invention, mean particle diameter and the standard deviation of particle diameter are found by measuring the particle diameter on 200 particles chosen at random on electron micrographs and using the equations below.

$$\text{Mean particle diameter } (\bar{X}) = \left[\sum_{i=1}^n X_i \right] / n$$

Standard deviation of particle diameter (σ) =

$$\left[\left(\sum_{i=1}^n (\bar{X} - X_i)^2 \right) / (n - 1) \right]^{1/2}$$

The organic-inorganic composite particles according to the second embodiment of the present invention include an organic polymer framework and a polysiloxane framework having organosilicon in its molecule in which the silicon atom is directly and chemically combined with at least one carbon atom in the organic polymer framework, and the quantity of SiO_2 composing the polysiloxane framework is ≥ 2 wt%; and hence they have the great hardness characteristic of the polysiloxane 3-dimensional framework and the high mechanical resilience and fracture strength characteristic



of the organic polymer framework. Consequently, the second embodiment of the organic-inorganic composite particles of the present invention has the mechanical resilience necessary in order to maintain a constant gap distance between a pair of members which should be arranged with the correct gap distance, and have the hardness and fracture strength necessary in order to maintain the aforementioned gap distance constant with smaller numbers, and which also do not readily cause physical damage to these members. Since the second embodiment of the organic-inorganic composite particles of the present invention further has a mean particle diameter of $\geq 0.5 \mu\text{m}$, they are useful in forming a gap distance between a pair of members.

The organic polymer framework includes at least a main chain but can include main chains, side chains, branching chains and crosslinking chains derived from an organic polymer. There are no particular restrictions as to the molecular weight, composition or structure of the organic polymer or the presence or absence of functional groups.

The organic polymer is, for example, at least one selected from the group consisting of (meth)acrylic resins, polystyrene, poly(vinyl chloride), poly(vinyl acetate), polyolefins and polyesters. Preferred organic polymer frameworks have a main chain constituted from the repeating unit $-\text{C}-\text{C}-$ (referred to as "vinyl polymers" hereafter),



because they form particles of particularly outstanding mechanical resilience.

A vinyl polymer is, for example, at least one selected from the group consisting of (meth)acrylic resins, polystyrene, poly(vinyl chloride), poly(vinyl acetate) and polyolefins. Preferably the vinyl polymer is at least one selected from the group consisting of (meth)acrylic resins and (meth)acrylic-styrene resins. More preferably the vinyl polymer is a (meth)acrylic resin.

With at least one carbon atom constituting the organic polymer framework, a silicon atom in polysiloxane is directly and chemically combined.

The quantity of SiO_2 which constitutes the polysiloxane is ≥ 25 wt%, preferably 30-80 wt%, more preferably 33-70 wt%, and most preferably 37-60 wt%, of the weight of the organic-inorganic composite particles of the present invention. When it is within the above range the particles have a beneficial hardness, mechanical resilience and fracture strength. When it is lower than 25 wt% the hardness characteristic of inorganic substances is not manifested, and there is the problem described hereafter that the elastic modulus in 10% compression is too small. When it exceeds the aforementioned range the mechanical resilience and fracture strength which organic polymers have are lost, and residual displacement may become large or the

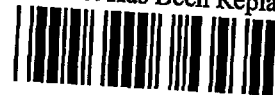


particles may break.

The quantity of SiO_2 which constitutes the polysiloxane framework is the percentage by weight found by determining the weight before and after calcining the particles at a temperature of $\geq 1000^\circ\text{C}$ in an oxidizing atmosphere such as air..

The second embodiment of the organic-inorganic composite particles of the present invention can also contain inorganic components other than polysiloxane. Examples of inorganic components other than polysiloxane include oxides of boron, aluminum, titanium and zirconium, etc. The quantity of inorganic components other than polysiloxane is preferably 0-20 wt%, and more preferably 0-10 wt%. When it is outside the aforementioned range there is a fear that the hardness, mechanical resilience or fracture strength may not be manifested effectively.

The second embodiment of the organic-inorganic composite particles of the present invention has a mean particle diameter of $\geq 0.5 \mu\text{m}$, preferably $0.5-50 \mu\text{m}$, more preferably $1-25 \mu\text{m}$, and most preferably $1.5-20 \mu\text{m}$. When it is under $0.5 \mu\text{m}$ it is difficult to form a gap distance between a pair of members. When it is outside the aforementioned range, the particle diameter is in a range which precludes use as spacers for liquid crystal displays or as conductive particles.



From the perspective of the uniformity of the gap distance when they are used as spacers, the second embodiment of the organic-inorganic composite particles of the present invention have a coefficient of variation in particle diameter of $\leq 20\%$, preferably $\leq 10\%$, and more preferably $\leq 8\%$. When it is greater than the aforementioned range the uniformity of the gap distance is prone to be lowered, producing image unevenness.

The second embodiment of the organic-inorganic composite particles of the present invention is a composite particle which contains both inorganic structural units represented by Formula (5) above and an organic polymer framework, and the inorganic structural units and the organic polymer are chemically combined. Therefore, the second embodiment of the organic-inorganic composite particles of the present invention is provided with both the great hardness characteristic of inorganic substances and the high mechanical resilience and fracture strength characteristic of organic polymers.

The second embodiment of the organic-inorganic composite particles can also be composite particles which contain inorganic structural units represented by Formula 5 above, and an organic polymer framework, and also organic groups as described above with respect to the first embodiment of the composite particles, in which the



inorganic structural units and the organic groups are chemically combined.

The measure indicating hardness is elastic modulus in 10% compression and the measure indicating mechanical resilience is residual displacement after 10% deformation.

Fracture strength can also be investigated by using the micro compression tester previously described. For single test particles scattered on the testing platform a load is applied at a constant loading rate towards the center of the particle using a round frustrum-shaped loading element as described previously, and the compression load at which the particle breaks can be found.

The hardness of the second embodiment of the organic-inorganic composite particles of the present invention can be regulated at will to give an elastic modulus 10% compression preferably in the range 350-3000 kg/mm², more preferably in the range 400-2500 kg/mm², and even more preferably in the range 500-2000 kg/mm². When the elastic modulus in 10% compression is lower than this range, as described previously, there are fears of giving a rise in production costs, lowering contrast, increasing image roughness, and is more than this range, as mentioned previously, there is a fear of physical damage to layers attached to the substrates and to coating layers, and a fear of low-temperature bubbling.



As regards residual displacement after 10% deformation, the residual displacement of uncalcined silica particles was 8%, but the second embodiment of the composite particles of the present invention is a composite particle with outstanding mechanical resilience having a residual displacement preferably in the range 0-5%, more preferably 0-4%, and even more preferably in the range 0-3%. When residual displacement after 10% deformation is greater than the aforementioned range, they are prone to cause image unevenness when employed as spacers for liquid crystal displays.

Similarly, as regards fracture strength the second embodiment of the composite particles of the present invention is a composite particle which preferably satisfies the following equation

$$G \geq 14 \times Y^{1.75}$$

(where G and Y are as described above)

and more preferably satisfy the following equation

$$G \geq 21 \times Y^{1.75}$$

(where G and Y are as described above)

When the fracture strength does not satisfy the aforementioned equations the particles may be broken in making liquid crystal displays because of their low fracture strength, making it impossible to maintain a constant gap distance between the electrode substrates.



An elastic modulus in 10% compression and residual displacement within the above ranges can be achieved by regulating the quantity of the polysiloxane framework or the polymer framework in the particles. For example, lowering the quantity of the polysiloxane framework lowers the elastic modulus in 10% compression and residual displacement; and raising the quantity of the polysiloxane framework increases the elastic modulus in 10% compression and residual displacement.

The first and second embodiments of the composite particles of the present invention can also be colored by including at least one selected from the group consisting of dyes and pigments. The color of the particles is preferably a color which does not transmit light. Non-transmitting colors are preferred for coloring spacers for liquid crystal displays because they can prevent light of the backlight lamp from escaping, and can improve contrast. Examples of non-transmitting colors include colors such as black, dark blue, navy blue, purple, blue, dark green, green, brown and red, etc.; but black, dark blue and navy blue are particularly preferred. Suitable pigments and/or dyes selected according to the intended color can be used: examples, according to classification of dyeing method, include disperse dyes, acidic dyes, basic dyes, reactive dyes and sulfur dyes, etc. Concrete examples of these dyes



are described in "The Chemical Handbook - Applied Chemistry" (edited by the Japanese Chemical Society), Maruzen KK (1986) pp 1399-1427, and "The Nippon Kayaku dye handbook" by Nippon Kayaku KK (1973).

A known method can be adopted as the method for coloring the first and second embodiments of the organic-inorganic composite particles of the present invention. It can be accomplished for example by the methods described in "The Chemical Handbook - Applied Chemistry" (edited by the Japanese Chemical Society) and "The Nippon Kayaku Dye Handbook" above. Colored composite particles of the present invention are provided with the hardness and mechanical resilience described above, and hence are particularly useful in raising the picture quality of liquid crystal displays.

The preferred specifications of the second embodiment of the organic-inorganic composite particles of the present invention for use as spacers for liquid crystal displays are as follows.

(1) A fracture strength G preferably $\geq 14 \times Y^{1.75}$ and more preferably $\geq 21 \times Y^{1.75}$.

(2) Polysiloxane framework ≥ 25 wt%; elastic modulus of $350-3000 \text{ kg/mm}^2$ in 10% compression; residual displacement of 0-5% after 10% deformation; mean particle diameter of $0.5-50 \text{ } \mu\text{m}$; and coefficient of variation of $\leq 20\%$ in



particle diameter.

(3) Polysiloxane framework 30-80 wt%; elastic modulus of 400-2900 kg/mm² in 10% compression; residual displacement of 0-4% after 10% deformation; mean particle diameter of 1-25 μ m; and coefficient of variation of $\leq 10\%$ in particle diameter.

(4) Polysiloxane framework 33-70 wt%; elastic modulus of 500-2800 kg/mm² in 10% compression; residual displacement of 0-3% after 10% deformation; mean particle diameter of 1.5-20 μ m; and coefficient of variation of $\leq 8\%$ in particle diameter.

(5) Polysiloxane framework 37-60 wt%; elastic modulus of 550-2700 kg/mm² in 10% compression; residual displacement of 0-2% after 10% deformation; mean particle diameter of 2-15 μ m; and coefficient of variation of $\leq 6\%$ in particle diameter.

(6) (2)-(5) above with a fracture strength G preferably $\geq 14 \times Y^{1.75}$ and more preferably $\geq 21 \times Y^{1.75}$.

(7) (1)-(6) above, the particle body being colored by including at least one selected from the group consisting of dyes and pigments.

There are no particular restrictions as to the shapes of the first and second embodiments of the organic-inorganic composite particles of the present invention, and they can be any particle shape, such as spheres, needles, sheets,

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flakes, splinters, rugby football-shaped, cocoon shaped or star-shaped; but for use as liquid crystal display spacers spheres are preferred on the grounds of giving a uniformly constant gap distance. This is because when the particles are spherical they have a constant or nearly constant diameter in all or nearly all directions.

Organic-inorganic composite particles of the present invention can be made by the production process described below; but they can also be produced by other processes.

Compounds used in the present invention represented by the aforementioned General Formula (1) have 1-4 hydrolyzable groups; the hydrolyzable groups being monovalent groups selected from the groups consisting of a hydroxyl group, alkoxy groups of 1-5 groups and acyloxy groups of 2-5 carbon atoms, and preferably methoxy groups, ethoxy groups, propoxy groups and/or acetoxy groups. These hydrolyzable groups are employed in the present invention because they are hydrolyzed by water and can produce polysiloxane by condensation. When $m = 1-3$ in compounds represented by the aforementioned General Formula (1) they have an organic group (or organosilicon) described above and are employed in order to introduce organic groups into the composite particles that are produced.

Concrete examples of compounds used in the present invention which are represented by General Formula (1)



include the following.

Compounds of $m = 0$ in Formula (1): tetraalkoxysilane compounds such as tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, tetrabutoxysilane and dimethoxy-diethoxysilane, etc.; and tetraacyloxysilane compounds such as tetraacetoxysilane, etc.

Compounds of $m = 1$ in Formula (1): organotrialkoxysilane compounds and organotriacyloxysilane compounds, such as methyltrimethoxysilane, methyltriethoxysilane, methyltripropoxysilane, methyltriisopropoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, propyltriethoxysilane, butyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-(2-aminoethylamino-propyl)trimethoxysilane, phenyltrimethoxysilane phenyltriethoxysilane, methyltriacetoxysilane and phenyltriacetoxysilane, etc.

Compounds of $m = 2$ in Formula (1): diorganodialkoxysilane compounds, diorganodiacyloxysilane compounds, diorganosilanediol compounds, such as dimethoxydimethylsilane, diethoxy-3-glycidoxypropylmethoxysilane, dimethoxydiphenylsilane, diacetoxymethylsilane and diphenylsilanediol, etc.

Compounds of $m = 3$ in Formula (1):



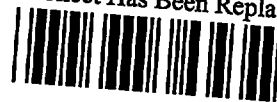
triorganoalkoxysilane compounds, triorganoacyloxysilane compounds, triorganosilanol compounds, such as trimethylmethoxysilane, trimethylethoxysilane, acetoxymethyltrimethylsilane and trimethylsilanol, etc.

Of the compounds represented by the aforementioned General Formula (1), organotrialkoxysilane compounds and tetraalkoxysilane compounds are preferred starting materials.

Derivatives of the compounds represented by the aforementioned General Formula (1) are other silicon compounds capable of hydrolysis and condensation. Examples include compounds in which some of the hydrolyzable groups are substituted by a carboxyl group, β -dicarbonyl group or other group which allow the formation of chelate compounds, or lowly condensed products obtained by partial hydrolysis and condensation of these silicon compounds or chelate compounds.

Silicon compounds capable of hydrolysis and condensation such as those described above can be employed as starting materials (here which mean members of metal compounds capable of hydrolysis and condensation) singly, or in mixtures of 2 or more types.

Of the aforementioned silicon compounds, only compounds selected from the group consisting of compounds of $m = 1$ in Formula (1) and derivatives thereof can be used



alone as the silicon compound; only in this case can the first embodiment of the composite particles of the present invention be obtained by employing a single compound.

When two or more of the aforementioned silicon compounds are used together, they need to include either or both of: a compound selected from the group consisting of compounds of $m = 1$ in Formula (1) and their derivatives; and a compound selected from the group consisting of compounds of $m = 0$ in Formula (1) and their derivatives. Only in this case can the first embodiment of the composite particles of the present invention be obtained by using 2 or more compounds together. In this case, the proportions of silicon compounds (having values of m of 0, 1, 2 and 3 in General Formula (1) and their derivatives) are preferably decided to give $n = 0.5-1$ in General Formula (6) below for the mean composition of the starting materials after mixing.



(In the formula, R'' indicates the mean composition of organic groups having carbon atoms directly combined with silicon atoms, and R''' indicates the mean composition of at least one monovalent group selected from the group consisting of a hydrogen atom, alkyl groups and acyl groups.)

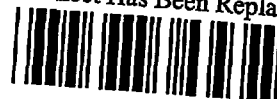
The first embodiment of the composite particles of the present invention cannot be obtained when at least one



selected from the group consisting of silicon compounds having $m = 2$ in Formula (1), silicon compounds having $m = 3$ in Formula (1) and derivatives thereof is exclusively used as the starting material, or when at least one selected from the group consisting of silicon compounds having $m = 0$ in Formula (1) and derivatives thereof is exclusively used as the starting material.

Silicon compounds capable of hydrolysis and condensation selected from compounds represented by the aforementioned General Formula (1) and derivatives thereof, which are starting materials for a polysiloxane component having organosilicon in its molecule described above, may be employed on their own as metallic compounds capable of hydrolysis and condensation employed to obtain the first embodiment of the composite particles of the present invention, or a mixture of aforementioned silicon compounds capable of hydrolysis and condensation in the presence of other metal compounds capable of hydrolysis and condensation, selected from organic metal compounds of boron, aluminum, gallium, indium, phosphorus, titanium or zirconium, etc. or inorganic compounds, can be employed. The proportions of these compounds is preferably decided to give a proportion accounted for by the aforementioned polysiloxane in the composite particles of ≥ 70 wt%.

The metal compounds capable of hydrolysis and



condensation as the starting materials described above are subjected to hydrolysis and condensation in a solution medium which includes water. A bulk, intermittent or continuous manner etc., can be adopted at will for hydrolysis and condensation. A catalyst such as ammonia, urea, ethanolamine, tetramethylammonium hydroxide, an alkali metal hydroxide or an alkaline earth metal hydroxide, etc., can be used for hydrolysis and condensation. An organic solvent can also be present in the solution medium in addition to water and a catalyst. Concrete examples of organic solvents include alcohols such as methanol, ethanol, isopropanol, n-butanol, isobutanol, sec-butanol, t-butanol, pentanol, ethylene glycol, propylene glycol and butane-1,4-diol, etc., ketones such as acetone and methyl ethyl ketone, etc., esters such as ethyl acetate, etc., (cyclo)paraffins such as isooctane and cyclohexane, etc., ethers such as dioxane and diethyl ether, etc., and aromatic hydrocarbons such as benzene and toluene, etc., can be used singly or in mixtures.

Hydrolysis and condensation can be performed, for example, by adding the metal compounds capable of hydrolysis and condensation of the above starting materials, or a solution thereof in an organic solvent, to a solution medium which includes water, and stirring at a temperature in the range 0-100°C, and preferably 0-70°C, for 30 minutes to 100



hours.

Particles obtained by a process such as the above can also be loaded beforehand into the synthetic system as seed particles, and the seed particles can be grown by adding the starting materials.

By hydrolyzing and condensing metal compound starting materials capable of hydrolysis and condensation which include a silicon compound capable of hydrolysis and condensation, under suitable conditions in a solution medium including water in this way, a suspension is formed from which particles with a spherical shape and a very sharp particle diameter distribution separate out. As the suitable conditions here, for example a starting material concentration of ≤ 20 wt%, a water concentration of ≥ 50 wt%, and a catalyst concentration of ≤ 10 wt% of the suspension obtained are preferably used.

Particles having a mean particle diameter within the range of mean particle diameter for the first embodiment of the composite particles described above can be produced by setting the water concentration, catalyst concentration, organic solvent concentration and starting materials concentration, the period of time of adding the starting materials, temperature and the seed particle concentration to 50-99.99 wt%, 0.01-10 wt%, 0-50 wt%, 0.1-30 wt%, 0.001-500 hours, 0-100°C and 0-10 wt% respectively.



Particles with a coefficient of variation in particle diameter within the above range for the coefficient of variation of mean particle diameter for the first embodiment of the composite particles described above can be produced by setting the water concentration, catalyst concentration and organic solvent concentration within the ranges above.

Next, the particles thus produced are isolated from the above suspension using a prior known method such as filtration, centrifugal separation or concentration at decreased pressure, etc., and heat treated at a temperature $\geq 100^{\circ}\text{C}$ and $\leq 1000^{\circ}\text{C}$, and preferably $\geq 300^{\circ}\text{C}$ and $\leq 900^{\circ}\text{C}$ in order to dry and calcine them, to obtain the particle body of the first embodiment of the organic-inorganic composite particles of the present invention. The main component of this particle body is polysiloxane which has in its molecule organosilicon in which at least one carbon atom in an organic group is directly and chemically combined with the silicon atom. With heat-treatment at a temperature lower than 100°C condensation of silanol groups represented by the following Formula (7) present in the siloxane units indicated by the aforementioned Formula (5)



with the elimination of water is inadequate, and consequently the necessary hardness is not obtained: thus,



the elastic modulus in 10% compression does not become ≥ 350 kg/mm². Similarly, with heat treatment at a temperature higher than 1000 °C there is marked decomposition of the organic groups, and consequently the necessary mechanical resilience is not obtained: thus, the residual displacement after 10% deformation does not become 0-5%, and the elastic modulus in 10% compression also exceeds 3000 kg/mm². Moreover, although any atmosphere can be used for the heat treatment without restriction, in order to suppress decomposition of organic groups and obtain the needed mechanical resilience a concentration of oxygen in the atmosphere of $\leq 10\%$ is preferred. When the temperature of heat treatment is in the range 350-1000 °C the oxygen concentration in the atmosphere is preferably $\leq 10\%$ in order to obtain the above first embodiment of the composite particles; and when the temperature of heat treatment is 100-350°C the above first embodiment of the composite particles is also produced in air.

With the process of the present invention the proportion of organic groups in the first embodiment of the composite particles can be chosen at will in the aforementioned range (the range described in explaining the first embodiment of the composite particles) by selecting the types and quantities of starting materials described above, the temperature and time of heat treatment, and the



concentration of oxygen in the atmosphere.

When hydrolyzing, when condensing, or when heat-treating, other compounds which possess reactive groups as described above and can react and form chemical bonds with silicon compounds capable of hydrolysis and condensation can also be present. In this case, a prior known coloring compound such as a dye and/or pigment, for example, can also be present.

A prior known surface treatment, such as surface modification by means of a coupling agent, surface modification by means of a previously described organo-metallic compound or inorganic compound, or surface modification by means of another organic compound, can be carried out on the first embodiment of the composite particles obtained as above before employing them as spacers, in order to improve ease of dispersing spacers on the electrode substrate when used as spacers for liquid crystal displays, or to prevent the abnormal orientation of liquid crystals at the surface of the spacers, or to fix the composite particles on the surface of the electrode substrate so that they do not move, or for other purposes. For example, the method of surface treatment described in Japanese Unexamined Patent Publication (Kokai) 62-269933 can be adopted. In this specification, when silica gel particles made by the sol-gel method are used as liquid

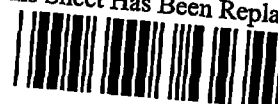


crystal display spacers the spacers are surface treated with an alcohol and/or a coupling agent, etc., in order to improve the ease of dispersing the spacers on the electrode substrate, or in order to suppress the production of abnormal liquid crystal orientation at the surface of the spacers.

The Si-C bonds and siloxane units in the particle body of the first embodiment of the composite particles of the present invention obtained can be confirmed by a prior known method such as FT-IR, NMR or ESCA, etc. and the proportion of the organic groups in the first embodiment of the composite particles, as the proportion accounted for by total carbon atoms, can be quantitatively determined by elemental analysis.

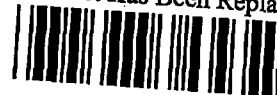
The condensation step can also be a step of hydrolysis and condensation using the aforementioned first silicon compound. The first silicon compound is at least one selected from the group consisting of compounds represented by General Formulae 2, 3 and 4 described above and their derivatives.

In the condensation step, both of the first and second silicon compounds described below can be used. The second silicon compound is at least one selected from the group consisting of compounds represented by the following General Formula (8) and their derivatives:



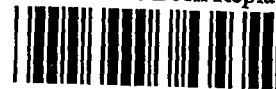
where: X indicates a monovalent radical-polymerizable functional group indicated by $CH_2=C(-R^1)-COOR^2-$, $CH_2=C(-R^4)-$ or $CH_2=C(-R^6)-R^7-$; R^1 , R^4 and R^6 indicate a hydrogen atom or a methyl group; R^2 and R^7 indicate an alkylene group of 1-10 carbon atoms, which may have a substituent group; R^9 indicates a hydrogen atom or at least one monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms; R^{10} indicates at least one monovalent group selected from the group consisting of alkyl groups of 1-10 carbon atoms and aryl groups of 6-10 carbon atoms, which may have a substituent group; m indicates an integer of 2-3; n indicates an integer of 0-2; and m + n indicates an integer of 2-3. The plural X may be different from each other, or 2 or more of X may be identical with each other. When n = 2, the two R^{10} s may be either different from or identical with each other. When 4 - m - n is 2, the two R^9 s may be either different from or identical with each other.

The radical-polymerizable groups in General Formulae 2-4 and 8 are $CH_2=C(-R^1)-COOR^2-$, $CH_2=C(-R^4)-$ or $CH_2=C(-R^6)-R^7-$. In General Formula 8, when there are 2 or more radical-polymerizable groups, they may be mutually different or 2 or more may be mutually identical. Subjecting the radical-polymerizable groups to radical polymerization



produces an organic polymer framework including the vinyl polymer described above. The radical-polymerizable group is an acryloxyalkyl group (R^1 in General Formulae 2 and 8 is a hydrogen atom), a methacryloxyalkyl group (R^1 in General Formulae 2 and 8 is a methyl group), a vinyl group (R^4 in General Formulae 3 and 8 is a hydrogen atom), an isopropenyl group (R^4 in General Formulae 3 and 8 is a methyl group), a 1-alkenyl group (R^6 in General Formulae 4 and 8 is a hydrogen atom), or an isoalkenyl group (R^6 in General Formulae 4 and 8 is a methyl group).

