

LIQUID CRYSTAL SEALANT AND LIQUID CRYSTAL DISPLAY CELL USING
SAME

TECHNICAL FIELD

The present invention relates to a liquid crystal sealant for the liquid crystal dropping process that has good thermosetting properties. More specifically, the present invention relates to a liquid crystal sealant for the liquid crystal dropping process that has good thermosetting properties, and excellent shelf life, and, furthermore, is also excellent in humidity resistance and the like in a cured product, and a liquid crystal display cell that is sealed with a cured product thereof.

BACKGROUND ART

The so-called liquid crystal dropping process that has a higher mass productivity was proposed as a method of manufacturing a liquid crystal display cell with an increased size of the liquid crystal display cell in recent years (Patent documents 1 and 2). The liquid crystal dropping process is specifically a method of manufacturing a liquid crystal display cell by dropping liquid crystal into the inside of a weir of a liquid crystal sealant formed on one substrate, and then bonding the other substrate whereby to seal the liquid crystal.

However, the liquid crystal dropping process has problems that the liquid crystal sealant in the uncured state is in

contact with the liquid crystal, and thus components of the liquid crystal sealant at this time are dissolved into the liquid crystal (elution) and the resistance value of the liquid crystal decreases, and display defects are generated in the vicinity of the seal.

In order to resolve this problem, a light-heat combination type liquid crystal sealant is currently used as a liquid crystal sealant for the liquid crystal dropping process, and practically applied (Patent documents 3 and 4). A liquid crystal dropping process using this liquid crystal sealant is characterized by irradiating the liquid crystal sealant interposed between substrates with light to perform first curing, and then performing secondary curing by heating. According to this method, it is possible to promptly cure uncured liquid crystal sealant with light and suppress dissolution (elution) of components of the liquid crystal sealant into the liquid crystal. Furthermore, with only photocuring, a problem of insufficient adhesive strength from curing shrinkage at the time of the photocuring and the like is generated. However, the light-heat combination type has an advantage that such a problem can be solved by the secondary curing by heating.

However, with the decrease in size of liquid crystal display devices in recent years, a light-shielded part where light does not reach is caused in a liquid crystal sealant by the metal wiring of an array substrate or by the black matrix part of a color filter substrate of a liquid crystal display

device, and thus the problem of display defects in the vicinity of the seal becomes more serious than before. In other words, due to the presence of the light-shielded part, the first curing by light is insufficient, and uncured components remain in large quantities in the liquid crystal sealant. If the secondary curing process by heat proceeds in this state, it leads to results that dissolution of the uncured components into the liquid crystal is promoted by this heat, and display defects are caused in the vicinity of the seal.

In order to resolve this problem, various investigations to improve thermal reactivity have been conducted. There was a trial to react a liquid crystal sealant not sufficiently cured by light in the light-shielded part quickly at a low temperature, whereby to suppress contamination of the liquid crystal. For example, Patent documents 5 and 6 disclose methods using thermal radical initiators. In addition, Patent documents 7 to 9 disclose methods using polyvalent carboxylic acids as a curing accelerator.

However, these methods have problems in that the thermal radical initiator or the curing accelerator used itself is eluted into the liquid crystal, which causes display defects even though the thermal reactivity is improved. In addition, it is known that presence of a functional group having high polarity, such as carboxylic acid, causes a problem of raising the water absorbency of a cured product of the sealant, and as a result thereof, decreasing the reliability of humidity

resistance. Furthermore, addition of the curing accelerator advances the reaction even at normal temperatures, whereas the curing accelerator improves the thermal reactivity, and thus extremely decreases shelf life.

As described above, development of the liquid crystal sealant for the liquid crystal dropping process has been very energetically performed, but a liquid crystal sealant having excellent thermal reactivity and also having good shelf life, and further having excellent cured product properties, has not yet been realized.

Patent Document 1: Japanese Unexamined Patent Application, Publication No. S63-179323

Patent Document 2: Japanese Unexamined Patent Application, Publication No. H10-239694

Patent Document 3: Japanese Patent Publication No. 3583326

Patent Document 4: Japanese Unexamined Patent Application, Publication No. 2004-61925

Patent Document 5: Japanese Unexamined Patent Application, Publication No. 2004-126211

Patent Document 6: Japanese Unexamined Patent Application, Publication No. 2009-8754

Patent Document 7: PCT International Publication No. WO2007/138870

Patent Document 8: Japanese Unexamined Patent Application, Publication No. 2008-15155

Patent Document 9: Japanese Unexamined Patent Application,

Publication No. 2009-139922

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The present invention relates to a liquid crystal sealant for the liquid crystal dropping process that is cured by heating only, or light-heat combination, and proposes a liquid crystal sealant for liquid crystal dropping process which reacts fast by heat, and thus has extremely little contamination with respect to the liquid crystal throughout the steps, and excellent shelf life, and is also excellent in cured product properties such as reliability of humidity resistance.

