

Description**FIELD OF THE INVENTION**

5 This invention relates to processes for preparing mono-dispersed particles of metal oxides or metal hydroxides having an average particle diameter of about 0.1-10 μm and a sharp (narrow) particle size distribution, said particles being preferably used in particular as spacer particles for display devices.

BACKGROUND OF THE INVENTION

10 Particles of metal oxides or metal hydroxides having a narrow particle size distribution are useful for a variety of applications, for example, as raw materials for ceramics, fillers for resins, spacers for liquid crystal display devices and the like. Insulators for liquid crystal spacers may also be formed of particles of metal oxides or metal hydroxides, particularly those which have a relatively large particle diameter such as greater
15 than 0.1 μm and have a sharp particle size distribution.

That is, liquid crystal display devices are widely used as display devices for watches, computers or wall-hanging televisions. These liquid crystal display devices use liquid crystals, the molecular arrangement of which changes slightly by application of a slight voltage and the direction of deflection varies, and usually have a structure comprising two plate electrodes having interposed a liquid crystal layer therebetween.

20 In display devices of this kind, it is desirable that the liquid crystal layer is thin and as uniform as possible. If the thickness of the liquid crystal layer is not uniform, partial unevenness is brought about in the strength of electric field to be applied to the layer, with the result that a contrast ratio of the image varies depending on the local area of the liquid crystal layer, resulting irregularities of the image. Furthermore, the rate of response to an input signal will vary according to the thickness of the liquid crystal layer and to the
25 strength of electric field. If, therefore, the thickness of the liquid crystal layer is not uniform, a difference will develop in the rate of response, and sharp images will not be obtained.

For the reasons mentioned above, it has been the usual practice in the manufacture of liquid crystal display devices that a spacer consisting of a thin insulator is interposed between two plate electrodes and liquid crystal is filled therebetween to form a thin and uniform liquid crystal layer between the two plate
30 electrodes.

As spacers adopted in the liquid crystal display devices mentioned above, there have been used spherical aluminum oxide for abrasives which have been classified into particles of 2-10 μm , glass fibers of 2-10 μm in diameter which have been cut into pieces of 50-100 μm in length, or a synthetic resin such as benzoguanamine formed into spheres of 2-10 μm .

35 In the liquid crystal display devices employing such conventionally known spacers, no particularly serious problem is brought about when the devices are of small size, but such problems as mentioned below are encountered in the devices when they are of large size.

(a) It is necessary to vary delicately the thickness of liquid crystal layer according to the kind of liquid crystal used, but it is practically impossible to control the shape of spacer capable of coping with this
40 slight variation in thickness of the liquid crystal layer.

(b) It is not possible to provide a liquid crystal layer having a uniform thickness because the spacer particles have a broad particle size distribution, with the result that irregularities occur in the displayed images or abnormal color tone is brought about in certain cases.

(c) Where a strong dielectric liquid crystal is used, it is necessary that the liquid crystal layer should
45 have a thickness of about 1/2 μm . However, no spacer is capable of controlling the thickness of such a liquid crystal layer.

(d) There are some cases wherein spacer particles in the liquid crystal layer aggregate and become visible to the naked eye in the displayed images or spacers having a long axis of 10-50 μm become visible themselves to the naked eye in the displayed images.

50 (e) When spacer particles used are not spherical, the spacer sometimes damages transparent electrodes, making the device defective.

(f) Where a resin is used as a spacer, it tends to change shape when heat or pressure is applied, whereby a liquid crystal layer having a uniform thickness cannot be obtained.

There is thus a need for spacer particles consisting of metal oxides or metal hydroxides for use in liquid
55 crystal display devices capable of solving the above-mentioned problems.

If black spacer particles consisting of metal oxides for use in liquid crystal devices were available, the display devices would be excellent particularly in the contrast of the displayed images, and hence such particles are highly desirable.

Furthermore, spacer particles coated on the surface thereof with synthetic resins do not move in the display devices, and hence are also desirable.

In preparing particles of metal oxides or metal hydroxides mentioned above, for example, silica particles, there has heretofore been known a process wherein silicic acid obtained from water-glass is allowed to grow in a liquid to produce a silica sol having dispersed particles of silica having an average particle diameter of 0.05-0.1 μm . However, micelles are formed if the particles in the sol have a particle diameter of less than 0.05 μm , and if the particles have a particle diameter exceeding 0.05 μm , the particle size distribution becomes sharp but the particles mono-dispersed in the sol are few in number. Moreover, this process involves such problems that it is difficult to obtain particles having a particle diameter of greater than 0.1 μm as it takes a long period of time such as from several days to scores of days at elevated temperatures, and, at the same time, new seeds are apt to form in the reaction system during the particle growth stage and consequently the particle size distribution becomes broad. Accordingly, it is not possible, according to this process, to obtain on a commercial scale mono-dispersed particles having a particle diameter of greater than 0.1 μm and a sharp particle size distribution.

There has also been known a process for obtaining metal oxide or metal hydroxide particles having a particle diameter of about 0.05-2 μm by hydrolyzing metal alkoxides in the presence of alkali catalysts in a water-alcohol solvent system. This process has such advantages that there is no need to keep the reaction system at elevated temperatures and particles having a particle diameter of about 1-2 μm and a relatively sharp particle size distribution are obtained by the reaction for several hour to scores of hours. In the process, however, there are such problems that when particles to be obtained by this process are, for example, those of silica, titania or zirconia, the particles having such properties as mentioned above are obtained only when the particle concentration in the reaction system is less than 0.5% by weight in terms of oxide concentration, and consequently the productivity decreases, large amounts of organic solvent such as alcohol are needed and the cost of production increases. In this process, moreover, when silica particles are required, the diameter of the particles obtained is 0.2-0.3 μm at the most. If particles having a diameter of greater than 0.5 μm are required, the starting metal alkoxide must have a slow rate of hydrolysis, i.e. alkoxides containing long ester groups having about 5-7 carbon atoms. However, such alkoxides are expensive, and their use involves such problems that, because of a slow rate of hydrolysis, a long period of time is required for carrying out the reaction, the alkoxides can be affected by the composition of the reaction system, reaction temperature, stirring method, stirring speed, etc., and mono-dispersed metal oxide or metal hydroxide particles of stable quality cannot be obtained.

EP-A-0216278 describes the preparation of spherical SiO_2 particles by hydrolytic polycondensation of a tetraalkoxysilane to form a sol, followed by conversion of the particles obtained to the desired size by the addition of further tetraalkoxysilane. We have found however that this method results in some aggregation of the particles, and satisfactory mono-dispersed particles cannot be obtained.

Under these circumstances, the present inventors conducted extensive research with the view to solving the above-mentioned problems associated with the prior art and obtaining particles of metal oxides or metal hydroxides which have a large diameter, are mono-dispersed and are usable particularly as spacer particles for display devices. We have found that such particles can be obtained in a short time by carrying out hydrolysis of metal alkoxides under specific conditions using a seed which becomes a nucleus of particle growth to allow the seed to grow.

OBJECT OF THE INVENTION

The present invention is intended to solve such problems associated with the prior art as mentioned hereinbefore, and an object of the invention is to provide a process for preparing mono-dispersed particles, through which metal oxide or metal hydroxide particles which are large in particle diameter, sharp in particle size distribution and mono-dispersed and which are usable particularly as spacer particles for display devices are obtained at low cost of production.

SUMMARY OF THE INVENTION

A first process for preparing mono-dispersed particles in accordance with the present invention is characterised in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds to effect particle growth thereof and subsequently the resulting particles are separated, if necessary, from the dispersion.

A second process for preparing mono-dispersed black particles in accordance with the present invention is characterised in that the particles obtained in the first process are subjected to heat treatment at a temperature above 250 ° C.

A third process for preparing particles coated with a synthetic resin in accordance with the present invention is characterised in that the particles obtained in the first process are coated on their surfaces with a synthetic resin.

Furthermore, the fourth process for preparing particles coated on the surface thereof with a synthetic resin in accordance with the present invention is further characterised in that the particles obtained in the second process are coated on the surface thereof with a synthetic resin.

In the processes for preparing mono-dispersed particles in accordance with the present invention, a metal alkoxide is hydrolyzed by adding it to a water-alcohol system containing seeds and a hydrolysis product of said metal alkoxide is allowed to attach to the seeds, thereby effecting particle growth of the seeds and hence form large diameter particles, sharp in particle size distribution and mono-dispersed in a highly efficient manner. In addition, the production cost of the particles can be reduced because the particle concentration in the reaction system can be increased.