In General Formulae 2-4 and 8 the hydrolyzable groups are R^3O , R^5O , R^8O and R^9O . Groups R^3O , R^5O , R^8O and R^9O are monovalent groups selected from the group consisting of a hydroxyl group, alkoxy groups of 1-5 carbon atoms and acyloxy groups of 2-5 carbon atoms. In General Formulae 2-4, the 3 R^3O group, 3 R^5O groups and 3 R^8O groups may be mutually different or 2 or more may be mutually identical. In General Formula 8 when there are two R^9O groups they may be mutually different or identical. On grounds of high speed of hydrolysis and condensation, the R^3O groups, R^5O groups, R^8O groups and R^9O groups are each preferably selected from the group consisting of a methoxy group, ethoxy group, propoxy group and acetoxy group; and methoxy groups and ethoxy groups are more preferred. By hydrolyzing the R^3O groups, R^5O groups, R^8O groups and R^9O groups of



first silicon compounds and second silicon compounds with water, and then condensing, a polysiloxane framework indicated by the aforementioned General Formula 5 is formed.

In General Formulae 2-4 and 8 the R^2 group and R^7 group are alkylene groups of 1-10 carbon atoms, which may have a substituent group. There are no particular restrictions as to these alkylene groups, but examples include an ethylene group, propylene group, butylene group, hexylene group and octylene group, etc. On grounds of ready availability, compounds having radical-polymerizable groups in which R^2 and R^7 are propylene groups are preferred.

In General Formula 8, the R^{10} groups are an alkyl group or aryl group combined with the silicon atom. An alkyl group here is an alkyl group of 1-10 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group or hexyl group, for example, which may have a substituent group. An aryl group here is an aryl group of 6-10 carbon atoms, for example a phenyl group or a tolyl group, etc. In General Formula 8, when there are two R^{10} groups they may be mutually different or identical.

Compounds represented by at least one General Formula selected from the General Formulae 2, 3 and 4 have one silicon atom, and three hydrolyzable groups combined with the silicon atom, and one radical-polymerizable group combined with the silicon atom.

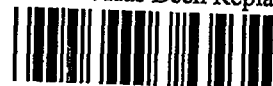


Concrete examples of compounds represented by General Formula 2 include γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -acryloxypropyltriethoxysilane and γ -methacryloxypropyltriacetoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

Concrete examples of compounds represented by General Formula 3 include vinyltrimethoxysilane, vinyltriethoxysilane and vinyltriacetoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

Concrete examples of compounds represented by General Formula 4 include 1-hexenyltrimethoxysilane and 1-octenyltrimethoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

A derivative of a compound represented by General Formula 2-4 is, for example, at least one selected from the group consisting of compounds in which some of the R^3O groups in a compound represented by General Formulae 2-4 are substituted by a β -dicarbonyl group and/or another group which allows the formation of a chelate compound, and lowly condensed products obtained by partial hydrolysis and condensation of compounds represented by General Formulae 2-4 and/or chelate compounds thereof.



As first silicon compounds, compounds indicated by General Formula 2 are preferred on grounds of the ease of forming the second embodiment of the organic-inorganic composite particles with a sharp particle diameter distribution; and at least one selected from the group consisting of γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -acryloxypropyltriethoxysilane and γ -methacryloxypropyltriacetoxysilane is particularly preferred.

The following 5 classes of compounds are represented by General Formula 8.

(1) Compounds which have one silicon atom, and one radical-polymerizable group combined with the silicon atom, and one alkyl group or aryl group combined with the silicon atom, and two hydrolyzable groups combined with the silicon atom ($m = 1$, $n = 1$). Concrete examples of such compounds include γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -acryloxypropylmethyldimethoxysilane, γ -acryloxypropylmethyldiethoxysilane, vinylmethyldimethoxysilane and vinylmethyldiethoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

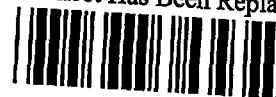
(2) Compounds having one silicon atom, and one radical-polymerizable group combined with the silicon atom,



and two alkyl and/or aryl groups combined with the silicon atom, and one hydrolyzable group combined with the silicon atom ($m = 1$, $n = 2$). Concrete examples of such compounds include γ -methacryloxypropyldimethylmethoxysilane, γ -methacryloxypropyldimethylethoxysilane, γ -acryloxypropyldimethylmethoxysilane, γ -acryloxypropyldimethylethoxysilane and vinyl dimethylmethoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

(3) Compounds having one silicon atom, and two radical-polymerizable groups combined with the silicon atom, and two hydrolyzable groups combined with the silicon atom ($m = 2$, $n = 0$). Concrete examples of such compounds include bis-(γ -acryloxypropyl)dimethoxysilane and bis(γ -methacryloxypropyl)dimethoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

(4) Compounds having one silicon atom, and two radical-polymerizable groups combined with the silicon atom, and one alkyl group or aryl group combined with the silicon atom, and one hydrolyzable group combined with the silicon atom ($m = 2$, $n = 1$). Concrete examples of such compounds include bis(γ -methacryloxypropyl)methylmethoxysilane, bis(γ -acryloxypropyl)methylmethoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used



together.

(5) Compounds having one silicon atom, and 3 radical-polymerizable groups combined with the silicon atom, and one hydrolyzable group combined with the silicon atom ($m = 3$, $n = 0$). Concrete examples of such compounds include tris(γ -methacryloxypropyl)methoxysilane, tris(γ -acryloxypropyl)methoxysilane, etc.; any one of these can be employed on its own, or 2 or more can be used together.

As a second silicon compound, a compound represented by General Formula 8 in which the radical-polymerizable group(s) in the compound is/are a $\text{CH}_2=\text{C}(-\text{R}^1)-\text{COOR}^2$ - group is preferred on grounds of the ease of forming the second embodiment of the organic-inorganic composite particles which have a sharp particle diameter distribution.

A derivative of a compound represented by General Formula 8 is, for example, at least one selected from the group consisting of compounds in which some of the R^9O groups in compounds represented by General Formula 8 are substituted by a β -dicarbonyl group and/or another group which allows the formation of a chelate compound, and lowly condensed products obtained by partial hydrolysis and condensation of compounds represented by General Formula 8 and/or chelate compounds thereof.

The first silicon compound is needed in the present invention because the particles obtained when a second



silicon compound is hydrolyzed and condensed without using a first silicon compound tend to have low hardness.

Other than the first and second silicon compounds described above, at least one metal compound capable of being hydrolyzed and condensed, selected from the group consisting of silane compounds represented by General Formula (9) below, and their derivatives, and organic metal compounds and inorganic metal compounds of boron, aluminum, gallium, indium, phosphorus, titanium and/or zirconium, etc., can also be used concurrently in order to obtain the second embodiment of the organic-inorganic composite particles of the present invention.



(In the formula, R^{11} is the same as R^3 , R^{12} is the same as R^{10} , and p is 0 or 1.)

On grounds of speed of hydrolysis and condensation the R^{11} group of the silane compound represented by General Formula 9 is preferably a methyl group or an ethyl group. p is 0 or 1, but on grounds of being able to give high hardness in the second embodiment of the organic-inorganic composite particles p is preferably 0.

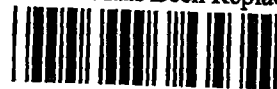
A derivative of a silane compound represented by General Formula 9 is, for example, at least one selected from the group consisting of compounds in which some of the $R^{11}O$ groups in compounds represented by General Formula 9



are substituted by a β -dicarbonyl group and/or another group which allow the formation of a chelate compound, and slowly condensed products obtained by partial hydrolysis and condensation of compounds represented by General Formula 9 and/or chelate compounds thereof.

There are no particular restrictions as to the quantity of metal compounds capable of hydrolysis and condensation other than the first and second silicon compounds, but if large quantities are employed the shape of the organic-inorganic composite particles obtained may not be spherical and particle diameter distribution may be broadened making them unsuitable as spacers. Consequently, the quantity of metal compounds capable of hydrolysis and condensation other than the first and second silicon compounds is preferably ≤ 200 wt%, more preferably ≤ 100 wt%, and even more preferably ≤ 50 wt%, of the total weight of first and second silicon compounds.

The first silicon compound, and optionally employed second silicon compound and/or metal compound capable of hydrolysis and condensation, (termed "starting materials" hereafter) is/are subjected to hydrolysis and condensation in a solution medium containing water. A bulk, intermittent or continuous manner, etc., can be adopted at will for the hydrolysis and condensation. A catalyst such as ammonia, urea, ethanolamine, tetramethylammonium hydroxide, an alkali



metal hydroxide or an alkaline earth hydroxide, etc., can be used for bringing about hydrolysis and condensation. An organic solvent may also be present in the solution medium in addition to water and a catalyst. Concrete examples of organic solvents include alcohols such as methanol, ethanol, isopropanol, n-butanol, isobutanol, sec-butanol, t-butanol, pentanol, ethylene glycol and 1,4-butanediol, etc., ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate, (cyclo)paraffins such as isooctane and cyclohexane, etc., ethers such as dioxane and diethyl ether and aromatic hydrocarbons such as benzene and toluene, etc., used singly or in mixtures.

Hydrolysis and condensation can be performed, for example, by adding the starting materials above, or a solution thereof in an organic solvent, to a solution medium including water, and stirring at a temperature in the range 0-100°C, and preferably 0-70°C, for 30 minutes to 100 hours.

Particles obtained by a process such as that above can also be loaded beforehand into the synthetic system as seed particles, and then the seed particles can be grown by adding the starting materials.

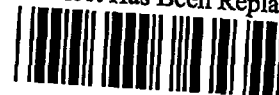
By hydrolyzing and condensing the starting materials under suitable conditions in a solution medium including water in this way, a slurry is produced from which the particles separate out. The particles which separate out



are the resulting product of hydrolysis and condensation of a silicon compound described above which has a radical-polymerizable group, and the particles have an optionally selected particle diameter $\geq 0.5 \mu m$, and a sharp particle diameter distribution. As the suitable conditions here, a starting material concentration in the slurry of ≤ 20 wt%, a water concentration of ≤ 50 wt% and a catalyst concentration of ≤ 10 wt% are preferably used.

Particles which have a mean particle diameter within the above range for particle diameter possessed by the second embodiment of the organic-inorganic composite particles of the present invention described above can be produced by hydrolysis and condensation by setting the water concentration, the catalyst concentration, the organic solvent concentration, the starting material concentration, the period of time of adding the starting materials, the temperature and seed particle concentration, for example, to 50-99.99%, 0.01-10 wt%, 0-90 wt%, 0.1-30 wt%, 0.001-500 hours, 0-100°C and 0-10 wt% respectively. By setting the water concentration, catalyst concentration and organic solvent concentration within the respective ranges above, particles can be produced which have a coefficient of variation in particle diameter within the range for the organic-inorganic composite particles of the present invention described above.

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REPLACED



Moreover, in hydrolyzing and condensing a first silicon compound, and an optionally employed second silicon compound and/or metal compound capable of hydrolysis and condensation, fine inorganic particles of a mean particle diameter $\leq 0.4 \mu\text{m}$ are preferably also used. The reason is that the organic-inorganic composite particles obtained are harder and have a raised fracture strength when they include fine inorganic particles chemically combined with the polysiloxane framework.

Concrete examples of fine inorganic particles include silica, alumina, aluminum hydroxide, titanium oxide and zirconium oxide, etc.; but on grounds of ease of introduction into particles obtained by hydrolysis and condensation, silica is preferred.

A mean particle diameter of the fine inorganic particles exceeding $0.4 \mu\text{m}$ is undesirable because it becomes difficult to introduce them into particles obtained by hydrolysis and condensation of the starting materials. Therefore, the smaller the mean particle diameter of the fine inorganic particles the better, and it is preferably $\leq 0.1 \mu\text{m}$, more preferably $\leq 30 \text{ nm}$, and even more preferably $\leq 10 \text{ nm}$. The fine inorganic particles are preferably silica of a mean particle diameter of preferably $\leq 0.1 \mu\text{m}$, more preferably $\leq 30 \text{ nm}$ or $\leq 10 \text{ nm}$.

On grounds of decreasing the number of particle



aggregates, these fine inorganic particles are preferably of sol dispersed in water or an organic solvent. More preferably they are of sol of fine inorganic particles of a mean particle diameter ≤ 30 nm, and even more preferably ≤ 10 nm. Concrete examples include, for example, sols of silica particles of mean particle diameter ≤ 30 nm (silica sols) such as "Snowtex 20", "Snowtex 0", "Snowtex C", "Snowtex N", "Snowtex S", "Snowtex 20L", "Snowtex XS", "Snowtex XL", "Snowtex YL", "Snowtex ZL", "Methanol Silica Sol" and "IPA-ST" (trade names, made by Nissan Chemical Industries, Ltd.), etc., and alumina sols such as "Alumina Sol 100", "Alumina Sol 200" and "Alumina Sol 520" (trade names, made by Nissan Chemical Industries, Ltd.), etc.

During the condensation step, and/or after the condensation step, the radical-polymerizable groups are subjected to radical polymerization. Thus, particles of an intermediate product obtained by hydrolysis and condensation of a first silicon compound, optionally employing a second silicon compound, are subjected to radical polymerization. The radical-polymerizable groups undergo radical polymerization to form an organic polymer framework.

As the method of radical polymerization, radical polymerization can be performed as it stands by dissolving a water-soluble or oil-soluble radical polymerization initiator in the slurry of a solution medium including water



which contains the particles obtained by hydrolysis and condensation, or the particles obtained by hydrolysis and condensation can be isolated from the slurry using a known method such as filtration, centrifugal separation or concentration at decreased pressure, etc., and then polymerized by dispersion in a solution of water or an organic solution medium, etc., containing a polymerization initiator; however, these are not the only possible methods. Performing hydrolysis and condensation in the presence of a polymerization initiator so that radical polymerization occurs simultaneously is particularly preferred. The reason is that because the organic polymer is produced by polymerization in parallel with the production of polysiloxane shown by Formula 5, it is easier to obtain the hardness characteristic of inorganic substances and the mechanical resilience and fracture strength characteristic of organic polymers which are possessed by the second embodiment of the organic-inorganic composite particles of the present invention, and the resulting particles express this hardness, mechanical resilience and fracture strength to particular advantage.

There are no particular restrictions as to the radical polymerization initiator here, and a prior known substance can be employed; but at least one selected from the group consisting of azo compounds and peroxy compounds



is preferred.

There are no particular restrictions as to the quantity of the radical polymerization initiator above; but since if too much is used a lot of heat is generated and it becomes difficult to control the reaction, and if too little is used radical polymerization may not proceed, for example, it will be in the range 0.1-5 wt%, and preferably 0.3-2 wt%, relative to the total weight of first and second silicon compounds.

The temperature for radical polymerization can be selected to suit the radical polymerization initiator that is employed, but to facilitate control of the reaction it will be in the range 30-100°C, and preferably 50-80°C.

Monomers having groups capable of radical polymerization with the radical-polymerizable groups can also be present when carrying out radical polymerization. Examples of monomers include unsaturated carboxylic acids such as acrylic acid and methacrylic acid, etc., esters of unsaturated carboxylic acids such as acrylic acid esters, methacrylic acid esters, crotonic acid esters, itaconic acid esters, maleic acid esters and fumaric acid esters, etc., acrylamides, methacrylamides, vinyl compounds such as aromatic vinyl compounds such as styrene, α -methylstyrene and divinyl benzene, etc., vinyl esters such as vinyl acetate, etc., and halogenated vinyl compounds such as vinyl



chloride, etc.; one or more of these can be employed. Of these, monomers which have 2 or more groups capable of radical polymerization, such as divinylbenzene, trimethylolpropane trimethacrylate and ethylene glycol dimethacrylate, etc., are preferred.

However, if too much monomer is employed and the polysiloxane content in the organic-inorganic composite particles becomes less than 25 wt%, hardness becomes inadequate, which is undesirable. Consequently, the quantity of monomers is, for example, 0-50 wt%, and preferably 0-30 wt%, of the total weight of first and second silicon compounds.

After radical polymerization, the further recondensation step described below is preferably carried out, since it raises the hardness, mechanical resilience and fracture strength of the organic-inorganic particles that are finally obtained. The recondensation step includes subjecting the polymerized particles (which are produced by the radical polymerization) to further condensation in an organic solvent. In order to speed up condensation the aforementioned catalysts can be used; catalysts preferred on grounds of speeding up condensation include organic titanium compounds such as titanium tetraisopropoxide, titanium tetrabutoxide and diisopropoxy-bis(acetylacetonate) titanate, etc., organic aluminum compounds such as aluminum



triisopropoxide, aluminum tri(sec-butoxide), aluminum tris-(acetylacetonate) and aluminum isopropoxide-bis(acetylacetonate), etc., organic zirconium compounds such as zirconium tetrabutoxide and zirconium tetrakis(acetylacetonate), etc., organic tin compounds such as dibutyltin diacetate, dibutyltin dilaurate, dibutyltin diethylhexanoate and dibutyltin dimaleate, etc., and acidic phosphate esters such as $(\text{CH}_3\text{O})_2\text{P}(=\text{O})\text{OH}$, $(\text{CH}_3\text{O})\text{P}(=\text{O})(\text{OH})_2$, $(\text{C}_4\text{H}_9\text{O})_2\text{P}(=\text{O})\text{OH}$ and $(\text{C}_8\text{H}_{17}\text{O})\text{P}(=\text{O})(\text{OH})_2$, etc.; any one of these can be used on its own, or two or more can be used together. Of these, at least one selected from the group consisting of organotin compounds and acidic phosphate esters is preferred.

In the recondensation step, it is preferable that the polymerized particles do not contain water. The reason for this is to facilitate the progress of condensation of silanol groups with the elimination of water. Therefore, when the slurry obtained by the polymerization step does not contain water the slurry can be employed as it stands in the recondensation step, but when the slurry contains water the polymerized particles are preferably isolated from the slurry using a prior known method such as filtration, centrifugal separation or concentration at decreased pressure, and then dispersed in an organic solvent before recondensation. The organic solvents employed will be, for example, at least one selected from the group consisting of



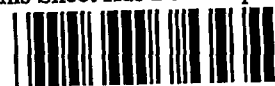
the alcohols, ketones, esters, paraffins, ethers and aromatic hydrocarbons mentioned previously. The recondensation step can be performed, for example, by stirring an organic solvent slurry containing the polymerized particles at a temperature of 50-200°C, and preferably 60-150°C, for 30 minutes to 100 hours. The pressure can be normal pressure, decreased pressure or increased pressure.

By isolating the polymerized particles produced by radical polymerization from the slurry using a prior known method such as filtration, centrifugal separation or concentration at decreased pressure, etc., and then heat-treating them at a temperature of $\leq 800^{\circ}\text{C}$, preferably a temperature of 100-600°C, and more preferably a temperature of 150-500°C in order to dry and calcine them, the second embodiment of the organic-inorganic composite particles of the present invention is obtained which possess suitable hardness, mechanical resilience and fracture strength. These composite particles include as their main components an organic polymer framework, and a polysiloxane framework which has in its molecule organosilicon in which the silicon atom is directly and chemically combined with at least one carbon atom in the organic polymer framework. However, with heat treatment at a low-temperature the condensation of silanol groups represented by Formula 7 present in the



siloxane units indicated by Formula 5 is incomplete, and consequently the necessary hardness is not obtained. Thus, the elastic modulus in 10% compression of the particles may not attain $\geq 350 \text{ kg/mm}^2$. Similarly, with heat treatment at a temperature higher than 800°C there is marked decomposition of the organic polymer, and consequently the necessary mechanical resilience and fracture strength are not obtained. Thus, the residual displacement of the particles after 10% deformation does not attain 0-5%; and the particles become too hard, with an elastic modulus in 10% compression in excess of 3000 kg/mm^2 . Moreover, although there are no restrictions as to the atmosphere used for heat treatment, in order to suppress decomposition of the organic polymer and obtain the necessary mechanical resilience an oxygen concentration of $\leq 10 \text{ vol\%}$ in the atmosphere is preferable. In order to obtain the second embodiment of the organic-inorganic composite particles of the present invention oxygen concentration in the atmosphere at heat treatment is preferably $\leq 10 \text{ vol\%}$ when the temperature of heat treatment is in the range $200-800^\circ\text{C}$, but when the temperature of heat treatment is $\leq 200^\circ\text{C}$ the second embodiment of the organic-inorganic composite particles of the present invention can also be obtained in air.

By appropriate selection of the types and/or



quantities of the starting materials, fine inorganic particles, water and catalyst for hydrolysis and condensation, and monomers and radical polymerization initiator described above, the temperature and period of time of heat treatment and the oxygen concentration in the atmosphere when making the second embodiment of the organic-inorganic composite particles, the quantity of SiO_2 in the polysiloxane framework of the organic-inorganic composite particles obtained can be controlled at will at ≥ 25 wt%, and the mean particle diameter can be controlled at will at $\geq 0.5 \mu\text{m}$.

Since the process of the present invention for producing the second embodiment of the organic-inorganic composite particles includes the condensation step, the hydrolysis step and the heat-treatment step described above, the polysiloxane framework and the organic polymer framework have a structure chemically combined by Si-C bonds, and organic-inorganic composite particles can be produced which have the great hardness characteristic of the polysiloxane 3-dimensional framework and the high mechanical resilience and fracture strength characteristic of the polymer framework. Consequently, the composite particles obtained have the mechanical resilience necessary to maintain a constant gap distance between a pair of members which should be placed with a proper gap distance, and the hardness and



fracture strength to maintain the aforementioned gap distance with smaller numbers, and they also do not readily cause physical damage to the members. Moreover, since the composite particles have a mean particle diameter $\geq 0.5 \mu m$, they are useful for forming a gap distance between a pair of members.

Colored organic-inorganic composite particles can be obtained by coloring the particles produced during and/or after at least one step selected from the group consisting of the condensation step, the polymerization step, the recondensation step and the heat-treatment step.

In the process of the present invention, colored organic-inorganic composite particles can be produced by introducing a dye and/or pigment into the particles by having a dye and/or pigment present in a suitable step during manufacture.

Within the process of the present invention the particles are preferably colored by using a dye and/or pigment in the condensation step. As dyes and/or pigments, those mentioned above can be cited. Of these, basic dyes are preferred. This is because the silanol groups in polysiloxane are acidic, and basic (cationic) dyes are readily absorbed so that coloring is easy. Examples of pigments include inorganic pigments such as carbon black, iron black, chrome vermillion, molybdenum red, red ochre,



yellow lead, chrome green, cobalt green, ultramarine blue and iron blue, etc., and organic pigments such as phthalocyanine, azo and quinacridone pigments, etc. However, since it may not be possible to introduce pigments into the composite particles of the present invention if the mean particle diameter thereof is not $\leq 0.4 \mu m$, the use of dyes is preferred. Organic-inorganic composite particles of the present invention which are colored in this way are particularly useful for raising the picture quality of liquid crystal displays because they are also provided with the aforementioned hardness, mechanical resilience and fracture strength.

Organic-inorganic composite particles of the present invention can also have a particle body described above and a conductive layer formed on the surface of the particle body.

The particle body of organic-inorganic composite particles of the present invention has the mechanical resilience necessary to maintain constant the gap distance between a pair of electrodes brought into electrical contact, and the hardness and fracture strength to maintain the aforementioned gap distance constant with smaller numbers; and they also do not readily cause physical damage to the electrodes. Consequently, it is easy to maintain the gap distance between a pair of electrodes constant, and to



avoid detachment and falling off of the conductive layer due to pressure which causes short circuit between the electrodes when they should not be in electrical contact and poor contact between the electrodes when they should be in electrical contact.

Metals employed in the conductive layer can be prior known metals: examples include nickel, gold, silver, copper and indium, and alloys of these, etc.; nickel, gold and indium are preferred, since they have particularly high conductivity. There are no particular restrictions as to the thickness of the conductive layer, provided that it gives adequate conduction; but it is preferably in the range 0.01-5 μ m, and particularly preferably in the range 0.02-2 μ m. When the thickness is thinner than the aforementioned range conductivity may be inadequate, and when it is thicker than the aforementioned range the conductive layer becomes prone to detach due to the difference in thermal conductivity between the particle and the conductive layer. The conductive layer can be a single layer or ≥ 2 layers; when there are ≥ 2 layers, layers including different conductors can be arranged one on top of the other.