Means for Solving the Problems

The present inventors earnestly investigated, and as a result thereof, found that a liquid crystal sealant for the liquid crystal dropping process containing a specific compound having a carboxyl group is excellent in terms of thermal reactivity, and as a result thereof, can suppress the contamination of the liquid crystal as well, and, furthermore, has excellent shelf life, and reliability of humidity resistance, and completed the present invention.

Specifically, the present invention relates to the following 1) to 10). Meanwhile, with respect to all of the component (a), it may be described as the "component (a) curable resin" or simply the "component (a)" in the

specification in order to avoid the complicated description of "a curable resin containing one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin". In addition, in the specification, the "(meth)acrylic" means either one or both of "acrylic" and "methacrylic". Likewise, in the specification, the "(meth)acryloyl" means either one or both of "acryloyl" and "methacryloyl".

1)

A liquid crystal sealant for the liquid crystal dropping process which is characterized in containing (a) a curable resin containing one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin, (b) a heat-curing agent, and (c) a compound having intramolecular carboxy groups and an acid value between 50 and 250 mg KOH/g.

2)

The liquid crystal sealant for the liquid crystal dropping process according to 1), in which the mass average molecular weight of the component (c) is 3000 to 10000 g/mol.

3)

The liquid crystal sealant for the liquid crystal dropping process according to 1) or 2), in which the content of the component (c) is from 0.1 to 20 parts by mass with respect to 100 parts by mass of the component (a).

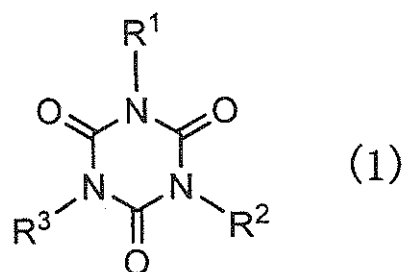
4)

The liquid crystal sealant for the liquid crystal

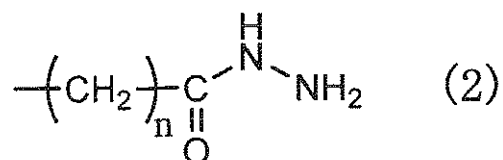
dropping process according to any one of 1) to 3), in which the component (b) heat-curing agent is a polyvalent hydrazide compound.

5)

The liquid crystal sealant for the liquid crystal dropping process according to 4), in which the component (b) heat-curing agent is one, or two or more of a hydrazide compound represented by formula (1) below:



in the formula, R^1 to R^3 each independently represent, a hydrogen atom, or a molecular skeleton represented by formula (2) below:



in the formula, n represents an integer of 1 to 6.

6)

The liquid crystal sealant for the liquid crystal dropping process according to any one of 1) to 5), in which the component (a) curable resin is a mixture of a (meth)acrylated epoxy resin and an epoxy resin.

7)

The liquid crystal sealant for the liquid crystal dropping process according to any one of 1) to 6), further containing a component (d) silane coupling agent.

8)

The liquid crystal sealant for the liquid crystal dropping process according to any one of 1) to 7), further containing a component (e) inorganic filler.

9)

The liquid crystal sealant for the liquid crystal dropping process according to any one of 1) to 8), further containing a component (f) photopolymerization initiator.

10)

A liquid crystal display cell sealed with a cured product obtained by curing the liquid crystal sealant for the liquid crystal dropping process according to any one of 1) to 9).

Effects of the Invention

The liquid crystal sealant for the liquid crystal dropping process of the present invention has fast reaction speed at the time of thermosetting, and thus has sufficient curability even under a wiring in which light is hardly delivered in the light-heat combination type liquid crystal dropping process, and thus makes it possible to secure flexibility in the design of the panel wiring, and to easily manufacture a liquid crystal display panel having high reliability, and, furthermore, to be applied to a liquid crystal dropping process in which a liquid crystal sealant is

cured with heat only.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

The liquid crystal sealant of the present invention contains a component (c) which is a compound having intramolecular carboxyl groups and an acid value between 50 and 250 mg KOH/g, which makes it possible to balance thermal reactivity and shelf life. The carboxyl group contained in this compound functions as a thermosetting accelerator. Accordingly, if the acid value is less than 50 mg, sufficient thermal reactivity is not obtained. In addition, if the acid value is greater than 250 mg, the polarity of the molecule increases, which deteriorates the reliability of humidity resistance of the cured product. The acid value is more preferably 50 to 180 mg KOH/g, further preferably 50 to 100 mg KOH/g, and particularly preferably 60 to 100 mg KOH/g. Meanwhile, the acid value is defined as the number of mg of potassium hydroxide necessary for neutralizing carboxylic acids that are present in 1 g of the component (c).

In addition, the component (c) preferably has a mass average molecular weight of 3000 to 10000 g/mol. If the mass average molecular weight is too small, the component (c) itself dissolves in the liquid crystal, and causes display defects. In addition, if the mass average molecular weight is too great, compatibility with other components becomes worse, and the thermal reaction promotion effect decreases remarkably. The mass average molecular weight is further preferably 4000

to 8000 g/mol.