Further, in the process for preparing black particles in accordance with the present invention, the particles obtained in the manner now described are heat treated at a temperature above 250 ° C., and when the black particles thus obtained are used as spacers in display devices, sharp and clear displayed images are obtained.

Furthermore, in the process for preparing particles coated on the surface thereof with a synthetic resin in accordance with the present invention, the particles obtained do not move when used as spacers in display devices.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a scanning type electron microscope photograph (magnification; 10,000) showing the shape of particle obtained in accordance with the present invention, Fig. 2 is a cross-sectional view of a particle coated on the surface thereof with a synthetic resin, and Fig. 3 is a schematic drawing showing the state of adhesion between a substrate and particles when the resin coated particles are used as spacer particles.

DETAILED DESCRIPTION OF THE INVENTION

The processes for preparing particles in accordance with the present invention are illustrated below in more detail.

In the present invention, a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed is first prepared. The seeds to be dispersed in the water-alcohol system are metal oxide or metal hydroxide particles, but other particles which are substantially uniform in particle diameter are also usable. The particles used as seeds are preferably those which have a particle diameter as uniform as possible, for example, ranging from about 0.05 to about 9 μ m.

The seeded water-alcohol system may be prepared by adding the seed to a water-alcohol mixture or by forming the seed in the water-alcohol system. We prefer to use systems in which the seeds have been formed by hydrolysing a metal alkoxide in a water-alcohol mixture. The process for forming the seeds has been described, for example, in "Particles and Particle Metallurgy", 23, (4), 19-24 (1976) or Journal Colloid & Interface Sci., 26, 62-69 (1968).

The water-alcohol dispersion is made stable by addition of alkali so that the seeds do not aggregate (hereinafter the thus stabilized dispersion called a "heel sol"). If the dispersion is not stabilized by the addition of alkali, the seeds in the dispersion aggregate and precipitate in certain cases. When the seeds aggregate, the hydrolysis product of the metal alkoxide attaches to the joint portion of the aggregated particles (the neck portion) and therefore particles of uniform diameter cannot be obtained.

The alkalis used for stabilizing the dispersions include ammonia, aqueous ammonia, alkali metal hydroxides such as sodium hydroxide, quaternary ammonium salts, amines, etc., which may be used either singly or in combination.

The alcohol concentration in the seeded water-alcohol system is preferably 35-97% by weight. The alcohol used include lower alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol, isobutyl alcohol, etc. Mixtures of these lower alcohols are also usable.

Further, there can also be used other organic solvents in addition to water and alcohol, such as organic solvents which are compatible with water and alcohol as well as with metal alkoxides.

The concentration of the seed in the dispersion of water-alcohol system is preferably 0.05-20.0% by weight in terms of oxide concentration. The use of a seed concentration of less than 0.05% by weight is not preferable, because new seeds will sometimes occur in the subsequent step of attaching the hydrolysed product of the alkoxide to the seed originally present, with the result that the particle size distribution of the resulting particles becomes broad. On the other hand, the use of a seed concentration exceeding 20.0% by weight is also not preferable, because the particles aggregate in the step of attaching the hydrolysed metal alkoxide product to the seed.

Next, to a heel sol, which is the seeded water-alcohol system stabilized with alkali, while keeping said heel sol under alkaline conditions, is added a metal alkoxide which is then hydrolyzed, and the seed particles are allowed to grow by attaching the hydrolysed product thereonto.

Any metal alkoxide may be used, for example an alkoxide of Si, Ti, Zr, Al, Sn, Mg and Zn. The alkyl groups are preferably those having 1-7 carbon atoms, desirably 1-4 carbon atoms. Such metal alkoxides may be used after dilution with a diluent such as alcohol, or in the form of a stock solution thereof.

It is preferable that the metal alkoxide is added together with a water-alcohol mixture to the dispersion (heel sol). The metal alkoxide and the water-alcohol mixture are preferably added to the heel sol gradually. When the metal alkoxide is added to the heel sol, the metal alkoxide begins to hydrolyze and at that time the pH suddenly changes. When the heel sol is no longer alkaline, the seed particles aggregate or new seeds occur, and consequently the particle size distribution of the resultant particles becomes undesirably broad. Therefore, the heel sol is kept under alkaline conditions when the metal alkoxide is added thereto. The heel sol has a pH of 10-13. In order to keep the heel sol alkaline, alkali is added thereto, for example ammonia, aqueous ammonia, amines, alkali metal hydroxides and quaternary ammonium salts which maybe used either singly or in combination.

The temperature employed in hydrolyzing the metal alkoxide is not particularly limited, but when a temperature above the boiling point of water or alcohol is adopted, preferably pressure is applied to the heel sol so as to retain its liquid phase. In this case, however, the hydrolysis of the metal alkoxide is preferably carried out at a temperature below the critical temperature of alcohol or the like in the reaction system because the composition in the liquid phase will change sometimes when the temperature adopted is above said critical temperature.

In the manner now described, the metal alkoxide hydrolysis product is allowed to attach onto the seeds, which thereby. In that case, the concentration of the grown particles in the reaction system is preferably 0.05-20.0% by weight, more preferably 0.05-15.0% by weight in terms of oxide concentration. When the particle concentration is less than 0.05% by weight, the productivity is low and large amounts of alcohol are needed, and thus the use of such a low concentration is not economical and, on the other hand, the use of such concentrations as exceeding 20% by weight is not preferable since the particles aggregate during growth thereof and a particle size distribution of the particles obtained becomes broad.

In attaching the metal alkoxide hydrolysis product onto the seeds, the alcohol concentration in the reaction system is preferably so adjusted to become 35-97% by weight. The use of the alcohol concentration of less than 35% by weight is not preferable as the compatibility of the alcohol with the metal alkoxide is poor and the emulsification thereof is brought about, with the result that the seed particles aggregate or the particles obtained are not spherical but indefinite in shape. On the other hand, the use of an alcohol concentration exceeding 97% by weight is not preferable as the rate of hydrolysis of the metal alkoxide becomes excessively slow. The alcohol concentration in the reaction system can be controlled by the addition of the metal alkoxide together with water and alcohol to the reaction system. In this case, it is preferable that the alcohol is added in a proportion of 0.4-1.1 mol based on the metal alkoxide, and water is added in a proportion of 2.0-24.0 mol based on the metal alkoxide.

The particles dispersed in the water-alcohol system obtained in the above manner are spherical with a particle diameter of about 0.1-10 μm , sharp in particle size distribution and mono-dispersed without aggregation. The particle concentration in terms of oxide concentration is 0.05-20.0% by weight, thus it is possible to markedly increase the particle concentration in the dispersion in comparison with the prior art process for preparing particles using metal alkoxides. Accordingly, in accordance with the present invention, not only the productivity of the particles can be enhanced but also a reduction in cost of production can be obtained.

Furthermore, the particle concentration can be increased to about 60.0% by weight by concentration of the solids obtained after subjecting the dispersion obtained to solid-liquid separation. In this case, the liquid component obtained by the solid-liquid separation can be used again as the reaction liquid.

When the dispersion obtained according to the present invention is aged by the addition of stabilizers such as alkali in order to improve the stability of the particles, the particles do not aggregate or do not undergo any other change over a long period of time. Furthermore, the alcohol in the dispersion may be

substituted with other organic solvents.

The particle dispersion obtained in the manner as mentioned above are spherical with a particle diameter of about 0.1-10 μm , sharp in the particle size distribution thereof ($\pm \sigma \leq 0.5$), and mono-dispersed in the dispersion. According to the process for preparing particles as mentioned above, it is possible to control the particle diameter of the resulting particles to any desired value falling within the range of from 0.1 to 10 μm .

Subsequently, when the dispersion is dried in the usual way, spherical particles are obtained having good dispersibility. The particles obtained at this stage are still white and may be used as spacer particles for display devices.

In accordance with the present invention, moreover, the water in the dispersion may be replaced with an organic solvent, and the resulting dispersion can also be used as spacer in the liquid crystal layer without separating said particles therefrom.

The white particles may be subjected to heat treatment at a temperature above 250 °C., preferably from 250 ° to 1000 °C, in an air atmosphere or in an atmosphere of inert gas, whereby they change in colour from white to black. The reason why the black particles are obtained is considered to be as follows. That is, organic matter such as unreacted metal alkoxide is present in the inside of particles prior to heat treatment, and when heated to a temperature above 250 °C, decompose or carbonize, whereby the particles blacken.