A prior known method can be adopted as the method for forming a conducting layer on the surface of the particle body of organic-inorganic composite particles of the present invention; there are no particular restrictions, and a



method such as a chemical plating method (electroless plating), a coating method, a PVD method (vacuum vapor deposition, sputtering, ion plating, etc.) etc., for example; can be used; of these chemical plating is preferred since it readily gives conductive particles of the present invention. Conductive particles of the present invention so obtained are also provided with the hardness and mechanical resilience of organic-inorganic composite particles of the present invention described above. Consequently, they are particularly useful as electrical connecting materials for electronics applications such as liquid crystal displays, LSIs and printed circuit boards, etc.

Organic-inorganic composite particles of the present invention have the mechanical resilience necessary to maintain a constant gap distance between a pair of electrode substrates which should be arranged with the correct gap distance between them, and the hardness and fracture strength necessary to maintain the aforementioned gap distance constant with smaller numbers; and they also do not readily cause physical damage to the electrode substrates. Consequently, it becomes easy to maintain a constant gap distance between a pair of electrode substrates, in low-temperature environments shrinkage approaches that of the liquid crystals, vapor deposition layers, orientating layers and coating layers do not readily get damaged, and the



number that needs to be dispersed between the electrode substrates is decreased.

As described above, because the first and second embodiments of the organic-inorganic composite particles of the present invention contain both of a polysiloxane framework and an organic group, or both of a polysiloxane framework and an organic polymer framework, or all of a polysiloxane framework, an organic group and an organic polymer framework together, and are composite particles in which the organic polymer framework and the polysiloxane framework are chemically combined, they are provided both with the great hardness characteristic of inorganic substances and with the high mechanical resilience and fracture strength characteristic of organic groups and/or organic polymers, and are ideal for use as spacers for liquid crystal displays.

When the organic-inorganic composite particles of the present invention are colored by including a dye and/or pigment in the particle body they are useful as colored spacers.

In liquid crystal displays an image is formed by applying a voltage between electrode substrates and producing a change in the optical properties of the liquid crystals. In this connection, the spacers do not show any change in optical properties as the result of applying a

voltage. Therefore, in the dark area of the portions when an image was displayed spacers which are not colored may allow light of the backlight lamp to escape and be recognizable as bright spots, and image contrast may be lowered.

When the organic-inorganic composite particles of the present invention have a particle body that has been colored by including a dye and/or pigment, light of the backlight lamp does not readily escape and the lowering of image contrast is prevented; since these composite particles are moreover also provided with a combination of characteristic hardness, mechanical resilience and fracture strength, they are particularly useful for improving the image quality of liquid crystal displays. The colors preferred for colored spacers for liquid crystal displays are colors which do not readily transmit light or which do not transmit light. Examples include black, dark blue, purple, blue, dark green, green, brown and red, etc., but black, dark blue and navy blue are particularly preferred.

The organic-inorganic composite particles of the present invention are also useful as adhesive spacers when they include a particle body and an adhesive layer formed on the surface of the particle body. The adhesive layer, for example can be an adhesive which becomes adhesive when heated.



When the composite particles of the present invention have an adhesive layer on the surface of the particle body, on being interposed between electrode substrates which constitute a liquid crystal display and being hot pressed the adhesive layer will melt and stick to the electrode substrate, and they can be fixed in place by cooling and hardening the adhesive layer. Consequently, since the composite particles become unable to move freely it is possible to prevent damage to orientating layers and to maintain the uniformity of the gap distance, and it is possible to achieve an improvement in image quality. As an adhesive layer a thermoplastic resin is preferred. The glass transition temperature of the thermoplastic resin is preferably $\leq 150^{\circ}\text{C}$, and more preferably $\leq 80^{\circ}\text{C}$. This is so that it can be stuck to the electrode substrates by hot pressing for a short time. When the glass transition temperature is too high the adhesive layer may not stick to the electrode substrate when heated, and when it is too low the composite particles are liable to stick together; hence, it is most preferably in the range $40\text{--}80^{\circ}\text{C}$. There are no particular restrictions as to the type of thermoplastic resin, but it is preferably a (meth)acrylic resin. The adhesive layer can be a single layer or it can be ≥ 2 layers, and when it is ≥ 2 layers it can be made up of layers of different thermoplastic resins on top of one



another.

Composite particles having an adhesive layer can be obtained, for example, by coating the particle body of organic-inorganic composite particles of the present invention with an adhesive layer. When a thermoplastic resin is used as the adhesive layer, a layer of thermoplastic adhesive can be coated onto the surface of organic-inorganic composite particles of the present invention by a prior known resin coating method such as in-situ polymerization, coacervation, interface polymerization, a liquid curing coating method, a liquid drying method, a high speed gas stream impact method, a gas spray coating or a spray drying method, etc. High-speed gas stream impact methods are preferred because coating is easier. A high-speed gas stream impact method, for example, involves mixing organic-inorganic composite particles of the present invention with a powdered thermoplastic resin, dispersing this mixture in a gas phase, applying to the composite particles and the powdered thermoplastic resin mechanical and thermal energy the main component of which is an impact force, and coating the surface of the organic-inorganic composite particles with the thermoplastic resin; this method is preferred because of the ease of coating.

Equipment employing such high-speed gas stream impact methods include the Hybridization System manufactured by



Nara Kikai Seisakusho KK, the Mechanofusion System manufactured by Hosokawa Mikron KK, and the Krypton System manufactured by Kawasaki Jukogyo KK [Kawasaki Heavy Industry], etc.

Composite particles having an adhesive coating are furnished with the hardness, mechanical resilience and fracture strength of organic-inorganic composite particles of the present invention described above, and have an adhesive coating; and hence they are particularly useful for improving the image quality of liquid crystal displays.

When composite particles having an adhesive layer are colored by including a dye and/or pigment in the particle body of organic-inorganic composite particles they do not readily allow light of the backlight lamp to escape and prevent a lowering of image contrast, and because they are adhesive they are not freely mobile, which prevents damage to orientating layers and enable a uniform gap distant to be maintained; since moreover they combine the hardness, mechanical resilience and fracture strength characteristic of the present invention described above, the adhesive spacers are also useful as colored spacers, and therefore particularly useful for improving the picture quality of liquid crystal displays.

In the liquid crystal displays of the present invention, the composite particles of the present invention



as described above are interposed between electrode substrates as spacers for the liquid crystal display instead of the prior spacers in prior liquid crystal displays; and they have a gap distance the same as the particle diameter of the composite particles, or almost the same. The quantity of composite particles employed is ordinarily 40-100/mm², and preferably 40-80/mm², which is of the order of 10-50% less than for prior organic spacers so that the area of the portions in which no image is formed becomes smaller and the quantity of impurities such as ions and molecules, etc., eluting from the inside of the spacers into the liquid crystal layer is greatly decreased. Consequently a high contrast, decrease in image roughness and an improvement in the picture quality can be expected.

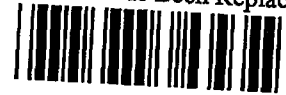
Liquid displays of the present invention are provided, for example, with the first electrode substrate, the second electrode substrate, a sealing material, and a spacer for the liquid crystal display, and a liquid crystal. The first electrode substrate has a first substrate and a first electrode formed in the surface of the first substrate. The second electrode substrate has a second substrate and a second electrode formed in the surface of the second substrate, and is opposite to the first electrode substrate. The spacers for the liquid crystal display, which are interposed between the first electrode substrate and the



second electrode substrate, are composite particles of the present invention. A sealing material bonds the first electrode substrate with the second electrode substrate at their respective circumferencial edges. The liquid crystals are packed into the space defined by the first electrode substrate, the second electrode substrate and the sealing material.

In the liquid crystal displays of the present invention the members other than the spacers, such as the electrode substrates, the sealing material and the liquid crystals can be the same materials employed in the same way as in prior liquid crystal displays. The electrode substrates include a substrate which is a glass sheet or a film sheet, etc., and an electrode formed in the surface of the substrate, and if necessary further have an orientating layer on the surface of the electrode substrate, formed so as to cover the electrode. As the sealing material an epoxy resin binder sealing material, etc., can be employed. The liquid crystals can be liquid crystals used in prior displays; for example, biphenyl, phenylcyclohexane, Schiff base, azo, azoxy, benzoic acid ester, terphenyl, cyclohexyl-carboxylic acid ester, biphenylcyclohexane, pyrimidine, dioxane, cyclohexylcyclohexane ester, cyclohexylethane or cyclohexene type liquid crystals, etc.

One method for making a liquid crystal display of the



present invention, for example, involves dispersing composite particles of the present invention evenly by a wet method or a dry method on one of the two electrode substrates as surface spacers, and then mounting the other electrode substrate, which has the portion to be sealed painted by a means such as screen printing with composite particles of the present invention as spacers for the sealed portion dispersed in a binder sealing material such as an epoxy resin, on top, and after heat curing the sealing binder material by applying a suitable pressure and heating at a temperature of 100-180°C for 1-60 minutes, or exposing to a quantity of ultraviolet radiation of 40-300 mJ/cm², injecting the liquid crystals, and then sealing the portion through which they are injected to obtain a liquid crystal display; but there are no restrictions in the present invention as to the method for making the liquid crystal display. Of the composite particles of the present invention, the aforementioned colored composite particles are preferred as surface spacers because they are not prone to allow light of the backlight lamp to escape, and the aforementioned composite particles having an adhesive layer are more preferred because they stick to the electrode substrates so that they cannot move freely; colored composite particles having an adhesive layer are even more preferred because they do not allow light of the backlight



lamp to escape and they stick to the electrode substrates so that they cannot move freely.

Liquid crystal displays of the present invention can be employed for the same purposes as prior liquid crystal displays, as image display elements for televisions, personal computers and word processors, etc.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention is illustrated by the following examples of some preferred embodiments in comparison with comparative examples not according to the invention.

The liquid crystal displays in the Examples below were made by the process described below. As shown in Figure 1, a lower electrode substrate 110 was first obtained by forming an electrode (for example, a transparent electrode) 5 and a polyimide orientating layer 4 on a lower glass substrate 11 of size 300 mm x 345 mm x 1.1 mm, and then rubbing. The spacers for the liquid crystal display (in this case surface spacers) 8, dispersed at 1 wt% in a mixed solvent including methanol 30 parts (v/v), isopropanol 20 parts (v/v) and water 50 parts (v/v) were spread over 1-10 seconds on this lower electrode substrate 110.

Meanwhile, an upper electrode substrate 120 was obtained by forming an electrode (for example a transparent electrode) 5 and a polyimide orientating layer 4 on an upper



glass substrate 12 of size 300 mm x 345 mm x 1.1 mm and then rubbing. And spacers for the liquid crystal display (in this case sealing spacers) 3 dispersed at 30 vol% in an epoxy resin binder sealing material 2 were screen printed onto the portion of the upper electrode substrate 120 that was to be sealed.

Finally, the upper and lower electrode substrates 120 and 110 were stuck together with the electrodes 5 and orientating layers 4 opposite to each other and the spacers 8 between; a pressure of 4 kg/cm^2 was applied, and the binder sealing material 2 was heat cured by heating at 150°C for 30 minutes. Then, by placing the space between the two electrode substrates 120 and 110 under vacuum and then returning it to atmospheric pressure, liquid crystals 7, including a mixture of biphenyl and phenylcyclohexane type liquid crystals, etc., according to the type of liquid crystal display being made, were injected and the portion through which they were injected was sealed. PVA (poly(vinyl alcohol)) polarizing films 6 were then stuck to the outside of the upper and lower glass substrates 12 and 11, to constitute the liquid crystal display.

As Figure 2 shows, the spacers 8 can be organic-inorganic composite particles of the present invention including an uncolored particle body 31. In this case, physical damage is not readily caused to the electrode



substrates by pressure during manufacture, and the display is not prone to occur low-temperature bubbling or image unevenness. Moreover, because the number of spacers is less than with prior spacers including polymer particles, the area of the portion in which no image is formed is decreased and the elution of impurities into the liquid crystals is also decreased. Consequently, it is possible to raise contrast and raise picture quality.

As Figure 3 shows, the spacers 8 can also be organic-inorganic composite particles of the present invention including a colored particle body 32. In this case there is the additional advantage that transmission of light of the backlight lamp through the spacers 8 does not readily occur, and hence conspicuous bright spots are eliminated and the quality of the pictures displayed is further raised.

As Figure 4 shows, the spacers 8 can also be organic-inorganic composite particles of the present invention which include an uncolored particle body 31 and an adhesive layer 33 formed on the surface of the particle body 31. In this case, there is the additional advantage that damage to the orientating layer is prevented because the spacers are not able to move freely, further raising the quality of the pictures displayed.

As Figure 5 shows, the spacers 8 can also be organic-inorganic composite particles of the present invention which



include a colored particle body 32 and an adhesive layer 33 formed on the surface of the particle body 32. In this case there is the additional advantage that transmission of light of the backlight lamp through the spacers 8 does not readily occur, eliminating conspicuous bright spots, and the additional advantage that damage to the orientating layer is prevented because the spacers are not able to move freely, further raising the quality of the pictures displayed.

As Figure 6 shows, the organic-inorganic composite particles of the present invention can also include a particle body 34 and a conductive layer 35 formed on the surface of the particle body 34. The conductive layer can be, for example, a metal layer formed by electroless coating, and can be one or more layers.

In relation to the methods for evaluating the liquid crystal displays obtained, low-temperature bubbling was assessed by the presence or absence of an image after holding for 1000 hours at -45°C , and the presence or absence of image unevenness and pixel faults was assessed visually at room temperature (25°C).

EXAMPLE A1

Methanol (307 parts by weight), 25% aqueous ammonia (6 parts by weight) and water (1225 parts by weight) were mixed evenly in a 2-liter glass reaction vessel provided with a stirrer, a dropping funnel and a thermometer. This mixture



was adjusted to $20 \pm 0.5^{\circ}\text{C}$ and stirred evenly at 100 rpm while methyltrimethoxysilane (60 parts by weight) was added dropwise over 6 hours from the dropping funnel. Stirring was continued evenly for 1 hour after the addition to perform hydrolysis and condensation and obtain a suspension of hydrated fine particles of condensed methyltrimethoxysilane (A). The solid and liquid in this suspension (A) were separated by filtration, the resulting cake was washed 3 times with methanol, and the resulting solid powder was dried in a vacuum drier at 100°C for 3 hours and then heat treated in an atmosphere of nitrogen at 350°C for 3 hours to obtain organic-inorganic composite particles of a mean particle diameter of $1.81 \mu\text{m}$ with a coefficient of variation of 7.6% in particle diameter.

When the hardness and mechanical resilience of the resulting composite particles was evaluated by the methods described previously, the elastic modulus in 10% compression was 711 kg/mm^2 and residual displacement after 10% deformation was 2.5%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was also confirmed by FT-IR analysis. From elemental analysis, the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 13.3 wt%.

When a B5 size ferroelectric liquid crystal display



was made by the known method using these composite particles, the number of spacers dispersed could be decreased by $\geq 10\%$ compared with current organic particle spacers (Epostar GP-H, made by Nippon Shokubai Co., Ltd.), and a liquid crystal display could be made which did not produce low-temperature bubbling or image unevenness which arise when calcined silica particles or non-calcined silica particles made by the sol-gel method were used.

EXAMPLE A2

Organic-inorganic composite particles of mean particle diameter $6.84 \mu\text{m}$ with a coefficient of variation of 5.9% in particle diameter were obtained as in Example A1 except that methanol (154 parts by weight) and n-propanol (153 parts by weight) were employed instead of the methanol (307 parts by weight) in Example A1, and heat treatment was performed at 750°C for 1 hour instead of at 350°C for 3 hours.

The elastic modulus in 10% compression of the resulting composite particles was 750 kg/mm^2 , and residual displacement after 10% deformation was 3.1%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 12.1 wt%.

When a B5 size STN (abbreviation for Super Twisted



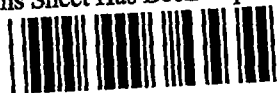
Nematic) liquid crystal display was made by the known method using these composite particles, the results obtained were similar to those in Example A1.

EXAMPLE A3

Organic-inorganic composite particles of mean particle diameter $4.47 \mu\text{m}$ with a coefficient of variation of 6.8% in particle diameter were obtained as in Example A1 except that methanol (154 parts by weight) and n-butanol (153 parts by weight) were employed instead of the methanol (307 parts by weight) in Example A1, and tetraethoxysilane (17 parts by weight) and methyltrimethoxysilane (43 parts by weight) were employed instead of methyltrimethoxysilane (60 parts by weight), and heat treatment was performed at 600°C for 2 hours instead of 350°C for 3 hours. Here n in Formula (6) was 0.8, since methyltrimethoxysilane was 80 mol% and tetraethoxysilane was 20 mol%.

The elastic modulus in 10% compression of the resulting composite particles was 1606 kg/mm^2 , and residual displacement after 10% deformation was 4.7%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 9.2 wt%.

When a B5 size TFT (abbreviation for Thin Film



Transistor) liquid crystal display was made by the known method using these composite particles, the results obtained were similar to those in Example A1; no pixel faults were noted.

EXAMPLE A4

Organic-inorganic composite particles of mean particle diameter $6.15 \mu\text{m}$ with a coefficient of variation of 6.7% in particle diameter were obtained as in Example A2 except that heat treatment was performed in a mixed atmosphere of nitrogen 95 vol% and oxygen 5 vol% at 450°C for 2 hours instead of at 750°C for 1 hour in Example A2.

The elastic modulus in 10% compression of the resulting composite particles was 1440 kg/mm^2 , and residual displacement after 10% deformation was 3.8%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 10.1 wt%.

When a B5 size STN was made by the known method using these composite particles, the results obtained were similar to those in Example A2.

EXAMPLE A5

Organic-inorganic composite particles of mean particle diameter $1.97 \mu\text{m}$ with a coefficient of variation of 6.9% in



particle diameter were obtained as in Example A1 except that methanol (154 parts by weight) and n-butanol (153 parts by weight) were employed instead of the methanol (307 parts by weight) in Example A1, and ethyltrimethoxysilane (60 parts by weight) was employed instead of methyltrimethoxysilane (60 parts by weight), and heat treatment was performed at 750°C for 3 hours instead of 350°C for 3 hours.

The elastic modulus in 10% compression of the resulting composite particles was 811 kg/mm², and residual displacement after 10% deformation was 3.2%. The presence of Si-CH₂- bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 12.0 wt%.

When a B5 size ferroelectric liquid crystal display was made by the known method using these composite particles, the results obtained were similar to those in Example A1.

EXAMPLE A6

Organic-inorganic composite particles of mean particle diameter 4.55 μ m with a coefficient of variation of 6.8% in particle diameter were obtained as in Example A3 except that heat treatment was performed in air at 200°C for 5 hours instead of at 600°C for 2 hours in Example A3.



The elastic modulus in 10% compression of the resulting composite particles was 630 kg/mm^2 , and residual displacement after 10% deformation was 2.3%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 14.3 wt%.

When a B5 size TFT liquid crystal display was made by the known method using these composite particles, the results obtained were similar to those in Example A1; no pixel faults were noted.

COMPARATIVE EXAMPLE A1

Particles were obtained as in Example A2 except that heat treatment was performed at 80°C for 2 hours instead of the heat treatment at 750°C for 1 hour in Example A2.

The elastic modulus in 10% compression of the resulting particles was 312 kg/mm^2 , and residual displacement after 10% deformation was 2.0%. The proportion of organic groups in the particles, representing the quantity of organic groups by the total weight of carbon atoms, was 18 wt%.

When a B5 size STN liquid crystal display was made by the known method using these particles, the number that needed to be dispersed was the same as for the current



organic polymer particle spacers.

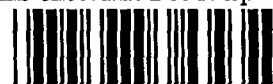
COMPARATIVE EXAMPLE A2

Particles were obtained as in Example A3 except that heat treatment was performed at 1150°C for 1 hour instead of the heat treatment at 600°C for 2 hours in Example A3.

The elastic modulus in 10% compression of the resulting particles was 3380 kg/mm², and residual displacement after 10% deformation was 6.4%. The proportion of organic groups in the particles, representing the quantity of organic groups by the total weight of carbon atoms, was 1 wt%.

When a B5 size TFT liquid crystal display was made by the known method using these particles, pixel faults were produced due to breakage of the TFT array on the substrate, and image unevenness was produced because mechanical resilience was inadequate.

As regards the numbers of composite particles of the present invention dispersed in the surface of the liquid crystal displays obtained in the Examples above, the numbers of composite particles of the present invention were counted under an optical microscope in arbitrary areas of 1 mm² in each of 9 fields formed by equal division of the surface (on which to be dispersed) into 3 widthwise and lengthwise, and the mean value of the 9 fields was taken to be the number dispersed. The results are given below.



Example A1 ... Number dispersed $73/\text{mm}^2$
Example A2 ... Number dispersed $70/\text{mm}^2$
Example A3 ... Number dispersed $69/\text{mm}^2$
Example A4 ... Number dispersed $68/\text{mm}^2$
Example A5 ... Number dispersed $69/\text{mm}^2$
Example A6 ... Number dispersed $66/\text{mm}^2$

COMPARATIVE EXAMPLE A3

When the current organic particle spacers described in Example A1 were used in making a B5 size STN liquid crystal display by the known method marked image unevenness appeared, and it was unsatisfactory for employment as a liquid crystal display. In this case the number of spacers dispersed, according to the counting method above, was $66/\text{mm}^2$

EXAMPLE B1

A mixed solution of 25% aqueous ammonia (2.9 g), methanol (10.1 g) and water (141.1 g) (Solution A) was put into a 4-mouthed flask fitted with a condenser, a thermometer and a dropping funnel, and was held at $25 \pm 2^\circ\text{C}$ and stirred as a mixed solution of γ -methacryloxypropyltrimethoxysilane (27 g), methanol (54 g) and 2,2'-azobis-(2,4-dimethylvaleronitrile) (0.14 g) as a radical polymerization initiator (Solution B) was added from the dropping funnel and γ -methacryloxypropyltrimethoxysilane was hydrolyzed and condensed. After stirring for a further

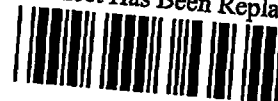


20 minutes, radical polymerization was performed by heating in an atmosphere of nitrogen at $70 \pm 5^\circ\text{C}$.

After heating continuously for 2 hours, the system was cooled to room temperature and a suspension of polymerized particles was obtained. The liquid and solid in this suspension were separated by filtration, the resulting cake was washed 3 times with methanol, and the resulting polymerized particles were vacuum dried in a vacuum drier at 200°C for 2 hours to give Composite Particles (1).

The resulting Composite Particles (1) had a mean particle diameter of $4.24 \mu\text{m}$ with a coefficient of variation of 3.8% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 34.7 wt%; the elastic modulus in 10% compression was 480 kg/mm^2 , residual displacement after 10% deformation 2.2% and fracture strength 2.4 g. A spectrum ($650\text{--}800 \text{ cm}^{-1}$) attributable to $-\text{CH}_2\text{--CH}_2-$ of the organic polymer framework and a spectrum ($1150\text{--}1300 \text{ cm}^{-1}$) attributable to $-\text{Si--CH}_2-$ were confirmed in Composite Particles (1) by FT-IR analysis.

From these results it is evident that Composite Particles (1) were organic-inorganic composite particles which included an organic polymer framework and a polysiloxane framework having in its molecule organosilicon in which the silicon atom was directly and chemically combined with at least one carbon atom in the organic



polymer framework.

A B5 size STN liquid crystal display was made by the known method using these Composite Particles (1). As a result, the number of particles dispersed could be decreased by $\geq 10\%$ compared with current organic particle spacers (Epostar GP-H, made by Nippon Shokubai Co., Ltd.), and there was neither low-temperature bubbling nor the image unevenness which are produced when calcined silica particles or uncalcined silica gel particles made by the sol/gel method are used.

EXAMPLE B2

Composite Particles (2) were obtained by repeating the procedure of Example B1 except that the composition of Solution B in Example B1 was changed to γ -methacryloxy-propyltrimethoxysilane (19.2 g), methanol (51 g), 2,2'-azobis-(2,4-dimethylvaleronitrile) (0.10 g), and tetraethoxysilane dimers-pentamers. (Tamakagaku KK [Tama Chemical Co.] "Silicate 40", 40 wt% as SiO_2) (4.2 g).