The content of the component (c) is preferably from 0.1 to 20 parts by mass, and particularly preferably from 1 to 10 parts by mass with respect to 100 parts by mass of the total amount of the component (a) curable resin. If the content is too small, sufficient heat curability is not obtained. If the content is too great, the liquid crystal sealant has higher viscosity, and thus may be restricted in blending with other components, and thus is inadequate.

Specific examples of the component (c) include compounds obtained by reacting an acid anhydride or a polyvalent carboxylic acid (including anhydride) with an epoxy (meth)acrylate having a hydroxy group, compounds obtained by reacting a polyvalent carboxylic acid (including anhydride) with a terminal alcoholic hydroxy group of a polyester resin obtained by dehydro-condensing one or more kinds of a polyvalent carboxylic acid and one or more kinds of a polyhydric alcohol, and the like. The compounds obtained by reacting an acid anhydride or a polyvalent carboxylic acid (including anhydride) with an epoxy (meth)acrylate having a hydroxy group can be obtained, for example, with the method described in JP 5-32746 A, or the like. Among them, compounds obtained by reacting an acid anhydride with a bisphenol A type epoxy (meth)acrylate are preferred. In addition, the compounds obtained by reacting a polyvalent carboxylic acid (including anhydride) with a terminal alcoholic hydroxy group of a polyester resin obtained by dehydro-condensing one or more

kinds of a polyvalent carboxylic acid and one or more kinds of a polyhydric alcohol are easily available from the market, for example, trademarks of U-Pica Coat GV230 or U-Pica Coat GV250 (Japan U-PICA Company Ltd). Among them, U-Pica Coat GV230 (acid value : 53 mg KOH/g, mass average molecular weight : 7900 g/mol) and U-Pica Coat GV250 (acid value : 74 mg KOH/g, mass average molecular weight : 5200 g/mol) are preferably used, and U-Pica Coat GV250 is particularly preferably used.

The heat-curing agent, which is the component (b) that is used in the liquid crystal sealant of the present invention, is not particularly limited, and examples thereof may include polyvalent amines, polyhydric phenols, hydrazide compounds and the like. However, the polyvalent hydrazide compounds are particularly suitably used. For example, the hydrazide compounds may include aromatic hydrazides such as terephthalic acid dihydrazide, isophthalic acid dihydrazide, 2,6-naphthoic acid dihydrazide, 2,6-pyridine dihydrazide, 1,2,4-benzene trihydrazide, 1,4,5,8-naphthoic acid tetrahydrazide, pyromellitic acid tetrahydrazide. In addition, examples of the aliphatic hydrazide compounds may include, for example, formhydrazide, acetohydrazide, propionic acid hydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, 1,4-cyclohexane dihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, N,N'-hexamethylene bis-semicarbazide, citric acid trihydrazide, nitriloacetic acid

trihydrazide, cyclohexane tricarboxylic acid trihydrazide; dihydrazide compounds having a hydantoin skeleton, preferably a valine hydantoin skeleton (skeleton where a carbon atom of a hydantoin ring is substituted with an isopropyl group), such as 1,3-bis(hydrazinocarboethylethyl)-5-isopropyl hydantoin; and the compounds represented by formula (1) and the like.

Examples of the compound represented by formula (1) may include, for example, tris(1-hydrazinocarbonylmethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(3-hydrazinocarbonylpropyl) isocyanurate, bis(2-hydrazinocarbonylethyl) isocyanurate and the like, and are not limited thereto if the compound has a structure of formula (1).

The compound represented by formula (1) is preferably isophthalic acid dihydrazide, malonic acid dihydrazide, adipic acid dihydrazide, tris(1-hydrazinocarbonylmethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate or tris(3-hydrazinocarbonylpropyl) isocyanurate, and particularly preferably tris(2-hydrazinocarbonylethyl) isocyanurate for the balancing of the curing reactivity and the potentiality.

The content of the component (b) is preferably from 0.1 to 20 parts by mass, and further preferably from 1 to 10 parts by mass with respect to 100 parts by mass of the total amount of the component (a) curable resin, and two or more kinds may be used in a mixture.

The liquid crystal sealant of the present invention

contains a curable resin that has one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin as the component (a). Examples of the component (a) include an epoxy resin, a mixture of an epoxy resin and a (meth)acrylated epoxy resin, a (meth)acrylated epoxy resin, a partially (meth)acrylated epoxy resin and the like. Any of the components (a) used in the present invention preferably have little contamination and solubility with respect to the liquid crystal. Examples of a suitable epoxy resin include a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a bisphenol S type epoxy resin, a phenol novolak type epoxy resin, a cresol novolak type epoxy resin, a bisphenol A novolak type epoxy resin, a bisphenol F novolak type epoxy resin, an alicyclic epoxy resin, an aliphatic chain-like epoxy resin, a glycidyl ester type epoxy resin, a glycidyl amine type epoxy resin, a hydantoin type epoxy resin, an isocyanurate type epoxy resin, a triphenol methane skeleton-containing phenol novolak type epoxy resin, and in addition, a diglycidyl ether of bifunctional phenols, a diglycidyl ether of bifunctional alcohols, and a halogenated material thereof, a hydrogenated material thereof and the like, but are not limited thereto. The (meth)acryloylated epoxy resin and the partial (meth)acryloylated epoxy resin may be obtained by a well-known reaction of an epoxy resin and a (meth)acrylic acid. For example, (meth)acryloylated epoxy resin and the partial (meth)acryloylated epoxy resin may be obtained by adding a

