

Liquid Crystal Display Devices

The invention relates to liquid crystal display devices.

5

Liquid crystal display devices are generally produced by interposing liquid crystal between two transparent electrodes. Since the electrooptical effect of the liquid crystal display device hinges heavily on the thickness of the liquid crystal layer, and the uniformity of that thickness, the control of that thickness is important. As liquid crystal display devices have become larger the control of accurate uniform thickness of the liquid crystal has become increasingly difficult. Variations in uniformity are liable to induce interference colours and uneven displays.

Various materials have been tried as spacers which serve to keep the two transparent electrodes at a fixed distance from each other. For example, spacers which are made of chopped glass fibres, metal oxides such as finely divided alumina particles, and the thermoplastic resins such as spherical polystyrene particles have been developed (Japanese Patent Laid-open Nos. 70522/1982, 210323/1982, 40809/1981 and 64945/1976).

These spacers, however, do not always keep the liquid crystal layer uniform in thickness. In the case of spacers made of glass fibres, for example, there is the possibility that the pressure exerted on the spacers when the substrates on which the electrodes are formed are pressed against each other will crush the glass fibres, and the spacers will consequently be deprived of their function. In the case of spacers made of metal oxide particles having

high rigidity, the same pressure will possibly cause the particles to eat into the inner walls of the substrates and, in an extreme case, destroy the transparent electrodes formed on the substrates. In the case of spacers made of thermoplastic resin, when the thermoplastic resin is used as mixed in an adhesive sealing agent such as epoxy resin and polyimide resin or when it is subjected to a heat treatment for adhesion, there is the possibility that the spacers will be attacked by the adhesive agent or the heat and prevented from keeping the liquid crystal layer constant in thickness.

The invention provides a liquid crystal display device comprising two transparent substrates facing each other, two transparent electrodes one on the inner face of each substrate, a liquid crystal and a mixture of an adhesive sealing agent and fine spherical cured particles of an amino-formaldehyde resin obtained from formaldehyde and at least one of benzoguanamine, melamine and urea, the mixture being applied to the periphery of the substrates to space them one from the other and to seal the liquid crystal therebetween.

The fine spherical cured particles of amino-formaldehyde resin used in the invention are obtained from formaldehyde and at least one amino compound selected from benzoguanamine, melamine and urea. They may be produced by any of the methods previously proposed by us and now proposed in this Specification. Representative of these methods are the following:

1. Fine spherical cured resin particles are obtained by a method which comprises causing benzoguanamine or a mixture of 100 to 50 parts by weight of benzoguanamine with 0 to 50 parts by weight of melamine to react with formaldehyde at a ratio of 1 mol of benzoguanamine or the mixture thereof to

- 1.2 to 3.5 mols of formaldehyde until the reaction product is rendered hydrophobic, adding the reaction product to a stirred aqueous protective colloid solution, polymerizing the resultant emulsion in the presence of a curing catalyst, separating the resultant fine spherical cured resin from the suspension, washing it with water, drying it and crushing it into fine spherical particles (see British Patent Specification No. 1433183).
- 10 These reactions are carried out at a pH of from 5 to 10 at a temperature of from 50° to 100°C. The curing of the reaction product in its emulsified state is effected by heating the emulsion in the presence of a curing catalyst at a temperature of 50° to 100°C. The curing catalyst
- 15 can be suitably selected from a host of polymerization curing catalysts used for amino type resins. Examples of the catalyst include mineral acids such as hydrochloric acid, sulphuric acid and phosphoric acid, carboxylic acids such as benzoic acid, phthalic acid, acetic acid, propionic
- 20 acid and salicylic acid, ammonium salts such as ammonium chloride and ammonium phosphate, benzenesulphonic acid, p-toluenesulphonic acid, dodecyl benzenesulphonic acid and various other latent curing catalysts. Among other catalysts, sulphonic acids prove particularly desirable.
- 25 The polymerization curing catalyst is effectively used in an amount of 0.01 to 5 parts by weight, preferably 0.2 to 2 parts by weight, based on 100 parts by weight of the reaction product.
- 30 2. The fine spherical cured resin particles are otherwise obtained by a method which comprises causing at least one amino compound selected from benzoguanamine, melamine and urea to react with formaldehyde at a ratio of 1 mol of the amino compound to 1.2 to 6.0 mols of formaldehyde, adding
- 35 the reaction product to a stirred aqueous surface active agent solution, polymerizing the resultant emulsion in

presence of a curing catalyst, separating the resultant fine spherical cured resin from the suspension, washing it with water, drying it and crushing it into fine spherical particles.