The use of a temperature below 250 °C. is not preferable as a long period of time is required to blacken the white particles, though they eventually blackens. On the other hand, the use of a temperature exceeding 1000 °C. is also not preferable as sintering occurs between the particles.

In general, the blackening takes place at a relatively low temperature range of from 250 ° to 1000 C. when the white particles are small in particle diameter, but higher temperature are required with increasing the particle diameter.

In the present invention, furthermore, when the metal alkoxide is added to the seeded water-alcohol system, an organic substance capable of dissolving or dispersing in said system may be added together with said metal alkoxide and this organic substance becomes attached, together with the metal alkoxide hydrolysis product, onto the seed. When particles obtained are subjected to heat treatment at a temperature above 250 °C., the black particles obtained are found to be further improved in black color tone. Alternatively, the white particles obtained by drying the dispersion are immersed, prior to heat treatment, in a solution of the organic substance (to attach said organic substance onto said particles) and the particles thus treated are the subjected to heat treatment, and the black particles further improved in black color tone are obtained.

The black particles obtained in the manner as mentioned above usually have a Y value of less than 10%, said value corresponding to brightness of color represented by tristimulus values X, Y, Z of color as measured on the basis JIS Z 8701-82. Thus the black particles are excellent in blackness. On that account, the black particles obtained by the present invention are used spacers for liquid crystals in addition to their application to ceramic raw materials, fillers for resin, etc. Particularly, when the black particles of the present invention are used as spacers for liquid crystals, there is obtained such an excellent effect that the displayed images obtained are sharp and clear.

The process for preparing particles coated on the surface thereof with a synthetic resin in accordance with the present invention is illustrated hereinbelow. Such particles are obtained by coating the white or black insulant particles obtained in the manner as aforesaid. Any coating method may be used so long as they are capable of coating the insulant particles on the surface almost uniformly with synthetic resin powders without causing aggregation of the coated insulant particles. As an example, the following method may be mentioned.

When insulant particles are placed under a dry atmosphere, the particles are electrostatically charged. For instance, when a metal of the metal alkoxide used in the preparation of particles is silicon, titanium, zirconium or tin, the resulting particles are negatively charged, and when the metal used is aluminum, magnesium or zinc, the resulting particles are positively charged. The particles thus charged are coated by adsorption of spherical synthetic resin powders having the opposite charge. In this case, however, the synthetic resin powders are held almost on the whole surface of the particles, but because of a weak electrostatic force of attraction, they are apt to fall off. Then, to increase the bonding force therebetween, an impact force is applied to the particles to fuse part of the synthetic resin powders by means of the heat generated on application of the impact force, whereby the synthetic resin powders adhere to one another and, at the same time, to the insulant particles. To apply the impact force, the particles may be charged into a grinder such as a ball mill.

When the particles thus coated on the surface thereof with a synthetic resin powders are used, for example, as spacer particles for display devices, the spacer particles are firmly fixed by means of the

synthetic resin to electrode bases or the like of the display devices and consequently the spacer particles used do not move.

As shown in its schematic drawing of Fig. 2, in each the particles 1 used as spacer particles for display devices, each of inorganic insulant particles 2 has been coated on the surface thereof with synthetic resin powder 3.

This insulant particle 2 has been coated practically the whole surface thereof with the synthetic resin powders 3, but it is not always necessary that the particle is wholly coated.

As shown in the schematic drawing of Fig. 2, the synthetic resin powders 3 may retain their spherical shape and are cemented to one another, or in certain case they may be partly fused to form a thin film.

When a diameter of the insulant particle 2 is taken as D, a diameter d of the synthetic resin powders 3 covering the insulant particle 2 is D/5 or less, preferably less than D/7, and more particularly the diameter of the synthetic resin powder is desirably 0.01-2.0 μm , preferably 0.01-1.0 μm . The use of this synthetic resin powder having a diameter d exceeding D/5 is not preferable since the synthetic resin powder 3 sometimes falls off under the weight thereof from the surface of the insulant particle 2.

The diameter D of insulant particle corresponds to a diameter of spacer particle, and said diameter D is preferably 0.1-10 μm .

In preparing the synthetic resin powders 3, there are used thermoplastic resins having a glass transition point of below 200°C. or thermosetting resins having a curing temperature of below 200°C. The use of thermoplastic resins having a glass transition point above 200°C. or thermosetting resins having a curing temperature of above 200°C. is not preferable since elevated temperatures should be adopted when spacer particles are fixed in display devices.

The particles thus obtained, when used as spacer particles for liquid crystal devices in the manner as will be mentioned later, are incorporated into thermosetting sealing resins and provided at the circumferential portions of substrates of the display devices and, at the same time, are provided at the liquid crystal layer portions wherein no sealing resin is provided. In this case, the two substrates are bonded together by heating and at the time of heating, the synthetic resin powders 3 coated on the surface of the insulant particles 2 fuse and are fixed, as shown in Fig. 3, through thin synthetic resins layers 4, to a pair of substrates 5a and 5b for the display device. In this case, the insulant particles 2 are bonded by heating, and hence no surplus synthetic resin is present therebetween, leaving the very thin synthetic resin films 4 therebetween. It is considered that the fused synthetic resin gather around the side portions 6 of insulant particles 2. In the present invention, accordingly the insulant particles 2 are almost equal in size to the spacer particles.

All particles prepared by the processes of the present invention as mentioned hereinbefore, when used as spacer particles for display devices, exhibit such excellent characteristics that they have a sharp particle size distribution, can controlled to have any desired particle size and can cope with delicate change in thickness because they do not aggregate, have a uniform thickness and are not visible by the naked eye.

Further, the particles prepared by the processes of the present invention do not damage transparent electrodes because they are spherical in shape, and also they do not change in shape by application of heat or pressure, and further they have such an effect that spacers high in purity are obtained therefrom since the particles of the present invention start from metal alkoxide.

Display devices in which the particles prepared by the processes of the present invention are preferably used include, in addition to liquid crystal display devices, electrochromic displays (ECD), plasma displays (PDP), liquid crystal printers, touch pannels, photomodulating elements, etc.

To assemble display devices such as liquid crystal devices using the dispersed particles obtained by the processes described hereinbefore, the methods, per se, known are applicable.

The present invention is illustrated below with reference to examples, but the invention is in no way limited thereto.

Example 1

A mixture of ethyl alcohol (486.50 g) and water (398.05 g) was kept with stirring at 35°C., and in this was dissolved ammonia gas (71.72 g). The resulting mixture was charged with 28% ethyl silicate (ethanol solution of 28% by weight of tetraethoxysilane in terms of SiO_2) (17.39 g) and thereafter stirred for 2 hours to obtain a white turbid liquid (I) in which 0.5% by weight, in terms of SiO_2 , of seed particles had been dispersed.

To this white turbid liquid (I) was immediately added an aqueous solution (3.3 g) in which NaOH (0.033 g) had been dissolved, and the mixture was subjected for 10 minutes to supersonic wave treatment to obtain a heel sol comprising a water-alcohol dispersion in which the seed particles had been dispersed.

The thus obtained heel sol (974 g) was kept with stirring at 35°C., while controlling the pH of the heel sol with ammonia gas to 11.5, and thereto were added gradually and simultaneously over 19 hours a mixture of ethyl alcohol (1508.6 g) and water (3006.8 g), and 28% ethyl silicate (2268 g). After completion of the addition, to the resulting mixture was added an aqueous solution (204 g) in which NaOH (2.04 g) had been dissolved, and the mixture was heated at 70°C. and kept at that temperature for 2 hours.

Physical properties of the dispersion thus obtained are shown in Table 1.

A shape of the particles obtained was examined by means of a scanning type electron microscope (SEM) to obtain a photograph (magnification: 10000) as shown in Fig. 1.

10 Example 2

Example 1 was repeated except that the mixture of ethyl alcohol and water, and the 28% ethyl silicate were added over 2 hours to the heel sol.

Physical properties of the dispersion obtained are shown in Table 1.

15 Example 3

Example 1 was repeated except that a mixture of ethyl alcohol (1507 g), water (2253 g) and 28% aqueous ammonia (1026 g), and 28% ethyl silicate (2268 g) were simultaneously added over 10 minutes to the heel sol in place of the addition of the mixture of ethyl alcohol and water, and the 28% ethyl silicate to the heel sol over 19 hours.

Physical properties of the dispersion obtained are shown in Table 1.