The resulting Composite Particles (2) had a mean particle diameter of $2.02 \mu\text{m}$ with a coefficient of variation of 7.4% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 42.7 wt%; the elastic modulus in 10% compression was 720 kg/mm^2 , residual displacement after 10% deformation 3.6% and fracture strength 1.0 g. As in Example B1, a spectrum (650-



800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (2).

When a B5 size ferroelectric liquid crystal display was made by the known method using these Composite Particles (2) the results obtained were as in Example B1.

EXAMPLE B3

Composite Particles (3) were obtained by repeating the procedure of Example B1 except that the composition of Solution B in Example B1 was changed to γ -methacryloxy-propyltrimethoxysilane (40.5 g), methanol (50.6 g), 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile) (0.20 g) and divinylbenzene (4.5 g), and radical polymerization was performed during hydrolyzing and condensing by holding Solution A at $50 \pm 5^\circ\text{C}$ and stirring in an atmosphere of nitrogen while Solution B was added dropwise over 20 minutes.

The resulting Composite Particles (3) had a mean particle diameter of 8.91 μm with a coefficient of variation of 4.8% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 29.5 wt%; the elastic modulus in 10% compression was 370 kg/mm^2 , residual displacement after 10% deformation 2.8% and fracture strength 9.7 g. As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-



1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (3).

When a B5 size TN liquid crystal display was made by the known method using these Composite Particles (3) the results obtained were as in Example B1.

EXAMPLE B4

Composite Particles (4) were obtained by repeating the procedure of Example B1 except that vinyltrimethoxysilane was used instead of the γ -methacryloxypropyltrimethylsilane in Example B1 and that the particles were calcined in an atmosphere of nitrogen at 600°C for 2 hours after drying at 200°C for 2 hours.

The resulting Composite Particles (4) had a mean particle diameter of 4.18 μm with a coefficient of variation of 7.2% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 40.9 wt%; the elastic modulus in 10% compression was 1050 kg/mm^2 , residual displacement after 10% deformation 3.2% and fracture strength 1.9 g. As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (4).

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (4) the results obtained were as in Example B1.



EXAMPLE B5

Composite Particles (5) were obtained by repeating the procedure of Example B1 except that a silica sol ("Snowtex-XS", made by Nissan Chemical Industries, Ltd.; SiO_2 20 wt%; particle diameter 4-6 nm) (15 g) was added to Solution A in Example B1.

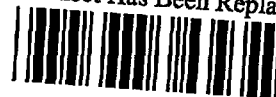
The resulting Composite Particles (5) had a mean particle diameter of 4.77 μm with a coefficient of variation of 4.0% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 42.0 wt%; the elastic modulus in 10% compression was 1130 kg/mm^2 , residual displacement after 10% deformation 2.5% and fracture strength 3.8 g. As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (5).

When a B5 size TFT liquid crystal display was made by the known method using these Composite Particles (5) the results obtained were as in Example B1.

EXAMPLES B6-B9

Composite Particles (6)-(9) were obtained by repeating the procedure of Example B5 except that the type and quantity of silica sol in Example B5 were changed as shown in Table 1.

The mean particle diameter, coefficient of variation



in particle diameter, quantity of SiO_2 which constitutes the polysiloxane framework, elastic modulus in 10% compression, residual displacement after 10% deformation and fracture strength of the resulting Composite Particles (6)-(9) are shown in Table 1. As in Example B1, a spectrum ($650\text{--}800\text{ cm}^{-1}$) attributable to $\text{--CH}_2\text{--CH}_2\text{--}$ and a spectrum ($1150\text{--}1300\text{ cm}^{-1}$) attributable to $\text{--Si--CH}_2\text{--}$ were confirmed in Composite Particles (6)-(9).

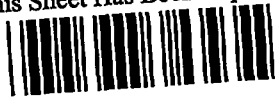
When B5 size STN liquid crystal displays were made by the known method using these Composite Particles (6)-(9), in all cases the results obtained were as in Example B1.

EXAMPLE B10

Composite Particles (10) were obtained by further heat-treating Composite Particles (8) obtained in Example B8 in a mixed atmosphere of nitrogen 95 vol% and oxygen 5 vol% at 400°C for 2 hours

The mean particle diameter, coefficient of variation in particle diameter, quantity of SiO_2 which constitutes the polysiloxane framework, elastic modulus in 10% compression, residual displacement after 10% deformation and fracture strength of the resulting Composite Particles (10) are shown in Table 1. As in Example B1, a spectrum ($650\text{--}800\text{ cm}^{-1}$) attributable to $\text{--CH}_2\text{--CH}_2\text{--}$ and a spectrum ($1150\text{--}1300\text{ cm}^{-1}$) attributable to $\text{--Si--CH}_2\text{--}$ were confirmed in Composite Particles (10).

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When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (10) the results obtained were as in Example B1.

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TABLE 1

Example	Type and quantity of silica sol (g)	Properties of organic-inorganic composite particles obtained					
		Mean particle diameter (μm)	Coefficient of variation in particle diameter (%)	Quantity of SiO_2 which constitutes polysiloxane framework (wt%)	Elastic modulus in 10% compression (kg/mm^2)	Residual displacement after 10% deformation (%)	Fracture strength (g)
6	ST-N 15	5.18	6.0	43.3	1340	3.2	3.6
7	ST-ZL 15	6.34	7.9	43.6	1280	3.6	5.5
8	ST-XS 9.7	4.52	5.0	40.5	980	2.4	3.6
9	ST-XS 70.9	4.83	4.8	59.8	2650	4.1	3.4
10	ST-XS 9.7	4.29	5.2	45.2	1610	3.0	3.0

(Footnote)

ST-N: Snowtex N made by Nissan Chemical Industries, Ltd.; SiO_2 20 wt%; particle diameter 10-20 nmST-ZL: Snowtex ZL made by Nissan Chemical Industries, Ltd.; SiO_2 20 wt%; particle diameter 70-100 nmST-XS: Snowtex XS made by Nissan Chemical Industries, Ltd.; SiO_2 20 wt%; particle diameter 4-6 nm

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EXAMPLE B11

A solution of the acidic dye Kayacyl Sky Blue R (Nippon Kayaku KK) (5 g) dissolved in water (100 g) and a dispersion of Composite Particles (8) obtained in Example B8 (10 g) in water (500 g) were mixed and heat-treated under pressure in an autoclave at 150°C for 1 hour. After treatment, the colored particles were collected by filtration, and after washing 3 times with water they were dried at 200°C, to obtain dark blue colored Composite Particles (11).

The resulting Composite Particles (11) had a mean particle diameter of 4.26 μm with a coefficient of variation of 6.3% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 40.0 wt%; elastic modulus in 10% compression was 920 kg/mm^2 , the residual displacement after 10% deformation was 3.0% and the fracture strength was 3.0 g. As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (11).

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (11) the results obtained were as in Example B8, and there were fewer bright spots (light escape).

EXAMPLE B12



Black colored Composite Particles (12) were obtained by dissolving the basic dye Kayacryl Black NP200 (Nippon Kayaku KK) (5 g) in water (300 g) and, after bringing the pH to 4 by adding acetic acid, adding Composite Particles (8) obtained in Example B8 (10 g) and stirring thoroughly while heat-treating at 95°C for 8 hours.

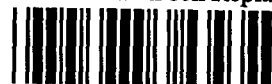
The resulting Composite Particles (12) had a mean particle diameter of 4.41 μm with a coefficient of variation of 5.7% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 40.2 wt%; the elastic modulus in 10% compression was 920 kg/mm^2 , the residual displacement after 10% deformation was 2.8% and the fracture strength was 3.4 g . As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (12).

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (12) the results obtained were as in Example B11.

EXAMPLE B13

Black colored Composite Particles (13) were obtained by repeating the procedure of Example B8 except for the addition of 1 g of the basic dye Kayacryl Black NP200 (Nippon Kayaku KK) to Solution A in Example B8.

The resulting Composite Particles (13) had a mean



particle diameter of $4.53 \mu\text{m}$ with a coefficient of variation of 5.1% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 40.4 wt%; the elastic modulus in 10% compression was 970 kg/mm^2 , the residual displacement after 10% deformation was 2.5% and the fracture strength was 3.6 g. As in Example B1, a spectrum ($650\text{--}800 \text{ cm}^{-1}$) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum ($1150\text{--}1300 \text{ cm}^{-1}$) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (13).

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (13) the results obtained were as in Example B11.

EXAMPLE B14

Composite Particles (14) having an adhesive layer on the surface were obtained by mixing Composite Particles (8) obtained in Example B8 (30 g) with thermoplastic resin particles (methyl methacrylate 84 wt% and n-butyl acrylate 16 wt% copolymer; glass transition temperature 70°C , mean particle diameter $0.3 \mu\text{m}$) (2 g) and then coating the surface of the Composite Particles (8) with the thermoplastic resin using a Nara Kikai Seisakusho Hybridization System Model NHS-O. When the resulting Composite Particles (14) were observed by SEM, the surface of the Composite Particles (8) was completely covered with thermoplastic resin, and when the cross-section was observed



by TEM, the thickness of the coating layer was $0.2 \mu\text{m}$.

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (14) having an adhesive layer the results obtained were as in Example B1. Moreover, the resulting liquid crystal display gave absolutely no change in image quality in the same picture before and after vibration using a vibrator.

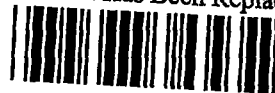
EXAMPLE B15

Black colored Composite Particles (15) having an adhesive layer on the surface were obtained by repeating the procedure of Example B14 except that the black colored Composite Particles (13) obtained in Example B13 were employed instead of Composite Particles (8) in Example B14. When the resulting Composite Particles (15) were observed by SEM, the surface of the Composite Particles (13) was completely covered with thermoplastic resin, and when the cross-section was observed by TEM, the thickness of the coating layer was $0.2 \mu\text{m}$.

When a B5 size STN liquid crystal display was made by the known method using these black colored Composite Particles (15) having an adhesive layer the results obtained were as in Example B14.

EXAMPLE B16

Composite Particles (16) having a conductive layer on the surface of the particle body were obtained by



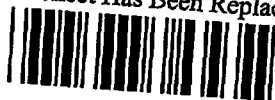
electroless Ni plating of Composite Particles (8) obtained in Example B8. The resulting Composite Particles (16) had a mean particle diameter of $4.92 \mu\text{m}$ and a coefficient of variation of 5.4% in particle diameter. When the resulting Composite Particles (16) were observed by SEM and XMA, the complete surface of the Composite Particles (16) was Ni plated; and when the cross-section was observed by TEM, the thickness of the coating layer was $0.3 \mu\text{m}$.

EXAMPLE B17

Composite Particles (17) having a conductive layer on the surface of the particle body were obtained by electroless Ni plating of Composite Particles (8) obtained in Example B8, followed by electroless gold plating. The resulting Composite Particles (17) had a mean particle diameter of $5.05 \mu\text{m}$ and a coefficient of variation of 5.5% in particle diameter. When the resulting Composite Particles (17) were observed by SEM and XMA, the complete surface of the Composite Particles (17) was Ni plated, with a covering of gold plate on top; and when the cross-section was observed by TEM, the thickness of the coating layer was $0.5 \mu\text{m}$.

EXAMPLE B18

The solid and liquid of the suspension of Polymerized Particles (1) obtained in Example B1 were separated by decantation, and the resulting cake was dried overnight at



room temperature. A portion of this dried cake (5g) was taken, and after dispersing in isopropyl alcohol (200 g) using ultrasonication, dibutyltin dilaurate (0.5 g) was added to the dispersion and the mixture was stirred as it was heated at 80°C for 2 hours. After obtaining in this way a suspension of recondensed particles (18), solid-liquid separation, washing and drying were performed as in Example B1, to obtain Composite Particles (18).

The resulting Composite Particles (18) had a mean particle diameter of 4.20 μm with a coefficient of variation of 3.9% in particle diameter; the quantity of SiO_2 which constitutes the polysiloxane framework was 35.1 wt%; the elastic modulus in 10% compression was 950 kg/mm^2 , the residual displacement after 10% deformation was 1.8% and the fracture strength was 3.0 g. As in Example B1, a spectrum (650-800 cm^{-1}) attributable to $-\text{CH}_2-\text{CH}_2-$ and a spectrum (1150-1300 cm^{-1}) attributable to $-\text{Si}-\text{CH}_2-$ were confirmed in Composite Particles (18).

When a B5 size STN liquid crystal display was made by the known method using these Composite Particles (18) the results obtained were as in Example B1.

COMPARATIVE EXAMPLE B1

Particles were obtained by further heat treatment of Composite Particles (1) obtained in Example B1 at 950°C for 2 hours. The quantity of SiO_2 which constitutes the



polysiloxane framework in these particles was 99.8 wt%; and it was also evident from FT-IR analysis that they were silica particles in which the polymer framework had decomposed and undergone combustion. The elastic modulus in 10% compression of the particles obtained was 3250 kg/mm^2 , residual displacement after 10% deformation was 6.2%. When a B5 size TFT liquid crystal display was made by the known method using these particles, pixel faults were produced due to breakage of the TFT array on the electrode substrates, and image unevenness was produced because mechanical resilience was inadequate.

As regards the numbers of composite particles of the present invention dispersed in the surface of the liquid crystal displays obtained in the examples above, the numbers of composite particles of the present invention were counted under an optical microscope in arbitrary areas of 1 mm^2 in each of 9 fields formed by equal division of the surface (on which to be dispersed) into 3 widthwise and lengthwise, and the mean value of the 9 fields was taken to be the number dispersed. The results are given below.

Example B1 ... Number dispersed $73/\text{mm}^2$

Example B2 ... Number dispersed $70/\text{mm}^2$

Example B3 ... Number dispersed $69/\text{mm}^2$

Example B4 ... Number dispersed $68/\text{mm}^2$

Example B5 ... Number dispersed $69/\text{mm}^2$



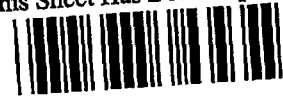
Example B6 ... Number dispersed $66/\text{mm}^2$
Example B7 ... Number dispersed $64/\text{mm}^2$
Example B8 ... Number dispersed $68/\text{mm}^2$
Example B9 ... Number dispersed $52/\text{mm}^2$
Example B10 ... Number dispersed $63/\text{mm}^2$
Example B11 ... Number dispersed $70/\text{mm}^2$
Example B12 ... Number dispersed $69/\text{mm}^2$
Example B13 ... Number dispersed $71/\text{mm}^2$
Example B14 ... Number dispersed $69/\text{mm}^2$
Example B15 ... Number dispersed $70/\text{mm}^2$
Example B18 ... Number dispersed $65/\text{mm}^2$

COMPARATIVE EXAMPLE B2

When a B5 size STN liquid crystal display was made by the known method using the current organic particles described in Example B1, considerable image unevenness was produced and it was unsuitable for employment as a liquid crystal display. In this case the number of spacers dispersed, according to the counting method above, was $66/\text{mm}^2$.

Various details of the invention may be changed without departing from its spirit not its scope. Furthermore, the foregoing description of the preferred embodiments according to the present invention is provided for the purpose of illustration only, and not for the

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purpose of limiting the invention as defined by the appended
claims and their equivalents..

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1 Claims

2

3 1. An organic-inorganic composite particle, which
4 comprises a particle body having an elastic
5 modulus of 350-3000 kg/mm² in 10% compression, a
6 residual displacement of 0-5% after 10%
7 deformation, a mean particle diameter of 0.5-50 μ m
8 and a coefficient of variation of 20% or less in
9 particle diameter, said particle body including:

10

11 an organic group; and

12

13 a polysiloxane framework which has in its molecule
14 an organosilicon containing a silicon atom
15 directly and chemically combined with at least one
16 carbon atom of said organic group.

17

18 2. An organic-inorganic composite particle, which
19 comprises a particle body having a mean particle
20 diameter of $\geq 0.5 \mu$ m and including:

21

22 an organic polymer framework; and

23

24 A polysiloxane framework which has in its molecule
25 an organosilicon containing a silicon atom
26 directly and chemically combined with at least one
27 carbon atom of said polymer framework, wherein the
28 quantity of SiO₂ which constitutes said
29 polysiloxane framework is ≥ 25 wt%.

30

31 3. An organic-inorganic composite particle as claimed
32 in Claim 2, wherein:

33

34 said particle body further includes an organic
35 group; and

36

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1 said polysiloxane framework has a silicon atom
2 directly and chemically combined with at least one
3 carbon atom of said organic group.

4

5 4. An organic-inorganic composite particle as claimed
6 in Claim 2, wherein said particle body further has
7 a fracture strength satisfying the following
8 equation:

9

10
$$G \geq 14 \times Y^{1.75}$$

11

12 where: G indicates a fracture strength (kg); and
13 Y indicates a particle diameter (mm).

14

15 5. An organic-inorganic composite particle as claimed
16 in any of Claims 2 to 4 wherein said particle body
17 has an elastic modulus of 350-3000 kg/mm² in 10%
18 compression, a residual displacement after 10%
19 deformation of 0-5%, a mean particle diameter of
20 0.5-50 μ m and a coefficient of variation of mean
21 particle diameter of $\leq$ 20%.

22

23 6. An organic-inorganic composite particle as claimed
24 in any one of Claims 1 to 5, wherein said organic
25 group is at least one monovalent group selected
26 from the group consisting of alkyl groups of 1-10
27 carbon atoms, aryl groups of 6-10 carbon atoms and
28 unsaturated aliphatic residual group of 2-14
29 carbon atoms, which may have a substituent group.

30

31 7. An organic-inorganic composite particle as claimed
32 in any one of Claims 1 to 6 which further
33 comprises a conductive layer formed on a surface
34 of said particle body.

35

36 8. An organic-inorganic composite particle as claimed

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in any one of Claims 1 to 7, which further comprises an adhesive layer formed on a surface of said particle body.

9. An organic-inorganic composite particle as claimed in any one of Claims 1 to 8 which is coloured by including in said particle body at least one colorant selected from the group consisting of dyes and pigments.

10. A process for producing organic-inorganic composite particles, which comprises:

a condensation step of hydrolyzing and condensing at least one silicon compound selected from the group consisting of compounds represented by General Formula (1) below and derivatives thereof:



where:

R' indicates a monovalent group selected from the group consisting of alkyl groups of 1-10 carbon atoms, aryl groups of 6-10 carbon atoms and unsaturated aliphatic residual groups of 2-14 carbon atoms, which may have a substituent group;

R'' indicates a hydrogen atom or a monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;

m indicates an integer of 0-3;

when m is 2, the two R' groups may be either





1 different from or identical with one another;

2

3 when m is 3, the three R' groups may differ from
4 one another, or two or more of the R' groups may
5 be identical;

6

7 when $4-m$ is 2, the two OR" groups may be either
8 different from or identical with one another;

9

10 when $4-m$ is 3, the three OR" groups may be
11 different from each other, or two or more of the
12 OR" groups may be identical; and

13

14 when $4-m$ is 4, the four OR" groups may be
15 different from each other, or two or more of the
16 OR" groups may be identical;

17

18 with the proviso that only a compound selected
19 from the group consisting of compounds of $m = 1$ in
20 said Formula (1) and derivatives thereof can be
21 employed alone as said silicon compound, and that
22 2 or more silicon compounds used together need to
23 include either or both of: a compound selected
24 from the group consisting of compounds of $m = 1$ in
25 said Formula (1) and derivatives thereof; and a
26 compound selected from the group consisting of
27 compounds of $m = 0$ in said Formula (1) and
28 derivatives thereof;

29

30 to give condensed particles; and

31

32 a heat treatment step of treating said condensed
33 particles by heating at a temperature of $\leq 1000^{\circ}\text{C}$
34 to obtain particle bodies of organic-inorganic
35 composite particles.

36

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- 1 11. A process as claimed in Claim 10, wherein said
2 heat-treatment step is performed in an atmosphere
3 having an oxygen concentration of ≤ 10 vol%.
- 4
- 5 12. A process as claimed in either one of Claims 10
6 and 11, which further comprises a conductive-
7 layer-forming step of forming a conductive layer
8 on a surface of said particle body.
- 9
- 10 13. A process as claimed in any one of Claims 10 to
11 12, which further comprises an adhesive-layer-
12 forming step of forming an adhesive layer on a
13 surface of said particle body.
- 14
- 15 14. A process as claimed in any one of Claims 10 to
16 13, which further comprises a colouring step of
17 colouring the produced particles during and/or
18 after at least one step selected from the group
19 consisting of said condensation step and said
20 heat-treatment step.
- 21
- 22 15. A process as claimed in any one of Claims 10 to
23 14, wherein said silicon compound is at least one
24 first silicon compound containing a radical-
25 polymerizable group and selected from the group
26 consisting of compounds represented by the
27 following general formulae and derivatives
28 thereof:
- 29
- $$\begin{array}{c} \text{R}^1 \\ | \\ \text{CH}_2 = \text{C} - \text{COOR}^2\text{Si}(\text{OR}^3)_3 \end{array} \quad (2)$$
- 30
- 31
- 32
- 33
- 34
- 35 where: R^1 indicates a hydrogen atom or a methyl
36 group;
- 37
- 38 R^2 indicates an alkylene group of 1-10 carbon atoms





1 which may have a substituent group; and

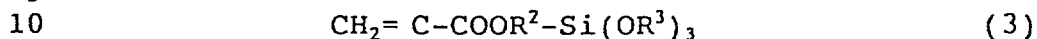
2

3 R^3 indicates a hydrogen atom or at least one
4 monovalent group selected from the group
5 consisting of alkyl groups of 1-5 carbon atoms and
6 acyl groups of 2-5 carbon atoms;

7

8

9



11

12

13

where:

14

15 R^4 indicates a hydrogen atom or a methyl group; and

16

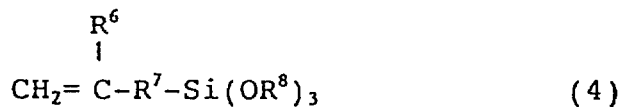
17 R^5 indicates a hydrogen atom or at least one
18 monovalent group selected from the group
19 consisting of alkyl groups of 1-5 carbon atoms and
20 acyl groups of 2-5 carbon atoms;

21

22

23

24



25

26

where:

27

28 R^6 indicates a hydrogen atom or a methyl group;

29

30 R^7 indicates an alkylene group of 1-10 carbon
31 atoms, which may have a substituent group; and

32

33 R^8 indicates a hydrogen atom or at least one
34 monovalent group selected from the group
35 consisting of alkyl groups of 1-5 carbon atoms and
36 acyl groups of 2-5 carbon atoms;

37

38 wherein the process further comprises a

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- 1 polymerization step of subjecting the radical-
2 polymerizable group of said silicon compound to
3 radical polymerization to obtain polymerized
4 particles, during and/or after said condensation
5 step, and before said heat-treatment step, and
6
7 wherein said heat-treatment step includes treating
8 said polymerized particles by heating at a
9 temperature of $\leq 800^{\circ}\text{C}$ to obtain particle bodies
10 of organic-inorganic composite particles.
11
- 12 16. A process as claimed in Claim 15, which further
13 comprises a colouring step of colouring the
14 produced particles during and/or after at least
15 one step selected from the group consisting of
16 said condensation step, said polymerization step
17 and said heat-treatment step.
18
- 19 17. A process as claimed in Claim 15, which further
20 comprises a recondensation step of further
21 condensing said polymerized particles to obtain
22 recondensed particles, between said polymerization
23 step and said heat-treatment step, wherein said
24 heat-treatment step includes treating said
25 recondensed particles by heating at a temperature
26 $\leq 800^{\circ}\text{C}$.
27
- 28 18. A process as claimed in Claim 17, which further
29 comprises a colouring step of colouring the
30 produced particles during and/or after at least
31 one step selected from the group consisting of
32 said condensation step, said polymerization step,
33 said recondensation step and said heat-treatment
34 step.
35
- 36 19. A liquid crystal display, which comprises:

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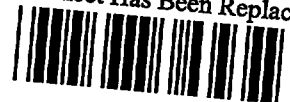


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1 a first electrode substrate;
2
3 a second electrode substrate arranged opposite to
4 said first electrode substrate;
5
6 a sealing material which binds said first
7 electrode substrate and said second electrode
8 substrate at their respective circumferential
9 edges;
10
11 a spacer for the liquid crystal display, which is
12 interposed between said first electrode substrate
13 and said second electrode substrate; and which
14 includes an organic-inorganic composite particle;
15 and
16
17 a liquid crystal packed into space defined by said
18 first electrode substrate and said second
19 electrode substrate and said sealing material;
20
21 wherein said organic-inorganic composite particle
22 is as claimed in any one of Claims 1 to 9.