5

These reactions are carried out at a pH of from 5 to 10 at a temperature of from 50° to 100°C. The curing of the reaction product in its emulsified state is effected by heating the emulsion in the presence of a curing catalyst at a temperature of 50° to 100°C. The curing catalyst can be suitably selected from a host of polymerization curing catalysts used for amino type resins. Examples of the catalyst include mineral acids such as hydrochloric acid, sulphuric acid and phosphoric acid, carboxylic acids such as benzoic acid, phthalic acid, acetic acid, propionic acid and salicylic acid, ammonium salts such as ammonium chloride and ammonium phosphate, benzenesulphonic acid, p-toluenesulphonic acid, dodecyl benzenesulphonic acid, and various other latent curing catalysts. Among other catalysts, sulphonic acids provide particularly desirable. The polymerization curing catalyst is effectively used in an amount of 0.01 to 20 parts by weight, preferably 0.2 to 10 parts by weight, based on 100 parts by weight of the reaction product.

25

The methods described above give insoluble, infusible fine spherical cured particles having a narrow particle distribution and having so surface irregularity. In order to obtain uniform spherical cured particles having a more narrow particle distribution, it is preferable to classify the particles by a method such as wet classification or pneumatic classification. By this method, the spherical cured particles can be easily prepared in a desired diameter. For use in liquid crystal display devices according to the invention, fine spherical cured particles

35

- 5 -

having a diameter falling in the range of 1 to 15 μm , preferably 2 to 12 μm , can be obtained with accuracy of $\pm 0.5 \mu\text{m}$.

- 5 The particles thus obtained are insoluble and infusible and are capable of resisting the action of the adhesive sealing agent, retaining rigidity intact under harsh heat treatments and withstanding various processing conditions. They are tough so that when the two transparent substrates
- 10 are pressed against each other across the cured particles, the cured particles are neither crushed nor caused to eat into the transparent substrates. Thus they permit a liquid crystal layer to be kept accurately in a uniform thickness. The fine spherical cured particles of benzoguanamine-
- 15 formaldehyde resin or benzoguanamine-melamine-formaldehyde resin, particularly, are excellent in resistance to chemicals and solvents, and capable of very easy production in a desired particle diameter. Optionally, benzoguanamine, melamine and urea may be partially
- 20 substituted by p-toluenesulphonamide. The amount of p-toluenesulphonamide must be carefully selected as an excessive amount may degrade the resistance of the particles to solvent.
- 25 From the fine spherical cured particles of amino-formaldehyde resin the spacers in a liquid crystal display device are produced by a method which comprises dispersing the fine spherical cured particles in an adhesive sealing agent such as epoxy resin or polyimide resin, applying the
- 30 resultant dispersion on the sealing portion of a given liquid crystal display device by means of screen printing, and thermally curing the dispersion or by a method which comprises dispersing the fine spherical cured particles in a solvent or in a solution of film-forming high

14

- 6 -

5 molecular substance in a solvent, applying the resultant dispersion on a transparent electrode substrate, thermally drying the applied layer of the dispersion thereby converting the solution into a film and, at the same time, fastening the particles on the transparent electrode substrate and giving rise to spacers. This invention does not discriminate the spacers for liquid crystal display devices by the methods used for their production.

10 The adhesive sealing agent keeps the liquid crystal display device sealed tightly and prevents moisture from entering the device and degrading the liquid crystal. Suitable adhesive sealing agents include those of thermosetting resin type, preferably epoxy type or polyimide resin.

15 Tin oxide, indium oxide or a mixture thereof can be used as the material for the electrodes. The transparent electrodes are obtained by depositing this material on a glass substrate by vacuum deposition or by sputtering.

20 Indium oxide excels tin oxide in transmittance of light and electric resistance but is vulnerable to acids. In the case of a transparent electrode using indium oxide, therefore, due care should be given when the substrate is washed.