(meth)acrylic acid, a catalyst (for example, benzyldimethyl amine, triethyl amine, benzyltrimethyl ammonium chloride, triphenyl phosphine, triphenyl stibine and the like), and a polymerization inhibitor (for example, methoquinone, hydroquinone, methyl hydroquinone, phenothiazine, dibutyl hydroxytoluene and the like) in a predetermined equivalent ratio to an epoxy resin, and performing an esterification reaction, for example, at 80 to 110°C. The epoxy resin, which is a raw material, is not particularly limited, but is preferably a bi-functional or higher-functional epoxy resin, and examples thereof include a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a bisphenol S type epoxy resin, a phenol novolak type epoxy resin, a cresol novolak type epoxy resin, a bisphenol A novolak type epoxy resin, a bisphenol F novolak type epoxy resin, an alicyclic epoxy resin, an aliphatic chain-like epoxy resin, a glycidyl ester type epoxy resin, a glycidyl amine type epoxy resin, a hydantoin type epoxy resin, an isocyanurate type epoxy resin, a triphenol methane skeleton-containing phenol novolak type epoxy resin, and in addition, a diglycidyl ether of bifunctional phenols, a diglycidyl ether of bifunctional alcohols, and a halogenated material thereof, a hydrogenated material thereof and the like. Among these, the epoxy resin is more preferably a bisphenol type epoxy resin or a novolak type epoxy resin from the viewpoint of the contamination of the liquid crystal. In addition, the ratio of the epoxy group to the (meth)acryloyl group is not limited, and is suitably selected from the

viewpoint of the process suitability and the contamination of the liquid crystal.

The content of the component (a) is suitably determined in consideration of the workability and the physical properties of the obtained liquid crystal sealant, and is typically from 25 to 80 wt%, and preferably from 25 to 75 wt% in the liquid crystal sealant.

In the liquid crystal sealant of the present invention, (d) a silane coupling agent may be used, to seek improvement of the adhesive strength and improvement of the reliability of humidity resistance. Examples of the silane coupling agent include 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 3-glycidoxypropyl methyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, N-phenyl- γ -aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-mercaptopropyl trimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)-3-aminopropyl trimethoxysilane hydrochloride, 3-methacryloxypropyl trimethoxysilane, 3-chloropropyl methyldimethoxysilane, 3-chloropropyl trimethoxysilane and the like. The content of the silane coupling agent (d) in the liquid crystal sealant is suitably from 0.05 to 3 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant of the present invention.

In the liquid crystal sealant of the present invention,

(e) an inorganic filler may be used to seek improvement of the adhesive strength and improvement of the reliability of humidity resistance. Examples of this (e) inorganic filler include molten silica, crystalline silica, silicon carbide, silicon nitride, boron nitride, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, magnesium oxide, zirconium oxide, aluminum hydroxide, magnesium hydroxide, calcium silicate, aluminum silicate, lithium aluminum silicate, zirconium silicate, barium titanate, glass fiber, carbon fiber, molybdenum bisulfide, asbestos and the like, preferably molten silica, crystalline silica, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate and aluminum silicate, and further preferably molten silica, crystalline silica, alumina and talc. These inorganic fillers may be used in a mixture of two or more kinds. If the average particle diameter is too great, it becomes a defect factor such that a gap cannot be formed well when the upper and the lower glass substrates are laminated at the time of manufacture of a liquid crystal display cell having a narrow gap, and thus the average particle diameter is appropriately 3 μm or less, and preferably 2 μm or less. The particle diameter can be measured by a laser diffraction/scattering type particle size distribution measurement apparatus (dry type) (manufactured by SEISHIN ENTERPRISE Co., Ltd.; LMS-30).

The content of the inorganic filler (e) in the liquid

crystal sealant, which may be used in the liquid crystal sealant of the present invention, is typically from 10 to 60 parts by mass, and preferably from 20 to 50 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant of the present invention. If the content of the inorganic filler is too small, the adhesive strength with respect to a glass substrate decreases, and the reliability of humidity resistance is also poor, and thus a decrease of the adhesive strength after moisture absorption may increase. On the other hand, if the content of the inorganic filler is too great, it is hard to perform crushing and the gap of the liquid crystal cell cannot be formed.

The liquid crystal sealant of the present invention may contain the component (f), a photopolymerization initiator in order to render the liquid crystal sealant to be a light-heat combination curing type liquid crystal sealant. The photopolymerization initiator is not particularly limited as long as it is a compound that generates radicals by irradiation of UV or visible light, and initiates a chain polymerization reaction, and examples thereof may include benzyldimethyl ketal, 1-hydroxycyclohexylphenylketone, diethylthioxanthone, benzophenone, 2-ethyl anthraquinone, 2-hydroxy-2-methyl propiophenone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane, 2,4,6-trimethyl benzoyldiphenyl phosphine oxide and the like. In addition, those having a (meth)acryloyl group in the molecule are preferably used, and for example, a reaction product of 2-

methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one is suitably used from the viewpoint of the contamination of the liquid crystal. This compound may be obtained by the manufacture according to the method described in WO 2006/027982.