25 Example 4

Example 1 was repeated except that ethyl alcohol (284 g), water (443 g) and 28% ethyl silicate (426 g) were added to the heel sol (184 g) while adjusting the heel sol to pH 12.0.

Physical properties of the dispersion obtained are shown in Table 1.

30 Example 5

Example 4 was repeated except that the amount ethyl alcohol added was 112 g and the water added was 164 g, while the heel sol was adjusted to pH 11.0.

Physical properties of the dispersion obtained are shown in Table 1.

35 Example 6

Example 1 was repeated except that there was used a seed dispersion (184 g) obtained by dispersing SiO₂ having an average particle size of 1 μm in a water-alcohol mixture (a weight ratio of 55/45 of ethyl alcohol/water) so that SiO₂ in the solution amounts to 0.5% by weight, and to this dispersion were added ethyl alcohol (266 g), water (521 g) and 28% ethyl silicate (467.4 g).

Physical properties of the dispersion obtained are shown in Table 1.

45 Example 7

Example 1 was repeated except that there was used a seed dispersion (184 g) obtained by dispersing SiO₂ having an average particle diameter of 8 μm in a water-alcohol mixture (a weight ratio of 55/45 of ethyl alcohol/water) so that SiO₂ in the solution amounts to 0.5% by weight, and to this dispersion were added over 3 hours ethyl alcohol (7.1 g), water (7.8 g) and 28% ethyl silicate (3.49 g).

Physical properties of the dispersion obtained are shown in Table 1.

50 Example 8

To water (81.6 g) having dispersed therein NaOH (0.006 g) was added silica sol (2.3 g)(SI-80P, a product of CATALYSTS & CHEMICALS INDUSTRIES CO.,LTD) and then ethyl alcohol (100.7 g), followed by stirring, and the heel sol obtained was kept at 35°C. To this heel sol were added over 19 hours gradually and simultaneously, while controlling the dispersion to pH 11.5 with ammonia gas, a mixture of ethyl alcohol (741 g) and water (676 g), and 28% ethyl silicate (407.4 g). After completion of the addition,

the dispersion was charged with an aqueous solution (37.0 g) having dissolved therein NaOH (0.37 g), heated at 70 °C., and kept at that temperature for 2 hours.

Physical properties of the dispersion obtained are shown in Table 1.

Example 9

A mixture of isopropyl alcohol (486.5 g) and water (398.05 g) was kept with stirring at 35 °C., and in this was dissolved ammonia gas (71.72 g). The mixture was charged with titanium tetrapropoxide (17.39 g), and stirred for 2 hours while adjusting the solution to pH of a level above 11, whereby a white turbid liquid [II] in which particles had been dispersed was obtained.

A heel sol was prepared by diluting the thus obtained white turbid liquid [II] with isopropyl alcohol so that the particles in the liquid amounts to 0.5% by weight in terms of TiO₂. To this heel sol (184 g) kept with stirring at 35 °C. were added over 4 hours gradually and simultaneously, while controlling the dispersion to pH 11.5 with ammonia gas, a mixture of isopropyl alcohol (166.5 g), water (311 g) and titanium tetrapropoxide (281.3 g). After completion of the addition, the dispersion was heated at 70 °C. and kept at that temperature for 2 hours.

Physical properties of the dispersion obtained are shown in Table 1.

Example 10

A mixture [A] (486.5 g), of n-butyl alcohol/isopropyl alcohol (weight ratio = 1/1) and water (398.05 g), was kept with stirring at 35 °C. and in this mixture was dissolved ammonia gas (71.72 g). The mixture was charged with zirconium tetrabutoxide (17.39 g) and stirred for 2 hours, while adjusting the pH of above 11, whereby a white turbid liquid [III] in which particles had been dispersed was obtained.

A heel sol was prepared by diluting the thus obtained white turbid liquid [III] with the above-mentioned mixture [A] so that the particles in the liquid amount to 0.5% by weight in terms of ZrO₂. The same procedure as in Example 9 was then followed except that to this heel sol (184 g) were added the above-mentioned mixture [A] (166.5 g) and zirconium tetrabutoxide (281.3 g).

Physical properties of the dispersion obtained are shown in Table 1.

Comparative Example 1

Example 1 was repeated except that aqueous NaOH solution as alkali was not added to the white turbid liquid [I].

Physical properties of the dispersion obtained are shown in Table 1.

Comparative Example 2

Example 4 was repeated except that the amount of ethyl alcohol added was 115 g, the amount of water added was 615 g, and no control of the pH with ammonia gas was effected on addition of the 28% ethyl silicate to the heel sol.

Physical properties of the dispersion obtained are shown in Table 1.

Comparative Example 3

Example 8 was repeated except that to water (81 g) was added silica sol (2.3 g)(SI-80P, a product of CATALYSTS & CHEMICALS INDUSTRIES CO.,LTD) and also ethyl alcohol (100.7 g), followed by stirring, and the mixture thus obtained was kept at 35 °C. without addition thereto of alkali.

Physical properties of the dispersion obtained are shown in Table 1.

Example 11

A mixture of ethyl alcohol (96.8 g) and water (0.186 g) was kept with stirring at 15 °C., and in this was dissolved ammonia gas (2.72 g). This mixture was charged with 28% ethyl silicate (0.375 g) and then stirred for 5 hours to obtain a white turbid liquid (IV) in which seed particles corresponding to 0.1% by weight in terms of SiO₂ had been dispersed. To this white turbid liquid (IV) was immediately added 0.06 g of an aqueous solution (0.6 g) of NaOH (0.006 g), and the mixture was subjected for 10 minutes to supersonic wave treatment to obtain a heel sol in which the seed particles had been dispersed in the water-alcohol

dispersion. To the thus obtained heel sol (100 g) kept with stirring at 35 °C., while controlling the heel sol to pH 11.5 with ammonia gas, were added over 19 hours gradually and simultaneously a mixture of ethyl alcohol (4558.7 g) and water (47.2 g), and 28% ethyl silicate (16.5 g). After completion of the addition, the dispersion was charged with an aqueous solution (3.0 g) of NaOH (0.03 g) and heated at 70 °C. and kept at that temperature for 2 hours.

Physical properties of the dispersion obtained are shown in Table 1.

Example 12

In a water-alcohol mixture (3238 g) with an ethyl alcohol/water weight ratio of 89/11 was dissolved ammonia gas (90.8 g), and to this was added SiO₂ particles (138.7 g) having an average particle diameter of 3.5 μm, whereby a seed dispersion was obtained, in which the seed particles amount to 4% by weight in terms of SiO₂. To this seed dispersion was immediately added an aqueous solution (90 g) of NaOH (0.9 g), and the mixture was subjected for 10 minutes to supersonic wave treatment, whereby a heel sol comprising a water-alcohol dispersion having dispersed therein the seed particles. To the thus obtained heel sol kept with stirring at 35 °C., while controlling the pH to 12.5 with ammonia gas, were added gradually over 5 hours a mixture of ethyl alcohol (1544.2 g) and water (263.5 g), and simultaneously with 28% ethyl silicate (557.4 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (101 g) of NaOH (1.01 g), heated at 65 °C. and kept at that temperature for 1 hour.

Physical properties of the dispersion obtained are shown in Table 1.

Example 13

In a water-alcohol mixture (5714 g) with an ethyl alcohol/water weight ratio of 64.5/35.5 was dissolved ammonia gas (258 g), and to this was added SiO₂ particles (248.8 g) having an average particle diameter of 5.0 μm to obtain a seed dispersion in which the seed particles amount to 4% by weight in terms of SiO₂. To this seed dispersion was immediately added an aqueous solution (161 g) of NaOH (1.61 g), and the resultant mixture was subjected for 10 minutes to supersonic wave treatment to obtain a heel sol in which the seed particles had been dispersed in a water-alcohol dispersion. The thus obtained heel sol was charged with stirring into an autoclave, a pressure of 7.5 kg/cm² was applied thereto with nitrogen gas, and the heel sol was then kept at 120 °C. To the heel sol thus kept were added gradually over 5 hours a mixture of ethyl alcohol (305.1 g), water (764.7 g) and dissolved ammonia gas (68.3 g), simultaneously with 28% ethyl silicate (647 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (117 g) of NaOH (1.17 g), heated at 150 °C., and kept at that temperature for 1 hour.

Physical properties of the dispersion obtained are shown in Table 1.