25 Examples of the liquid crystal material include nematic liquid crystals such as azomethine compounds, azo compounds, azoxy compounds, ester compounds and biphenyl compounds, smectic liquid crystals such as terephthal-bis-

30 -(4-n-butylaniline), 4,4'-azoxybenzoic acid di-ethylester, 4,4'-di-n-dodecyloxy-azoxybenzene, 4-p-substituted-benzylidene-aminocinnamic ester compounds, chloestic liquid crystals such as 3-methyl-2,6-bis-(4-methoxybenzylidene)-cyclohexanone, 2-(4-methoxybenzylidene)-6-(4-

5 -amyloyloxy-benzylidene)-cyclohexanone and heptyl-p-(methoxybenzylidene amino)-cinnamate, and mixed liquid crystals thereof. Desired sealing of such liquid crystal in the opposed panels can be accomplished by utilizing surface tension or pressure difference.

The invention is illustrated with reference to the drawing, of which:

10 Figure 1 is a cross sectional view illustrating a liquid crystal display device according to the invention; and Figure 2 is a cross sectional view illustrating another liquid crystal display device according to the invention.

15 With reference to Figure 1, a liquid crystal display device is obtained by thoroughly mixing the aforescribed fine spherical cured amino-formaldehyde resin particles having a diameter equal to the desired thickness of a liquid crystal layer 5 in a proportion falling in the range of 1 to 10% by weight, preferably 2 to 8% by weight, with an adhesive
20 sealing agent 3; applying the resultant mixture to the periphery portion of one of two transparent substrates 1 provided with a transparent electrode 2 by means of screen printing, for example; pressing the other transparent substrate 1 similarly provided with a transparent electrode
25 2 against the applied layer of the mixture; keeping the opposed transparent substrates 1 pressed against each other with proper pressure and, at the same time, heating them at a temperature in the range of 50° to 300°C, preferably 100° to 150°C, for 10 to 90 minutes, preferably 30 to
30 60 minutes thereby thermally curing the adhesive sealing agent as deposited; and sealing liquid crystal in a space formed between the transparent electrodes 2.

A liquid crystal display device constructed as illustrated

16

- 8 -

in Figure 2 is obtained by dispersing minute spherical cured amino-formaldehyde resin particles in a solvent or in a solution of a film-forming high molecular substance such as epoxy resin in a solvent; applying the resultant dispersion by means of the spinner method on one of two transparent substrates 1 provided with a transparent electrode 2; heating the layer of the dispersion as applied on the transparent substrate 1 thereby drying the high molecular substance into a film 6 and, at the same time, fastening the particles 4a on the transparent substrate 1; subsequently applying a dispersion of other particles 4 in an adhesive sealing agent 3 on the periphery portion of the transparent substrate 1; combining the other transparent substrate 1 similarly provided with a transparent electrode 2; keeping the opposed transparent substrates 1 pressed against each other with proper pressure and, at the same time heating them at a temperature in the range of 50° to 300°C, preferably 100° to 150°C, for 10 to 90 minutes, preferably 30 to 60 minutes thereby thermally curing the adhesive sealing agent as deposited; and sealing liquid crystal in a space formed between the transparent electrodes 2.

The following Examples further illustrate the invention.

Example 1

75 parts of benzoguanamine, 75 parts of melamine, 290 parts of formalin (formaldehyde content 37%) and 1.16 parts of 10% aqueous sodium carbonate solution were mixed in a four-necked flask provided with a stirrer, a reflux condenser and a thermometer. The resultant mixture was adjusted to pH 8.0 and was stirred and heated to 85°C. It was held at this temperature for 1.5 hours to induce reaction and afford a soluble resinous solution having a degree of water tolerance of 200%.

The expression "degree of water tolerance", as used herein, is a measure which indicates the affinity for water of the foregoing soluble and fusible resin. It can be determined by adding water dropwise to 2 grams of an aqueous reaction product of formaldehyde and at least one amino compound selected from benzoguanamine, melamine and urea, while holding the temperature of the solution at 15°C. The amount of water (W₁ grams) required to cause the solution to become turbid is measured, and the degree of water tolerance (x) is then calculated as follows:

$$x = \frac{W_1}{2} \times 100(\%)$$

7.5 parts of a nonionic surface active agent (Emulgen 430, product of Kao Chemical Kabushiki Kaisha, polyoxyethylene oleil ether) was dissolved in 2455 parts of water. The solution was raised to a temperature of 50°C and stirred. The resinous solution prepared above was poured into the solution of the nonionic surface active agent under stirring to obtain a white suspension. 90 parts of 5% aqueous dodecyl benzenesulphonic acid solution was poured into the suspension, which was maintained at a temperature of 50° to 60°C for 3 hours. It was then diluted by adding 2000 parts of cold water and was subjected to separation by sedimentation. The resin paste obtained by sedimentation separation was added to 3000 parts of a solution of 7.5 parts of Emulgen 430 and 4.5 parts of dodecyl benzenesulphonic acid in water and dispersed using an ultrasonic disperser. The mixture was raised to a temperature of 90°C under stirring and cured completely to obtain a suspension of fine cured resin particles, which were filtered from the suspension in vacuo. The resultant filter cake was dried in a hot air drier at a temperature

②

- 10 -

of 150°C for 4 hours to obtain 120 parts of a conglomerate of fine cured resin particles.

5 This conglomerate was disintegrated in a ball mill to obtain fine white cured resin particles. By a test with a particle size distribution tester (product of Coulter Electronics Inc. of the USA, marketed under trademark designation of "Coulter Counter, Model TAPI C1000"), the fine cured resin particles were found to be spheres 8.0 ±
10 0.5 μm in diameter. This result was confirmed by scanning electron microscopy.

The fine cured resin particles showed absolutely no sign of swelling or solution in various organic solvents including
15 methanol, ethanol, butanol, ethyl acetate, butyl acetate, methyl cellosolve, ethyl cellosolve, acetone, dimethyl ketone, toluene and xylene. When the fine cured resin particles were heated to temperatures exceeding 250°C, they showed no discernible sign of fusion or solution.

20

Example 2

150 parts of benzoguanamine, 130 parts of formalin (formaldehyde content 37%) and 0.52 part of a 10% aqueous sodium carbonate solution were mixed in the same
25 four-necked flask as was used in Example 1. The resultant mixture was adjusted to pH 8.0 and was stirred and heated to 95°C. It was held at this temperature for four hours to induce reaction and obtain a soluble, fusible resin having a degree of modified water tolerance of 100%.

30

The expression "degree of modified water tolerance", as used herein, is a measure which indicates the affinity of water of the foregoing soluble and fusible resin. It can be determined by adding water dropwise to a solution in 5
35 grams of methanol of 2 grams of an aqueous reaction product

of formaldehyde and at least one amino compound selected of benzoguanamine, melamine and urea, while holding the temperature of the solution at 25°C. The amount of water (W₂ grams) required to cause the solution to become
5 turbid is measured, and the degree of modified water tolerance (Y) is then calculated as follows:

$$Y = \frac{W_2}{2} \times 100(\%)$$

10 8 parts of partially saponified polyvinyl alcohol having a polymerization degree of 500 (product of Kuraray Co. Ltd., marketed under trademark designation of Kuraray Poval 205) was dissolved in 750 parts of cold water. The solution was
15 heated to 90°C and stirred in a mixer (product of Tokushuki Kako Co. Ltd., marketed under trademark designation of "Homomixer" HU-M type) at a rotational speed of 3000rpm. The soluble, fusible resin prepared above was added to the Kuraray Poval 205 solution kept in a
20 stirred state, and there was obtained a white emulsion. The emulsion was cooled to 40°C. 2 parts of dodecyl benzenesulphonic acid were added to the cooled emulsion in an anchor type stirrer. The mixture was gently stirred at 40°C for two hours, and then stirred for two
25 hours each at 50°C, 60°C and 90°C to cure the resin. There was obtained a suspension of fine cured resin particles. The whole of the suspension was poured into 3400 parts of water, homogenized and cooled to room temperature. Classification by natural sedimentation was
30 repeated. Fine cured resin particles classified from the suspension were filtered in vacuo and the resultant filter cake was washed with water. The whole filter cake was dried in a hot air drier at a temperature of 80°C for 2 hours, and then heated at a temperature of 140°C for 3
35 hours to obtain 50 parts of a conglomerate of the fine cured resin particles. With finger tip pressure this

conglomerate was disintegrated to afford fine white cured resin particles. Scanning electron microscopy showed the fine cured resin particles to be spheres $10 \pm 0.5 \mu\text{m}$ in diameter.