The content of the component (f) photopolymerization initiator in the liquid crystal sealant, which may be used in the liquid crystal sealant of the present invention, is typically from 0.1 to 5 parts by mass, and preferably from 0.2 to 3 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant of the present invention.

In the liquid crystal sealant of the present invention, a monomer or an oligomer of (meth)acrylic acid ester may be also used as necessary. Examples of such monomer or oligomer include a reaction product of dipentaerythritol and (meth)acrylic acid, a reaction product of dipentaerythritol caprolactone and (meth)acrylic acid and the like, but are not particularly limited as long as the monomer or oligomer has little contamination with respect to the liquid crystal.

In the liquid crystal sealant of the present invention, organic fillers, and additives such as pigments, leveling agents, antifoam agents and solvents may be also blended as necessary.

As one example of a method for obtaining the liquid crystal sealant of the present invention, there is a method to be described below. First, the (a) component is dissolved in

an organic solvent, and then the (c) component is added, and heating-mixing is performed to dissolve the (c) component. Then, the organic solvent is removed by heating and the like, and, furthermore, as necessary, the (f) component is dissolved and mixed under heating. The solution is cooled to room temperature and then combined with the (b) component, and combined with the (d) component, the (e) component, and an organic filler, an antifoam agent, a leveling agent, a solvent and the like as necessary, and uniformly mixed with a known mixing apparatus, for example, a three-roller milling machine, a sand mill, a ball mill or the like, and filtered with a metal mesh, whereby to manufacture the liquid crystal sealant of the present invention.

The liquid crystal display cell of the present invention is obtained by disposing one pair of substrates on which prescribed electrodes are formed in opposition to the substrate at a prescribed interval, sealing the circumference with the liquid crystal sealant of the present invention, and enclosing a liquid crystal into the space. The kind of the enclosed liquid crystal is not particularly limited. Herein, the substrates are formed of a combination of substrates such as glass, quartz, plastic, and silicon, in which at least one of the substrates is light-transmissive. As the manufacturing method thereof, the liquid crystal sealant of the present invention is combined with a spacer such as a glass fiber (space control material), and then the liquid crystal sealant is applied onto one of the pair of substrates using a

dispenser, or a screen print apparatus or the like, and then temporary curing is performed at 80 to 120°C as necessary. Then, liquid crystal is dropped into the inside of the weir of the liquid crystal sealant, and the other glass substrate is superposed in a vacuum to perform gap formation. After the gap formation, curing is performed at 90 to 130°C for 1 to 2 hours to obtain the liquid crystal display cell of the present invention. In addition, when a light-heat combination type is used, the portion of the liquid crystal sealant is irradiated with ultraviolet light using an ultraviolet light irradiation machine to perform the photocuring. The irradiation amount of ultraviolet light is preferably 500 to 6000 mJ/cm², and more preferably 1000 to 4000 mJ/cm². Then, as necessary, curing is performed at 90 to 130°C for 1 to 2 hours to obtain the liquid crystal display cell of the present invention. The liquid crystal display cell thus obtained of the present invention does not have display defects due to contamination of the liquid crystal, and is excellent in the adhesiveness and the reliability of humidity resistance. Examples of the spacer include glass fibers, silica beads, polymer beads and the like. The diameter thereof varies depending on the purpose, but typically from 2 to 8 μm, and preferably from 4 to 7 μm. The amount used is typically from 0.1 to 4 parts by mass, preferably from 0.5 to 2 parts by mass, and further preferably from 0.9 to 1.5 parts by mass with respect to 100 parts by mass of the liquid crystal sealant of the present invention.

The liquid crystal sealant of the present invention has

very good heat curability, and is promptly cured in the heating process in the liquid crystal dropping process. Accordingly, elution of the constituting components into the liquid crystal is extremely low, and the display defects of the liquid crystal display cell can be reduced. In addition, the liquid crystal sealant of the present invention also has excellent shelf life, and thus is suitable for the manufacture of a liquid crystal display cell. Furthermore, a cured product thereof is also excellent in various cured product properties such as adhesive strength, heat resistance and humidity resistance, and thus by using the liquid crystal sealant of the present invention, it is possible to prepare a liquid crystal display cell having excellent reliability. In addition, a liquid crystal display cell prepared using the liquid crystal sealant of the present invention has a high voltage-holding rate, and low ion density, and thus meets the properties necessary for a liquid crystal display cell.

EXAMPLES

Hereinafter, the present invention is further specifically described with Synthesis Examples and Examples, but the present invention is not limited to the Examples. Meanwhile, "part" and "%" in the text are on a mass basis unless otherwise stated.