The average particle size (D_p) of spherical particles present in the dispersions obtained in the foregoing examples and comparative examples was measured by means of an optical transmission type particle size measuring instrument (manufactured and sold by Horiba Seisakusho K.K.), and the particle size and state aggregation of said particles were examined by means of a scanning type electron microscope (SEM). Furthermore, uniformity of particle size distribution was represented by a coefficient of uniformity (C_v) indicated by the following equation.

$$\text{Coefficient of uniformity } (C_v) = \frac{D_2 - D_1}{2D_p}$$

- D_1 : Particle diameter of the particles when the cumulative total of the particles was 16% by weight.
 D_2 : Particle diameter of the particles when the cumulative total of the particles was 84% by weight.
 D_p : Average particle diameter.

Table 1

	D _p		Coefficient of uniformity C _v	Stage of Aggregation
	*1 SEM(μm)	*2 CaPa(μm)		
Example 1	0.9	1.0	0.10	o
2	0.9	0.9	0.10	o
3	1.4	1.5	0.19	o
4	1.2	1.2	0.11	o
5	1.1	1.1	0.20	o
6	5.0	5.0	0.15	o
7	9.9	10.0	0.19	o
8	0.3	0.35	0.15	o
9	1.1	1.1	0.18	o
10	1.0	1.0	0.10	o
11	1.5	1.5	0.02	o
12	4.5	4.6	0.08	o
13	6.0	6.1	0.12	o
Comparative Example 1	1.0	2.8	-	x
2	1.2	1.9	-	x
3	0.3	0.8	-	x

o : No state of aggregation is observed.

x : Aggregation is observed.

*1 : Value as measured by means of SEM.

*2 : Value as measured by means of the optical transmission type particle size measuring instrument.

The fact that no substantial difference is observed between particle sizes as measured by SEM and the optical transmission type particle size measuring instrument means that the particles obtained are mono-dispersed.

Accordingly, it is understood from Table 1 that the particles obtained in the present invention are mono-dispersed and moreover the coefficient of uniformity C_v thereof is small, and also from Fig. 1 that the present particles have excellent uniformity.

Example 14

In a mixture of ethyl alcohol (487 g) and water (389 g) kept with stirring at 35°C. was dissolved ammonia gas (71.7 g). This solution was charged with 28% ethyl silicate (17.4 g) and then stirred for 2 hours to obtain a white turbid liquid in which seed particles corresponding to 0.5% by weight in terms of SiO₂ had been dispersed.

To this white turbid liquid was immediately added an aqueous solution (3.3 g) of NaOH (0.03 g), whereby a heel sol (A) comprising the seed particles dispersed in a water-alcohol dispersion was obtained.

To 97 g out of the thus obtained heel sol (A) kept with stirring at 35°C., while controlling the heel sol (A) to pH11.5 with ammonia gas, were added gradually over 19 hours a mixture of ethyl alcohol (455 g) and

water (886 g), simultaneously with 28% ethyl silicate (570 g). After completion of the addition, the dispersion was charged with an aqueous solution (103 g) of NaOH (1.0 g), heated at 70°C., and kept at that temperature for 2 hours, whereby a dispersion (I) was obtained. This dispersion (I) was dried at 200°C. to obtain powder particles.

5 The thus obtained powder particles (1 g) were dispersed in a sealing resin (100 g) (an epoxy resin, produced and sold by Mitsui Toatsu Chemicals, Inc.) to prepare an ink composition. Substrates for large liquid crystal display devices were obtained by printing the thus obtained ink composition on the circumference of the orientation membrane of a laminate comprising the glass substrate on which transparent electrodes and orientation membrane had been formed.

10 Subsequently, in 1 litre of ethyl alcohol was dispersed the powder particles (0.01 g) obtained in the manner as above, and the dispersion thus obtained was sprayed over portions of the substrate for a large crystal display device placed in a spraying chamber kept at 60°C. and 3 % humidity, said portions being not provided with the sealing resin. The substrate was then subjected to predrying at 90°C. for 30 minutes, and then placed upon the surface of another substrate for a large liquid crystal display device, comprising a
15 glass substrate on which transparent electrodes and an orientation membrane had been formed. The substrates thus assembled was heated for 1 hour at 150°C. under a pressure of 3 kg/cm² to cure the resin, whereby 100 pieces of cells for large liquid crystal display devices were prepared.

Into the portion of the thus obtained cells for large liquid crystal display devices, said portion not being provided with the sealing resin, was injected liquid crystals as will be mentioned below, whereby a large
20 liquid crystal display device was obtained.

Example 15

To the dispersion (I) (114 g) kept with stirring at 35°C. were added ethyl alcohol (63 g) and water (51
25 g). To the resulting mixture, while controlling the pH at 11.5 with ammonia gas, were added gradually over 19 hours a mixture of ethyl alcohol (638 g) and water (814 g), simultaneously with 28% ethyl silicate (325 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (65 g) of NaOH (0.7 g), heated at 70°C., and kept at that temperature for 2 hours to obtain a heel sol (B). To this heel sol (B) (94.6 g) kept with stirring at 65°C. were added ethyl alcohol (116 g) and water (95 g). To the
30 resulting mixture, while controlling the pH to 11.5 with ammonia gas, were gradually added over 19 hours a mixture of ethyl alcohol (307 g) and water (438 g), simultaneously with 28% ethyl silicate (207 g). After completion of the addition, the resulting dispersion was charged with an aqueous solution (65 g) of NaOH (0.7 g), heated at 70°C., and kept at that temperature for 2 hours to obtain a dispersion (II). This dispersion (II) was dried at 200°C. to obtain powder particles.

35 A large liquid crystal display device was then prepared according to the same procedure as in Example 14 except that the thus obtained powder particles (1.5 g) were dispersed in the sealing resin (100 g) to prepare an ink composition and the powder particles (0.05 g) were dispersed in 1 litre of ethyl alcohol to prepare a dispersion.

Example 16

To the dispersion (II) (1126 g) obtained in Example 15 kept with stirring at 65°C. were added ethyl alcohol (155 g) and water (127 g). To the resulting mixture, while controlling the mixture to pH 11.5 with ammonia gas, were added gradually over 19 hours a mixture of ethyl alcohol (164 g) and water (275 g),
45 simultaneously with 28% ethyl silicate (156 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (65 g) of NaOH (0.7 g), heated at 70°C., and kept at that temperature for 2 hours to obtain a heel sol (C).

To this heel sol (C) (1324 g) kept with stirring at 65°C. were added ethyl alcohol (185 g) and water (151 g). To the resulting mixture, while controlling the mixture to pH 11.5 with ammonia gas, were added
50 gradually over 19 hours a mixture of ethyl alcohol (93 g) and water (150 g), simultaneously with 28% ethyl silicate (82 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (58 g) of NaOH (0.6 g), heated at 70°C., and kept at that temperature for 2 hours to obtain a dispersion (III), which was dried at 200°C. to obtain powder particles.

A large liquid crystal display device was then prepared according to the same procedure as in Example
55 14 except that the thus obtained powder particles (1.8 g) were dispersed in the sealing resin (100 g) to prepare an ink composition and the powder particles (0.1 g) were dispersed in 1 litre of ethyl alcohol to prepare a dispersion.

Example 17

To the heel sol (A) obtained in Example 14 kept with stirring at 35°C., while controlling the heel sol to pH 11.5 with ammonia gas, were gradually added over 19 hours a mixture of ethyl alcohol (1509 g) and water (3007 g), simultaneously with 28% ethyl silicate (2268 g). After completion of the addition, the resulting mixture was charged with an aqueous solution (204 g) of NaOH (2 g), heated at 70°C., and kept at that temperature for 2 hours to obtain a dispersion (IV). This dispersion (IV) was dried at 200°C. to obtain powder particles.

A large liquid crystal display device was then prepared according to the same procedure as in Example 14 except that the thus obtained powder particles (0.5 g) were dispersed in the sealing resin (100 g) to prepare an ink composition and the powder particles (0.1 g) were dispersed in 1 litre of ethyl alcohol to prepare a dispersion.

Comparative Examples 4-9

Large liquid crystal display devices were prepared according to the same procedure as Example 14 except that conventionally known spacers as indicated in Table 2 were also used in some cases.

Characteristics of large liquid crystal display devices as prepared were evaluated according to the following method.

(1) The cell was cut off with a diamond cutter at its centre portion, right side portion and left side portion, and the thickness of liquid crystal layer of each portion was measured by means of an electron microscope.

(2) The presence in the image portions of coarse spacer particles (aggregated particles) was examined by the naked eye, and when even one coarse spacer particle was observed, said device was graded as defective.