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ABSTRACT

"Organic-Inorganic Composite Particles and Production
Process Therefor"

Organic-inorganic composite particles which include a (meth)acrylic resin framework and a polysiloxane framework having in its molecule an organosilicon containing a silicon atom directly and chemically combined with at least one carbon atom of the (meth)acrylic resin framework, and also containing 25 wt% or more of SiO_2 which constitutes the polysiloxane framework and has a mean particle diameter of $\geq 0.5 \mu\text{m}$. The particles have the mechanical resilience necessary to maintain a constant gap distance between a pair of members to be arranged with the correct gap distance between them, and the hardness and fracture strength necessary to maintain the gap constant with smaller numbers; and also do not readily cause physical damage to the members. The composite particles can be employed as spacers for a liquid crystal display as they stand or with an adhesive layer formed on the surface. The composite particles can also have a conductive layer formed on the surface, and be employed as conductive particles.

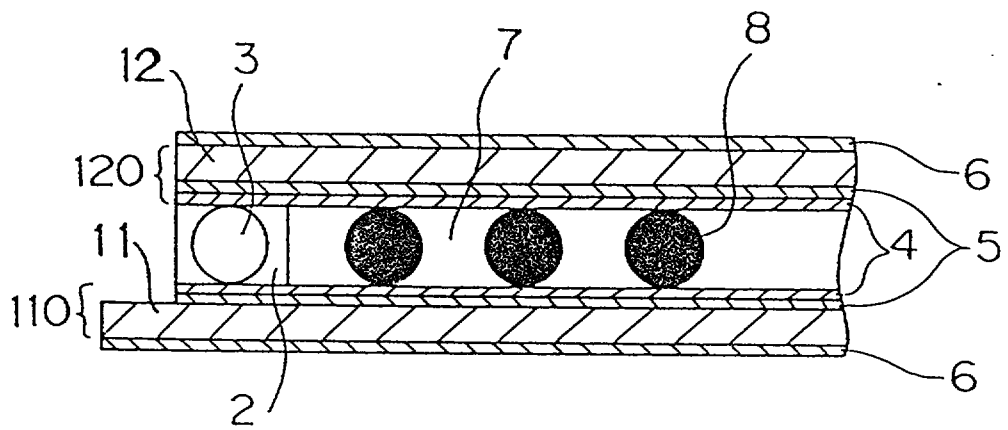
(If necessary, Figure 1 should accompany the Abstract when published.)

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Figure 1



2

Figure 2

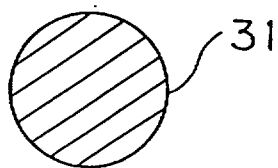


Figure 3

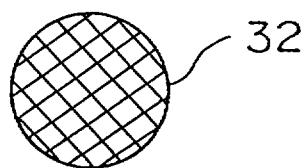


Figure 4

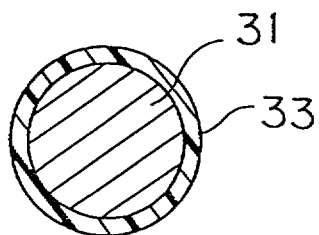


Figure 5

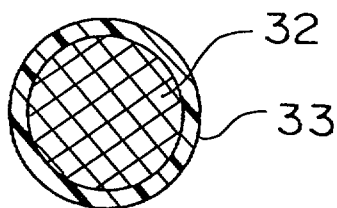
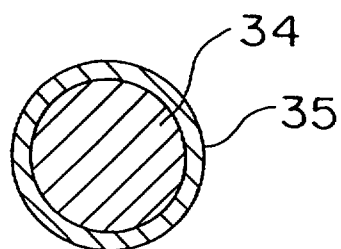


Figure 6



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TITLE OF THE INVENTION

"Organic-Inorganic Composite Particles"

BACKGROUND OF THE INVENTION

The present invention relates to organic-inorganic composite particles, and to liquid crystal displays which employ the organic-inorganic composite particles.

Liquid crystal displays (LCD) typically include two opposed electrode substrates, and spacers and a liquid crystal substance interposed between the aforementioned -electrode substrates. The spacers are employed in order to maintain a liquid crystal layer uniform and constant in thickness.

High speed of response, high contrast, and a wide viewing angle, etc. are among display performance characteristics cited as required in practice in liquid crystal displays. For these performance characteristics to be manifested, the thickness of the liquid crystal layers, and in the final analysis, the

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1 distance separating the two electrode substrates, must
2 be maintained strictly constant.

3

4 Spacers for liquid crystal displays which meet such a
5 need include silica particles made by the sol-gel
6 method (Japanese Unexamined Patent Publication (Kokai)
7 62-269933), the calcined product of the aforementioned
8 silica particles (Japanese Unexamined Patent
9 Publication (Kokai) 1-234826), and styrene or
10 divinylbenzene type polymer particles obtained by
11 suspension polymerization of styrene monomers of
12 divinylbenzene monomers, etc. (Japanese Unexamined
13 Patent Publication (Kokai) 61-95016), etc. These are
14 all spherical particles with a narrow particle diameter
15 distribution and a well ordered particle diameter.

16

17 However, the above prior art has the following
18 problems.

19

20 (A) Calcined products of silica particles made by the
21 sol-gel method are not readily deformable and are very
22 hard, and consequently when they are pressed in
23 constructing liquid crystal displays they may cause
24 physical damage to coating layers on the substrates
25 such as vapor deposited electrodes, etc., orientating
26 layers and color filters, etc., and cause faults in the
27 display due to image unevenness or breakages of TFT
28 array. There is also a large difference between the
29 thermal expansion coefficient of these calcined silica
30 particles and that of liquid crystals, and consequently
31 in liquid crystal displays using such calcined silica
32 particles the problem of so-called low temperature
33 bubbling is produced, so that when cooled in a low
34 temperature environment, of -40°C for example, the
35 particles do not shrink to the same extent as the
36 liquid crystals; voids are produced between the liquid

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1 crystals and the electrode substrates, and the display
2 function becomes completely inoperative.

3
4 (B) Silica particles made by the sol-gel method are
5 more pliant than calcined silica particles. However,
6 because these uncalcined silica particles are weak in
7 mechanical resilience the gap distance is prone to
8 become uneven, producing image unevenness. Moreover,
9 uncalcined silica particles give rise to the
10 low-temperature bubbling problem as well as the
11 calcined silica particles do.

12
13 (C) Since styrene or divinylbenzene type polymer
14 particles are organic particles and are very pliant,
15 they must be dispersed in large numbers onto an
16 electrode substrate. This not only tends to raise
17 manufacturing costs, but results in an increase in the
18 area of the portion of the display screen where no
19 image is formed. Moreover, the quality of the display
20 is lowered due to lowering contrast and increasing
21 image roughness, etc. due to the fact that that the
22 quantity of ionic and molecular impurities eluting from
23 the spacers into the liquid crystal layer increases.

24
25 Accordingly, polymer particles have been proposed
26 which are not easily deformed, formed by suspension
27 polymerization using crosslinkable monomers such as
28 divinyl-benzene, etc., and using a large quantity of
29 polymerization initiator (Japanese Unexamined Patent
30 Publication (Kokai) 4-313727).

31
32 Polymer particles made by suspension polymerization of
33 tetramethylolmethane tetraacrylate or
34 tetramethylolmethane tetraacrylate and divinylbenzene,
35 and then classified to regulate mean particle diameter
36 and standard deviation of particle diameter have also

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1 been proposed (Japanese Patent Publication (Kohyo)
2 6-503180).

3
4 These polymer particles have the problem that they are
5 prone to produce abnormal orientation in the liquid
6 crystals on the surfaces of these particles. In liquid
7 crystal displays no display is possible in spots in
8 which the liquid crystals are abnormally orientated.

9
10 The present inventors have proposed spacers for liquid
11 crystal displays which have a residual displacement
12 after 10% deformation and an elastic modulus in
13 compression at the 10% displacement of the particle
14 diameter (an elastic modulus in 10% compression) within
15 specified ranges, and which includes specific
16 organic-inorganic composite particles (Japanese Patent
17 Application 5-288536). The fact that these spacers for
18 liquid crystal displays are harder than prior polymer
19 particles means that the number of the particles
20 dispersed on the electrode substrate can be decreased.
21 However, the decrease in numbers means that the load
22 per particle is increased, and the fracture strength is
23 inadequate.

24
25 Prior electrically conductive particles are inorganic
26 particles such as silica particles, etc., or polymer
27 particles provided with a conductive layer formed on
28 the surface of the particles. Commonly, conductive
29 particles are employed in the electronics field for
30 connecting between pairs of electrodes. Thus, by
31 pressing a pair of electrodes with conducting particles
32 interposed between them, an electrical connection is
33 established between the two electrodes via the
34 conductive particles.

35
36 Conductive particles including a polymer are too

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1 pliant, and consequently when pressed the conductive
2 layer cannot accompany the deformation of the
3 particles, and the conductive layer may detach and fall
4 from the particle surface, and the electrodes may
5 become too close and short. On the other hand,
6 conductive particles including inorganic particles are
7 too hard, and consequently it is impossible to broaden
8 the area of contact with the electrodes to lower
9 contact resistance, and if unreasonable pressure is
10 applied when deforming so as to get large contact area,
11 the conductive layer may detach and fall away. There
12 are also problems with the poor mechanical resilience
13 of the conductive particles, and it becomes difficult
14 to maintain a constant gap distance, causing poor
15 contact.

16
17 SUMMARY OF THE INVENTION

18
19 One purpose of the present invention is to provide
20 organic-inorganic composite particles which have the
21 mechanical resilience needed in order to maintain
22 constant the aforementioned gap distance between a pair
23 of members placed with the proper gap, together with
24 the hardness and fracture strength needed in order to
25 maintain the aforementioned gap distance constant with
26 smaller numbers of particles, and which do not readily
27 cause physical damage to the aforementioned members.

28
29 Another purpose of the present invention is to reduce
30 physical damage to the electrode substrates of liquid
31 crystal displays, and to improve picture quality of the
32 liquid crystal displays.

33
34 An organic-inorganic composite particle according to
35 the present invention includes a particle body having
36 an elastic modulus of $350\text{--}3000\text{kg/mm}^2$ in 10% compression,

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1 a residual displacement of 0-5% after 10% deformation,
2 a mean particle diameter of 0.5-50 μ m and a coefficient of
3 variation of 20% or less in particle diameter, the
4 particle body including :

5

6 an organic group ; and

7

8 a polysiloxane framework which has in its molecule an
9 organosilicon containing a silicon atom directly and
10 chemically combined with at least one carbon atom of
11 the organic group.

12

13 BRIEF DESCRIPTION OF THE DRAWINGS

14

15 Figure 1 is a fragmentary cross-sectional diagram
16 representing an embodiment of a liquid crystal display
17 of the present invention.

18

19 Figure 2 is a cross-sectional diagram of an embodiment
20 of an organic-inorganic composite particle of the
21 present invention.

22

23 Figure 3 is a cross-sectional diagram of an embodiment
24 of an organic-inorganic composite particle of the
25 present invention.

26

27 Figure 4 is a cross-sectional diagram of an embodiment
28 of an organic-inorganic composite particle of the
29 present invention.

30

31 Figure 5 is a cross-sectional diagram of an embodiment
32 of an organic-inorganic composite particle of the
33 present invention.

34

35 Figure 6 is a cross-sectional diagram of an embodiment
36 of an organic-inorganic composite particle of the

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1 present invention.

2

3 DETAILED DISCLOSURE OF THE INVENTION

4

5 An organic-inorganic composite particle according to
6 the present invention includes a particle body having
7 an elastic modulus of $350-3000\text{kg/mm}^2$ in 10% compression,
8 a residual displacement of 0-5% after 10% deformation,
9 a mean particle diameter of $0.5-50\mu\text{m}$ and a coefficient
10 of variation of 20% or less in particle diameter, the
11 particle body including:

12

13 an organic group; and

14

15 a polysiloxane framework which has in its molecule an
16 organosilicon containing a silicon atom directly and
17 chemically combined with at least one carbon atom of
18 the organic group.

19

20 In the embodiment of the organic-inorganic composite
21 particle of the present invention, for example, the
22 organic group is at least one monovalent group selected
23 from the group consisting of alkyl groups of 1-10
24 carbon atoms, aryl groups of 6-10 carbon atoms and
25 unsaturated aliphatic residual groups of 2-14 carbon
26 atoms. These monovalent groups may have a substituent
27 group.

28

29 The embodiment of the organic-inorganic composite
30 particle of the present invention may further
31 include a conductive layer formed on a surface of the
32 particle body.

33

34 The embodiment of the organic-inorganic composite
35 particle of the present invention may further include
36 an adhesive layer formed on a surface of the particle

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1 body.

2

3 The embodiment of the organic-inorganic composite
4 particle of the present invention may be colored
5 by including in the particle body at least one selected
6 from the group, consisting of dyes and pigments.

7

8 The silicon compound is at least one silicon compound
9 selected from the group consisting of compounds
10 represented by General Formula (1) below and
11 derivatives thereof:

12



14

15 where:

16

17 R' indicates a monovalent group selected from the
18 group consisting of alkyl groups of 1-10 carbon atoms,
19 aryl groups of 6-10 carbon atoms and unsaturated
20 aliphatic residual groups of 2-14 carbon atoms, which
21 may have a substituent group;

22

23 R'' indicates a hydrogen atom or a monovalent group
24 selected from the group consisting of alkyl groups of
25 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;
26 m indicates an integer of 0-3;

27 when m is 2, the two R's may be either different from
28 or identical with one another;

29 when m is 3, the three R's may differ from one another,
30 or two or more of the R's may be identical;

31 when 4-m is 2, the two OR"s may be either different
32 from or identical with one another;

33 when 4-m is 3, the three OR"s may be different from
34 each other, or two or more of the OR"s may be
35 identical; and

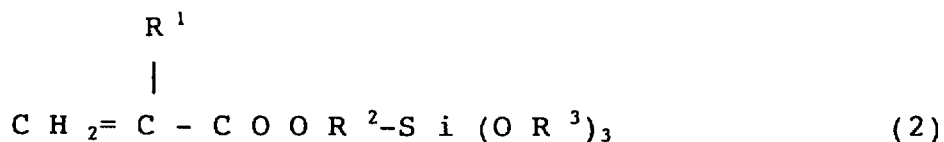
36 when 4-m is 4, the four OR"s may be different from

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each other, or two or more of the OR"s may be identical;

with the proviso that only a compound selected from the group consisting of compounds of $m = 1$ in the Formula (1) and derivatives thereof can be employed alone as the silicon compound, and that 2 or more silicon compounds used together need to include either or both of: a compound selected from the group consisting of compounds of $m = 1$ in the Formula (1) and derivatives thereof; and a compound selected from the group consisting of compounds of $m = 0$ in the Formula (1) and derivatives thereof.

The first silicon compound which contains a radical-polymerizable group is at least one selected from a group consisting of compounds represented by the following general formulae and derivatives thereof:



where:

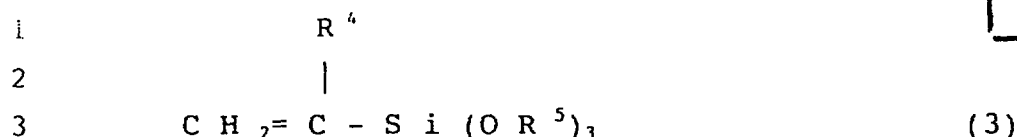
R^1 indicates a hydrogen atom or a methyl group; -

R^2 indicates an alkylene group of 1-10 carbon atoms which may have a substituent group; and

R^3 indicates a hydrogen atom or at least one monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms;

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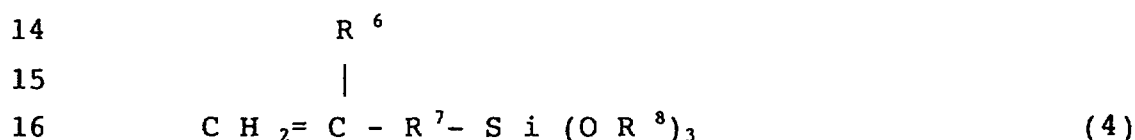
10



4
5 where:

6
7 R⁴ indicates a hydrogen atom or a methyl group; and

8
9 R⁵ indicates a hydrogen atom or at least one monovalent
10 group selected from the group consisting of alkyl
11 groups of 1-5 carbon atoms and acyl groups of 2-5
12 carbon atoms;



17
18 where:

19
20 R⁶ indicates a hydrogen atom or a methyl group;

21
22 R⁷ indicates an alkylene group of 1-10 carbon atoms,
23 which may have a substituent group; and

24
25 R⁸ indicates a hydrogen atom or at least one monovalent
26 group selected from the group consisting of alkyl
27 groups of 1-5 carbon atoms and acyl groups of 2-5
28 carbon atoms.

29
30 A liquid crystal display according to an embodiment of
31 the present invention includes a first electrode
32 substrate, a second electrode substrate, a sealing
33 material, a spacer for the liquid crystal display, and
34 a liquid crystal. The second electrode substrate is
35 arranged opposite to the first electrode substrate.
36 The sealing material binds (joins) the first electrode

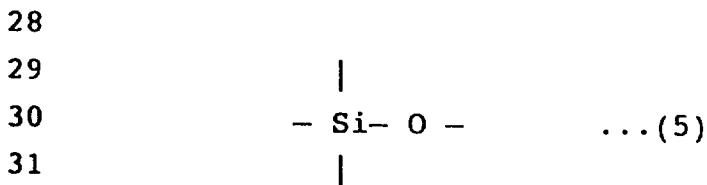
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1 substrate and the second electrode substrate at their
2 respective circumferential edges. The spacer for the
3 liquid crystal display is interposed between the first
4 electrode substrate and the second electrode substrate,
5 functions to maintain a gap distance between the two
6 electrode substrates, and includes the organic-
7 inorganic composite particles according to the first
8 embodiment of the present invention described above.
9 The liquid crystal is packed into space defined by the
10 first electrode substrate, the second electrode
11 substrate and the sealing material.

12
13 In the embodiment of the crystal display of the present
14 invention, the first embodiment of the organic-
15 inorganic composite particles may further have an
16 adhesive layer formed on a surface of the particle
17 body.

18
19 In the embodiment of the crystal display of the
20 present invention, the embodiment of the organic-
21 inorganic composite particles may be colored by
22 including in the particle body at least one selected
23 from the group consisting of dyes and pigments.

24
25 In the present invention, the polysiloxane is defined
26 as a compound in which siloxane units represented by
27 the following Formula (5)



32
33 are chemically combined with each other in sequence to
34 constitute a 3-dimensional network.

35
36 The organic group in the present invention is at least

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1 one selected from the group consisting of monovalent,
2 divalent and trivalent groups which have 1-10, and
3 preferably 1-5, carbon atoms and in which at least one
4 carbon atom is directly and chemically combined with
5 one or more hydrogen atoms. As the aforementioned
6 organic groups, monovalent groups selected from the
7 group consisting of alkyl groups of 1-10 carbon atoms,
8 aryl groups of 6-10 carbon atoms and unsaturated
9 aliphatic residual groups of 2-14 carbon atoms, which
10 may have a substituent group, are preferred; monovalent
11 groups selected from the group consisting of alkyl
12 groups of 1-5 carbon atoms, and unsaturated aliphatic
13 residual groups of 2-5 carbon atoms (e.g. vinyl groups,
14 allyl groups, ethynyl groups, propynyl groups) are more
15 preferred. These organic groups have the advantages
16 that they are cheaper and more easily obtained than
17 other organic groups, and are easier to handle, etc.
18 Examples of the substituent groups allowable in the
19 case of alkyl groups include glycidoxy groups, mercapto
20 groups and amino groups, etc.; from one to all of the
21 hydrogen atoms of the alkyl group can be substituted,
22 but preferably 1-3 hydrogen atoms are substituted.
23 Concrete examples of the aforementioned organic groups
24 include methyl, ethyl, propyl, butyl, vinyl,
25 3-glycidoxypropyl, 3-mercaptopropyl,
26 3-(2-aminoethylaminopropyl) and phenyl, etc.

27
28 Organosilicon in the present invention means that at
29 least one of the carbon atoms of an organic group is
30 directly and chemically combined with at least one of
31 the silicon atoms contained in the siloxane unit above.
32 One to three organic groups can be chemically combined
33 per silicon atom.

34
35 Because the embodiment of the organic-inorganic
36 composite particles of the present invention has

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1 simultaneously both inorganic structural units
2 represented by Formula (5) above and organosilicon, the
3 particles are provided simultaneously with the great
4 hardness characteristic of inorganic substances, and
5 the high mechanical resilience characteristic of
6 organic substances. The measures indicating the
7 hardness and mechanical resilience referred to above
8 are the elastic modulus in compression and the residual
9 displacement; these will be discussed in more detail
10 hereafter. In order to satisfy the aforementioned
11 ranges for the elastic modulus in 10% compression and
12 the displacement after 10% deformation; the proportion
13 of polysiloxane in the organic-inorganic composite
14 particles which has organosilicon in its molecule is
15 preferably $\geq 70\text{wt}\%$, and more preferably 100%. Examples
16 of components other than polysiloxane having
17 organosilicon in its molecule include oxides of boron,
18 aluminum, gallium, indium, phosphorus, titanium and
19 zirconium, etc.

20
21 The elastic modulus in 10% compression referred to in
22 the present invention is the value determined by the
23 method of determination below. Using a Shimadzu micro
24 compression tester (KK Shimadzu Seisakusho MCTM-200),
25 at room temperature (25°C) the test particles are
26 scattered on a testing platform (material: flat SKS
27 disk) and a load is applied to a single particle at a
28 constant loading rate towards the centre of the
29 particle using a round frustrum-shaped loading element
30 (material : diamond) with $50\mu\text{m}$ in diameter; the
31 particle is deformed until compression displacement is
32 10% of the particle diameter, and the load in
33 kilogramme and compression displacement in millimetres
34 at 10% deformation are found. The elastic modulus in
35 compression calculated by substituting the load and
36 compression displacement found and the radius of the

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1 particles into the following equation

2

3
$$E = \{3 \times F \times (1 - K^2)\} / (2^{1/2} \times S^{3/2} \times R^{1/2})$$

4 (where E: Elastic modulus in compression (kg/mm²)

5 F: Compression load (kg)

6 K: Poisson ratio of the particle (constant 0.38)

7 S: Compression displacement (mm)

8 R: Particle radius (mm))

9

10 is the elastic modulus in 10% compression. Directly
11 after this, the load is removed at the same rate as
12 when applying the load, until the load becomes 0.1g,
13 and the extent of the residual displacement assumed by
14 the particle to which no load is applied is found by
15 extrapolating tangent at 0.1g in the diagram obtained
16 to the horizontal axis at which the load applied is
17 zero. The residual displacement is this deformation as
18 a percentage of particle diameter. This procedure is
19 repeated on 3 different particles, and the mean values
20 for the elastic modulus in 10% compression and residual
21 displacement of the particles are taken as the measures
22 of the hardness and mechanical resilience of the
23 particles.

24

25 When the elastic modulus in 10% compression of prior
26 spacer particles were determined by the method above,
27 the values were 4400kg/mm² for calcined silica particles
28 and 300kg/mm² for styrene type polymer particles.

29

30 By contrast, with the embodiment of the composite
31 particles of the present invention, the particle body
32 can be regulated to have a hardness chosen at will to
33 give an elastic modulus in 10% compression in the range
34 350-3000kg/mm², and preferably in the range 550-
35 2500kg/mm², and even more preferably in the range 550-
36 2000kg/mm². If the elastic modulus in 10% compression

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15

1 falls below the aforementioned range, there are the
2 previously mentioned problems of giving a rise in
3 production costs due to an increase in the number of
4 spacer particles that have to be used, lowering
5 contrast and increasing image roughness, etc.; and if
6 it is greater there are the previously described
7 problems of physical damage to vapour deposited layers
8 and coating layers on the substrates, and low-
9 temperature bubbling, etc.

10

11 Similarly, as far as residual displacement after 10%
12 deformation is concerned, the residual displacement of
13 non-calcined silica particles was 8%; but the
14 embodiment of the composite particles of the present
15 invention is a composite particle with superior
16 mechanical resilience, having a residual displacement
17 in the range 0-5%, and preferably 0-4%. A residual
18 displacement after 10% deformation above the
19 aforementioned range causes the previously mentioned
20 problem of image unevenness, etc.