Synthesis Example 1: Synthesis of epoxy acrylate of bisphenol
A type epoxy resin

282.5 g bisphenol A type epoxy resin (product name: YD-8125, manufactured by NIPPON STEEL & SUMIKIN CHEMICAL CO., LTD.) was dissolved in 266.8 g of toluene, and 0.8 g of dibutyl hydroxytoluene as a polymerization inhibitor was added thereto, and the reaction liquid was heated to 60°C. Then, 117.5 g of acrylic acid as 100% equivalent to the epoxy group was added, and the reaction liquid was further heated to 80°C, combined with 0.6 g of trimethyl ammonium chloride as a reaction catalyst, and stirred at 98°C for about 30 hours to give the reaction liquid.

Synthesis Example 1-1

The reaction liquid obtained in Synthesis Example 1 was washed with water, and the toluene was distilled, whereby to give 395 g of the intended bisphenol A type epoxy acrylate (KAYARAD^{RTM} R-93100).

Synthesis Example 1-2

The reaction liquid obtained in Synthesis Example 1 was also combined with 151.6 g of tetrahydrophthalic anhydride, and stirred at 98°C for about 30 hours. The obtained reaction liquid was washed with water 6 times, and then the toluene was distilled with an evaporator whereby to give 640 g of the intended compound (acid anhydride adduct of bisphenol A type epoxy acrylate). The mass average molecular weight of this compound measured with GPC (gel permeation chromatography) was 828 g/mol.

(Preparation of liquid crystal sealant for the liquid crystal dropping process)

Examples 1 and 2

Each of the resin components (component (a)) was mixed in the ratio shown in Table 1 to be described below, and stirred, and then combined with acetone to dissolve the resin components. Then, the component (c) was added, and heat-dissolved at 70°C, and then the acetone was distilled with an evaporator. Then, a radical polymerization initiator (component (f)) was added, and the solution was heat-dissolved, and then was cooled to room temperature, and combined with the silane coupling agent (component (d)), the inorganic filler (component (e)) and the heat-curing agent (component (b)), and stirred, and then dispersed with a three-roller milling machine and filtered with a metal mesh (635 mesh) to prepare the liquid crystal sealant for the liquid crystal dropping process of Examples 1 and 2.

Example 3

Each of the resin components (component (a)) was mixed in the ratio shown in Table 1 to be described below, and stirred, and then combined with the component (c) and heat-dissolved at 90°C. Then, a radical polymerization initiator (component (f)) was heat-dissolved, and then the solution was cooled to room temperature, and combined with the silane coupling agent (component (d)), the inorganic filler (component (e)) and the

heat-curing agent (component (b)), and stirred, and then dispersed with a three-roller milling machine, and filtered with a metal mesh (635 mesh) to prepare the liquid crystal sealant for the liquid crystal dropping process of Example 3.

Comparative Examples 1 to 3

Each of the resin components (component (a)) was mixed in the ratio shown in Table 1 to be described below and stirred, and then the radical polymerization initiator (component (f)) was heat-dissolved at 90°C. The solution was cooled to room temperature, and combined with the component (c), the silane coupling agent (component (d)), the inorganic filler (component (e)) and the heat-curing agent (component (b)), and stirred, and then dispersed with a three-roller milling machine, and filtered with a metal mesh (635 mesh) to prepare the liquid crystal sealant for the liquid crystal dropping process of Comparative Examples 1 to 3.

Hereinafter, the descriptions for evaluation items of each of the prepared liquid crystal sealants for liquid crystal dropping process and results thereof are shown.

(Test for heat curability)

Each of the liquid crystal sealants for the liquid crystal dropping process was applied between polyethylene terephthalate films, and then stretched to a thickness of 100 μm using a laminater, and irradiated with 3000 mJ/cm^2 ultraviolet light (Sample 1). The prepared film was heat-cured

at 120°C for 1 hour (Sample 2). The enthalpies of Samples 1 and 2 were measured using a differential scan type calorimeter (manufactured by Seiko Instruments Inc., measurement condition: 30°C to 250°C, 10°C temperature-elevation speed), and the thermal reaction rate was calculated using the calculation formula to be described below.

Thermal reaction rate = $[1 - (\text{Enthalpy of Sample 1} - \text{Enthalpy of Sample 2}) / \text{Enthalpy of Sample 1}] \times 100$

The results were judged as described below.

A: 90% or more of thermal reaction rate

C: Less than 90% of thermal reaction rate

The thermal reaction rate of Example 1 was 92%, the thermal reaction rate of Example 2 was 91%, and the thermal reaction rate of Example 3 was 94%.

(Test for contamination of liquid crystal)

The film of the liquid crystal sealant for the liquid crystal dropping process irradiated with 3000 mJ/cm² of ultraviolet light (Sample 1) was cut to a size of about 5 mm², and about 100 mg was put into a 10 ml vial, and then liquid crystal (MLC-6866-100: manufactured by Merck KGaA, Darmstadt, Germany) was added in a ten-fold amount based on the weight. The vial was heated at 120°C for 1 hour, and then cooled for 30 minutes. Each of the supernatant liquids was isolated with decantation, and the value of specific resistance was measured with a digital super-high ohmmeter (R8340: manufactured by Advantest Corporation), and compared with the value of specific resistance of those containing no sealant. Evaluation

was performed as described below.