In Examples 14 and 17, and Comparative Examples 4 and 7, Smc* liquid crystal (a strongly dielectric liquid crystal, a product of Merck) was used, in Example 15 and Comparative Examples 5 and 8, SBE liquid crystal (Merck) was used, in Example 16 and Comparative Examples 6 and 9, TN liquid crystal (Merck) was used. The large liquid crystal display devices as prepared were examined for their performance to obtain the results as shown in Table 3.

Table 2

Item	Shape of spacer		Weight of spacer particles per 100 g of the resin in the ink composition [g]	Weight of spacer particles per litre of ethanol in the dispersion [g]	Remarks
	Diameter λ [μm]	Irregularity β [μm]			
Example 14	2.03	0.02	1.0	0.01	Spherical
15	6.02	0.09	1.5	0.05	
16	8.04	0.14	1.8	0.10	
17	1.01	0.02	0.5	0.01	
Comparative Example 4	2.20	0.39	2.2	0.02	Hexagonally columnar Alfit (a trade name) a product of Showa Denko K.K.
5	6.66	1.25	3.0	0.10	
6	8.05	1.90	3.6	0.20	
Comparative Example 7	2.20	0.17	0.9	0.01	Spherical Epistar (a trade name) a product of Nippon Shokubai Kagaku Kogyo K.K.
8	5.67	0.33	1.0	0.04	
9	7.94	0.25	1.2	0.08	

σ : Population standard deviation of d
Number of samples = 100

Table 3

Item	Thickness of liquid crystal layer $[\mu\text{m}]$	Irregularity in thickness of liquid crystal layer σ $[\mu\text{m}]$	Percent defective	
			Coarse Particle	Poor Performance
Example 14	2.08	0.06	0/100	0/100
15	6.40	0.16	0/100	0/100
16	8.90	0.20	0/100	0/100
17	1.05	0.05	0/100	0/100
Comparative Example 4	2.50	0.40	0/100	8/100
5	7.91	1.31	0/100	6/100
6	9.62	1.95	0/100	3/100
7	2.30	0.15	50/100	0/100
8	5.90	0.35	10/100	1/100
9	8.50	0.28	10/100	0/100

σ : Population standard deviation of thickness

Number of samples = 300

Example 18

The dispersion (I) obtained in Example 14 was dried at 110°C. to obtain white powder particles.

Subsequently, the thus obtained white powder particles were subjected in an air atmosphere to heat treatment at 350°C. for 3 hours, whereupon black particles were obtained.

A large liquid crystal display device was then prepared according to the same procedure as in Example 14 except that the black powder particles (1g) were dispersed in the sealing resin (100g) to prepare an ink composition and the powder particles (0.01g) were dispersed in 1 litre of ethyl alcohol.

Example 19

The dispersion (II) obtained in Example 15 was dried at 110°C. to obtain white powder particles.

Subsequently, the thus obtained white powder particles were subjected in a nitrogen atmosphere to heat treatment at 750°C. for 3 hours, whereupon black particles were obtained.

A large liquid crystal display device was prepared according to the same procedure as in Example 18 except that the black particles (1.5 g) obtained above were dispersed in the sealing resin (100 g) to prepare an ink composition and the black particles (0.05 g) were dispersed in 1 litre of ethyl alcohol.

Example 20

The dispersion (III) obtained in Example 16 was dried at 110°C. to obtain white powder particles.

Subsequently, the thus obtained white powder particles were subjected in an air atmosphere to heat treatment at 750°C. for 3 hours to obtain black particles.

A large liquid crystal display device was then prepared according to the same procedure as in Example 18 except that the black particles (1.8 g) obtained above were dispersed in the sealing resin (100 g) to prepare an ink composition and the black particles (0.1 g) were dispersed in 1 litre of ethyl alcohol.

Example 21

The dispersion (IV) was then prepared according to the same procedure as in Example 17 except that to the heel sol [A] of Example 14 were added a mixture of ethyl alcohol (1509g) and water (3007g) in which a water-soluble phenol resin (9.5g) (a product of Dainippon Ink and Chemicals, Inc.) had been dissolved.

This dispersion (IV) was dried at 110°C. to obtain white powder particles.

Subsequently, the thus obtained white powder particles were subjected in a nitrogen atmosphere to heat treatment at 300°C. for 1 hour to obtain black particles.

A large liquid crystal display device was then prepared according to the same procedure as in Example 18 except that the black particles (0.5 g) obtained above were dispersed in the sealing resin (100 g) to prepare an ink composition and the black particles (0.1 g) were dispersed in 1 litre of ethyl alcohol.

Comparative Example 10-15

Large liquid crystal display devices were prepared according to the same procedure as in Example 18 except that such conventionally known spacers as indicated in Table 4 were also used in some cases.

Characteristics of large liquid crystal display devices as prepared were evaluated according to the same method as described in Comparative Examples 14-17.

In Examples 18 and 21, Comparative Examples 10 and 14, Smc* liquid crystal (a strongly dielectric liquid crystal, a product of Merk) was used, in Example 19 and Comparative Examples 11 and 15, SBE liquid crystal (a product of Merk) was used, and in Example 20 and Comparative Examples 12 and 13, TN liquid crystal (a product of Merk) was used. The large liquid crystal display devices as prepared were examined with respect to their performance to obtain the results as shown in Table 5.

The Y value (a value represented on the basis of JIS Z 8701) of the black and white particles obtained in the foregoing examples and comparative examples was measured in the following manner.

Each of the black and white particles was placed in a cylindrical cell and measured for Y value with S & M color computer (SM4-CH Model, manufactured and sold by Suga Shikenki K.K.).

It is understood from Table 4 that the black particles obtained in the present invention have a particle diameter of 0.1-10 µm, a sharp particle size distribution and, moreover, they are black in colour.

Furthermore, it is understood from Table 5 that when the black particles obtained in the present invention are used as liquid crystal spacers, the liquid crystal layers comprising the same are found to be

less irregular in thickness and excellent in operating efficiency and, moreover, also excellent in display performance.

Table 4

Item	Shape of particle		γ value %	Weight of spacer particles per 100 g of resin in the ink Composition [g]	Weight of spacer particles per litre of ethanol in the dispersion [g]	Remarks
	Diameter [μ m]	Irregularity σ [μ m]				
Example 18	2.03	0.02	7.0	1.0	0.01	Spherical
19	6.02	0.09	2.9	1.5	0.05	
20	8.04	0.14	1.5	1.8	0.10	
21	1.01	0.02	0.5	0.5	0.01	
Comparative						Hexagonal columns Alfit (a trade name) a product of Showa Denko K.K.
Example 10	2.20	0.39	91.1	2.2	0.02	
11	6.66	1.25	93.7	3.0	0.10	
12	8.05	1.90	93.5	3.6	0.20	Spherical Epostar (a trade name) a product of Nippon Shokubai Kagaku Kogyo K.K.
Comparative						
Example 13	2.20	0.17	93.0	0.9	0.01	
14	5.67	0.33	94.2	1.0	0.04	
15	7.94	0.25	93.8	1.2	0.08	

σ : Population standard deviation
of d

Number of samples = 100

Table 5

Item	Thickness of liquid crystal layer [μm]	Irregularity in thickness of crystal layer σ [μm]	Percent defective		Contrast display efficiency
			Coarse particles	Poor performance	
Example 18	2.08	0.06	0/100	0/100	Good
19	6.40	0.16	0/100	0/100	Good
20	8.90	0.20	0/100	0/100	Good
21	1.05	0.05	0/100	0/100	Good
Comparative Example 10	2.50	0.40	0/100	8/100	Decreased
11	7.91	1.31	0/100	6/100	Decreased
12	9.62	1.95	0/100	3/100	Decreased
13	2.30	0.15	50/100	0/100	Decreased
14	5.90	0.35	10/100	1/100	Decreased
15	8.50	0.28	10/100	0/100	Decreased

σ : Population standard deviation of thickness
Number of samples = 100

Example 22

The dispersion (III) obtained in Example 16 was dried at 110°C., and powder particles (1) were separated. The thus obtained powder particles (95 g) and methyl methacrylate resin powder (5 g) (a trade name MP-1000, particle diameter 0.4 μm , a product of Soken Kagaku K.K.) were mixed together to adsorb

the resin on the particles. Further, the particles were stirred by means of a ball mill to coat the resin on the particles (powder particles (2)).