21

22 An elastic modulus in 10% compression and residual
23 displacement within the above ranges are achieved by
24 regulating the proportion of organic groups in the
25 particles. For example, raising the proportion of
26 organic groups lowers the elastic modulus in 10%
27 compression and residual displacement, and lowering the
28 proportion of organic groups increases the elastic
29 modulus in 10% compression and the residual
30 displacement.

31

32 In the embodiment of the composite particles of the
33 present invention the proportion accounted for organic
34 groups in the particles, representing the quantity of
35 organic groups by the total weight of carbon atoms, is
36 usually 5-17wt%, and is preferably 7-17wt%. The reason

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1 is that if there are fewer organic groups than the
2 above range, elastic modulus in compression and
3 residual displacement become large and the particles
4 become too hard, or adequate mechanical resilience
5 cannot be obtained; and if there are more, the elastic
6 modulus in compression becomes too small and the
7 particles become more pliant than necessary. When the
8 quantity of organic groups is within the aforementioned
9 range hardness and mechanical resilience which are
10 effective to avoid the aforementioned problems are
11 obtained.

12
13 In the embodiment of the composite particles of the
14 present invention the mean particle diameter of the
15 particle body can be regulated at will according to the
16 size of the intended gap distance, but will usually be
17 0.5-50 μ m and is preferably 1-20 μ m, and more preferably
18 1-15 μ m. With diameter outside the aforementioned range
19 it is impossible to achieve the gap distance of a
20 liquid crystal display for practical use, and the
21 particle diameter is in a range which precludes use as
22 an ordinary spacer.

23
24 From the point of view of the uniformity of the gap
25 distance, the coefficient of variation in the particle
26 diameter of the particle body in the first embodiment
27 of the composite particles of the present invention is
28 $\leq 20\%$, preferably $\leq 10\%$, and more preferably $\leq 8\%$. When it
29 is over the above upper limit the uniformity of gap
30 distance is prone to be lowered, causing image
31 unevenness. The coefficient of variation of particle
32 diameter is defined by the following equation

33
34 Coefficient of variation in particle diameter (%) =

$$(\sigma / \bar{x}) \times 100$$

35
36 (σ : Standard deviation of particle diameter

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1 $\bar{X}$: Mean particle diameter).

2
3 In the present invention, mean particle diameter and
4 the standard deviation of particle diameter are found
5 by measuring the particle diameter on 200 particles
6 chosen at random on electron micrographs and using the
7 equations below.

8
9
10 Mean particle diameter $(\bar{X}) = \left[\sum_{i=1}^n X_i \right] / n$

11
12
13 Standard deviation of particle diameter $(\sigma) =$

14
15
$$\left[\left(\sum_{i=1}^n (\bar{X} - X_i)^2 \right) / (n - 1) \right]^{1/2}$$

16
17
18
19 The embodiment of the composite particles of the
20 present invention can also be colored by including at
21 least one selected from the group consisting of dyes
22 and pigments. The color of the particles is preferably
23 a color which does not transmit light. Non-
24 transmitting colors are preferred for colouring spacers
25 for liquid crystal displays because they can prevent
26 light of the backlight lamp from escaping, and can
27 improve contrast. Examples of non-transmitting
28 colors include colors such as black, dark blue, navy
29 blue, purple, blue, dark green, green, brown and red,
30 etc.; but black, dark blue and navy blue are
31 particularly preferred. Suitable pigments and/or dyes
32 selected according to the intended color can be used:
33 examples according to classification of dyeing method,
34 include disperse dyes, acidic dyes, basic dyes,
35 reactive dye and sulfur dyes, etc. Concrete examples
36 of these dyes are described in "The Chemical Handbook -

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1 Applied Chemistry" (edited by the Japanese Chemical
2 Society), Maruzen KK (1986) pp 1399-1427, and "The
3 Nippon Kayaku dye handbook" by Nippon Kayaku KK (1973).
4

5 A known method can be adopted as the method for
6 coloring embodiments of the organic-inorganic composite
7 particles of the present invention. It can
8 be accomplished for example by the methods described in
9 "The Chemical Handbook-Applied Chemistry" (edited by
10 the Japanese Chemical Society) and "The Nippon Kayaku
11 Dye Handbook" above. Colored composite particles of
12 the present invention are provided with the hardness
13 and mechanical resilience described above, and hence
14 are particularly useful in raising the picture quality
15 of liquid crystal displays.
16

17 There are no particular restrictions as to the shapes
18 of the embodiments of the organic-inorganic composite
19 particles of the present invention, and they can be any
20 particle shape, such as spheres, needles, sheets,
21 flakes, splinters, rugby football-shaped, cocoon shaped
22 or star-shaped; but for use as liquid crystal display
23 spacers spheres are preferred on the grounds of giving
24 a uniformly constant gap distance. This is because
25 when the particles are spherical they have a constant
26 or nearly constant diameter in all or nearly all
27 directions.
28

29 Organic-inorganic composite particles of the present
30 invention can be made by the production process
31 described below; but they can also be produced by other
32 processes.
33

34 Compounds used in the present invention represented by
35 the aforementioned General Formula (1) have 1-4
36 hydrolyzable groups; the hydrolyzable groups being
37 monovalent groups selected from the groups consisting

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1 of a hydroxyl group, alkoxy groups of 1-5 groups and
2 acyloxy groups of 2-5 carbon atoms, and preferably
3 methoxy groups, ethoxy groups, propoxy groups and/or
4 acetoxy groups. These hydrolyzable groups are employed
5 in the present invention because they are hydrolyzed by
6 water and can produce polysiloxane by condensation.
7 When $m = 1-3$ in compounds represented by the
8 aforementioned General Formula (1), they have an organic
9 group (or organosilicon) described above and are
10 employed in order to introduce organic groups into the
11 composite particles that are produced.

12

13 Concrete examples of compounds used in the present
14 invention which are represented by General Formula (1)
15 include the following.

16

17 Compounds of $m = 0$ in Formula (1): tetraalkoxysilane
18 compounds such as tetramethoxysilane,
19 tetraethoxysilane, tetraisopropoxysilane,
20 tetrabutxysilane and dimethoxy-diethoxysilane, etc.
21 and tetraacyloxysilane compounds such as
22 tetraacetoxysilane, etc.

23

24 Compounds of $m = 1$ in Formula (1);
25 organotrialkoxysilane compounds and
26 organotriacyloxysilane compounds, such as
27 methyltrimethoxysilane, methyltriethoxysilane,
28 methyltripropoxysilane, methyltriisopropoxysilane,
29 ethyltrimethoxysilane, ethyltriethoxysilane
30 propyltriethoxysilane, butyltrimethoxysilane,
31 vinyltrimethoxysilane, vinyltriethoxysilane,
32 3-glycidoxypropyltrimethoxysilane,
33 3-mercaptopropyltrimethoxysilane,
34 3-(2-aminoethylamino-propyl)trimethoxysilane,
35 phenyltrimethoxysilane phenyl-triethoxysilane,
36 methyltriacetoxysilane and phenyltriacetoxysilane, etc.

37

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1 Compounds of $m = 2$ in Formula (1):
2 diorganodialkoxysilane compounds,
3 diorganodiacyloxysilane compounds, diorganosilanediol
4 compounds, such as dimethoxydimethylsilane,
5 diethoxy-3-glycidoxypropylmethylsilane,
6 dimethoxydiphenylsilane, diacetoxymethylsilane and
7 diphenylsilanediol, etc.

8
9 Compounds of $m = 3$ in Formula (1):
10 triorganoalkoxysilane compounds, triorganoacyloxysilane
11 compounds, triorganosilanol compounds, such as
12 trimethylmethoxysilane, trimethylethoxysilane,
13 acetoxymethylsilane and trimethylsilanol, etc.

14
15 Of the compounds represented by the aforementioned
16 General Formula (1), organotrialkoxysilane compounds
17 and tetraalkoxysilane compounds are preferred starting
18 materials.

19
20 Derivatives of the compounds represented by the
21 afore-mentioned General Formula (1) are other silicon
22 compounds capable of hydrolysis and condensation.
23 Examples include compounds in which some of the
24 hydrolyzable groups are substituted by a carboxyl
25 group, β -dicarbonyl group or other group which allow
26 the formation of chelate compounds, or lowly condensed
27 products obtained by partial hydrolysis and
28 condensation of these silicon compounds or chelate
29 compounds.

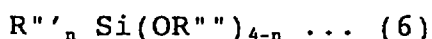
30
31 Silicon compounds capable of hydrolysis and
32 condensation such as those described above can be
33 employed as starting materials (here which mean members
34 of metal compounds capable of hydrolysis and
35 condensation) singly, or in mixtures of 2 or more
36 types.

37

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Of the aforementioned silicon compounds, only compounds selected from the group consisting of compounds of $m = 1$ in Formula (1) and derivatives thereof can be used alone as the silicon compound; only in this case can the embodiment of the composite particles of the present invention be obtained by employing a single compound.

When two or more of the aforementioned silicon compounds are used together, they need to include either or both of: a compound selected from the group consisting of compounds of $m = 1$ in Formula (1) and their derivatives; and a compound selected from the group consisting of compounds of $m = 0$ in Formula (1) and their derivatives. Only in this case can the embodiment of the composite particles of the present invention be obtained by mixing 2 or more compounds together. In this case, the proportions of silicon compounds (having values of m of 0, 1, 2 and 3 in General Formula (1) and their derivatives) are preferably decided to give $n = 0.5-1$ in General Formula (6) below for the mean composition of the starting materials after mixing.



(In the formula, R'' indicates the mean composition of organic groups having carbon atoms directly combined with silicon atoms, and R''' indicates the mean composition of at least one monovalent group selected from the group consisting of a hydrogen atom, alkyl groups and acyl groups.)

The embodiment of the composite particles of the present invention cannot be obtained when at least one selected from the group consisting of silicon compounds having $m = 2$ in Formula (1), silicon compounds having

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1 m = 3 in Formula (1) and derivatives thereof is
2 exclusively used as the starting material, or when at
3 least one selected from the group consisting of silicon
4 compounds having m = 0 in Formula (1) and derivatives
5 thereof is exclusively used as the starting material.

6
7 Silicon compounds capable of hydrolysis and
8 condensation selected from compounds represented by the
9 aforementioned General Formula (1) and derivatives
10 thereof, which are starting materials for a
11 polysiloxane component having organosilicon in its
12 molecule described above, may be employed on their own
13 as metallic compounds capable of hydrolysis and
14 condensation employed to obtain the first embodiment of
15 the composite particles of the present invention, or a
16 mixture of aforementioned silicon compounds capable of
17 hydrolysis and condensation in the presence of other
18 metal compounds capable of hydrolysis and condensation,
19 selected from organic metal compounds of boron,
20 aluminum, gallium, indium, phosphorus, titanium or
21 zirconium, etc. or inorganic compounds, can be
22 employed. The proportions of these compounds is
23 preferably decided to give a proportion accounted for
24 by the aforementioned polysiloxane in the composite
25 particles of $\geq 70\text{wt}\%$.

26 -
27 The metal compounds capable of hydrolysis and
28 condensation as the starting materials described above
29 are subjected to hydrolysis and condensation in a
30 solution medium which includes water. A bulk,
31 intermittent or continuous manner etc., can be adopted
32 at will for hydrolysis and condensation. A catalyst
33 such as ammonia, urea, ethanolamine,
34 tetramethylammonium hydroxide, an alkali metal
35 hydroxide or an alkaline earth metal hydroxide, etc.,
36 can be used for hydrolysis and condensation. An
37 organic solvent can also be present in the solution

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1 medium in addition to water and a catalyst. Concrete
2 examples of organic solvents include alcohols such as
3 methanol, ethanol, isopropanol, n-butanol, isobutanol,
4 sec-butanol, t-butanol, pentanol, ethylene glycol,
5 propylene glycol and butane-1, 4-diol, etc., ketones
6 such as acetone and methyl ethyl ketone etc., esters such
7 as ethyl acetate, etc., (cyclo)paraffins such as
8 isooctane and cyclohexane, etc., ethers such as dioxane
9 and diethyl ether, etc., and aromatic hydrocarbons such
10 as benzene and toluene, etc., can be used singly or in
11 mixtures.

12

13 Hydrolysis and condensation can be performed, for
14 example, by adding the metal compounds capable of
15 hydrolysis and condensation of the above starting
16 materials, or a solution thereof in an organic solvent,
17 to a solution medium which includes water, and
18 stirring at a temperature in the range 0-100°C, and
19 preferably 0-70°C, for 30 minutes to 100 hours.

20

21 Particles obtained by a process such as the above can
22 also be loaded beforehand into the synthetic system as
23 seed particles, and the seed particles can be grown by
24 adding the starting materials.

25

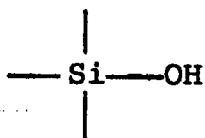
26 By hydrolizing and condensing metal compound starting
27 materials capable of hydrolysis and condensation which
28 include a silicon compound capable of hydrolysis and
29 condensation, under suitable conditions in a solution
30 medium including water in this way, a suspension is
31 formed from which particles with a spherical shape and
32 a very sharp particle diameter distribution separate
33 out. As the suitable conditions here, for example a
34 starting material concentration of $\leq 20\text{wt}\%$, a water
35 concentration of $\geq 50\text{wt}\%$, and a catalyst concentration
36 of $\leq 10\text{wt}\%$, of the suspension obtained are preferable
37 used.

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1 Particles having a mean particle diameter within the
 2 range of mean particle diameter for the embodiment of
 3 the composite particles described above can be produced
 4 by setting the the water concentration, catalyst
 5 concentration, organic solvent concentration and
 6 starting materials concentration, the period of time of
 7 adding the starting materials, temperature and the seed
 8 particle concentration to 50-99.99wt%, 0.01-10wt%,
 9 0-50wt%, 0.1-30wt%, 0.001-500 hours, 0-100°C and
 10 0-10wt% respectively.

11
 12 Particles with a coefficient of variation in particle
 13 diameter within the above range for the coefficient of
 14 variation of mean particle diameter for the embodiment
 15 of the composite particles described above can be
 16 produced by setting the water concentration, catalyst
 17 concentration and organic solvent concentration within
 18 the ranges above.

19
 20 Next, the particles thus produced are isolated from the
 21 above suspension using a prior known method such as
 22 filtration, centrifugal separation or concentration at
 23 decreased pressure, etc., and heat treated at a
 24 temperature $\geq 100^{\circ}\text{C}$ and $\leq 1000^{\circ}\text{C}$, and preferably $\geq 300^{\circ}\text{C}$
 25 and $\leq 900^{\circ}\text{C}$ in order to dry and calcine them, to obtain
 26 the particle body of the embodiment of the organic-
 27 inorganic composite particles of the present invention.
 28 The main component of this particle body is
 29 polysiloxane which has in its molecule organosilicon in
 30 which at least one carbon atom in an organic group is
 31 directly and chemically combined with the silicon atom.
 32 With heat-treatment at a temperature lower than 100°C
 33 condensation of silanol groups represented by the
 34 following Formula (7) present in the siloxane units
 35 indicated by the aforementioned Formula (5)



...(7)

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1 with the elimination of water is inadequate, and
2 consequently the necessary hardness is not obtained:
3 thus, the elastic modulus in 10% compression does not
4 become $\geq 350\text{kg/mm}^2$. Similarly, with heat treatment at a
5 temperature higher than 1000°C there is marked
6 decomposition of the organic groups, and consequently
7 the necessary mechanical resilience is not obtained:
8 thus, the residual displacement after 10% deformation
9 does not become 0-5%, and the elastic modulus in 10%
10 compression also exceeds 3000kg/mm^2 . Moreover, although
11 any atmosphere can be used for the heat treatment without
12 restriction, in order to suppress decomposition of
13 organic groups and obtain the needed mechanical
14 resilience a concentration of oxygen in the atmosphere
15 of $\leq 10\%$ is preferred. When the temperature of heat
16 treatment is in the range $350-1000^\circ\text{C}$ the oxygen
17 concentration in the atmosphere is preferably $\leq 10\%$ in
18 order to obtain the above embodiment of the composite
19 particles; and when the temperature of heat treatment
20 is $100-350^\circ\text{C}$ the above embodiment of the composite
21 particles is also produced in air.

22

23 With the process of the present invention the
24 proportion of organic groups in the embodiment of the
25 composite particles can be chosen at will in the
26 aforementioned range (the range described in explaining
27 the embodiment of the composite particles) by selecting
28 the types and quantities of starting materials
29 described above, the temperature and time of heat
30 treatment, and the concentration of oxygen in the
31 atmosphere.

32

33 When hydrolizing, when condensing, or when heat-
34 treating, other compounds which possess reactive groups
35 as described above and can react and form chemical
36 bonds with silicon compounds capable of hydrolysis and
37 condensation can also be present. In this case, a

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1 prior known coloring compound such as a dye and/or
2 pigment, for example, can also be present.

3
4 A prior known surface treatment, such as surface
5 modification by means of a coupling agent, surface
6 modification by means of a previously described
7 organo-metallic compound or inorganic compound, or
8 surface modification by means of another organic
9 compound, can be carried out on the embodiment of the
10 composite particles obtained as above before employing
11 them as spacers, in order to improve ease of dispersing
12 spacers on the electrode substrate when used as spacers
13 for liquid crystal displays, or to prevent the abnormal
14 orientation of liquid crystals at the surface of the
15 spacers, or to fix the composite particles on the
16 surface of the electrode substrate so that they do not
17 move, or for other purposes. For example, the method
18 of surface treatment described in Japanese Unexamined
19 Patent Publication (Kokai) 62-269933 can be adopted.
20 In this specification, when silica gel particles made
21 by the sol-gel method are used as liquid crystal
22 display spacers the spacers are surface treated with an
23 alcohol and/or a coupling agent, etc., in order to
24 improve the ease of dispersing the spacers on the
25 electrode substrate, or in order to suppress the
26 production of abnormal liquid crystal orientation at
27 the surface of the spacers.

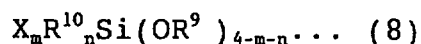
28
29 The Si-C bonds and siloxane units in the particle body
30 of the embodiment of the composite particles of the
31 present invention obtained can be confirmed by a prior
32 known method such as FT-IR, NMR or ESCA, etc. and the
33 proportion of the organic groups in the embodiment of
34 the composite particles, as the proportion accounted
35 for by total carbon atoms, can be quantitatively
36 determined by elemental analysis.

37

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The condensation step can also be a step of hydrolysis and condensation using the aforementioned first silicon compound. The first silicon compound is at least one selected from the group consisting of compounds represented by General Formulae 2, 3 and 4 described above and their derivatives.

In the condensation step, both of the first and second silicon compounds described below can be used. The second silicon compound is at least one selected from the group consisting of compounds represented by the following General Formula (8) and their derivatives:



where: X indicates a monovalent radical-polymerizable functional group indicated by $CH_2=C(-R^1)-COOR^2-$, $CH_2=C(-R^4)-$ or $CH_2=C(-R^6)-R^7-$; R^1 , R^4 and R^6 indicate a hydrogen atom or a methyl group; R^2 and R^7 indicate an alkylene group of 1-10 carbon atoms, which may have a substituent group; R^9 indicates a hydrogen atom or at least one monovalent group selected from the group consisting of alkyl groups of 1-5 carbon atoms and acyl groups of 2-5 carbon atoms; R^{10} indicates at least one monovalent group selected from the group consisting of alkyl groups of 1-10 carbon atoms and aryl groups of 6-10 carbon atoms, which may have a substituent group; m indicates an integer of 2-3; n indicates an integer of 0-2; and $m + n$ indicates an integer of 2-3. The plural X may be different from each other, or 2 or more of X may be identical with each other. When $n = 2$, the two R^{10} s may be either different from or identical with each other. When $4 - m - n$ is 2, the two R^9 s may be either different from or identical with each other.

The radical-polymerizable groups in General Formulae 2-4 and 8 are $CH_2=C(-R^1)-COOR^2-$, $CH_2=C(-R^4)-$ or

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1 $\text{CH}_2=\text{C}(-\text{R}^6)-\text{R}^7-$. In General Formula 8, when there are 2
2 or more radical-polymerizable groups, they may be
3 mutually different or 2 or more may be mutually
4 identical. Subjecting the radical-polymerizable groups
5 to radical polymerization produces an organic polymer
6 framework including the vinyl polymer described above.
7 The radical-polymerizable group is an acryloxyalkyl
8 group (R^1 in General Formulae 2 and 8 is a hydrogen
9 atom), a methacryloxyalkyl group (R^1 in General
10 Formulae 2 and 8 is a methyl group), a vinyl group (R^4
11 in General Formulae 3 and 8 is a hydrogen atom), an
12 isopropenyl group (R^4 in General Formulae 3 and 8 is a
13 methyl group), a 1-alkenyl group (R^6 in General Formulae
14 4 and 8 is a hydrogen atom), or an isoalkenyl group (R^6
15 in General Formulae 4 and 8 is a methyl group).
16

17 In General Formulae 2-4 and 8 the hydrolyzable groups
18 are R^3O , R^5O , R^8O and R^9O . Groups R^3O , R^5O , R^8O and R^9O
19 are monovalent groups selected from the group
20 consisting of a hydroxyl group, alkoxy groups of 1-5
21 carbon atoms and acyloxy groups of 2-5 carbon atoms.
22 In General Formulae 2-4, the 3 R^3O groups, 3 R^5O groups
23 and 3 R^8O groups may be mutually different or 2 or more
24 may be mutually identical. In General Formula 8 when
25 there are two R^9O groups they may be mutually different
26 or identical. On grounds of high speed of hydrolysis
27 and condensation, the R^3O groups, R^5O groups, R^8O groups
28 and R^9O groups are each preferably selected from the
29 group consisting of a methoxy group, ethoxy group,
30 propoxy group and acetoxy group; and methoxy groups and
31 ethoxy groups are more preferred. By hydrolyzing the
32 R^3O groups, R^5O groups, R^8O groups and R^9O groups of
33 first silicon compounds and second silicon compounds
34 with water, and then condensing, a polysiloxane
35 framework indicated by the aforementioned General
36 Formula 5 is formed.
37

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1 In General Formulae 2-4 and 8 the R^2 group and R^7
2 group are alkylene groups of 1-10 carbon atoms, which
3 may have a substituent group. There are no particular
4 restrictions as to these alkylene groups, but examples
5 include an ethylene group, propylene group, butylene
6 group, hexylene group and octylene group, etc. On
7 grounds of ready availability, compounds having
8 radical-polymerizable groups in which R^2 group and R^7 are
9 propylene groups are preferred.

10

11 In General Formula 8, the R^{10} groups are an alkyl
12 group or aryl group combined with the silicon atom. An
13 alkyl group here is an alkyl group of 1-10 carbon atoms
14 such as a methyl group, ethyl group, propyl group,
15 butyl group or hexyl group, for example, which may have
16 a substituent group. An aryl group here is an aryl
17 group of 6-10 carbon atoms, for example a phenyl group
18 or a tolyl group, etc. In General Formula 8, when
19 there are two R^{10} groups they may be mutually different
20 or identical.

21

22 Compounds represented by at least one General Formula
23 selected from the General Formulae 2, 3 and 4 have one
24 silicon atom, and three hydrolyzable groups combined
25 with the silicon atom, and one radical-polymerizable
26 group combined with the silicon atom.

27

28 Concrete examples of compounds represented by General
29 Formula 2 include γ -methacryloxypropyltrimethoxysilane,
30 γ -methacryloxypropyltriethoxysilane, γ -acryloxy-
31 propyltrimethoxysilane, γ -acryloxypropyltriethoxysilane
32 and γ -methacryloxypropyltriacetoxysilane, etc.; any one
33 of these can be employed on its own, or 2 or more can
34 be used together.

35

36 Concrete examples of compounds represented by General
37 Formula 3 include vinyltrimethoxysilane, vinyl-

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1 triethoxysilane and vinyltriacetoxysilane, etc. ~~any~~
2 one of these can be employed on its own, or 2 or more
3 can be used together.