A: $9.5E + 11$ or more of the value of specific resistance

B: $1.0E + 11$ or more and less than $9.5E + 11$ of the value of specific resistance

C: Less than $1.0E + 11$ of the value of specific resistance

Meanwhile, " $1.0E + 12$ " of the value of specific resistance represents " 1.0×10^{12} ". The same applies to the other descriptions. The value of specific resistance of Example 1 was $3.8E + 12$, the value of specific resistance of Example 2 was $9.7E + 11$, and the value of specific resistance of Example 3 was $2.7E + 12$.

(Test for shelf life)

Each of the liquid crystal sealants for the liquid crystal dropping process was kept warm in a 23°C thermostatic bath, and the viscosity after 24 hours was measured. The viscosity was compared with the initial viscosity, and evaluated as described below. Meanwhile, the viscosity was measured using an E type viscometer (manufactured by TOKI SANGYO CO., LTD).

A: Less than 5% of viscosity increase rate

B: 5% or more and less than 10% of viscosity increase rate

C: 10% or more of viscosity increase rate, or gelled

The viscosity increase rate of Example 1 was 3%, the viscosity increase rate of Example 2 was 3%, and the viscosity increase rate of Example 3 was 4%.

(Test for moisture-resistant adhesiveness)

100 g of each of the liquid crystal sealants for the liquid crystal dropping process was combined with 1 g of 5 μm glass fiber as a spacer, and mixed and stirred. This liquid crystal sealant was applied onto a 50 mm $\times$ 50 mm glass substrate, and 1.5 mm $\times$ 1.5 mm glass fragments were laminated onto the liquid crystal sealant, and irradiated with 3000 mJ/cm^2 ultraviolet light using a UV irradiation machine, and then placed in an oven at 120°C for 1 hour and cured. The shear adhesive strength of the glass fragment was measured. In addition, a PCT test (condition: 120°C temperature, 100% humidity, 2 atm atmosphere, 12 hours of test time) was performed using the glass substrate after the curing, and then the shear adhesive strength of the glass fragment was measured. Then, the adhesive holding rate before and after the PCT test was calculated, and evaluated as described below.

A: 50% or more of adhesive holding rate

B: 25% or more and less than 50% of adhesive holding rate

C: Less than 25% of adhesive holding rate

The adhesive holding rate of Example 1 was 69%, the adhesive holding rate of Example 2 was 65%, and the adhesive holding rate of Example 3 was 55%.

(Test for panel display property)

Each of the liquid crystal sealants for the liquid crystal dropping process was filled into a syringe and degassed, and then was applied onto a glass substrate with a dispenser (SHOT MASTER 300 manufactured by Musashi Engineering,

Inc.), and a suitable amount of the liquid crystal was dropped into the frame of the seal. The substrate was installed in a vacuum lamination apparatus, and the other substrate was superposed under vacuum, and then cured at 120°C for 1 hour. The prepared simulation panel was electrically charged, and observed on a polarizing film. The observation results are evaluated as described below.

A: Alignment defect was not found

C: Alignment defect was found

F: Bubbles were generated from the sealant, and leakage of the liquid crystal was caused

[Table 1]

			Example 1	Example 2	Example 3
Component (a)	#1	Resorcin diglycidyl ether	1.5 parts	1.5 parts	1.5 parts
	#2	Bisphenol A type epoxy acrylate	16 parts	16 parts	16 parts
Component (b)	#3	Tris(2-hydrazinocarbonylethyl) isocyanurate	0.96 parts	0.96 parts	0.96 parts
Component (c)	#4	U-Pica Coat GV250	1 part		
	#5	U-Pica Coat GV230		1 part	
	#6	Acid anhydride adduct of bisphenol A type epoxy acrylate			1 part
	#7	1,3,5-tris(2-carboxylethyl) isocyanurate			
	#8	VPE-0201			
Component (d)	#9	3-glycidoxypropyl trimethoxysilane	0.3 parts	0.3 parts	0.3 parts
Component (e)	#10	Talc	1.5 parts	1.5 parts	1.5 parts
	#11	Silica	6 parts	6 parts	6 parts
Component (f)	#12	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-prop an-1-one	1 part	1 part	1 part
Curability			A	A	A
Liquid crystal contamination			A	A	A
Shelf life			A	A	A
Moisture-resistant adhesiveness (holding rate)			A	A	B
Panel display property			A	A	A