A large liquid crystal display device was then prepared according to the same procedure as in Example 14 except that the powder particles (1) (1g) were dispersed in the sealing resin (100g) to prepare an ink composition and the powder particles (2) (0.01g) were dispersed in 1 litre of ethyl alcohol to prepare a dispersion and the substrate assembled was heated at 180°C.

Example 23

A cell for large liquid crystal display devices was obtained in the same procedure as in Example 22 except that the powder particle (1) obtained in Example 22 was subjected in a nitrogen atmosphere to heat treatment at 750°C. for 3 hours to obtain black powder particles (3) and the thus obtained black powder particles (3) were used.

The characteristics of the devices prepared were evaluated by the methods of Examples 14-17.

The cells for liquid crystal display devices (LCD) were evaluated by the following methods.

(1) Display performance of LCD was confirmed when the LCD was obtained by assembling polarized light films so that transparent light is obtained when TN iniquid crystal (Merck) was injected and an electric field applied. Further, LCD cell was subjected to centrifuging with a centrifugal separator at 800G for 1 hour so that the spacer particles were rendered movable in the liquid crystal layer, and thereafter the LCD was confirmed with respect to its display performance.

(2) Large liquid crystal display devices were subjected to a heat cycle test wherein the heating and cooling cycle was repeated 4 times between -20°C. and 80°C., and display performance of the devices was confirmed.

The results obtained are shown in Table 6.

Table 6

Item	Shape of spacer particles		Thickness		percent defective			
	d [μm]	d' [μm]	[μm]	ρ_z [μm]	Coarse particle performance	Poor performance after centrifuging	Heat cycle	
Example 1	8.06			0.18	8.95	0.23	0/100	0/100
2	8.04			0.14	8.90	0.20	0/100	0/100

σ_z : Population
standard
deviation of
thickness

Number of
samples = 100

σ_d : Population
standard
deviation of d
Number of
samples = 100

Claims

1. A process for preparing mono-dispersed particles, characterized in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds



The results obtained are shown in Table 6.

Table 6

Item	Shape of spacer particles		Thickness		percent defective			
	d [μ m]	σ_d [μ m]	[μ m]	ρ_z [μ m]	Coarse particle percentage	Poor performance after centrifuging	Poor performance after centrifuging	Heat cycle
Example 1	8.06	0.16	8.95	0.23	0/100	0/100	0/100	0/100
2	8.04	0.14	8.90	0.20	0/100	0/100	0/100	0/100

σ_d : Population
standard
deviation of d
Number of
samples = 100

ρ_z : Population
standard
deviation of
thickness
Number of
samples = 100

Claims

1. A process for preparing mono-dispersed particles, characterized in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds



to effect particle growth thereof.

- 5 2. The process as claimed in claim 1 wherein the alcohol concentration in the water-alcohol system is 35-97% by weight.
3. The process as claimed in claim 1 wherein the alcohol is methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol or isobutyl alcohol.
- 10 4. The process as claimed in claim 1 wherein the concentration of the seed in the water-alcohol system is 0.05-20.0% by weight in terms of the oxide concentration.
- 15 5. A process for preparing black particles, characterized in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds to effect particle growth thereof, and in that the particles separated from the dispersion are subsequently subjected to heat treatment at a temperature above 250 °C.
- 20 6. The process as claimed in claim 5 wherein the alcohol concentration in the water-alcohol system is 35-97% by weight.
7. The process as claimed in claim 5 wherein the alcohol is methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol or isobutyl alcohol.
- 25 8. The process as claimed in claim 5 wherein the concentration of the seed in the water-alcohol system is 0.05-20.0% by weight in terms of the oxide concentration.
- 30 9. The process as claimed in claim 5 wherein the particles separated from the dispersion are subjected to heat treatment at a temperature of from 250 ° to 1000 °C.
- 35 10. A process for preparing particles for use as spacers for display devices, characterized in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds to effect particle growth thereof, and in that the particles separated from the dispersion are subsequently coated on their surfaces with a synthetic resin.
- 40 11. The process as claimed in claim 10 wherein the alcohol concentration in the water-alcohol system is 35-97% by weight.
- 45 12. The process as claimed in claim 10 wherein the alcohol is methanol, ethanol, n-propanol isopropanol, n-butyl alcohol or isobutyl alcohol.
13. The process as claimed in claim 10 wherein the concentration of the seed in the water-alcohol system is 0.05-20.0% by weight in terms of the oxide concentration.
- 50 14. A process for preparing particles for use as spacers for display devices, characterised in that hydrolysis of a metal alkoxide is carried out by adding said metal alkoxide to a water-alcohol system having dispersed therein a metal oxide or metal hydroxide as a seed, and, while keeping said dispersion under controlled alkaline conditions at pH 10-13, allowing the hydrolysis product of said metal alkoxide to attach onto said seeds to effect particle growth thereof, and in that black particles obtained by subjecting the particles separated from the dispersion to heat treatment at a temperature above 250 °C are subsequently coated on their surfaces with a synthetic resin.
- 55 15. The process as claimed in claim 14 wherein the alcohol concentration in the water-alcohol system is 35-97% by weight.



16. The process as claimed in claim 14 wherein the alcohol is methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol or isobutyl alcohol.
- 5 17. The process as claimed in claim 14 wherein the concentration of the seed in the water-alcohol system is 0.05-20.0% by weight in terms of the oxide concentration.
18. The use of particles prepared by a process as claimed in any preceding claim as spacers for display devices.
- 10 19. The use as claimed in claim 18, wherein the particles are prepared by a process as claimed in any of claims 10 to 17 and are for use in liquid crystal display devices.