5

The fine cured resin particles showed absolutely no sign of swelling or solution in various organic solvents including methanol, ethanol, isopropanol, butanol, ethyl acetate, butyl acetate, methyl cellosolve, ethyl cellosolve, acetone, methyl ethyl ketone, toluene and xylene. When the fine cured resin particles were heated to temperatures exceeding 250°C , they showed no discernible sign of fusion or solution.

10

15 Example 3

150 parts of melamine, 290 parts of formalin (formaldehyde content 37%) and 1.16 parts of a 10% aqueous sodium carbonate solution were mixed in the same four-necked flask as was used in Example 1 and the resultant mixture was adjusted to pH 8.0. The mixture was stirred and heated to 70°C . It was held at this temperature for one hour to induce reaction and afford a soluble resinous solution having degree of water tolerance of 180%.

20

25 12 parts of an anionic surface active agent (Neopellex 05 powder, product of Kao Chemical Kabushiki Kaisha, sodium dodecyl benzenesulphonate) was dissolved in 2241 parts of water. The solution was raised to a temperature of 40°C and stirred. The resinous solution prepared above was poured into the anionic surface active agent solution under stirring and 30 parts of 10% aqueous solution of dodecyl benzenesulphonic acid was added to obtain a white suspension. The suspension was maintained at a temperature of 40°C for 1 hour, then raised to a temperature of 90°C at a rate of 10°C/hr and cured to obtain a

30

35

suspension of fine cured resin particles.

The whole suspension of the fine cured resin particles was poured into 2800 parts of water, homogenized, and cooled to room temperature. Classification was repeated by the method described in Example 2. Fine cured resin particles were separated by centrifugation from the suspension of classified fine cured resin particles. The whole of a paste of fine cured resin particles obtained by the centrifugal separation was dispersed into 1000 parts of 0.1 N aqueous hydrochloric acid, washed by ultrasonics and separated by centrifuge. This operation was repeated three times. The whole of the fine cured resin paste was then dispersed into 1000 parts of water, washed by ultrasonics and separated by centrifuge. This operation was repeated twice. The whole of the fine cured resin particle paste after washing was dried in a hot air drier at a temperature of 160°C for two hours to obtain 80 parts of a conglomerate of fine cured resin particles. With finger tip pressure this conglomerate was disintegrated to afford fine white cured resin particles. Scanning electron microscopy showed the fine cured resin particles to be spheres $3.0 \pm 0.5 \mu\text{m}$ in diameter.

The fine cured resin particles showed absolutely no sign of swelling or solution in various organic solvents, including methanol, ethanol, isopropanol, butanol, ethyl acetate, butyl acetate, methyl cellosolve, ethyl cellosolve, acetone, methyl ethyl ketone, toluene and xylene. When the fine cured resin particles were heated to temperatures exceeding 250°C, they showed no discernible sign of fusion or solution.

Example 4

120 parts of benzoguanamine, 30 parts of urea, 266 parts of

formalin (formaldehyde content 37%) and 1.1 parts of a 10% aqueous sodium carbonate solution were mixed in the same four-necked flask as was used in Example 1. The resultant mixture was adjusted to pH 8.0. The mixture was stirred and held at 85°C for three hours to induce reaction and afford a soluble, fusible resin having degree of modified water tolerance of 150%.

8.5 parts of completely saponified polyvinyl alcohol having a polymerization degree of 1700 (product of Kuraray Co. Ltd., marketed under trademark designation of "Kuraray Poval 117") were dissolved in 500 parts of cold water. The solution was heated to 80°C and stirred in the same mixer as was used in Example 2 at a rotational speed of 300 rpm. The soluble, fusible resin prepared above was added to the Kuraray Poval 117 solution kept in a stirred state to obtain a white emulsion. The emulsion was cooled to 40°C. 3 parts of dodecyl benzenesulphonic acid were added to the cooled emulsion and the whole was gently stirred in an anchor type stirrer at 50°C for 1.5 hours. It was then held for two hours each at 60°C, 70°C and 90°C to obtain a suspension of fine cured resin particles. The whole of this suspension was poured into 4600 parts of water, homogenized, cooled to room temperature and repeatedly classified by the method described in Example 2. The classified fine cured resin particles were filtered from the suspension in vacuo and the resultant filter cake was washed with water. The whole filter cake was dried in a hot air drier at a temperature of 80°C for two hours and then heated at a temperature of 150°C for three hours to obtain 75 parts of a conglomerate of fine cured resin particles. With finger tip pressure the conglomerate was disintegrated to afford fine white cured resin particles. Scanning electron microscopy showed the fine white cured resin particles to

- 15 -

be spheres $6.5 \pm 0.5 \mu\text{m}$ in diameter.