			Compara tive Example 1	Compara tive Example 2	Compara tive Example 3
Component (a)	#1	Resorcin diglycidyl ether	1.5 parts	1.5 parts	1.5 parts
	#2	Bisphenol A type epoxy acrylate	16 parts	16 parts	16 parts
Component (b)	#3	Tris(2-hydrazinocarbonylethyl) isocyanurate	0.96 parts	0.96 parts	0.96 parts
Component (c)	#4	U-Pica Coat GV250			
	#5	U-Pica Coat GV230			
	#6	Acid anhydride adduct of bisphenol A type epoxy acrylate			
	#7	1,3,5-tris(2-carboxylethyl) isocyanurate	1 part		
	#8	VPE-0201		1 part	
Component (d)	#9	3-glycidoxypropyl trimethoxysilane	0.3 parts	0.3 parts	0.3 parts
Component (e)	#10	Talc	1.5 parts	1.5 parts	1.5 parts
	#11	Silica	6 parts	6 parts	6 parts
Component (f)	#12	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-prop an-1-one	1 part	1 part	1 part
Curability			A	A	C
Liquid crystal contamination			A	C	B
Shelf life			B	C	A
Moisture-resistant adhesiveness (holding rate)			C	C	A
Panel display property			A	F	C

#1 : 1,3-bis(oxiranylmethoxy)benzene (manufactured by Nagase Chemtex Corporation)

#2 : Synthesized from Synthesis Example 1-1

#3 : HCIC (Manufactured by JAPAN FINECHEM COMPANY, INC.)

#4 : Manufactured by U-PICA Company Ltd.

#5 : Manufactured by U-PICA Company Ltd.

#6 : Synthesized from Synthesis Example 1-2

142 mg KOH/g acid value (calculation value)

#7 : CIC acid (manufactured by SHIKOKU CHEMICALS CORPORATION)

492 mg KOH/g acid value (calculation value)

#8 : Azo-type thermal radical initiator (manufactured by Wako Pure Chemical Industries, Ltd.)

#9 : Sila-Ace S-510 (manufactured by CHISSO CORPORATION)

#10 : D-600 (Manufactured by Nippon Talc Co., Ltd.)

#11 : Admafine SEZ (manufactured by Admatechs)

#12 : Synthesized with the method described in WO 2006/027982 A

From the results of Table 1, Comparative Example 3 not containing a curing accelerator component has poor curability, and as a result thereof, has occurrence of the alignment defect in the panel display property. In addition, those using a thermal radical initiator or a CIC acid as a curing accelerator have shortcomings regarding the liquid crystal contamination and the moisture-resistant adhesiveness although they achieve the improvement of the curability. On the contrary, it is confirmed that with Examples 1 to 3, improvement of curability is realized, and other properties are also at the level of being usable. Particularly, Examples 1 and 2 show very excellent results in all of the properties.

From these results, it can be said that the liquid crystal sealant of the present invention has excellent shelf life and curability, and thus is excellent in workability, and it can be said that the liquid crystal sealant of the present invention is excellent in terms of liquid crystal contamination, moisture-resistant adhesiveness, panel display

property, and thus realizes high reliability of a liquid crystal display cell.

INDUSTRIAL APPLICABILITY

Since the liquid crystal sealant of the present invention is excellent in terms of workability, the liquid crystal sealant of the present invention allows stable production of the liquid crystal display cell, and, furthermore, contributes to securing long term reliability of the liquid crystal display cell.

CLAIMS

1. A liquid crystal sealant for the liquid crystal dropping process, comprising:

(a) a curable resin containing one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and partially (meth)acrylated epoxy resin,

(b) a heat-curing agent, and

(c) a compound having intramolecular carboxy groups and an acid value between 50 and 250 mg KOH/g.

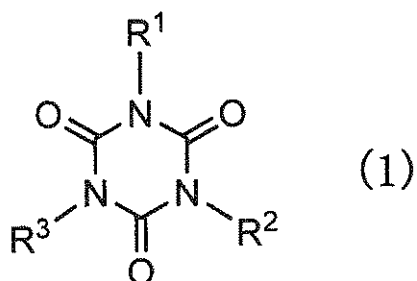
2. The liquid crystal sealant for the liquid crystal dropping process according to claim 1, wherein the mass average molecular weight of the component (c) is 3000 to 10000 g/mol.

3. The liquid crystal sealant for the liquid crystal dropping process according to claim 1 or 2, wherein the content of the component (c) is from 0.1 to 20 parts by mass with respect to 100 parts by mass of the component (a).

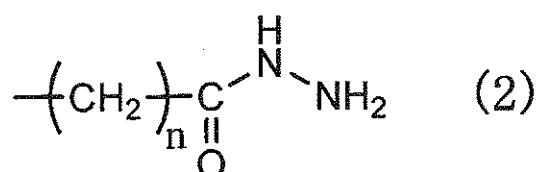
4. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 3, wherein the component (b) heat-curing agent is a polyvalent hydrazide compound.

5. The liquid crystal sealant for the liquid crystal

dropping process according to claim 4, wherein the component (b) heat-curing agent is one, or two or more of a hydrazide compound represented by formula (1) below:



wherein R^1 to R^3 each independently represent a hydrogen atom or a molecular skeleton represented by formula (2) below:



wherein n represents an integer of 1 to 6.

6. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 5, wherein the component (a) curable resin is a mixture of a (meth)acrylated epoxy resin and an epoxy resin.

7. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 6, further comprising a component (d) silane coupling agent.

8. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 7,

further comprising a component (e) inorganic filler.

9. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 8, further comprising a component (f) photopolymerization initiator.

10. A liquid crystal display cell sealed with a cured product obtained by curing the liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 9.