4
5 Concrete examples of compounds represented by General
6 Formula 4 include 1-hexenyltrimethoxysilane and 1-
7 octenyltrimethoxysilane, etc.; any one of these can be
8 employed on its own, or 2 or more can be used together.
9 A derivative of a compound represented by General
10 Formula 2-4 is, for example, at least one selected from
11 the group consisting of compounds in which some of the
12 R³O groups in a compound represented by General Formulae
13 2-4 are substituted by a β -dicarbonyl group and/or
14 another group which allows the formation of a chelate
15 compound, and lowly condensed products obtained by
16 partial hydrolysis and condensation of compounds
17 represented by General Formulae 2-4 and/or chelate
18 compounds thereof.

19
20 The following 5 classes of compounds are represented
21 by General Formula 8.

22
23 (1) Compounds which have one silicon atom, and one
24 radical-polymerizable group combined with the silicon
25 atom, and one alkyl group or aryl group combined with
26 the silicon atom, and two hydrolyzable groups combined
27 with the silicon atom ($m = 1$, $n = 1$). Concrete examples
28 of such compounds include
29 γ -methacryloxypropylmethyldimethoxysilane,
30 γ -methacryloxypropylmethyldiethoxysilane,
31 γ -acryloxypropyl-methyldimethoxysilane,
32 γ -acryloxypropylmethyldiethoxy silane,
33 vinylmethyldimethoxysilane and vinylmethyldiethoxy-
34 silane, etc.; any one of these can be employed on its
35 own, or 2 or more can be used together.

36
37 (2) Compounds having one silicon atom, and one

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1 radical-polymerizable group combined with the silicon
2 atom, and two alkyl and/or aryl groups combined with
3 the silicon atom, and one hydrolyzable group combined
4 with the silicon atom ($m = 1$, $n = 2$). Concrete examples
5 of such compounds include
6 γ -methacryloxypropyldimethylmethoxysilane,
7 γ -methacryloxypropyldimethylethoxysilane,
8 γ -acryloxy-propyldimethylmethoxysilane,
9 γ -acryloxypropyldimethyl-ethoxysilane and vinyl-
10 dimethylmethoxysilane, etc.; any one of these can be
11 employed on its own, or 2 or more can be used together.

12
13 (3) Compounds having one silicon atom, and two
14 radical-polymerizable groups combined with the silicon
15 atom, and two hydrolyzable groups combined with the
16 silicon atom ($m = 2$, $n = 0$). Concrete examples of such
17 compounds include bis-(γ -acryloxypropyl) dimethoxy
18 silane and bis(γ -methacryloxypropyl) dimethoxysilane,
19 etc.; any one of these can be employed on its own, or 2
20 or more can be used together.

21
22 (4) Compounds having one silicon atom, and two
23 radical-polymerizable groups combined with the silicon
24 atom, and one alkyl group or aryl group combined with
25 the silicon atom, and one hydrolyzable group combined
26 with the silicon atom ($m = 2$, $n = 1$). Concrete
27 examples of such compounds include bis-
28 (γ -methacryloxypropyl) methylmethoxysilane, bis-
29 (γ -acryloxypropyl) methylmethoxysilane, etc.; any one
30 of these can be employed on its own, or 2 or more can
31 be used together.

32
33 (5) Compounds having one silicon atom, and 3 radical-
34 polymerizable groups combined with the silicon atom,
35 and one hydrolyzable group combined with the silicon
36 atom ($m = 3$, $n = 0$). Concrete examples of such
37 compounds include tris-(γ -methacryloxypropyl)-

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1 methoxysilane, tris- (γ -acryloxypropyl)methoxysilane,
2 etc.; any one of these can be employed on its own, or 2
3 or more can be used together.

4
5 A derivative of a compound represented by General
6 Formula 8 is, for example, at least one selected from
7 the group consisting of compounds in which some of the
8 R⁹O groups in compounds represented by General Formula 8
9 are substituted by a β -dicarbonyl group and/or another
10 group which allows the formation of a chelate compound,
11 and lowly condensed products obtained by partial
12 hydrolysis and condensation of compounds represented by
13 General Formula 8 and/or chelate compounds thereof.

14
15 The first silicon compound is needed in the present
16 invention because the particles obtained when a second
17 silicon compound is hydrolyzed and condensed without
18 using a first silicon compound tend to have low
19 hardness.

20
21 There are no particular restrictions as to the
22 quantity of metal compounds capable of hydrolysis and
23 condensation other than the first and second silicon
24 compounds, but if large quantities are employed the
25 shape of the organic-inorganic composite particles
26 obtained may not be spherical and particle diameter
27 distribution may be broadened making them unsuitable as
28 spacers. Consequently, the quantity of metal compounds
29 capable of hydrolysis and condensation other than the
30 first and second silicon compounds is preferably
31 $\leq 200\text{wt}\%$, more preferably $\leq 100\text{wt}\%$, and even more
32 preferably $\leq 50\text{wt}\%$, of the total weight of first and
33 second silicon compounds.

34
35 The first silicon compound, and optionally employed
36 second silicon compound and/or metal compound capable
37 of hydrolysis and condensation, (termed "starting

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1 materials" hereafter) is/are subjected to hydrolysis
2 and condensation in a solution medium containing water;
3 a bulk, intermittent or continuous manner, etc., can be
4 adopted at will for the hydrolysis and condensation. A
5 catalyst such as ammonia, urea, ethanolamine,
6 tetramethylammonium hydroxide, an alkali metal
7 hydroxide or an alkaline earth hydroxide, etc., can be
8 used for bringing about hydrolysis and condensation.
9 An organic solvent may also be present in the solution
10 medium in addition to water and a catalyst. Concrete
11 examples of organic solvents include alcohols such as
12 methanol, ethanol, isopropanol, n-butanol, isobutanol,
13 sec-butanol, t-butanol, pentanol, ethylene glycol and
14 1,4-butanediol, etc., ketones such as acetone and
15 methyl ethyl ketone, esters such as ethyl acetate,
16 (cyclo)paraffins such as isooctane and cyclohexane,
17 etc., ethers such as dioxane and diethyl ether and
18 aromatic hydrocarbons such as benzene and toluene,
19 etc., used singly or in mixtures.

20
21 Hydrolysis and condensation can be performed, for
22 example, by adding the starting materials above, or a
23 solution thereof in an organic solvent, to a solution
24 medium including water, and stirring at a temperature
25 in the range 0-100°C, and preferable 0-70°C, for 30
26 minutes to 100 hours.

27
28 Particles obtained by a process such as that above can
29 also be loaded beforehand into the synthetic system as
30 seed particles, and then the seed particles can be
31 grown by adding the starting materials.

32
33 By hydrolyzing and condensing the starting materials
34 under suitable conditions in a solution medium
35 including water in this way, a slurry is produced from
36 which the particles separate out. The particles which
37 separate out are the resulting product of hydrolysis

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1 and condensation of a silicon compound described above
2 which has a radical-polymerizable group, and the
3 particles have an optionally selected particle diameter
4 $\geq 0.5\mu\text{m}$, and a sharp particle diameter distribution. As
5 the suitable conditions here, a starting material
6 concentration in the slurry of $\leq 20\text{wt}\%$, a water
7 concentration of $\leq 50\text{wt}\%$ and a catalyst concentration
8 of $\leq 10\text{wt}\%$ are preferably used.

9
10 Moreover, in hydrolyzing and condensing a first
11 silicon compound, and an optionally employed second
12 silicon compound and/or metal compound capable of
13 hydrolysis and condensation, fine inorganic particles
14 of a mean particle diameter $\leq 0.4\mu\text{m}$ are preferably also
15 used. The reason is that the organic-inorganic
16 composite particles obtained are harder and have a
17 raised fracture strength when they include fine
18 inorganic particles chemically combined with the
19 polysiloxane framework.

20
21 Concrete examples of fine inorganic particles include
22 silica, alumina, aluminum hydroxide, titanium oxide and
23 zirconium oxide, etc.; but on grounds of ease of
24 introduction into particles obtained by hydrolysis and
25 condensation, silica is preferred.

26
27 A mean particle diameter of the fine inorganic
28 particles exceeding $0.4\mu\text{m}$ is undesirable because it
29 becomes difficult to introduce them into particles
30 obtained by hydrolysis and condensation of the starting
31 materials. Therefore, the smaller the mean particle
32 diameter of the fine inorganic particles the better,
33 and it is preferably $\leq 0.1\mu\text{m}$, more preferably $\leq 30\text{nm}$, and
34 even more preferably $\leq 10\text{nm}$. The fine inorganic
35 particles are preferably silica of a mean particle
36 diameter of preferably $\leq 0.1\mu\text{m}$, more preferably $\leq 30\text{nm}$ or
37 $\leq 10\text{nm}$.

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1 On grounds of decreasing the number of particle
2 aggregates, these fine inorganic particles are
3 preferably of sol dispersed in water or an organic
4 solvent. More preferably they are of sol of fine
5 inorganic particles of a mean particle diameter $\leq 30\text{nm}$,
6 and even more preferably $\leq 10\text{nm}$. Concrete examples
7 include, for example, sols of silica particles of mean
8 particle diameter $\leq 30\text{nm}$ (silica sols) such as "Snowtex
9 20", "Snowtex 0", "Snowtex C", "Snowtex N", "Snowtex
10 S", "Snowtex 20L", "Snowtex XS", "Snowtex XL", "Snowtex
11 YL", "Snowtex ZL", "Methanol Silica Sol" and "IPA-ST"
12 (trade names, made by Nissan Chemical Industries,
13 Ltd.), etc., and alumina sols such as "Alumina Sol
14 100", "Alumina Sol 200" and "Alumina Sol 520" (trade
15 names, made by Nissan Chemical Industries, Ltd.), etc.

16
17 During the condensation step, and/or after the
18 condensation step, the radical-polymerizable groups are
19 subjected to radical polymerization. Thus, particles
20 of an intermediate product obtained by hydrolysis and
21 condensation of a first silicon compound, optionally
22 employing a second silicon compound, are subjected to
23 radical polymerization. The radical-polymerizable
24 groups undergo radical polymerization to form an
25 organic polymer framework.

26
27 As the method of radical polymerization, radical
28 polymerization can be performed as it stands by
29 dissolving a water-soluble or oil-soluble radical
30 polymerization initiator in the slurry of a solution
31 medium including water which contains the particles
32 obtained by hydrolysis and condensation, or the
33 particles obtained by hydrolysis and
34 condensation can be isolated from the slurry using a
35 known method such as filtration, centrifugal separation
36 or concentration at decreased pressure, etc., and then
37 polymerized by dispersion in a solution of water or an

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1 organic solution medium, etc., containing a
2 polymerization initiator; however, these are not the
3 only possible methods. Performing hydrolysis and
4 condensation in the presence of a polymerization
5 initiator so that radical polymerization occurs
6 simultaneously is particularly preferred.

7
8 There are no particular restrictions as to the
9 radical polymerization initiator here, and a prior
10 known substance can be employed; but at least one
11 selected from the group consisting of azo compounds and
12 peroxy compounds is preferred.

13
14 There are no particular restrictions as to the
15 quantity of the radical polymerization initiator above;
16 but since if too much is used a lot of heat is
17 generated and it becomes difficult to control the
18 reaction, and if too little is used radical
19 polymerization may not proceed, for example, it will be
20 in the range 0.1-5wt%, and preferably 0.3-2wt%,
21 relative to the total weight of first and second
22 silicon compounds.

23
24 The temperature for radical polymerization can be
25 selected to suit the radical polymerization initiator
26 that is employed, but to facilitate control of the
27 reaction it will be in the range 30-100°C, and
28 preferably 50-80°C.

29
30 Monomers having groups capable of radical
31 polymerization with the radical-polymerizable groups
32 can also be present when carrying out radical
33 polymerization. Examples of monomers include
34 unsaturated carboxylic acids such as acrylic acid and
35 methacrylic acid, etc., esters of unsaturated
36 carboxylic acids such as acrylic acid esters,
37 methacrylic acid esters, crotonic acid esters, itaconic

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1 acid esters, maleic acid esters and fumaric acid
2 esters, etc., acrylamides, methacrylamides, vinyl
3 compounds such as aromatic vinyl compounds such as
4 styrene, α -methylstyrene and divinyl benzene, etc.,
5 vinyl esters such as vinyl acetate, etc., and
6 halogenated vinyl compounds such as vinyl chloride,
7 etc.; one or more of these can be employed. Of these,
8 monomers which have 2 or more groups capable of radical
9 polymerization, such as divinylbenzene,
10 trimethylolpropane trimethacrylate and ethylene glycol
11 dimethacrylate, etc., are preferred.

12
13 However, if too much monomer is employed and the
14 polysiloxane content in the organic-inorganic composite
15 particles becomes less than 25wt%, hardness becomes
16 inadequate, which is undesirable. Consequently, the
17 quantity of monomers is, for example, 0-50wt%, and
18 preferably 0-30wt%, of the total weight of first and
19 second silicon compounds.

20
21 After radical polymerization, the further
22 recondensation step described below is preferably
23 carried out, since it raises the hardness, mechanical
24 resilience and fracture strength of the organic-
25 inorganic particles that are finally obtained. The
26 recondensation step includes subjecting the polymerized
27 particles (which are produced by the radical
28 polymerization) to further condensation in an organic
29 solvent. In order to speed up condensation the
30 aforementioned catalysts can be used; catalysts
31 preferred on grounds of speeding up condensation
32 include organic titanium compounds such as titanium
33 tetraisopropoxide, titanium tetrabutoxide and
34 diisopropoxy-bis (acetylacetonate) titanate, etc.,
35 organic aluminum compounds such as aluminum
36 triisopropoxide, aluminium tri(sec-butoxide),
37 aluminium tris (acetylacetonate) and aluminium

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1 isopropoxide-bis(acetyl-acetonate), etc., organic
2 zirconium compounds such as zirconium tetrabutoxide and
3 zirconium tetrakis(acetyl-acetonate), etc., organic tin
4 compounds such as dibutyltin diacetate, dibutyltin
5 dilaurate, dibutyltin diethylhexanoate and dibutyltin
6 dimaleate, etc., and acidic phosphate esters such as
7 $(\text{CH}_3\text{O})_2\text{P}(=\text{O})\text{OH}$, $(\text{CH}_3\text{O})\text{P}(=\text{O})(\text{OH})_2$, $(\text{C}_4\text{H}_9\text{O})_2\text{P}(=\text{O})\text{OH}$ and
8 $(\text{C}_8\text{H}_{17}\text{O})\text{P}(=\text{O})(\text{OH})_2$, etc.; any one of these can be used on
9 its own, or two or more can be used together. Of
10 these, at least one selected from the group consisting
11 of organotin compounds and acidic phosphate esters is
12 preferred.

13
14 In the recondensation step, it is preferable that the
15 polymerized particles do not contain water. The reason
16 for this is to facilitate the progress of condensation
17 of silanol groups with the elimination of water.
18 Therefore, when the slurry obtained by the
19 polymerization step does not contain water the slurry
20 can be employed as it stands in the recondensation
21 step, but when the slurry contains water the
22 polymerized particles are preferably isolated from the
23 slurry using a prior known method such as filtration,
24 centrifugal separation or concentration at decreased
25 pressure, and then dispersed in an organic solvent
26 before recondensation. The organic solvents employed
27 will be, for example, at least one selected from the
28 group consisting of the alcohols, ketones, esters,
29 paraffins, ethers and aromatic hydrocarbons mentioned
30 previously. The recondensation step can be performed,
31 for example, by stirring an organic solvent slurry
32 containing the polymerized particles at a temperature
33 of 50-200°C, and preferably 60-150°C, for 30 minutes
34 to 100 hours. The pressure can be normal pressure,
35 decreased pressure or increased pressure.

36
37 Colored organic-inorganic composite particles can be

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1 obtained by coloring the particles produced during
2 and/or after at least one step selected from the group
3 consisting of the condensation step, the polymerization
4 step, the recondensation step and the heat-treatment
5 step.

6
7 In the process of the present invention, colored
8 organic-inorganic composite particles can be produced
9 by introducing a dye and/or pigment into the particles
10 by having a dye and/or pigment present in a suitable
11 step during manufacture.

12
13 Within the process of the present invention the
14 particles are preferably colored by using a dye and/or
15 pigment in the condensation step. As dyes and/or
16 pigments, those mentioned above can be cited. Of
17 these, basic dyes are preferred. This is because the
18 silanol groups in polysiloxane are acidic, and basic
19 (cationic) dyes are readily absorbed so that coloring
20 is easy. Examples of pigments include inorganic
21 pigments such as carbon black, iron black, chrome
22 vermillion, molybdenum red, red ochre, yellow lead,
23 chrome green, cobalt green, ultramarine blue and iron
24 blue, etc., and organic pigments such as
25 phthalocyanine, azo and quinacridone pigments, etc.
26 However, since it may not be possible to introduce
27 pigments into the composite particles of the present
28 invention if the mean particle diameter thereof is not
29 $\leq 0.4\mu\text{m}$, the use of dyes is preferred. Organic-
30 inorganic composite particles of the present invention
31 which are colored in this way are particularly useful
32 for raising the picture quality of liquid crystal
33 displays because they are also provided with the
34 aforementioned hardness, mechanical resilience and
35 fracture strength.

36
37 Organic-inorganic composite particles of the present

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1 invention can also have a particle body described above
2 and a conductive layer formed on the surface of the
3 particle body.

4
5 The particle body of organic-inorganic composite
6 particles of the present invention has the mechanical
7 resilience necessary to maintain constant the gap
8 distance between a pair of electrodes brought into
9 electrical contact, and the hardness and fracture
10 strength to maintain the aforementioned gap distance
11 constant with smaller numbers; and they also do not
12 readily cause physical damage to the electrodes.
13 Consequently, it is easy to maintain the gap distance
14 between a pair of electrodes constant, and to avoid
15 detachment and falling off of the conductive layer due
16 to pressure which causes short circuit between the
17 electrodes when they should not be in electrical
18 contact and poor contact between the electrodes when
19 they should be in electrical contact.

20
21 Metals employed in the conductive layer can be prior
22 known metals: examples include nickel, gold, silver,
23 copper and indium, and alloys of these, etc.; nickel,
24 gold and indium are preferred, since they have
25 particularly high conductivity. There are no
26 particular restrictions as to the thickness of the
27 conductive layer, provided that it gives adequate
28 conduction; but it is preferably in the range 0.01-5 μ m,
29 and particularly preferably in the range 0.02-2 μ m.
30 When the thickness is thinner than the aforementioned
31 range conductivity may be inadequate, and when it is
32 thicker than the aforementioned range the conductive
33 layer becomes prone to detach due to the difference in
34 thermal conductivity between the particle and the
35 conductive layer. The conductive layer can be a single
36 layer or ≥ 2 layers; when there are ≥ 2 layers, layers
37 including different conductors can be arranged one on

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1 top of the other.

2

3 A prior known method can be adopted as the method for
4 forming a conducting layer on the surface of the
5 particle body of organic-inorganic composite particles
6 of the present invention; there are no particular
7 restrictions, and a method such as a chemical plating
8 method (electroless plating), a coating method, a PVD
9 method (vacuum vapour deposition, sputtering, ion
10 plating, etc.) etc., for example, can be used; of these
11 chemical plating is preferred since it readily gives
12 conductive particles of the present invention.
13 Conductive particles of the present invention so
14 obtained are also provided with the hardness and
15 mechanical resilience of organic-inorganic composite
16 particles of the present invention described above.
17 Consequently, they are particularly useful as
18 electrical connecting materials for electronics
19 applications such as liquid crystal displays,
20 LSIs and printed circuit boards, etc.

21

22 Organic-inorganic composite particles of the present
23 invention have the mechanical resilience necessary to
24 maintain a constant gap distance between a pair of
25 electrode substrates which should be arranged with the
26 correct gap distance between them, and the hardness and
27 fracture strength necessary to maintain the
28 aforementioned gap distance constant with smaller
29 numbers; and they also do not readily cause physical
30 damage to the electrode substrates. Consequently, it
31 becomes easy to maintain a constant gap distance
32 between a pair of electrode substrates, in low-
33 temperature environments shrinkage approaches that of
34 the liquid crystals, vapour deposition layers,
35 orientating layers and coating layers do not readily
36 get damaged, and the number that needs to be dispersed
37 between the electrode substrates is decreased.

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1 As described above, because the embodiments of the
2 organic-inorganic composite particles of the present
3 invention contain both of a polysiloxane framework and
4 an organic group, they are provided both with the great
5 hardness characteristic of inorganic substances and
6 with the high mechanical resilience and fracture
7 strength characteristic of organic groups, and are
8 ideal for use as spacers for liquid crystal displays.
9

10 When the organic-inorganic composite particles of the
11 present invention are colored by including a dye and/or
12 pigment in the particle body they are useful as colored
13 spacers.
14

15 In liquid crystal displays an image is formed by
16 applying a voltage between electrode substrates and
17 producing a change in the optical properties of the
18 liquid crystals. In this connection, the spacers do
19 not show any optical properties as the result of
20 applying a voltage. Therefore, in the dark area of the
21 portions when an image was displayed spacers which are
22 not colored may allow light of the backlight lamp to
23 escape and be recognisable as bright spots, and image
24 contrast may be lowered.
25

26 When the organic-inorganic composite particles of the
27 present invention have a particle body that has been
28 colored by including a dye and/or pigment, light of the
29 backlight lamp does not readily escape and the lowering
30 of image contrast is prevented; since these composite
31 particles are moreover also provided with a combination
32 of characteristic hardness, mechanical resilience and
33 fracture strength, they are particularly useful for
34 improving the image quality of liquid crystal displays.
35 The colors preferred for colored spacers for liquid
36 crystal displays are colors which do not readily
37 transmit light or which do not transmit light.

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1 Examples include black, dark blue, purple, blue, dark
2 green, green, brown and red, etc., but black, dark blue
3 and navy blue are particularly preferred.

4
5 The organic-inorganic composite particles of the
6 present invention are also useful as adhesive spacers
7 when they include a particle body and an adhesive layer
8 formed on the surface of the particle body. The
9 adhesive layer, for example can be an adhesive which
10 becomes adhesive when heated.

11
12 When the composite particles of the present invention
13 have an adhesive layer on the surface of the particle
14 body, on being interposed between electrode substrates
15 which constitute a liquid crystal display and being hot
16 pressed the adhesive layer will melt and stick to the
17 electrode substrate, and they can be fixed in place by
18 cooling and hardening the adhesive layer.

19 Consequently, since the composite particles become
20 unable to move freely it is possible to prevent damage
21 to orientating layers and to maintain the uniformity of
22 the gap distance, and it is possible to achieve an
23 improvement in image quality. As an adhesive layer a
24 thermoplastic resin is preferred. The glass transition
25 temperature of the thermoplastic resin is preferably
26 $\leq 150^{\circ}\text{C}$, and more preferably $\leq 80^{\circ}\text{C}$. This is so that it
27 can be stuck to the electrode substrates by hot
28 pressing for a short time. When the glass transition
29 temperature is too high the adhesive layer may not
30 stick to the electrode substrate when heated, and when
31 it is too low the composite particles are liable to
32 stick together; hence, it is most preferably in the
33 range $40-80^{\circ}\text{C}$. There are no particular restrictions as
34 to the type of thermoplastic resin, but it is
35 preferably a (meth)acrylic resin. The adhesive layer
36 can be a single layer or it can be ≥ 2 layers, and when
37 it is ≥ 2 layers it can be made up of layers of

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1 different thermoplastic resins on top of one another.

2
3 Composite particles having an adhesive layer can be
4 obtained, for example, by coating the particle body of
5 organic-inorganic composite particles of the present
6 invention with an adhesive layer. When a thermoplastic
7 resin is used as the adhesive layer, a layer of
8 thermoplastic adhesive can be coated onto the surface
9 of organic-inorganic composite particles of the present
10 invention by a prior known resin coating method such as
11 in-situ polymerization, coacervation, interface
12 polymerization, a liquid curing coating method, a
13 liquid drying method, a high speed gas stream impact
14 method, a gas spray coating or a spray drying method,
15 etc. High-speed gas stream impact methods are prefer
16 red because coating is easier. A high-speed gas stream
17 impact method, for example, involves mixing
18 organic-inorganic composite particles of the present
19 invention with a powdered thermoplastic resin,
20 dispersing this mixture in a gas phase, applying to the
21 composite particles and the powdered thermoplastic
22 resin mechanical and thermal energy the main component
23 of which is an impact force, and coating the surface of
24 the organic-inorganic composite particles with the
25 thermoplastic resin; this method is preferred because
26 of the ease of coating.

27
28 Equipment employing such high-speed gas stream impact
29 methods include the Hybridization System manufactured
30 by Nara Kikai Seisakusho KK, the Mechanofusion System
31 manufactured by Hosokawa Mikron KK, and the Kryptron
32 System manufactured by Kawasaki Jukogyo KK [Kawasaki
33 Heavy Industry], etc.