The fine cured resin particles showed absolutely no sign of swelling or solution in the same organic solvents as tested in Example 1. When the fine cured resin particles were heated to temperatures exceeding 250°C , they showed no discernible sign of fusion or solution.

Example 5

Referring to Figure 1 of the drawings fine cured spherical particles 4, prepared as described in Example 1, were thoroughly mixed in a proportion in the range of 1 to 10% by weight in epoxy resin 3 as an adhesive sealing agent. The resultant mixture was applied on one of the transparent substrates 1 provided with a transparent electrode 2 by means of screen printing. The remaining transparent substrate 1 was superposed on the applied layer of the mixture. The resultant composite was held under suitable pressure and heated at a temperature of 100° to 150°C for 30 to 60 minutes to cure the mixture. The liquid crystal 5 was poured into the space formed by the spacers between the opposed transparent substrates to obtain a liquid crystal display device.

The particles 4 were not corroded by the epoxy resin used as the adhesive sealing agent, not softened when cured by heating, and not crushed under application of pressure. They served to keep the space between the transparent substrates accurately in a fixed thickness.

30

The example represents the invention embodied advantageously in a small liquid crystal display device.

Example 6

With reference to Figure 2 of the drawings, fine cured



- 16 -

spherical particles 4a, prepared as described in Example 2, were dispersed in a solution of a film-forming high molecular substance such as epoxy resin in a solvent. The resultant dispersion was applied on one of two transparent substrates 1 provided with a transparent electrode 2 by means of screen printing. The applied dispersion was thermally dried to convert the solution of high molecular substance into a film 6 and, at the same time, fasten the particles 4a on the transparent substrate 1. Thereafter, the particles 4 were dispersed in epoxy resin as an adhesive sealing agent 3. The resultant dispersion was applied on the periphery of the transparent substrate 1. The two transparent substrates are combined and held under proper pressure at a temperature of 100° to 150°C for 30 to 60 minutes to cure the dispersion. Then, liquid crystal was poured into a space formed between the opposed transparent substrates to afford a liquid crystal display device.

The resin particles 4 and 4a were not corroded by either the epoxy resin as the adhesive sealing agent or the high molecular substance, not softened when heated, or not crushed or caused to eat into the transparent substrate under applied pressure. They served to keep the space between the transparent substrate accurately at a uniform thickness.

In this example, the resin particles control the space not merely in the sealed portion of the liquid crystal display device but also in the entire area of the transparent electrodes. Thus, this example represents the invention embodied advantageously in a large liquid crystal display device.



25

- 17 -

CLAIMS:

1. A liquid crystal display device comprising two transparent substrates facing each other, two transparent electrodes one on the inner face of each substrate, a
5 liquid crystal and a mixture of an adhesive sealing agent and fine spherical cured particles of an amino-formaldehyde resin obtained from formaldehyde and at least one of benzoguanamine, melamine and urea, the mixture being applied to the periphery of the substrates to space them
10 one from the other and to seal the liquid crystal therebetween.
 2. A liquid crystal display device according to claim 1 wherein the amino-formaldehyde resin is benzoguanamine-
15 formaldehyde resin or benzoguanamine-melamine-formaldehyde resin.
 3. A liquid crystal display device according to claim 1 or claim 2 wherein the fine spherical particles have an
20 average particle diameter of from 1 to 15 μ m.
 4. A liquid crystal display device according to any preceding claim wherein the adhesive sealing agent is a thermosetting type resin adhesive agent.
25
 5. A liquid crystal display device according to any of claim 1 to 3 wherein the thermosetting resin type adhesive agent is an epoxy resin type adhesive agent.
 - 30 6. A liquid crystal display device according to any preceding claim further comprising fine spherical cured particles of the amino-formaldehyde resin between the two transparent substrates at non-peripheral positions
-