Patentansprüche

- 15 1. Verfahren zur Herstellung von monodispersen Teilchen, dadurch gekennzeichnet, daß man eine Hydrolyse eines Metallalkoxids durchführt, indem man das Metallalkoxid zu einem Wasser-Alkohol-System gibt, das hierin dispergiert ein Metalloxid oder Metallhydroxid als Keime enthält, und während man diese Dispersion unter kontrollierten alkalischen Bedingungen bei pH 10 bis 13 hält, man das Hydrolyseprodukt des Metallalkoxids an den Keimen anhaften läßt, um deren Teilchenwachstum zu bewirken.
- 20 2. Verfahren gemäß Anspruch 1, worin die Alkoholkonzentration in dem Wasser-Alkohol-System 35 bis 97 Gew.-% beträgt.
- 25 3. Verfahren gemäß Anspruch 1, worin der Alkohol Methanol, Ethanol, n-Propanol, Isopropanol, n-Butylalkohol oder Isobutylalkohol ist.
4. Verfahren gemäß Anspruch 1, worin die Konzentration der Keime in dem Wasser-Alkohol-System 0,05 bis 20,0 Gew.-%, ausgedrückt als Oxidkonzentration, beträgt.
- 30 5. Verfahren zur Herstellung von schwarzen Teilchen, dadurch gekennzeichnet, daß man eine Hydrolyse eines Metallalkoxids durchführt, indem man das Metallalkoxid zu einem Wasser-Alkohol-System gibt, das hierin dispergiert ein Metalloxid oder Metallhydroxid als Keime enthält, und während man diese Dispersion unter kontrollierten alkalischen Bedingungen bei pH 10 bis 13 hält, man das Hydrolyseprodukt des Metallalkoxids an den Keimen anhaften läßt, um deren Teilchenwachstum zu bewirken, und daß die aus der Dispersion abgetrennten Teilchen anschließend einer Wärmebehandlung bei einer Temperatur oberhalb 250 °C unterzogen werden.
- 35 6. Verfahren gemäß Anspruch 5, worin die Alkoholkonzentration in dem Wasser-Alkohol-System 35 bis 97 Gew.-% beträgt.
- 40 7. Verfahren gemäß Anspruch 5, worin der Alkohol Methanol, Ethanol, n-Propanol, Isopropanol, n-Butylalkohol oder Isobutylalkohol ist.
- 45 8. Verfahren gemäß Anspruch 5, worin die Konzentration der Keime in dem Wasser-Alkohol-System 0,05 bis 20,0 Gew.-%, ausgedrückt als Oxidkonzentration, beträgt.
9. Verfahren gemäß Anspruch 5, worin die aus der Dispersion abgetrennten Teilchen einer Wärmebehandlung bei einer Temperatur von 250 bis 1000 °C unterzogen werden.
- 50 10. Verfahren zur Herstellung von Teilchen für die Verwendung als Abstandshalter für Displayvorrichtungen, dadurch gekennzeichnet, daß man eine Hydrolyse eines Metallalkoxids durchführt, indem man das Metallalkoxid zu einem Wasser-Alkohol-System gibt, welches hierin dispergiert ein Metalloxid oder Metallhydroxid als Keime enthält, und während man diese Dispersion unter kontrollierten alkalischen Bedingungen bei pH 10 bis 13 hält, man das Hydrolyseprodukt des Metallalkoxids an den Keimen anhaften läßt, um deren Teilchenwachstum zu bewirken, und daß die aus der Dispersion abgetrennten Teilchen anschließend auf ihrer Oberfläche mit einem synthetischen Harz beschichtet werden.
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11. Verfahren gemäß Anspruch 10, worin die Alkoholkonzentration in dem Wasser-Alkohol-System 35 bis 97 Gew.-% beträgt.
12. Verfahren gemäß Anspruch 10, worin der Alkohol Methanol, Ethanol, n-Propanol, Isopropanol, n-Butylalkohol oder Isobutylalkohol ist.
13. Verfahren gemäß Anspruch 10, worin die Konzentration der Keime in dem Wasser-Alkohol-System 0,05 bis 20,0 Gew.-%, ausgedrückt als Oxidkonzentration, beträgt.
- 10 14. Verfahren zur Herstellung von Teilchen für die Verwendung als Abstandshalter für Displayvorrichtungen, dadurch gekennzeichnet, daß man eine Hydrolyse eines Metallalkoxids durchführt, indem man das Metallalkoxid zu einem Wasser-Alkohol-System gibt, das hierin dispergiert ein Metalloxid oder Metallhydroxid als Keime enthält, und während man die Dispersion unter kontrollierten alkalischen Bedingungen bei pH 10 bis 13 hält, man das Hydrolyseprodukt des Metallalkoxids an den Keimen anhaften läßt, 15 um deren Teilchenwachstum zu bewirken, und daß schwarze Teilchen, erhalten durch Unterziehen der aus der Dispersion abgetrennten Teilchen einer Wärmebehandlung bei einer Temperatur oberhalb 250 ° C, anschließend an ihrer Oberfläche mit einem synthetischen Harz beschichtet werden.
15. Verfahren gemäß Anspruch 14, worin die Alkoholkonzentration in dem Wasser-Alkohol-System 35 bis 97 Gew.-% beträgt. 20
16. Verfahren gemäß Anspruch 14, worin der Alkohol Methanol, Ethanol, n-Propanol, Isopropanol, n-Butylalkohol oder Isobutylalkohol ist.
- 25 17. Verfahren gemäß Anspruch 14, worin die Konzentration der Keime in dem Wasser-Alkohol-System 0,05 bis 20,0 Gew.-%, ausgedrückt als Oxidkonzentration, beträgt.
18. Verwendung der nach einem Verfahren der vorhergehenden Ansprüche hergestellten Teilchen als Abstandshalter für Displayvorrichtungen. 30
19. Verwendung gemäß Anspruch 18, worin die Teilchen nach einem Verfahren, wie in einem der Ansprüche 10 bis 17 beansprucht, hergestellt werden und für die Verwendung in Flüssigkristall-Displayvorrichtungen vorgesehen sind.

35 Revendications

1. Procédé de préparation de particules monodispersées, caractérisé en ce qu'il consiste à effectuer l'hydrolyse d'un alcoolate métallique en ajoutant cet alcoolate métallique à un système eau-alcool ayant dispersé en son sein un oxyde métallique ou un hydroxyde métallique en tant que germe et, tout en maintenant la dispersion dans des conditions alcalines contrôlées à un pH de 10 à 13, à laisser le produit d'hydrolyse de l'alcoolate métallique se fixer aux germes pour en effectuer une croissance de particules. 40
2. Procédé suivant la revendication 1, dans lequel la concentration d'alcool du système eau-alcool est de 35 à 97 % en poids. 45
3. Procédé suivant la revendication 1, dans lequel l'alcool est le méthanol, l'éthanol, le propanol normal, l'isopropanol, l'alcool butylique normal ou l'alcool isobutylique.
- 50 4. Procédé suivant la revendication 1, dans lequel la concentration du germe dans le système eau-alcool est de 0,05 à 20,0 % en poids, exprimée en la concentration d'oxyde.
5. Procédé de préparation de particules de noir, caractérisé en ce qu'il consiste à effectuer l'hydrolyse d'un alcoolate métallique par addition de cet alcoolate métallique à un système eau-alcool ayant dispersé en son sein un oxyde métallique ou un hydroxyde métallique en tant que germe et, tout en maintenant cette dispersion dans des conditions alcalines contrôlées à un pH de 10 à 13, à laisser le produit d'hydrolyse de l'alcoolate métallique se fixer sur les germes pour en effectuer une croissance de particules, et à soumettre ensuite les particules séparées de la dispersion à un traitement thermique 55



à une température supérieure à 250 ° C.

- 5 6. Procédé suivant la revendication 5, dans lequel la concentration d'alcool dans le système eau-alcool est de 35 à 97 % en poids.
7. Procédé suivant la revendication 5, dans lequel l'alcool est le méthanol, l'éthanol, le propanol normal, l'isopropanol, l'alcool butylique normal ou l'alcool isobutylique.
- 10 8. Procédé suivant la revendication 5, dans lequel la concentration du germe dans le système eau-alcool est de 0,05 à 20,0 % en poids, exprimée en la concentration d'oxyde.
9. Procédé suivant la revendication 5, qui consiste à soumettre les particules séparées de la dispersion à un traitement thermique à une température de 250 à 1000 ° C.
- 15 10. Procédé de préparation de particules destinées à être utilisées comme intercalaire dans des dispositifs d'affichage, caractérisé en ce qu'il consiste à effectuer l'hydrolyse d'un alcoolate métallique en ajoutant cet alcoolate métallique à un système eau-alcool ayant dispersé dans son sein un oxyde métallique ou un hydroxyde métallique en tant que germe et, tout en maintenant la dispersion dans des conditions alcalines contrôlées à un pH de 10 à 13, à laisser le produit d'hydrolyse de l'alcoolate métallique se fixer aux germes pour en effectuer une croissance de particules, et à revêtir ensuite les surfaces des particules séparées de la dispersion d'une résine synthétique.
- 20 11. Procédé suivant la revendication 10, dans lequel la concentration d'alcool du système eau-alcool est de 35 à 97 % en poids.
- 25 12. Procédé suivant la revendication 10, dans lequel l'alcool est le méthanol, l'éthanol, le propanol normal, l'isopropanol, l'alcool butylique normal ou l'alcool isobutylique.
- 30 13. Procédé suivant la revendication 10, dans lequel la concentration du germe dans le système eau-alcool est de 0,05 à 20,0 % en poids, exprimée en la concentration d'oxyde.
- 35 14. Procédé de préparation de particules destinées à être utilisées comme intercalaire dans des dispositifs d'affichage, caractérisé en ce qu'il consiste à effectuer l'hydrolyse d'un alcoolate métallique en ajoutant cet alcoolate métallique à un système eau-alcool ayant dispersé dans son sein un oxyde métallique ou un hydroxyde métallique en tant que germe et, tout en maintenant la dispersion dans des conditions alcalines contrôlées à un pH de 10 à 13, à laisser le produit d'hydrolyse de l'alcoolate métallique se fixer aux germes pour en effectuer une croissance de particules et à revêtir les surfaces des particules de noir obtenues en soumettant les particules séparées de la dispersion à un traitement thermique à une température supérieure à 250 ° C, d'une résine synthétique.
- 40 15. Procédé suivant la revendication 14, dans lequel la concentration d'alcool du système eau-alcool est de 35 à 97 % en poids.
- 45 16. Procédé suivant la revendication 14, dans lequel l'alcool est le méthanol, l'éthanol, le propanol normal, l'isopropanol, l'alcool butylique normal ou l'alcool isobutylique.
- 50 17. Procédé suivant la revendication 14, dans lequel la concentration du germe dans le système eau-alcool est de 0,05 à 20,0 % en poids, exprimée en la concentration d'oxyde.
- 55 18. Utilisation de particules préparées par un procédé tel que revendiqué à l'une quelconque des revendications précédentes, comme intercalaires pour des dispositifs d'affichage.
19. Utilisation suivant la revendication 18, dans laquelle les particules sont préparées par un procédé tel que revendiqué à l'une quelconque des revendications 10 à 17 et sont destinées à être utilisées dans des dispositifs d'affichage à cristaux liquides.