34
35 Composite particles having an adhesive coating are
36 furnished with the hardness, mechanical resilience and
37 fracture strength of organic-inorganic composite

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1 particles of the present invention described above, and
2 have an adhesive coating; and hence they are
3 particularly useful for improving the image quality of
4 liquid crystal displays.

5
6 When composite particles having an adhesive layer are
7 colored by including a dye and/or pigment in the
8 particle body of organic-inorganic composite particles
9 they do not readily allow light of the backlight lamp
10 to escape and prevent a lowering of image contrast, and
11 because they are adhesive they are not freely mobile,
12 which prevents damage to orientating layers and enable
13 a uniform gap distant to be maintained; since moreover
14 they combine the hardness, mechanical resilience and
15 fracture strength characteristic of the present
16 invention described above, the adhesive spacers are
17 also useful as colored spacers, and therefore
18 particularly useful for improving the picture quality
19 of liquid crystal displays.

20
21 In the liquid crystal displays of the present
22 invention, the composite particles of the present
23 invention as described above are interposed between
24 electrode substrates as spacers for the liquid crystal
25 display instead of the prior spacers in prior liquid
26 crystal displays; and they have a gap distance the same
27 as the particle diameter of the composite particles, or
28 almost the same. The quantity of composite particles
29 employed is ordinarily 40-100/mm², and preferably
30 40-80/mm², which is of the order of 10-50% less than for
31 prior organic spacers so that the area of the portions
32 in which no image is formed becomes smaller and the
33 quantity of impurities such as ions and molecules,
34 etc., eluting from the inside of the spacers into the
35 liquid crystal layer is greatly decreased.
36 Consequently a high contrast, decrease in image
37 roughness and an improvement in the picture quality can

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1 be expected.

2
3 Liquid displays of the present invention are provided,
4 for example, with the first electrode substrate, the
5 second electrode substrate, a sealing material, and a
6 spacer for the liquid crystal display, and a liquid
7 crystal. The first electrode substrate has a first
8 substrate and a first electrode formed in the surface
9 of the first substrate. The second electrode substrate
10 has a second substrate and a second electrode formed in
11 the surface of the second substrate, and is opposite to
12 the first electrode substrate. The spacers for the
13 liquid crystal display, which are interposed between
14 the first electrode substrate and the second electrode
15 substrate, are composite particles of the present
16 invention. A sealing material bonds the first
17 electrode substrate with the second electrode substrate
18 at their respective circumferential edges. The liquid
19 crystals are packed into the space defined by the first
20 electrode substrate, the second electrode substrate and
21 the sealing material.

22
23 In the liquid crystal displays of the present
24 invention the members other than the spacers, such as
25 the electrode substrates, the sealing material and the
26 liquid crystals can be the same materials employed in
27 the same way as in prior liquid crystal displays. The
28 electrode substrates include a substrate which is a
29 glass sheet or a film sheet, etc., and an electrode
30 formed in the surface of the substrate, and if
31 necessary further have an orientating layer on the
32 surface of the electrode substrate, formed so as to
33 cover the electrode. As the sealing material an epoxy
34 resin binder sealing material, etc., can be employed.
35 The liquid crystals can be liquid crystals used in
36 prior displays; for example, biphenyl,
37 phenylcyclohexane, Schiff base, azo, azoxy, benzoic

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1 acid ester, terphenyl, cyclohexyl-carboxylic acid
2 ester, biphenylcyclohexane, pyrimidine, dioxane,
3 cyclohexylcyclohexane ester, cyclohexylethane or
4 cyclohexene type liquid crystals, etc.

5
6 One method for making a liquid crystal display of the
7 present invention, for example, involves dispersing
8 composite particles of the present invention evenly by
9 a wet method or a dry method on one of the two
10 electrode substrates as surface spacers, and then
11 mounting the other electrode substrate, which has the
12 portion to be sealed painted by a means such as screen
13 printing with composite particles of the present
14 invention as spacers for the sealed portion dispersed
15 in a binder sealing material such as an epoxy resin, on
16 top, and after heat curing the sealing binder material
17 by applying a suitable pressure and heating at a
18 temperature of 100-180°C for 1-60 minutes, or exposing
19 to a quantity of ultraviolet radiation of 40-300mJ/cm²,
20 injecting the liquid crystals, and then sealing the
21 portion through which they are injected to obtain a
22 liquid crystal display; but there are no restrictions
23 in the present invention as to the method for making
24 the liquid crystal display. Of the composite particles
25 of the present invention, the aforementioned colored
26 composite particles are preferred as surface spacers
27 because they are not prone to allow light of the
28 backlight lamp to escape, and the aforementioned
29 composite particles having an adhesive layer are more
30 preferred because they stick to the electrode
31 substrates so that they cannot move freely; colored
32 composite particles having an adhesive layer are even
33 more preferred because they do not allow light of the
34 backlight lamp to escape and they stick to the
35 electrode substrates so that they cannot move freely.
36 Liquid crystal displays of the present invention can
37 be employed for the same purposes as prior liquid

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1 crystal displays, as image display elements for
2 televisions, personal computers and word processors,
3 etc.

4
5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

6
7 Hereinafter, the present invention is illustrated by
8 the following examples of some preferred embodiments in
9 comparison with comparative examples not according to
10 the invention.

11
12 The liquid crystal displays in the Examples below were
13 made by the process described below. As shown in
14 Figure 1, a lower electrode substrate 110 was first
15 obtained by forming an electrode (for example, a
16 transparent electrode) 5 and a polyimide orientating
17 layer 4 on a lower glass substrate 11 of size 300mm x
18 345mm x 1.1mm, and then rubbing. The spacers for the
19 liquid crystal display (in this case surface spacers)
20 8, dispersed at 1wt% in a mixed solvent including
21 methanol 30 parts (v/v), isopropanol 20 parts (v/v) and
22 water 50 parts (v/v) were spread over 1-10 seconds on
23 this lower electrode substrate 110.

24
25 Meanwhile, an upper electrode substrate 120 was
26 obtained by forming an electrode (for example a
27 transparent electrode) 5 and a polyimide orientating
28 layer 4 on an upper glass substrate 12 of size 300mm x
29 345mm x 1.1mm and then rubbing. And spacers for the
30 liquid crystal display (in this case sealing spacers) 3
31 dispersed at 30vol% in an epoxy resin binder sealing
32 material 2 were screen printed onto the portion of the
33 upper electrode substrate 120 that was to be sealed.

34
35 Finally, the upper and lower electrode substrates 120
36 and 110 were stuck together with the electrodes 5 and
37 orientating layers 4 opposite to each other and the

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1 spacers 8 between; a pressure of 4kg/cm^2 was applied,
2 and the binder sealing material 2 was heat cured by
3 heating at 150°C for 30 minutes. Then, by placing the
4 space between the two electrode substrates 120 and 110
5 under vacuum and then returning it to atmospheric
6 pressure, liquid crystals 7, including a mixture of
7 biphenyl and phenylcyclohexane type liquid crystals,
8 etc., according to the type of liquid crystal display
9 being made, were injected and the portion through which
10 they were injected was sealed. PVA (poly(vinyl
11 alcohol)) polarizing films 6 were then stuck to the
12 outside of the upper and lower glass substrates 12 and
13 11, to constitute the liquid crystal display.
14

15 As Figure 2 shows, the spacers 8 can be organic-
16 inorganic composite particles of the present invention
17 including an uncolored particle body 31. In this case,
18 physical damage is not readily caused to the electrode
19 substrates by pressure during manufacture, and the
20 display is not prone to occur low-temperature bubbling
21 or image unevenness. Moreover, because the number of
22 spacers is less than with prior spacers including
23 polymer particles, the area of the portion in which no
24 image is formed is decreased and the elusion of
25 impurities into the liquid crystals is also decreased.
26 Consequently, it is possible to raise contrast and
27 raise picture quality.
28

29 As Figure 3 shows, the spacers 8 can also be organic-
30 inorganic composite particles of the present invention
31 including a colored particle body 32. In this case
32 there is the additional advantage that transmission of
33 light of the backlight lamp through the spacers 8 does
34 not readily occur, and hence conspicuous bright spots
35 are eliminated and the quality of the pictures
36 displayed is further raised.
37

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1 As Figure 4 shows, the spacers 8 can also be organic-
2 inorganic composite particles of the present invention
3 which include an uncolored particle body 31 and an
4 adhesive layer 33 formed on the surface of the particle
5 body 31. In this case, there is the additional
6 advantage that damage to the orientating layer is
7 prevented because the spacers are not able to move
8 freely, further raising the quality of the pictures
9 displayed.

10

11 As Figure 5 shows, the spacers 8 can also be organic-
12 inorganic composite particles of the present invention
13 which include a colored particle body 32 and an
14 adhesive layer 33 formed on the surface of the particle
15 body 32. In this case there is the additional
16 advantage that transmission of light of the backlight
17 lamp through the spacers 8 does not readily occur,
18 eliminating conspicuous bright spots, and the
19 additional advantage that damage to the orientating
20 layer is prevented because the spacers are not able to
21 move freely, further raising the quality of the
22 pictures displayed.

23

24 As Figure 6 shows, the organic-inorganic composite
25 particles of the present invention can also include a
26 particle body 34 and a conductive layer 35 formed on
27 the surface of the particle body 34. The conductive
28 layer can be, for example, a metal layer formed by
29 electroless coating, and can be one or more layers.

30

31 In relation to the methods for evaluating the liquid
32 crystal displays obtained, low-temperature bubbling was
33 assessed by the presence or absence of an image after
34 holding for 1000 hours at -45°C , and the presence or
35 absence of image unevenness and pixel faults was
36 assessed visually at room temperature (25°C).

37

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EXAMPLE A1

Methanol (307 parts by weight), 25% aqueous ammonia (6 parts by weight) and water (1225 parts by weight) were mixed evenly in a 2-litre glass reaction vessel provided with a stirrer, a dropping funnel and a thermometer. This mixture was adjusted to $20 \pm 0.5^{\circ}\text{C}$ and stirred evenly at 100 rpm while methyltrimethoxysilane (60 parts by weight) was added dropwise over 6 hours from the dropping funnel. Stirring was continued evenly for 1 hour after the addition to perform hydrolysis and condensation and obtain a suspension of hydrated fine particles of condensed methyltrimethoxysilane (A). The solid and liquid in this suspension (A) were separated by filtration, the resulting cake was washed 3 times with methanol, and the resulting solid powder was dried in a vacuum drier at 100°C for 3 hours and then heat treated in an atmosphere of nitrogen at 350°C for 3 hours to obtain organic-inorganic composite particles of a mean particle diameter of $1.81\mu\text{m}$ with a coefficient of variation of 7.6% in particle diameter.

When the hardness and mechanical resilience of the resulting composite particles was evaluated by the methods described previously, the elastic modulus in 10% compression was 711kg/mm^2 and residual displacement after 10% deformation was 2.5%. The presence of Si-CH_3 bonds and siloxane units in the composite particles was also confirmed by FT-IR analysis. From elemental analysis, the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was 13.3wt%.

When a B5 size ferroelectric liquid crystal display was made by the known method using these composite

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particles, the number of spacers dispersed ~~could be~~ decreased by $\geq 10\%$ compared with current organic particle spacers (Epostar GP-H, made by Nippon Shokubai Co., Ltd.), and a liquid crystal display could be made which did not produce low-temperature bubbling or image unevenness which arise when calcined silica particles or non-calcined silica particles made by the sol-gel method were used.

EXAMPLE A2

Organic-inorganic composite particles of mean particle diameter $6.84\mu\text{m}$ with a coefficient of variation of 5.9% in particle diameter were obtained as in Example A1 except that methanol (154 parts by weight) and n-propanol (153 parts by weight) were employed instead of the methanol (307 parts by weight) in Example A1, and heat treatment was performed at 750°C for 1 hour instead of at 350°C for 3 hours.

The elastic modulus in 10% compression of the resulting composite particles was 750kg/mm^2 , and residual displacement after 10% deformation was 3.1% . The presence of Si-CH₃ bonds and siloxane units in the composite particles was confirmed by FT-IR analysis, and the proportion of organic groups in the composite particles, representing the quantity of organic groups by the total weight of carbon atoms, was $12.1\text{wt}\%$.

When a B5 size STN (abbreviation for Super Twisted Nematic) liquid crystal display was made by the known method using these composite particles, the results obtained were similar to those in Example A1.

EXAMPLE A3

Organic-inorganic composite particles of mean particle

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1 diameter 4.47 μ m with a coefficient of variation of 6.8%
2 in particle diameter were obtained as in Example A1
3 except that methanol (154 parts by weight) and
4 n-butanol (153 parts by weight) were employed instead
5 of the methanol (307 parts by weight) in Example A1,
6 and tetraethoxysilane (17 parts by weight) and
7 methyltrimethoxysilane (43 parts by weight) were
8 employed instead of methyltrimethoxysilane (60 parts by
9 weight), and heat treatment was performed at 600°C for
10 2 hours instead of 350°C for 3 hours. Here n in Formula
11 (6) was 0.8, since methyltrimethoxysilane was 80 mol%
12 and tetraethoxysilane was 20 mol%.

13

14 The elastic modulus in 10% compression of the
15 resulting composite particles was 1606kg/mm², and
16 residual displacement after 10% deformation was 4.7%.
17 The presence of Si-CH₃ bonds and siloxane units in the
18 composite particles, particles was confirmed by FT-IR
19 analysis, and the proportion of organic groups in the
20 composite particles, representing the quantity of
21 organic groups by the total weight of carbon atoms, was
22 9.2wt%.

23

24 When a B5 size TFT (abbreviation for Thin Film
25 Transistor) liquid crystal display was made by the
26 known method using these composite particles, the -
27 results obtained were similar to those in Example A1;
28 no pixel faults were noted.

29

30 EXAMPLE A4

31

32 Organic-inorganic composite particles of mean particle
33 diameter 6.15 μ m with a coefficient of variation of 6.7%
34 in particle diameter were obtained as in Example A2
35 except that heat treatment was performed in a mixed
36 atmosphere of nitrogen 95 vol% and oxygen 5 vol% at
37 450°C for 2 hours instead of at 750°C for 1 hour in

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1 Example A2.

2
3 The elastic modulus in 10% compression of the
4 resulting composite particles was 1440kg/mm², and
5 residual displacement after 10% deformation was 3.8%.
6 The presence of Si-CH₃ bonds and siloxane units in the
7 composite particles was confirmed by FT-IR analysis,
8 and the proportion of organic groups in the composite
9 particles, representing the quantity of organic groups
10 by the total weight of carbon atoms, was 10.1wt%.

11
12 When a B5 size STN was made by the known method using
13 these composite particles, the results obtained were
14 similar to those in Example A2.

15
16 EXAMPLE A5

17
18 Organic-inorganic composite particles of mean particle
19 diameter 1.97μm with a coefficient of variation of 6.9%
20 in particle diameter were obtained as in Example A1
21 except that methanol (154 parts by weight) and
22 n-butanol (153 parts by weight) were employed instead
23 of the methanol (307 parts by weight) in Example A1,
24 and ethyltrimethoxysilane (60 parts by weight) was
25 employed instead of methyltrimethoxysilane (60 parts by
26 weight), and heat treatment was performed at 750°C for
27 3 hours instead of 350°C for 3 hours.

28
29 The elastic modulus in 10% compression of the
30 resulting composite particles was 811kg/mm², and
31 residual displacement after 10% deformation was 3.2%.
32 The presence of Si-CH₂- bonds and siloxane units in the
33 composite particles was confirmed by FT-IR analysis,
34 and the proportion of organic groups in the composite
35 particles, representing the quantity of organic groups
36 by the total weight of carbon atoms, was 12.0 wt%.

37

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1 When a B5 size ferroelectric liquid display
2 was made by the known method using these composite
3 particles, the results obtained were similar to those
4 in Example A1.

5

6 EXAMPLE A6

7

8 Organic-inorganic composite particles of mean particle
9 diameter 4.55 μ m with a coefficient of variation of 6.8%
10 in particle diameter were obtained as in Example A3
11 except that heat treatment was performed in air at
12 200°C for 5 hours instead of at 600°C for 2 hours in
13 Example A3.

14

15 The elastic modulus in 10% compression of the
16 resulting composite particles was 630kg/mm², and
17 residual displacement after 10% deformation was 2.3%.
18 The presence of Si-CH₃ bonds and siloxane units in the
19 composite particles was confirmed by FT-IR analysis,
20 and the proportion of organic groups in the composite
21 particles, representing the quantity of organic groups
22 by the total weight of carbon atoms, was 14.3wt%.

23

24 When a B5 size TFT liquid crystal display was made by
25 the known method using these composite particles, the
26 results obtained were similar to those in Example A1;
27 no pixel faults were noted.

28

29

30 COMPARATIVE EXAMPLE A1

31

32 Particles were obtained as in Example A2 except that
33 heat treatment was performed at 80°C for 2 hours
34 instead of the heat treatment at 750°C for 1 hour in
35 Example A2.

36

37 The elastic modulus in 10% compression of the

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1 resulting particles was 312kg/mm², and residual
2 displacement after 10% deformation was 2.0%. The
3 proportion of organic groups in the particles,
4 representing the quantity of organic groups by the
5 total weight of carbon atoms, was 18wt%.

6
7 When a B5 size STN liquid crystal display was made by
8 the known method using these particles, the number that
9 needed to be dispersed was the same as for the current
10 organic polymer particle spacers.

11
12 COMPARATIVE EXAMPLE A2

13
14 Particles were obtained as in Example A3 except that
15 heat treatment was performed at 1150°C for 1 hour
16 instead of the heat treatment at 600°C for 2 hours in
17 Example A3.

18
19 The elastic modulus in 10% compression of the
20 resulting particles was 3380kg/mm², and residual
21 displacement after 10% deformation was 6.4%. The
22 proportion of organic groups in the particles,
23 representing the quantity of organic groups by the
24 total weight of carbon atoms, was 1wt%.

25
26 When a B5 size TFT liquid crystal display was made by
27 the known method using these particles, pixel faults
28 were produced due to breakage of the TFT array on the
29 substrate, and image unevenness was produced because
30 mechanical resilience was inadequate.

31
32 As regards the numbers of composite particles of the
33 present invention dispersed in the surface of the
34 liquid crystal displays obtained in the Examples above,
35 the numbers of composite particles of the present
36 invention were counted under an optical microscope in
37 arbitrary areas of 1mm² in each of 9 fields formed by

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57

1 equal division of the surface (on which to be
2 dispersed) into 3 widthwise and lengthwise, and
3 the mean value of the 9 fields was taken to be the
4 number dispersed. The results are given below.

5
6 Example A1 ... Number dispersed 73/mm²

7 Example A2 ... Number dispersed 70/mm²

8 Example A3 ... Number dispersed 69/mm²

9 Example A4 ... Number dispersed 68/mm²

10 Example A5 ... Number dispersed 69/mm²

11 Example A6 ... Number dispersed 66/mm²

12
13 COMPARATIVE EXAMPLE A3

14
15 When the current organic particle spacers described in
16 Example A1 were used in making a B5 size STN liquid
17 crystal display by the known method marked image
18 unevenness appeared, and it was unsatisfactory for
19 employment as a liquid crystal display. In this case
20 the number of spacers dispersed, according to the
21 counting method above, was 66/mm².

22
23 /home/mur/specs14/p14399B
24
25



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1 Claims

- 2
- 3 1. An organic-inorganic composite particle, which
- 4 comprises a particle body having an elastic
- 5 modulus of 350-3000 kg/mm² in 10% compression, a
- 6 residual displacement of 0-5% after 10%
- 7 deformation, a mean particle diameter of 0.5-50 μ m
- 8 and a coefficient of variation of 20% or less in
- 9 particle diameter, said particle body including:
- 10
- 11 an organic group; and
- 12
- 13 a polysiloxane framework which has in its molecule
- 14 an organosilicon containing a silicon atom
- 15 directly and chemically combined with at least one
- 16 carbon atom of said organic group.
- 17
- 18 2. An organic-inorganic composite particle as claimed
- 19 in Claim 1, wherein said organic group is at least
- 20 one monovalent group selected from the group
- 21 consisting of alkyl groups of 1-10 carbon atoms,
- 22 aryl groups of 6-10 carbon atoms and unsaturated
- 23 aliphatic residual group of 2-14 carbon atoms,
- 24 which may have a substituent group.
- 25
- 26 3. An organic-inorganic composite particle as claimed
- 27 in any one of Claims 1 to 2 which further
- 28 comprises a conductive layer formed on a surface
- 29 of said particle body.
- 30
- 31 4. An organic-inorganic composite particle as claimed
- 32 in any one of Claims 1 to 3, which further
- 33 comprises an adhesive layer formed on a surface of
- 34 said particle body.
- 35
- 36 5. An organic-inorganic composite particle as claimed



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1 in any one of Claims 1 to 4 which is coloured by
2 including in said particle body at least one
3 colorant selected from the group consisting of
4 dyes and pigments.

5

6 6. A liquid crystal display, which comprises:

7

8 a first electrode substrate;

9

10 a second electrode substrate arranged opposite to
11 said first electrode substrate;

12

13 a sealing material which binds said first
14 electrode substrate and said second electrode
15 substrate at their respective circumferential
16 edges;

17

18 a spacer for the liquid crystal display, which is
19 interposed between said first electrode substrate
20 and said second electrode substrate; and which
21 includes an organic-inorganic composite particle;
22 and

23

24 a liquid crystal packed into space defined by said
25 first electrode substrate and said second
26 electrode substrate and said sealing material;

27

28 wherein said organic-inorganic composite particle
29 is as claimed in any one of Claims 1 to 5.

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ABSTRACT

"Organic-Inorganic Composite Particles and Production
Process Therefor"

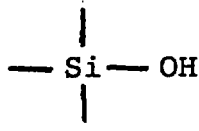
Organic-inorganic composite particles which include a (meth)acrylic resin framework and a polysiloxane framework having in its molecule an organosilicon containing a silicon atom directly and chemically combined with at least one carbon atom of the (meth)acrylic resin framework, and also containing 25 wt% or more of SiO_2 which constitutes the polysiloxane framework and has a mean particle diameter of $\geq 0.5 \mu\text{m}$. The particles have the mechanical resilience necessary to maintain a constant gap distance between a pair of members to be arranged with the correct gap distance between them, and the hardness and fracture strength necessary to maintain the gap constant with smaller numbers; and also do not readily cause physical damage to the members. The composite particles can be employed as spacers for a liquid crystal display as they stand or with an adhesive layer formed on the surface. The composite particles can also have a conductive layer formed on the surface, and be employed as conductive particles.

09 MAR 1998

1 Particles having a mean particle diameter within the
 2 range of mean particle diameter for the embodiment of
 3 the composite particles described above can be produced
 4 by setting the the water concentration, catalyst
 5 concentration, organic solvent concentration and
 6 starting materials concentration, the period of time of
 7 adding the starting materials, temperature and the seed
 8 particle concentration to 50-99.99wt%, 0.01-10wt%,
 9 0-50wt%, 0.1-30wt%, 0.001-500 hours, 0-100°C and
 10 0-10wt% respectively.

11
 12 Particles with a coefficient of variation in particle
 13 diameter within the above range for the coefficient of
 14 variation of mean particle diameter for the embodiment
 15 of the composite particles described above can be
 16 produced by setting the water concentration, catalyst
 17 concentration and organic solvent concentration within
 18 the ranges above.

19
 20 Next, the particles thus produced are isolated from the
 21 above suspension using a prior known method such as
 22 filtration, centrifugal separation or concentration at
 23 decreased pressure, etc., and heat treated at a
 24 temperature $\geq 100^{\circ}\text{C}$ and $\leq 1000^{\circ}\text{C}$, and preferably $\geq 300^{\circ}\text{C}$
 25 and $\leq 900^{\circ}\text{C}$ in order to dry and calcine them, to obtain
 26 the particle body of the embodiment of the organic-
 27 inorganic composite particles of the present invention.
 28 The main component of this particle body is
 29 polysiloxane which has in its molecule organosilicon in
 30 which at least one carbon atom in an organic group is
 31 directly and chemically combined with the silicon atom.
 32 With heat-treatment at a temperature lower than 100°C
 33 condensation of silanol groups represented by the
 34 following Formula (7) present in the siloxane units
 35 indicated by the aforementioned Formula (5)



...(7)